PB-276 624
PART 1 OF 2

NIOSH MANUAL OF ANALYTICAL METHODS

SECOND EDITION

Part II
Standards Completion Program Validated Methods

David G. Taylor, Ph.D.
Manual Coordinator

VOLUME 2

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Center for Disease Control
National Institute for Occupational Safety and Health
Cincinnati, Ohio
April 1977

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

DISCLAIMER

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

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

DHEW (NIOSH) Publication No. 77-157-B

BIBLIOGRAPHIC DATA SHEET	1. Report No. 77-NIOSH-75-157-B	2.	3. Recipient's Accession No. PB 270624
4. Title and Subtitle NIOSH MANUAL OF ANALYTICAL METHODS SECOND EDITION - PART II STANDARDS COMPLETION PROGRAM VALIDATED METHODS VOLUME 2			5. Report Date April 1977 6.
7. Author(s)			8. Performing Organization Rept. No.
9. Performing Organization Name and Address National Institute for Occupational Safety and Health 4676 Columbia Parkway Cincinnati, Ohio 45226			10. Project/Task/Work Unit No. 11. Contract/Grant No.
12. Sponsoring Organization Name and Address Same as Box 9			13. Type of Report & Period Covered 14.

15. Supplementary Notes

16. Abstracts

The second volume of the NIOSH Manual of Analytical Methods, Part II, Standards Completion Program Validated Methods, Second Edition, contains a series of data sheets for a total of 115 chemicals of varied nature. Validation data are given for concentrations of the compounds in the air ranging from about half as much to twice as great as levels established by the prevailing OSHA standards. For each compound, details are given as to the principle of the method, range and sensitivity, interference, precision and accuracy, advantages and disadvantages of the method, apparatus, reagents, procedure, collection and shipping of samples, analysis of samples, determination of desorption efficiency, calibration and standards, and calculations.

17. Key Words and Document Analysis. 17a. Descriptors

Industrial hygiene
Microanalysis
Atmosphere contamination control
Air pollution
Industrial plants
Industrial atmospheres
Toxicology
Chemical analysis

17b. Identifiers/Open-Ended Terms

Exposure limits
Air quality measurement

17c. COSATI Field/Group 06/J

18. Availability Statement	19. Security Class (This Report)	21.
Release unlimited	UNCLASSIFIED	
	20. Security Class (This Page) UNCLASSIFIED	22. Price PC A01

ii-A

CONTENTS OF VOLUME 2

PART II
Standards Completion Program Validated Methods

Acetone S1
Antimony and compounds (as Sb) S2
2-Butanone S3
Hydrogen sulfide S4
Manganese and compounds (as Mn) S5
Ozone S8
Camphor S10
Mesityl oxide S12
5-Methyl-3-heptanone S13
Methyl (n-amyl) ketone S15
Ethyl butyl ketone S16
Hexone S18
Cyclohexanone S19
2-Pentanone S20
p-tert-Butyltoluene S22
Cumene S23
Vinyl toluene S25
alpha-Methyl styrene S26
Terphenyls S27
Cyclohexane S28
Ethyl benzene S29
Styrene S30
sec-Amyl acetate S31
tert-Butyl acetate S32
Dibutyl phthalate S33
Ethyl acrylate S35
Ethyl formate S36
Methyl isoamyl acetate S37
Methyl acrylate S38
Methyl cellosolve acetate S39
Di-2-Ethylhexyl phthalate S40
2-Ethoxyethyl acetate S41
Methyl acetate S42
Isobutyl acetate S44
Isoamyl acetate S45
sec-Butyl acetate S46
Butyl acetate S47
n-Propyl acetate S48
Ethyl acetate S49
Isopropyl acetate S50
n-Amyl acetate S51
Allyl alcohol S52
sec-Butyl alcohol S53
Cyclohexanol S54
Diacetone alcohol S55
Ethyl alcohol S56
Hydroquinone S57

Isoamyl alcohol S58
Methyl alcohol S59
Methyl isobutyl carbinol S60
Propyl alcohol S62
tert-Butyl alcohol S63
Isobutyl alcohol S64
Isopropyl alcohol S65
Butyl alcohol S66
Chlorinated camphene S67
Dipropylene glycol methyl ether S69
Glycidol S70
Methylal S71
Phenyl ether S72
Phenyl ether-Biphenyl mixture (vapor) S73
Phenyl glycidyl ether S74
Propylene oxide S75
2-Butoxy ethanol S76
Isopropyl glycidyl ether S77
Tetrahydrofuran S78
Methyl cellosolve S79
Ethyl ether S80
n-Butyl glycidyl ether S81
Cyclohexene S82
Naphtha, coal tar S86
Propane S87
Turpentine S88
Heptane S89
Hexane S90
Butadiene S91
Ketene S92
LPG (Liquified petroleum gas) S93
Methylcyclohexane S94
Propylene dichloride S95
Pentachloronaphthalene S96
Octachloronaphthalene S97
Methyl iodide S98
Hexachloronaphthalene S100
Hexachloroethane S101
Fluorotrichloromethane S102
Ethylene chlorohydrin S103
Ethylene dibromide S104
Ethyl bromide S106
Difluorodibromomethane S107
Dichlorotetrafluoroethane S108
Dichloromonofluoromethane S109
1,2-Dichloroethylene S110
Dichlorodifluoromethane S111
Chloroprene S112
Chlorobromomethane S113
Bromoform S114
Benzyl chloride S115

Allyl chloride S116
Acetylene tetrabromide S117
Epichlorohydrin S118
Chlorinated diphenyl oxide S119
Chlorodiphenyl, 54% chlorine S121
Ethylene dichloride S122
1,1-Dichloroethane S123
1,1,2,2-Tetrachloroethane S124
Trifluoromonobromomethane S125
1,2,3-Trichloropropane S126
Trichloronaphthalene S128
1,1,2-Trichloro-1,2,2-trifluoroethane S129
Tetrachloronaphthalene S130
1,1,1,2-Tetrachloro-2,2-difluoroethane S131
1,1,2,2-Tetrachloro-1,2-difluoroethane S132
Chlorobenzene S133
1,1,2-Trichloroethane S134

Index

Acetone

Analyte:	Acetone	Method No.: S1
Matrix:	Air	Range: 1200-4500 mg/cu m
OSHA Standard:	1000 ppm (2380 mg/cu m)	Precision (CV_T): 0.082
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 9/13/74

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 1200-4500 mg/cu m at an atmospheric temperature and pressure of 24°C and 762 mm Hg, using a 2 liter sample. Under the conditions of sample size (2 liters) the probable useful range of this method is 350-5000 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for the 10 mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of acetone and other substances in the air. The first section of the charcoal tube was found to hold no more than 18 mg of acetone when a test atmosphere of 4300 mg/cu m

of acetone in air was sampled at 0.2 (0.195) liter per minute. Under these experimental conditions, after 22 minutes a 5% breakthrough was observed, i.e. the concentration of acetone in the effluent was 5% (215 mg/cu m) of that in the influent (4300 mg/cu m). (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample, since, with differences in polarity, one may displace another from the charcoal.

3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Hence, retention time data on a single column, or even on a number of columns, cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 1200-4500 mg/cu m is 0.082. The relative standard deviation of the method is 4.1%. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 2% lower than the "true" values.

5. Advantages and Disadvantages of the Method

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

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 An approved and calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (4 ft x 1/4 in) packed with 50/80 mesh Porapak, Type Q.

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

6.6 One-milliliter sample containers with glass stoppers or Teflon®-lined caps.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 0.5-ml delivery pipets or 1.0-ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 Acetone, reagent grade.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 2 liters is recommended. This can be accomplished by sampling for 20 minutes at a rate of 0.10 liter per minute. The flow rate should be known with an accuracy of at least $\pm 5\%$.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

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

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process for a given compound, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

For this validation study, the amount injected is equivalent to that present in a 2-liter sample at the selected level.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon®-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 0.5 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period.

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

1. 50 cc/min. (60 psig) nitrogen carrier gas flow
2. 65 cc/min. (24 psig) hydrogen gas flow to detector
3. 500 cc/min. (50 psig) air flow to detector
4. 175°C injector temperature
5. 200°C manifold temperature (detector)
6. 125°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation

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

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

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

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the total mg/sample.

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$mg/cu\ m = \frac{\text{total mg (Section 10.4) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

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

where:

P	= pressure (mm Hg) of air sampled
T	= temperature (°C) of air sampled
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	= molecular weight
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete absorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 0.5 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for absorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/0.5 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.26-1.1 mg/cu m was 0.059. This value corresponds to a 0.03 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in References 11.4 and 11.5.

4.2 A collection efficiency of 99.7% was determined for the collection medium; thus, no bias was introduced in the sample collection step, and the collected samples have been verified to be stable upon storage. Likewise, there was no bias due to analytical method recovery, average recovery was found to be 100.8%. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

5.1 The reliability of this method has been tested using antimony potassium tartrate, antimony metal, and antimony trisulfide as representative compounds. These compounds would exist as particulates at the OSHA standard concentration levels of interest.

5.2 This method will not work for compounds of antimony which exist as a vapor such as stibine.

6. Apparatus

6.1 Sampling Equipment - The sampling unit for the collection of personal air samples for the determination of metal content has the following components:

6.1.1 The filter unit, consisting of the filter media (Section 6.2) and 37-mm, 3-piece cassette filter holder.

6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of ±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 micrometer pore size.

Antimony and Compounds (as Sb)

Analyte:	Antimony	Method No:	S2
Matrix:	Air	Range:	0.258-1.08 mg/cu m
OSHA Standard:	0.5 mg/cu m	Precision ($\overline{CV}_T$):	0.059
Procedure:	Filter collection, Acid digestion, Atomic absorption	Validation Date:	9/30/76

1. Principle of the Method

1.1 Samples are wet ashed using nitric acid to destroy the organic matrix and the antimony (including antimony compounds) is then solubilized in a hydrochloric acid solution maintaining a pH of 1; tartaric acid is added to prevent formation of SbOCl.

1.2 The solutions of samples and standards are aspirated into the air-acetylene flame of an atomic absorption (AA) spectrophotometer. An electrodeless discharge lamp or a hollow cathode lamp for antimony is used to provide a characteristic antimony line at 217.6 nm. The absorbance is proportional to the antimony concentration.

2. Range and Sensitivity

2.1 This method was validated over the range of 0.258-1.08 mg/cu m at an atmospheric temperature and pressure of 24°C and 766 mm Hg, using a 360-liter sample. Under the conditions of sample size (360 liters), the linear working range of the method is estimated to be 0.05-3.0 mg/cu m.

2.2 The method may be extended to higher values by further dilution of the sample solution or by collecting a smaller sample volume.

2.3 The sensitivity of the method can be expressed as 0.5 µg Sb per ml/1% absorption (Reference 11.1).

3. Interferences

3.1 Solutions containing lead at concentrations of 10000 µg/ml showed absorption at 217.6 nm. Similarly, copper when present at 1000 µg/ml would be a positive interference at this wavelength. In the presence of high lead and copper concentrations, the 231.2 nm line should be used. (Reference 11.2)

8.1.2 After initial cleaning, glassware must be cleaned by immersion in chromic acid (a saturated solution of sodium dichromate in concentrated sulfuric acid) and then rinsed thoroughly with warm tap water, concentrated nitric acid, tap water and distilled water, in that order, and then dried.

8.1.3 For glassware which has been previously subjected to the entire cleaning procedure a nitric acid rinse can be used in place of the chromic acid cleaning solution.

8.2 Sampling Requirements and Shipping of Samples

8.2.1 To collect particulate antimony compounds, a personal sampler pump is used to pull air through a cellulose ester membrane filter (Section 6.1). The filter holder is held together by tape or a shrinking band. If the middle piece of the filter holder does not fit snugly into the bottom piece of the filter holder, the contaminant will leak around the filter. A piece of flexible tubing is used to connect the filter holder to the pump. Sample at a flow rate of 1.5 liters per minute with face cap on and small plugs removed. After sampling, replace small plugs.

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

8.2.3 Shipping. The filter cassette should be shipped in a suitable container, designed to prevent damage in transit.

8.3 Analysis of Samples

8.3.1 Open the cassette filter holder and carefully remove the cellulose membrane filter from the holder and cellulose backup pad with the aid of appropriate tweezers and transfer filter to a 125-ml Phillips beaker.

8.3.2 Wet Ashing: To destroy the organic filter matrix, treat the sample in each beaker with 2 ml of concentrated nitric acid. Cover each beaker with a watchglass and heat on a hotplate (140°C) in a fume hood until the filter is dissolved and most of the acid has evaporated. Repeat this process two more times using 2 ml of concentrated nitric acid each time and being careful not to allow the sample to evaporate to dryness.

8.3.3 Antimony dissolution. To ensure complete dissolution of antimony compounds, digest the resulting nitric acid liquor by treating with HCl and heating on a hot plate. This is

6.3 Atomic absorption spectrophotometer, having a monochromator with a reciprocal linear dispersion of about 6.5 Angstrom/mm in the ultraviolet region. The instrument must have the burner head for an acetylene-air flame and a background corrector.

6.3.1 Antimony hollow cathode lamp or electrodeless discharge lamp

6.3.2 Oxidant: compressed air

6.3.3 Fuel: purified acetylene

6.3.4 Pressure-reducing valves, a 2-gauge, 2-stage pressure reducing valve and appropriate hose connections are needed for each compressed gas tank used.

6.4 Glassware, borosilicate:

6.4.1 125 ml Phillips beakers with watchglass covers

6.4.2 Pipets, delivery or graduated, 1, 2, 5, 10 ml

6.4.3 25 ml volumetric flasks

6.4.4 Microliter syringes, 100 µl or other convenient sizes

6.5 Adjustable thermostatically controlled hot plate.

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 Hydrochloric acid, 1:1 aqueous solution and 0.1N

7.4 Tartaric acid, 10% solution

7.5 Commercially prepared aqueous standard stock solution , 1000 µg/ml as antimony.

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.

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

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

9. Calibration and Standards

9.1 From the 1000 µg/ml antimony stock standard solution, prepare at least six standard solutions to cover the antimony concentration range from 20-1000 µg/25 ml. Prepare these standard solutions fresh daily by dilution of appropriate aliquots of the antimony stock standard solution with 2.5 ml of 10% tartaric acid and diluting to volume with 0.1N HCl.

9.2 Proceed as in Section 8.3.6.

9.3 Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard in µg/25 ml. A set of standards should be run both before and after the analysis of a series of samples. It is also advisable to aspirate a standard after every six samples to determine if instrument conditions are changing.

10. Calculations

10.1 Read the weight, in µg, corresponding to the total absorbance from the standard curve. No volume corrections are needed, because the standard curve is based on µg per 25 ml.

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

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

where:

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

10.3 Divide the total weight by the recovery to obtain the corrected µg/sample

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

10.4 For personal sampling pumps with rotameters only, the following correction for air volume sampled should be made.

done by adding 2 ml of 6N aqueous HCl and evaporating to about 0.5 ml; repeat this process three times. Do not allow the solution to evaporate to dryness at any point.

8.3.4 Cool solutions and add 2.5 ml of 10% tartaric acid and 5 ml of distilled water.

8.3.5 Quantitatively transfer the sample solutions into the 25-ml volumetric flasks. Rinse Phillips beaker with distilled water at least 3 times and transfer each rinsing to the 25-ml volumetric flask and dilute to volume.

8.3.6 Aspirate the solutions into an oxidizing air-acetylene flame and record the absorbance at 217.6 nm. The absorbance is proportional to the antimony concentration in the sample and can be determined from the appropriate calibration curve.

Note: Follow instrument manufacturer's recommendations for specific operating parameters.

8.3.7 Appropriate filter blanks must be analyzed following the above 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 from the filter and analyzed as described in Section 8.3. Duplicate determination should agree within $\pm$5%.

For the experimental studies conducted to determine the precision and accuracy of this method, an amount of the analyte equivalent to that present in a 360-liter sample at the selected level has been used for the recovery studies. Six filters at each of the three levels (0.5X, 1X, and 2X the OSHA standard) were spiked accordingly by adding aliquots of an aqueous solution of antimony potassium tartrate. A parallel blank filter was also treated in the same manner except that no sample was added to it. All filters were then digested and analyzed as described in Section 8.3. The average recovery value obtained was found to be 100.8%.

2-Butanone

Analyte:	2-Butanone	Method No.: S3
Matrix:	Air	Range: 380-1240 mg/cu m
OSHA Standard:	200 ppm (590 mg/cu m)	Precision (CV_T): 0.072
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 9/13/74

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 380-1240 mg/cu m at an atmospheric temperature and pressure of 25°C and 761 mm Hg, using a 10 liter sample. Under the conditions of sample size (10 liters) the probable useful range of this method is 70-1500 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for the 15 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of 2-butanone and other substances in the air. The first section of the charcoal tube was found to hold no more than 19 mg of 2-butanone when a test atmosphere of 1260 mg/cu m of 2-butanone in air was sampled at 0.17 liter

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

where:

f = sample flow rate
t = sampling time
P_1= pressure during calibration of sampling pump (mm Hg)
P_2= pressure of air sampled (mm Hg)
T_1= temperature during calibration of sampling pump (°K)
T_2= temperature of air sampled (°K)

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m (µg per liter = mg per cu m).

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

11. References

11.1 Analytical Methods for Atomic Absorption Spectrophototometry, the Perkin-Elmer Corporation, Norwalk, Conn., 1976.

11.2 Christian, Gary and Feldman, Fredric, Atomic Absorption Spectroscopy, Wiley-Interscience, N.Y., p. 422, 1970.

11.3 Methods for Emission Spectrochemical Analysis, ASTM Committee E-2, Philadelphia, 1971.

11.4 Memoranda, Kenneth A. Busch (Chief, Statistical Services, DLCD), to Deputy Director, DLCD, dated 1/6/75, 11/8/74, subject: "Statistical Protocol for Analysis of Data from Contract CDC-99-74-45."

11.5 Backup Data Report for S2, Antimony and Compounds (as Sb) prepared under NIOSH Contract No. 210-76-0123.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 An approved and calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10 ft x 1/8 in) packed with 10% FFAP stationary phase on 80/100 mesh, acid washed DMCS Chromosorb W solid support.

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

6.6 One-milliliter sample containers with glass stoppers or Teflon®-lined caps.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 0.5-ml delivery pipets or 1.0-ml type graduated in 0.1-ml increments.

per minute. Under these experimental conditions, after 86 minutes a 5% breakthrough was observed, i.e. the concentration of 2-butanone in the effluent was 5% (63 mg/cu m) of that in the influent (1260 mg/cu m). (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample, since, with differences in polarity, one may displace another from the charcoal.

3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Hence, retention time data on a single column, or even on a number of columns, cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 380-1240 mg/cu m is 0.072. The standard deviation at the OSHA standard level is 46 mg/cu m. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 9% higher than the "true" values at the OSHA standard level.

5. Advantages and Disadvantages of the Method

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

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon®-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 0.5 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period.

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

1. 50 cc/min. (60 psig) nitrogen carrier gas flow
2. 65 cc/min. (24 psig) hydrogen gas flow to detector
3. 500 cc/min. (50 psig) air flow to detector
4. 100°C injector temperature
5. 200°C manifold temperature (detector)
6. 50°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 2-Butanone, reagent grade.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 10 liters is recommended. This can be accomplished by sampling for 50 minutes at a rate of 0.20 liter per minute. The flow rate should be known with an accuracy of at least $\pm 5\%$.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete absorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 0.5 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for absorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/0.5 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

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

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process for a given compound, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

For this validation study, the amount injected is equivalent to that present in a 10-liter sample at the selected level.

Hydrogen Sulfide

Analyte:	Hydrogen Sulfide	Method No.: S4
Matrix:	Air	Range: 8.5-63 mg/cu m
OSHA Standard:	20 ppm (30 mg/cu m) - Ceiling 50 ppm (70 mg/cu m) - Peak	Precision ($\overline{CV}_T$): 0.121
Procedure:	Absorption - Methylene Blue Spectrophotometric	Validation Date: 9/13/74

1. Principle of the Method

1.1 Hydrogen sulfide is collected by aspirating a measured volume of air through an alkaline suspension of cadmium hydroxide (Reference 11.1). The sulfide is precipitated as cadmium sulfide to prevent air oxidation of the sulfide which occurs rapidly in an aqueous alkaline solution. STRactan 10® is added to the cadmium hydroxide slurry to minimize photo-decomposition of the precipitated cadmium sulfide (Reference 11.2). The collected sulfide is subsequently determined by spectrophotometric measurement of the methylene blue produced by the reaction of the sulfide with an acid solution of N,N-dimethyl-p-phenylenediamine and ferric chloride (References 11.3, 11.4, 11.5).

1.2 Collection efficiency is variable below 10 µg/cu m and is affected by the type of scrubber, the size of the gas bubbles, and the contact time with the absorbing solution and the concentration of hydrogen sulfide (References 11.6, 11.7, 11.8).

2. Range and Sensitivity

2.1 This method was validated over the range of 8.5-63 mg/cu m at an atmospheric temperature and pressure of 25°C and 760 mm Hg, using a 2 liter sample. Under the conditions of sample size (2 liters) the probable useful range of the method is 5-100 mg/cu m. For sample concentrations outside this range the sampling volume should be modified.

3. Interferences

3.1 The methylene blue reaction is highly specific for sulfide at the low concentrations usually encountered in ambient air. Strong

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

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

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

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the total mg/sample.

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$mg/cu\ m = \frac{\text{total mg (Section 10.4) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

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

where:

P	= pressure (mm Hg) of air sampled
T	= temperature (°C) of air sampled
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	= molecular weight
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

5. Advantages and Disadvantages of the Method

5.1 Effect of Light and Storage - Disadvantage

5.1.1 Hydrogen sulfide is readily volatilized from aqueous solution when the pH is below 7.0. Alkaline, aqueous sulfide solutions are very unstable, because sulfide ion is rapidly oxidized by exposure to the air.

5.1.2 Cadmium sulfide is not appreciably oxidized even when aspirated with pure oxygen in the dark. However, exposure of an impinger containing cadmium sulfide to laboratory or to more intense light sources produces an immediate and variable photo-decomposition. Losses of 50-90 per cent of added sulfide have been routinely reported by a number of laboratories. Even though the addition of STRactan 10® to the absorbing solution controls the photo-decomposition (Reference 11.2), it is necessary to protect the impinger from light at all times. This is achieved by the use of low actinic glass impingers, paint on the exterior of the impingers, or an aluminum foil wrapping.

6. Apparatus

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

6.1.1 A graduated 25-ml midget impinger with a standard glass-tapered gas delivery tube containing the absorbing solution or reagent. The impinger should be wrapped in aluminum foil to protect the sample from exposure to light.

6.1.2 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. The sampling pump is protected from splashover or water condensation by an adsorption tube loosely packed with a plug of glass wool and inserted between the exit arm of the impinger and the pump.

6.1.3 An integrating volume meter such as a dry gas or wet test meter or rotameter capable of measuring 2 liters of air at 0.2 liter per minute with an accuracy of ±5%. Instead of these, calibrated hypodermic needles may be used as critical orifices if the pump is capable of maintaining greater than 0.7 atmospheric pressure differential across the needle (Reference 11.10).

6.1.4 Thermometer.

6.1.5 Manometer.

6.1.6 Stopwatch.

reducing agents (e.g. SO_2) inhibit color development. Even sulfide solutions containing several micrograms sulfite per ml show this effect and must be diluted to eliminate color inhibition. If sulfur dioxide is absorbed to give a sulfite concentration in excess of 10 μg/ml color formation is retarded. The use of 0.5 ml of ferric chloride solution during analysis eliminates the SO_2 interference up to 40 μg/ml.

3.2 Nitrogen dioxide gives a pale yellow color with the sulfide reagents at 0.5 μg/ml or more. No interference is encountered when 0.3 ppm NO_2 is aspirated through a midget impinger containing a slurry of cadmium hydroxide-cadmium sulfide-STRactan 10®. If H_2S and NO_2 are simultaneously aspirated through cadmium hydroxide-STRactan 10® slurry, lower H_2S results are obtained, probably because of gas phase oxidation of the H_2S prior to precipitation as CdS (Reference 11.8).

3.3 Ozone at 57 ppb reduced the recovery of sulfide previously precipitated as CdS by 15 per cent (Reference 11.8).

3.4 Substitution of other cation precipitants for the cadmium in the absorbent (i.e. zinc, mercury, etc.) will shift or eliminate the absorbance maximum of the solution upon addition of the acid-amine reagent.

3.5 Cadmium sulfide decomposes significantly when exposed to light unless protected by the addition of 1 per cent STRactan® to the absorbing solution prior to sampling (Reference 11.2).

3.6 The choice of impinger used to trap H_2S with the $Cd(OH)_2$ slurry is very important when measuring concentration in the range 5-100 mg/cu m. Impingers or bubblers having fritted-end gas delivery tubes are a problem source if the sulfide in solution is oxidized to free sulfur by oxygen from the atmosphere. The sulfur collects on the fritted glass membrane and may significantly change the flow rate of the air sample through the system. One way of avoiding this problem is to use a midget impinger with standard glass-tapered tips.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 8.5-63 mg/cu m was 0.121. This value corresponds to a 3.6 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.9.

4.2 On the average the values obtained using the overall sampling and analytical method were 10% higher than the "true" values at the OSHA standard level.

6.2 Associated laboratory glassware.

6.3 Colorimeter with red filter or spectrophotometer at 670 nm.

6.4 Matched cells, 1-cm path length.

7. Reagents

All reagents must be ACS analytical reagent quality. Distilled water should conform to the ASTM Standards for Referee Reagent Water.

All reagents should be refrigerated when not in use.

7.1 Amine-sulfuric Acid Stock Solution. Add 50 ml concentrated sulfuric acid to 30 ml water and cool. Dissolve 12 g of N,N-dimethyl-p-phenylene-diamine dihydrochloride* (para-aminodimethylaniline) (redistilled if necessary) in the acid. Do not dilute. The stock solution may be stored indefinitely under refrigeration.

7.2 Amine Test Solution. Dilute 25 ml of the Stock Solution to 1 liter with 1:1 sulfuric acid.

7.3 Ferric Chloride Solution. Dissolve 100 g of ferric chloride, $FeCl_3 \cdot 6H_2O$ in water and dilute to 100 ml.

7.4 Ethanol, 95%.

7.5 STRactan 10®. (Arabinogalactan) Available from Chicago Scientific, Inc., 716 W. Irving Park Road, Bensenville, IL 60106. Arabinogalactan sold under other brand names may be used.

7.6 Cadmium Sulfate-STRactan® Solution. Dissolve 8.6 g of $3CdSO_4 \cdot 8H_2O$ in approximately 600 ml of water. Add 20 g STRactan 10® and dilute to 1 liter.

7.7 Sodium Hydroxide Solution. Dissolve 0.6 g sodium hydroxide in approximately 600 ml of water and dilute to 1 liter.

7.8 Cadmium Hydroxide-STRactan® Absorbing Solution. This absorbing solution is prepared by pipeting 5 ml of cadmium sulfate-STRactan® solution (7.6) and 5 ml of sodium hydroxide solution (7.7) directly into the midget impinger and mixing. This solution is stable for 3 to 5 days.

7.9 Stock Sodium Sulfide Standard. Place 35.28 g of $Na_2S \cdot 9H_2O$ into a 1 liter volumetric flask and add enough oxygen free distilled water to bring the volume to 1 liter. Store under nitrogen and refrigerate. Standardize with standard iodine and thiosulfate solution in an iodine flask under a nitrogen atmosphere to minimize air oxidation. The approximate concentration of the sulfide solution will be 4700 μg sulfide/ml of solution. The exact concentration must be determined by iodine-thiosulfate standardization immediately prior to dilution.

* 10.5 g N,N-dimethyl-p-phenylenediamine oxalate may be used.

7.10 Working Sodium Sulfide Solution. Dilute 25 ml of stock solution (7.9) with oxygen free water to 250 ml. This solution contains the sulfide equivalent of approximately 500 µg/ml of H_2S. Make fresh working sulfide solution daily. The actual concentration of this solution can be determined from the titration results on the stock sodium sulfide standard (7.9).

For the most accurate results in the iodometric determination of sulfide in aqueous solution, the following general procedure is recommended:

1. Replace the oxygen from the flask by flushing with an inert gas such as carbon dioxide or nitrogen.

2. Add an excess of standard iodine, acidify, and back titrate with standard thiosulfate and starch indicator (Reference 11.14).

8. Procedure

8.1 Cleaning of Equipment. All glassware should be thoroughly cleaned; the following procedure is recommended:

8.1.1 Wash with a detergent and tap water solution followed by tap water and distilled water rinses.

8.1.2 Soak in 1:1 or concentrated nitric acid for 30 minutes and then follow with tap, distilled, and double distilled water rinses.

8.2 Collection and Shipping of Samples

8.2.1 Prepare 10 ml of absorbing solution as described in Section 7.8 directly in the midget impinger. The addition of 5 ml of 95% ethanol to the absorbing solution just prior to aspiration controls foaming for 2 hours (induced by the presence of STRactan 10®). In addition, 1 or 2 Teflon demister discs may be slipped up over the impinger air inlet tube to a height approximately 1 to 2" from the top of the tube. Wrap the impinger with aluminum foil.

8.2.2 Connect the impinger (via the absorption tube) to the sampling pump with a short piece of flexible tubing.

8.2.3 Air being sampled should not be passed through any other tubing or other equipment before entering the impinger.

8.2.4 At the ceiling and peak concentrations, a sample size of 2 liters is recommended. Sample for 10 minutes at a flow of 0.20 liter per minute. The flow rate should be known with an accuracy of at least ±5%.

8.3.5 Measure the absorbance of the color at 670 nm in a spectrophotometer or colorimeter set at 100 per cent transmission against the zero reference.

9. Calibration and Standards

9.1 Aqueous Sulfide

9.1.1 Place 5 ml of each of the absorbing solutions (Sections 7.6 and 7.7) into each of a series of 250 ml volumetric flasks. Add standard sulfide solution equivalent to 0, 20, 40, 80, 120, 160 μg of hydrogen sulfide to the different flasks.

9.1.2 Add 90 ml of distilled water.

9.1.3 Add 15 ml of amine-acid test solution to each flask and mix gently.

9.1.4 Add 0.5 ml of ferric chloride solution to each flask. Mix, make up to volume, and allow to stand for 20 minutes.

9.1.5 Determine the absorbance in a spectrophotometer at 670 nm against the sulfide-free reference solution.

9.1.6 Prepare a standard curve of absorbance versus μg H_2S.

9.2 Gaseous Sulfide. Cylinders of hydrogen sulfide in dry nitrogen in the range desired are available commercially, and may be used to prepare calibration curves for use at the 10-60 mg/cu m levels. Nitrogen containing hydrogen sulfide in the 450-600 mg/cu m range can be diluted to the desired concentrations. Analyses of these known concentrations give calibration curves which simulate all of the operational conditions performed during the sampling and chemical procedure. This calibration curve includes the important correction for collection efficiency at various concentrations of hydrogen sulfide.

9.2.1 Prepare or obtain a cylinder of nitrogen containing hydrogen sulfide in the range of 450-600 mg/cu m.

9.2.2 To obtain standard concentrations of hydrogen sulfide, assemble the apparatus consisting of appropriate pressure regulators, needle valves and flow meters for the nitrogen and for a dry air diluent stream. All stainless steel, glass or rubber tubing must be used for the hydrogen sulfide mixture. Flow of hydrogen sulfide in nitrogen is controlled by a needle valve operated in conjunction with a previously calibrated flow meter in the range of 0.2 to 2.0 liters per minute. Diluent dry air from a cylinder is controlled by a similar needle valve-flow meter combination in the range of 1 to 20 liters per minute. The hydrogen sulfide in nitrogen and the diluent air are combined in a mixing chamber at atmospheric

8.2.5 Turn on the pump to begin sample collection. Care should be taken to measure the flow rate, time and/or volume as accurately as possible.

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

8.2.7 After sampling, the impinger stem must not be removed since it contains CdS deposits. It is necessary to ship the impingers with the stems in so the outlets of the stem should be sealed with Parafilm or other non-rubber covers, and the ground glass joints should be sealed (i.e. taped) to secure the top tightly.

8.2.8 Care should be taken to minimize spillage or loss by evaporation at all times. Refrigerate samples if analysis cannot be done within a day.

8.2.9 Whenever possible, hand delivery of the samples is recommended. Otherwise, special impinger shipping cases designed by NIOSH should be used to ship the samples.

8.2.10 A "blank" impinger should be handled as the other samples (fill, seal, and transport) except that no air is sampled through this impinger.

8.3 Analysis

8.3.1 Remove the impinger top and drain it thoroughly into the impinger bottom. Set aside. Transfer the solution and deposit in the impinger bottom to a 250-ml volumetric flask. Using 50 ml of distilled water rinse the bottom twice with the aid of a clean rubber policeman on a glass stirring rod. Add the rinse solutions to the volumetric flask. With the aid of the rubber policeman wash the outside of the impinger stem with 20 ml of distilled water and add the washings to the flask and drain 20 ml of distilled water through it into the flask. The total wash water volume should be 90 ml.

8.3.2 Add 15 ml of amine test solution through the impinger inlet tube into the volumetric flask. This is necessary to dissolve the CdS deposited inside the inlet tube. Mix gently to avoid loss of H_2S.

8.3.3 Add 0.5 ml of ferric chloride solution and mix. Bring to volume with distilled water. Allow to stand 20 minutes.

8.3.4 Prepare a zero reference solution in the same manner using a 10-ml volume of absorbing solution, through which no air has been aspirated.

9.2.5 If hydrogen sulfide is present at much lower concentrations (1.5 to 140 μg/cu m), commercially available permeation tubes containing liquified hydrogen sulfide may be used to prepare calibration tubes (Reference 11.8, 11.11, 11.12, 13, 14).

10. Calculations

10.1 Gaseous Sulfide

10.1.1 Using the Beers-Law Standard curve of absorbance versus μg H_2S determine μg H_2S in the sampling impinger corresponding to its absorbance reading at 670 nm.

10.1.2 The concentration of H_2S in the air sampled can be expressed in mg/cu m which is numerically equal to μg/liter.

$$\text{mg/cu m} = \mu\text{g/liter} = \frac{\mu\text{g } H_2S \text{ (Section 10.1)}}{\text{Air volume sampled (liter)}}$$

10.1.3 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	= pressure (mm Hg) of air sampled
T	= temperature (°C) of air sampled
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	= molecular weight (g/mole) of analyte
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

11. References

11.1 Jacobs, M.B., Braverman, M.M., and Hochheiser, S. "Ultramicro Determination of Sulfides in Air," Anal. Chem., 29: 1349 (1957).

11.2 Ramesberger, W.L., and Adams, D.F., "Improvements in the Collection of Hydrogen Sulfides in Cadmium Hydroxide Suspension," Environ. Sci. & Tech., 3: 258, (1969).

11.3 Mecklenburg, W., and Rozenkranzer, R., "Colorimetric Determination of Hydrogen Sulfide," A. Anorg. Chem., 86: 143, (1914).

11.4 Almy, L.H., "Estimation of Hydrogen Sulfide in Proteinaceous Food Products," J. Am. Chem. Soc., 47: 1381, (1925).

11.5 Sheppard, S.E., and Hydson, J.H., "Determination of Labile Sulfide in Gelatin and Proteins," Ind. Eng. Chem. Anal. Ed., 2: 73 (1930).

pressure, from which they flow through a baffle tube in which mixing takes place into a 1 liter sampling flask which is provided with one or more nipples from which samples can be taken. Sampling is done by connecting a midget impinger to the nipple and drawing a known volume of the mixture through the impinger for a measured length of time, using a critical orifice to control flow at a constant known rate.

9.2.3 Procedure for Preparing Simulated Calibration Curves. The following description represents a typical procedure for air sampling of short duration.

1. The system is designed to provide an accurate measure of hydrogen sulfide in the 10-60 mg/cu m range. It can be easily modified to meet special needs.

2. The dynamic range of the colorimetric procedure fixes the total volume of the sample at 2 liters; then, to obtain linearity between the absorbance of the solution and the concentration of hydrogen sulfide in mg/cu m, select a constant sampling time. This fixing of the sampling time is desirable also from a practical standpoint. In this case, select a sampling time of 10 minutes. To obtain a 2 liter sample of air requires a flow rate of 0.2 liter per minute. The concentration of standard H_2S in air is computed as follows:

$$C = \frac{cf}{F + f}$$

where:

C = concentration of H_2S in mg/cu m

c = concentration of H_2S in nitrogen, before dilution

F = flow of diluent air, as measured by calibrated flow meter

f = flow of H_2S in nitrogen, as measured by calibrated flow meter.

9.2.4 Commercially prepared hydrogen sulfide in nitrogen can be obtained with a known concentration, as analyzed by the laboratory preparing the gas. If it is desired to check this concentration, measured volume of the gas can be bubbled through the absorbing solutions, and the collected sulfide titrated against iodine-thiosulfate. The volume of gas can be measured using a wet test meter.

MANGANESE AND COMPOUNDS (as Mn)

Analyte:	Manganese	Method No: S5
Matrix:	Air	Range: 2.5 - 10 mg/cu m
OSHA Standard:	5 mg/cu m (ceiling)	Precision ($\overline{CV}_T$): 0.065
Procedure:	Filter collection Acid digestion Atomic absorption	Validation Date: 8/23/74

1. Principle of the Method

1.1 Samples are ashed using nitric acid to destroy the organic matrix and the manganese (including manganese compounds) is then solubilized in a hydrochloric acid solution maintaining a pH of 1.

1.2 The solutions (samples and standards) are aspirated into the oxidizing air-acetylene flame of an atomic absorption (AA) spectrometer flame. A hollow cathode lamp for manganese provides the characteristic and most intense line at 2795 nm. The absorption of this line by the ground state atoms in the flame is proportional to the manganese concentration in the aspirated sample.

2. Range and Sensitivity

2.1 This method was validated over the range of 2.5 - 10 mg/cu m at an atmospheric temperature and pressure of 24°C and 749 mm Hg, using a 20 - 26 liter sample. Under the conditions of sample size (22.5 liters), the working range of the method is estimated to be 0.2 - 20 mg/cu m.

2.2 The sensitivity of this method using the 100 ml final assay solution volume should be adequate for most cases. Since the standard is a ceiling value, measurement of lower atmospheric concentrations should be made by using smaller final solution volumes. The method may similarly be extended to higher values by further dilution of the sample.

11.6 Bostrom, C.E., "The Absorption of Sulfur Dioxide at Low Concentrations (ppnm) Studied by an Isotopic Tracer Method," Air & Water Pollut. Int. J., 9: 333 (1965).

11.7 Bostrom, C.E., "The Adsorption of Low Concentrations (ppmn) of Hydrogen Sulfide in a $Cd(OH)_2$ Suspension as Studied by an Isotopic Tracer Method," Air & Water Pollut. Int. J., 10: 435 (1966).

11.8 Thomas, B.L., and Adams, D.F., Unpublished information.

11.9 Documentation of NIOSH Validation Tests, Contract No. CDC-99-74-45.

11.10 Lodge, J.P., Pate, J.B., Ammons, B.E., Swanson, G.A., "The Use of Hypodermic Needles as Critical Orifices," J. Air Poll. Control Assoc., 16: 197 (1966).

11.11 O'Keeffe, A.E., and Ortman, G.C., "Primary Standards for Trace Gas Analysis," Anal. Chem., 38: 760 (1966).

11.12 O'Keeffe, A.E., and Ortman, G.C., "Precision Picogram Dispenser for Volatile Substances," Anal. Chem., 39: 1047 (1967).

11.13 Scaringelli, F.P., Frey, S.A., and Saltzman, B.E., "Evaluation of Teflon Permeation Tubes for Use with Sulfur Dioxide," Am. Ind. Hyg. Assoc. J., 28: 260 (1967).

11.14 Scaringelli, F.P., Rosenberg, E., and Rehme, K., "Stoichiometric Comparison Between Permeation Tubes and Nitrite Ion as Primary Standards for the Colorimetric Determination of Nitrogen Dioxide," Presented before the Division of Water, Air and Waste Chemistry of the American Chemical Society, 157th National Meeting, Minneapolis, Minn., April 1969.

11.15 Kolthoff, I.M., and Elving, P.J., Eds. Treatise on Analytical Chemistry, Part II, Analytical Chemistry of the Elements, V. 7, Interscience Publishers, New York, 1961.

11.16 Bock, R., and Puff, H.J., "Bestimmung Von Sulfid Mit Einer Sulfidionenempfindlichen Elektrode," Z. Anal. Chem., 240: 381 (1968).

6.3.1 Manganese hollow cathode lamp

6.3.2 Oxidant: compressed air

6.3.3 Fuel: purified acetylene

6.3.4 Pressure-reducing valves, a 2-gauge, 2-stage pressure reducing valve and appropriate hose connections are needed for each compressed gas tank 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

6.4.3 100 ml volumetric flasks

6.4.4 125 ml polyethylene bottles

6.5 Adjustable thermostatically controlled hot plate capable of reaching 400°C.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Distilled or deionized water

7.2 Concentrated nitric acid

7.3 Hydrochloric acid, 1:1 aqueous solution

7.4 Commercially prepared aqueous standard stock solutions; 1000 µg/ml of Manganese

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 by immersion in chromic acid (a saturated solution of sodium dichromate in concentrated sulfuric acid) and then rinsed thoroughly with warm tap water, concentrated nitric acid, tap water and distilled water, in that order, and then dried.

3. Interferences

There are no known interferences for the manganese AA assay.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 2.5 - 10 mg/cu m was 0.065. This value corresponds to a 0.30 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.3.

4.2 On the average the values obtained using the overall sampling and analytical method were 9% lower than the "true" value at the OSHA standard level.

5. Advantages and Disadvantages of the Method

(not applicable)

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 appropriate 37 mm 3-piece cassette filter holder.

6.1.2 Personal Sampling Pump - A calibrated personal sampling pump whose flow can be determined to an accuracy of ±5% (reference 11.4) at the recommended flow rate. The pump must be calibrated with a representative filter holder and filter in the line.

6.2 Mixed cellulose ester membrane filter; 37 mm diameter, 0.8 micrometer pore size.

6.3 Atomic absorption spectrophotometer, having a monochromotor with a reciprocal linear dispersion of about 6.5 Å/mm in the ultraviolet region. The instrument must have the necessary burner heads for the indicated flame.

by three successive additions of 2 ml of aqueous HCl, followed by evaporation to about 0.5 ml after each addition. It is suggested that the solution should not be allowed to evaporate to dryness at any point.

8.3.4 Cool solutions and add 10 ml of distilled (or deionized) water to each one.

8.3.5 Quantitatively transfer the clear solutions into a 100 ml volumetric flask.

8.3.6 Rinse each beaker at least twice with 10 ml portions of distilled water, and quantitatively transfer each rinsing to the solution in the volumetric flask. Dilute all samples to 100 ml with distilled water.

8.3.7 Aspirate the solutions into an oxidizing air-acetylene flame and record the absorbance at 2795 nm. The absorbance is proportional to the sample concentration and can be determined from the appropriate calibration curve. When very low metal concentrations are found in the sample, scale expansion can be used to increase instrument response or the sample could be concentrated to some smaller volume such as 10 ml before aspiration. In such a case, one should not use any more water in 8.3.6 than is necessary to effect a quantitative transfer.

Note: Follow instrument manufacturer's recommendations for specific operating parameters.

8.3.8 Appropriate filter blanks must be analyzed in accordance with the total procedure.

9. Calibration and Standards

9.1 From each of the 1000 µg/ml stock manganese standard solutions, prepare at least 4 working standards to cover the range from 0.05 to 4 µg/ml. All standard solutions are made 0.3 N in HCl and are stored in polyethylene bottles. Since the low concentration standards may deteriorate, the standard solutions should be remade each day.

9.2 Aspirate each of the standards samples 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/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.

8.1.3 For glassware which has previously been subjected to the entire cleaning procedure, a nitric acid rinse will be adequate.

8.2 Sampling Requirements and Shipping of Samples

8.2.1 The OSHA standard (ceiling value) for manganese is 5 mg/cu m.

8.2.2 To collect particulate manganese a personal sampler pump is used to pull air through a cellulose ester membrane filter (Section 6.1). The filter holder is held together by tape or a shrinking band. If the middle piece of the filter holder does not fit snugly into the bottom piece of the filter holder, the contaminant will leak around the filter. A piece of flexible tubing is used to connect the filter holder to the pump. Sample at a flow rate of 1.5 liters per minute with face cap on and small plugs removed. After sampling, replace small plugs.

8.2.3 Sample size: A series of 15 minute samples at a sampling rate of 1.5 lpm is required since the standard is limited to a ceiling value.

8.2.4 Blank: With each batch of samples submit one filter which is subjected to exactly the same handling as for the samples except that no air is drawn through it. Label this as a Blank.

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

8.3 Analysis of Samples

8.3.1 Transfer each sample to a clean 125 ml Phillips beaker.

8.3.2 Wet ashing: To destroy the organic filter matrix, treat the sample in each beaker with 2 ml of concentrated nitric acid. Cover each beaker with a watch glass and heat on a hot plate (140°C) in a fume hood until all the filter is dissolved and most of the acid has evaporated. Repeat this process two more times using 2 ml of concentrated nitric acid each time. It is advisable not to allow the solution to evaporate to dryness.

8.3.3 Manganese dissolution: To ensure complete dissolution of manganese compounds, digest the resulting nitric acid solution by treating with HCl and heating on a high temperature hot plate (400°C). Do this digestion process

OZONE

Analyte:	Ozone	Method No.: S8
Matrix:	Air	Range: 0.1-0.4 mg/cu m
OSHA Standard:	0.1 ppm (0.2 mg/cu m)	Precision (CV_T) = 0.0806
Procedure:	Colorimetric-Alkaline KI Method	Validation Date: 10/11/74

1. Principle of the Method

   1.1 Air containing ozone is drawn through a midget impinger containing 10 ml of 1 percent potassium iodide in 1 N sodium hydroxide. A stable product is formed that can be stored with little loss for several days.

   1.2 The analysis is completed in the laboratory by the addition of phosphoric-sulfamic acid reagent, which liberates the iodine.

   1.3 The yellow iodine color is read in a spectrophotometer at 352 nm.

2. Range and Sensitivity

   2.1 This method has been validated over the range 0.1 to 0.4 mg/cu m. This is the limit of the useful range for the 45 liter sample size. The method is capable of measuring smaller or larger concentrations if the sampling size is adjusted, but it has not been validated for other sample sizes.

3. Interferences

   3.1 Chlorine, hydrogen peroxide, organic peroxides, and various other oxidants will liberate iodine by this method.

   3.2 The response to nitrogen dioxide is limited to 10 percent by the use of sulfamic acid in the procedure to destroy nitrite, thus minimizing any error due to the collection of NO_2.

   3.3 The negative interferences from reducing gases such as sulfur dioxide and hydrogen sulfide are very serious (probably on a mole-to-mole equivalency).

   3.4 The procedure is very sensitive to reducing dusts that may be present in the air or on the glassware. Losses of iodine also occur even on clean glass surfaces and thus the manipulations should minimize this exposure.

10. Calculations

10.1 From the calibration curve, read the concentration (µg/ml) in the analyzed samples.

10.2 Blank values, if any, are to be subtracted from each observed sample value.

10.3 Convert the volume of air collected to normal conditions of 25°C and 760 mm Hg as follows:

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

where:

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

V = volume of air in liters as measured

P = Barometric pressure in mm Hg

T = Temperature of air in degrees Celsius

10.4 To determine the concentration of Mn in the air sample the observed solution concentration is multiplied by the final solution volume which was used for analysis and divided by the volume of air sampled (in liters, referenced to normal conditions of 25°C and 760 mm Hg).

$$\text{Mn mg/cu m} = \frac{\text{µg Mn/ml} \times \text{solution volume}}{\text{liters of air collected}}$$

11. References

11.1 Analytical Methods for Atomic Absorption Spectrophotometry, The Perkin-Elmer Corp., Norwalk, Conn., 1971.

11.2 Methods for Emission Spectrochemical Analysis, ASTM Committee E-2, Philadelphia, 1971.

11.3 "Documentation of NIOSH Validation Tests", Contract No. CDC-99-74-45, NIOSH TR.

11.4 NIOSH TR (pump reference)

make the mixture to 1 liter. Store in a clean glass bottle with a screw cap (with inert liner) or rubber stopper (previously boiled for 30 minutes in alkali and washed). Age for at least 1 day before using. The reagent should be used within two weeks.

7.3 Acidifying reagent. Dissolve 5.0 g of sulfamic acid in 100 ml of water, then add 84 ml of 85 percent phospheric acid and dilute to 200 ml.

7.4 Standard potassium iodate solution. Dissolve 0.758 g of potassium iodate in water and dilute to 1 liter. One ml of this stock solution is equivalent to 400 µl of ozone. Prepare a dilute standard solution just before it is required by pipetting exactly 5 ml of stock solution into a 50-ml volumetric flask and making to mark with distilled water.

8. Procedure

8.1 Cleaning of equipment. All glassware should be cleaned with dichromate cleaning solution followed by 3 tap and 3 distilled water rinses.

8.2 Collection of samples

8.2.1 Assemble a train composed of a midget impinger, a rotameter, and pump. Use ground glass connections upstream from the impinger. Insure that all fittings are vacuum tight.

8.2.2 Pipette exactly 10 ml of the absorbing solution into the midget impinger and sample at a flow rate of 1 liter per minute. Note the volume of air sampled. Record atmospheric temperature and pressure.

8.2.3 Cap the impinger with the stopper supplied for shipment to the laboratory.

8.3 Analysis

8.3.1 If the liquid level is below the 10-ml mark in the impinger, add distilled water to bring the level up to the mark.

8.3.2 Add 2 ml of the acidifying reagent with a volumetric pipette. Swirl gently to expel the carbon dioxide released immediately. Then cap and shake vigorously until bubbling ceases. It is imperative that all of the carbon dioxide is expelled, otherwise more may be released while the u.v. measurement is being made.

8.3.3 Place the stoppered impinger in a water bath at room temperature for 5 to 10 minutes to dissipate the heat of neutralization.

4. Precision and Accuracy

4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 0.1 to 0.4 mg/cu m is 0.0806. The standard deviation at the OSHA standard level is 0.0077 mg/cu m. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average, the values obtained using the overall sampling and analytical method were the same as the true value at the OSHA standard level.

4.3 These data are based on validation experiments in which neutral buffered KI was used to determine the actual ozone concentration.

5. Advantages and Disadvantages of the Method

5.1 The method is simple, accurate and precise.

5.2 Those compounds listed in 3.1 will liberate iodine by this method.

5.3 A delay of several days is permissable between sampling and completion of analysis. However, the relationship between delay and analytical results has not been established.

6. Apparatus

6.1 Midget impinger with 1 mm ID nozzle, graduation marks and Teflon-coated ground glass stopper.

6.2 Personal sampling pump capable of drawing the required sample flow for intervals of up to 45 minutes.

6.3 Air metering device capable of measuring a flow of 1 to 2 liters per minute, including a prefilter to prevent liquid droplets from reaching the measuring device.

6.4 Spectrophotometer capable of measuring the yellow color at 352 nm with stoppered tubes or cuvettes.

6.5 Associated laboratory glassware.

7. Reagents

The reagents described must be made up using ACS reagent grade or better grade of chemical.

7.1 Double distilled water.

7.2 Absorbing reagent. Dissolve 40.0 g of sodium hydroxide in almost a liter of water, then dissolve 10.0 g of potassium iodide and

$$O_3\ (mg/m^3) = \frac{\text{ozone equivalence}}{\text{air volume (liters)}}$$

The reaction of ozone with alkaline KI is not quantitative and the yield of iodine is concentration dependent. The following correction equation was developed during validation of the method.

$$O_3\ (mg/cu\ m) = 0.038 + 1.038A - 0.010505A^2$$

where A is the concentration of ozone (also in mg/cu m) read from the absorbance curve.

10.3 Another method of expressing concentration is ppm, defined as µl of ozone per liter of air

$$ppm\ O_3 = O_3\ (mg/cu\ m) \times \frac{24.45}{48} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (C) of air sampled
24.45 = molar volume (l/mole) at 25 C and 760 mm Hg
48 = molecular weight (g/mole) of ozone
760 = standard pressure (mm Hg)
298 = standard temperature (K)

11. References

11.1 "Selected Methods for the Measurement of Air Pollutants" USDHEW Public Health Service Publication Number 999-AP-11, 1965.

11.2 "Documentation of NIOSH Validation Tests", Contract No. CDC-99-74-45.

8.3.4 Transfer a portion of the sample to a cuvette and determine the absorbance at 352 nm. A cuvette containing distilled water is used as the reference. Do not delay the reading since reducing impurities sometimes causes rapid fading of the color.

8.3.5 Prepare a reagent blank by adding 2 ml of the acidifying reagent to ml of unexposed absorbing reagent. Cool and determine the blank absorbance. The blank absorbance should be determined each day and should be subtracted from the absorbance of the samples.

8.3.6 Samples may be aliquoted before or after acidification if very large concentrations of oxidant are expected. In the former case dilute the aliquot to 10 ml with unexposed absorbing reagent and proceed in the usual manner. In the latter case dilute the aliquot to 10 ml with reagent blank mixture. Aliquoting after acidifcation is not as reliable as before acidification and should be used only to save a sample when unexpectedly large concentrations of oxidant are encountered. The calculations should include the aliquoting factor.

9. Calibration and Standards

9.1 Add the freshly prepared, dilute standard iodate solution in graduated amounts of 0.10 to 0.5 ml (measured accurately in a graduated pipette or small burette) to a series of 25-ml glass stoppered volumetric flasks. Make at least 4 standards.

9.2 Add alkaline potassium iodide solution (measured accurately in a graduated pipette) to make the total volume of each exactly 10 ml.

9.3 Acidify and determine the absorbance of each standard as with the samples.

10. Calculations

10.1 Plot the absorbance of the standards (corrected for the blank) against the concentration of dilute standard iodate solution. One (1) ml of the diluted standard iodate solution (in a total of 10-ml absorbing solution per Section 9) is equivalent to 51 mg of ozone. To readily determine ambient ozone concentrations in units of mg/m^3, it is convenient to plot absorbance versus mg equivalents of ozone per 10 ml of absorbing solution.

10.2 Upon determining the absorbance of the sample solutions, use the standard absorbance curve to find the ozone equivalence. The concentration of ozone in the air sample equals the ozone equivalence divided by the air volume in liters.

CAMPHOR

Analyte:	Camphor	Method No.: S10
Matrix:	Air	Range: 6-27 mg/cu m
OSHA Standard:	2 ppm (12.5 mg/cu m)	Precision (CV_T): 0.0737
Procedure:	Adsorption on charcoal, desorption with eluent, GC	Validation Date: 10/11/74

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide containing 1% methanol.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 6-25 mg/cu m at an atmospheric temperature and pressure of 25 C and 751 mm Hg, using a nominal 20 liter sample. Under the conditions of sample size (20 liters) the probable range of this method is 1-40 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 0.75 mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of the analyte and other substances in the air. The first section of the charcoal tube was found to hold at least 1 mg of the analyte when a test atmosphere of 26.8 mg/cu m of the analyte in dry air was sampled at 0.2 liters per minute.

After 48 liters of the test atmosphere was sampled, there was no detectable change in the concentration of the analyte in the effluent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2.) If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments indicate that high humidity severely decreases the breakthrough volume.

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

3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 115 to 460 mg/cu m was 0.0737. The standard deviation at the OSHA standard level was 0.21 mg/cu m. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 The average values obtained using the overall sampling and analytical method were 1% higher than the "true" value at the OSHA standard level.

4.3 The above data are based on validation experiments using the internal standard method. (Reference 11.2)

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more compounds suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 An approved and calibrated personal sampling pump whose flow can be determined accurately (±5%) at the recommended flow rate. (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600 C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10 ft x 1/8 in. stainless steel) packed with 10% FFAP on 80/100 Chromosorb W-AW.

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

6.6 Two-milliliter glass sample containers with glass stoppers or Teflon®-lined caps. If an automatic sample injector is used, the sample injector vials can be used.

6.7 Microliter syringes: 10-µl, and other convenient sizes for making standards.

6.8 Pipets: 1.0-ml delivery type.

6.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Eluent: Carbon disulfide (chromatographic grade) containing 1% methanol (reagent grade).

7.2 Camphor (reagent grade).

7.3 Internal Standard: n-Tridecane (99+%).

7.4 n-Heptane (reagent grade).

7.5 Purified nitrogen.

7.6 Prepurified hydrogen.

7.7 Filtered compressed air.

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 10 liters is recommended. This can be accomplished by sampling for 100 minutes at a rate of 0.20 liters per minute. The flow rate should be known with an accuracy of at least ±5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available the elevation should be recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

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

8.3.10 A sample of the suspected compound should be submitted to the laboratory in glass containers with Teflon®-lined caps. These liquid bulk samples should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container or automatic sample injector vial. The separating section of foam is removed and discarded; the second section is transferred to another sample container or vial. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of the eluent is pipetted into each sample container. For the internal standard method a 0.1 percent solution of internal standard in the eluent is used. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period.

If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization.

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

1. 30 ml/min (80 psig) nitrogen carrier gas flow.
2. 30 ml/min (50 psig) hydrogen gas flow to detector.
3. 300 ml/min (50 psig) air flow to detector.
4. 200 C injector temperature.
5. 300 C manifold temperature (detector).

6. 120 C column temperature.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-µl syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 µl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-µl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 µl to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 µl in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique. In this case 2-µl injections are satisfactory.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below (see Section 9).

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided that the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.0-ml sample container. This charcoal must be from

the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. A 6.23 percent stock solution of the analyte in n-heptane is prepared. A known amount of this solution is injected directly into the activated charcoal with a 10-µl syringe, and the container is capped. The amount injected is equivalent to that present in a 10-liter sample at the selected level. It is not practical to inject the neat liquid directly because the amounts to be added would be too small to measure accurately.

At least six tubes at each of three levels (0.5X, 1X, and 2X the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete absorption of the analyte onto the charcoal. These six tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

The weight of analyte found in each tube is determined from the standard curve (Section 9). Desorption efficiency is determined by the following equation:

$$\text{D.E.} = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/ml of eluent. To minimize error due to the volatility of the eluent, one can add 10 times the weight to 10 ml of the eluent. (For the internal standard method use eluent containing 0.1 percent of the internal standard.) A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentrations in mg/ml versus peak area. In the case of the internal standard method plot the concentration versus the ratio of peak area of analyte to peak area of internal standard.

Note: Whether the absolute area of internal standard method is used standard solutions should be analyzed at the same time that the sample analysis is done. This will minimize the effect variations of FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area (area ratio in case of the internal standard method) from the standard curve. No volume corrections are needed, because the standard curve is based on mg/ml eluent and the volume of sample injected is identical to the volume of the standards injected.

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

$$mg = mg_s - mg_b$$

where:

mg_s = mg found in front section of sample tube

mg_b = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

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

10.4 Read the desorption efficiency from the curve (Section 8.5.2) for the amount of analyte found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

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

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm:

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (C) of air sampled
24.45 = molar volume (liter/mole) at 25 C and 760 mm Hg
MW = molecular weight (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (K)

11. References

11.1 White L. D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 "Documentation of NIOSH Validation Tests", Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract No. HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes, September 15, 1972."

MESITYL OXIDE

Analyte:	Mesityl Oxide	Method No.: S12
Matrix:	Air	Range: 45-210 mg/cu m
OSHA Standard:	25 ppm (100 mg/cu m)	Precision (CV_T): 0.0708
Procedure:	Adsorption on charcoal, desorption with eluent, GC	Validation Date: 10/11/74

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide containing 1% methanol.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 45-210 mg/cu m at an atmospheric temperature and pressure of 25 C and 754 mm Hg, using a nominal 10 liter sample. Under the conditions of sample size (10 liters) the probable range of this method is 10-300 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 3 mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of the analyte and other substances in the air. The first section of the charcoal tube was found to hold at least 9.6 mg of the analyte when a test atmosphere of 210 mg/cu m of the analyte in dry air was sampled at 0.2 liters per minute.

After 48 liters of the test atmosphere was sampled, the concentration of the analyte in the effluent was less than 0.25% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2.) If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments indicate that high humidity severely decreases the breakthrough volume.

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

3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 45 to 210 mg/cu m was 0.0708. The standard deviation at the OSHA standard level was 7.8 mg/cu m. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 The average values obtained using the overall sampling and analytical method were 7% higher than the "true" value at the OSHA standard level.

4.3 The above data are based on validation experiments using the internal standard method. (Reference 11.2)

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more compounds suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 An approved and calibrated personal sampling pump whose flow can be determined accurately (±5%) at the recommended flow rate. (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600 C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10 ft x 1/8 in. stainless steel) packed with 10% FFAP on 80/100 Chromosorb W-AW.

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

6.6 Two-milliliter glass sample containers with glass stoppers or Teflon®-lined caps. If an automatic sample injector is used, the sample injector vials can be used.

6.7 Microliter syringes: 10-µl, and other convenient sizes for making standards.

6.8 Pipets: 1.0-ml delivery type.

6.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Eluent: Carbon disulfide (chromatographic grade) containing 1% methanol (reagent grade).

7.2 Mesityl Oxide (reagent grade).

7.3 Internal Standard: n-Tridecane (99+%).

7.4 n-Heptane (reagent grade).

7.5 Purified nitrogen.

7.6 Prepurified hydrogen.

7.7 Filtered compressed air.

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 10 liters is recommended. This can be accomplished by sampling for 50 minutes at a rate of 0.20 liters per minute. The flow rate should be known with an accuracy of at least ±5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available the elevation should be recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

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

8.3.10 A sample of the suspected compound should be submitted to the laboratory in glass containers with Teflon®-lined caps. These liquid bulk samples should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container or automatic sample injector vial. The separating section of foam is removed and discarded; the second section is transferred to another sample container or vial. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of the eluent is pipetted into each sample container. For the internal standard method a 0.1 percent solution of internal standard in the eluent is used. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period.

If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization.

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

1. 30 ml/min (80 psig) nitrogen carrier gas flow.
2. 30 ml/min (50 psig) hydrogen gas flow to detector.
3. 300 ml/min (50 psig) air flow to detector.
4. 200 C injector temperature.
5. 300 C manifold temperature (detector).

6. 120 C column temperature.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-µl syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 µl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-µl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 µl to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 µl in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique. In this case 2-µl injections are satisfactory.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below (see Section 9).

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided that the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.0-ml sample container. This charcoal must be from

the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. An 8 percent stock solution of the analyte in n-heptane is prepared. A known amount of this solution is injected directly into the activated charcoal with a 10-µl syringe, and the container is capped. The amount injected is equivalent to that present in a 10-liter sample at the selected level. It is not practical to inject the neat liquid directly because the amounts to be added would be too small to measure accurately.

At least six tubes at each of three levels (0.5X, 1X, and 2X the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete absorption of the analyte onto the charcoal. These six tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

The weight of analyte found in each tube is determined from the standard curve (Section 9). Desorption efficiency is determined by the following equation:

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/ml of eluent. To minimize error due to the volatility of the eluent, one can add 10 times the weight to 10 ml of the eluent. (For the internal standard method use eluent containing 0.1 percent of the internal standard.) A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentrations in mg/ml versus peak area. In the case of the internal standard method plot the concentration versus the ratio of peak area of analyte to peak area of internal standard.

Note: Whether the absolute area of internal standard method is used standard solutions should be analyzed at the same time that the sample analysis is done. This will minimize the effect variations of FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area (area ratio in case of the internal standard method) from the standard curve. No volume corrections are needed, because the standard curve is based on mg/ml eluent and the volume of sample injected is identical to the volume of the standards injected.

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

$$mg = mg_s - mg_b$$

where:

mg_s = mg found in front section of sample tube

mg_b = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

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

10.4 Read the desorption efficiency from the curve (Section 8.5.2) for the amount of analyte found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

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

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm:

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (C) of air sampled
24.45 = molar volume (liter/mole) at 25 C and 760 mm Hg
MW = molecular weight (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (K)

11. References

11.1 White L. D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 "Documentation of NIOSH Validation Tests", Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract No. HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes, September 15, 1972."

5-METHYL-3-HEPTANONE*

Analyte:	5-Methyl-3-heptanone	Method No.:	S13
Matrix:	Air	Range:	60-270 mg/cu m
OSHA Standard:	25 ppm (130 mg/cu m)	Precision (CV_T):	0.1043
Procedure:	Adsorption on charcoal, desorption with eluent, GC	Validation Date:	10/11/74

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide containing 1% methanol.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 60-270 mg/cu m at an atmospheric temperature and pressure of 25 C and 754 mm Hg, using a nominal 10 liter sample. Under the conditions of sample size (10 liters) the probable range of this method is 15-400 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 2.6 mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of the analyte and other substances in the air. The first section of the charcoal tube was found to hold at least 9 mg of the analyte when a test atmosphere of 250 mg/cu m of the analyte in dry air was sampled at 0.2 liters per minute.

*Listed incorrectly as Ethyl sec-amyl ketone in 29 CFR 1910.63.

After 36 liters of the test atmosphere was sampled, the concentration of the analyte in the effluent was 1.25% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2.) If a particular atmosphere is suspected of containing a large amount of contaminants, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments indicate that high humidity severely decreases the breakthrough volume.

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

3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 60 to 270 mg/cu m was 0.1043. The standard deviation at the OSHA standard level was 12.8 mg/cu m. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 The average values obtained using the overall sampling and analytical method were 15% higher than the "true" value at the OSHA standard level.

4.3 The above data are based on validation experiments using the internal standard method. (Reference 11.2)

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more compounds suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 An approved and calibrated personal sampling pump whose flow can be determined accurately (±5%) at the recommended flow rate. (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600 C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10 ft x 1/8 in. stainless steel) packed with 10% FFAP on 80/100 Chromosorb W-AW.

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

6.6 Two-milliliter glass sample containers with glass stoppers or Teflon®-lined caps. If an automatic sample injector is used, the sample injector vials can be used.

6.7 Microliter syringes: 10-µl, and other convenient sizes for making standards.

6.8 Pipets: 1.0-ml delivery type.

6.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Eluent: Carbon disulfide (chromatographic grade) containing 1% methanol (reagent grade).

7.2 5-Methyl-3-heptanone (reagent grade).

7.3 Internal Standard: n-Tridecane (99+%).

7.4 n-Heptane (reagent grade).

7.5 Purified nitrogen.

7.6 Prepurified hydrogen.

7.7 Filtered compressed air.

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 10 liters is recommended. This can be accomplished by sampling for 50 minutes at a rate of 0.20 liters per minute. The flow rate should be known with an accuracy of at least ±5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available the elevation should be recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

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

8.3.10 A sample of the suspected compound should be submitted to the laboratory in glass containers with Teflon®-lined caps. These liquid bulk samples should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container or automatic sample injector vial. The separating section of foam is removed and discarded; the second section is transferred to another sample container or vial. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of the eluent is pipetted into each sample container. For the internal standard method a 0.1 percent solution of internal standard in the eluent is used. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period.

If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization.

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

1. 30 ml/min (80 psig) nitrogen carrier gas flow.
2. 30 ml/min (50 psig) hydrogen gas flow to detector.
3. 300 ml/min (50 psig) air flow to detector.
4. 200 C injector temperature.
5. 300 C manifold temperature (detector).

6. 120 C column temperature.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-µl syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 µl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-µl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 µl to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 µl in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique. In this case 2-µl injections are satisfactory.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below (see Section 9).

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided that the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.0-ml sample container. This charcoal must be from

the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. A 10.4 percent stock solution of the analyte in n-heptane is prepared. A known amount of this solution is injected directly into the activated charcoal with a 10-µl syringe, and the container is capped. The amount injected is equivalent to that present in a 10-liter sample at the selected level. It is not practical to inject the neat liquid directly because the amounts to be added would be too small to measure accurately.

At least six tubes at each of three levels (0.5X, 1X, and 2X the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete absorption of the analyte onto the charcoal. These six tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

The weight of analyte found in each tube is determined from the standard curve (Section 9). Desorption efficiency is determined by the following equation:

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/ml of eluent. To minimize error due to the volatility of the eluent, one can add 10 times the weight to 10 ml of the eluent. (For the internal standard method use eluent containing 0.1 percent of the internal standard.) A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentrations in mg/ml versus peak area. In the case of the internal standard method plot the concentration versus the ratio of peak area of analyte to peak area of internal standard.

Note: Whether the absolute area of internal standard method is used standard solutions should be analyzed at the same time that the sample analysis is done. This will minimize the effect variations of FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area (area ratio in case of the internal standard method) from the standard curve. No volume corrections are needed, because the standard curve is based on mg/ml eluent and the volume of sample injected is identical to the volume of the standards injected.

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

$$mg = mg_s - mg_b$$

where:

mg_s = mg found in front section of sample tube

mg_b = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

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

10.4 Read the desorption efficiency from the curve (Section 8.5.2) for the amount of analyte found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

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

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm:

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (C) of air sampled
24.45 = molar volume (liter/mole) at 25 C and 760 mm Hg
MW = molecular weight (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (K)

11. References

11.1 White L. D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 "Documentation of NIOSH Validation Tests", Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract No. HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes, September 15, 1972."

METHYL n-AMYL KETONE

Analyte:	Methyl n-Amyl Ketone	Method No.: S15
Matrix:	Air	Range: 200-925 mg/cu m
OSHA Standard:	100 ppm (465 mg/cu m)	Precision (CV_T): 0.0660
Procedure:	Adsorption on charcoal, desorption with eluent, GC	Validation Date: 10/11/74

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide containing 1% methanol.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 200-925 mg/cu m at an atmospheric temperature and pressure of 25 C and 755 mm Hg, using a nominal 10 liter sample. Under the conditions of sample size (10 liters) the probable range of this method is 50-1000 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 9.6 mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of the analyte and other substances in the air. The first section of the charcoal tube was found to hold at least 15 mg of the analyte when a test atmosphere of 925 mg/cu m of the analyte in dry air was sampled at 0.2 liters per minute.

After 36 liters of the test atmosphere was sampled, the concentration of the analyte in the effluent was less than 1% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2.) If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments indicate that high humidity severely decreases the breakthrough volume.

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

3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 200 to 925 mg/cu m was 0.0660. The standard deviation at the OSHA standard level was 15.7 mg/cu m. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 The average values obtained using the overall sampling and analytical method were 2% higher than the "true" value at the OSHA standard level.

4.3 The above data are based on validation experiments using the internal standard method. (Reference 11.2)

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more compounds suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 An approved and calibrated personal sampling pump whose flow can be determined accurately (±5%) at the recommended flow rate. (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600 C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10 ft x 1/8 in. stainless steel) packed with 10% FFAP on 80/100 Chromosorb W-AW.

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

6.6 Two-milliliter glass sample containers with glass stoppers or Teflon®-lined caps. If an automatic sample injector is used, the sample injector vials can be used.

6.7 Microliter syringes: 10-µl, and other convenient sizes for making standards.

6.8 Pipets: 1.0-ml delivery type.

6.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Eluent: Carbon disulfide (chromatographic grade) containing 1% methanol (reagent grade).

7.2 Methyl m-amyl ketone (2-heptanone, reagent grade).

7.3 Internal Standard: n-Tridecane (99+%).

7.4 n-Heptane (reagent grade).

7.5 Purified nitrogen.

7.6 Prepurified hydrogen.

7.7 Filtered compressed air.

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 10 liters is recommended. This can be accomplished by sampling for 50 minutes at a rate of 0.20 liters per minute. The flow rate should be known with an accuracy of at least ±5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available the elevation should be recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

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

8.3.10 A sample of the suspected compound should be submitted to the laboratory in glass containers with Teflon®-lined caps. These liquid bulk samples should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container or automatic sample injector vial. The separating section of foam is removed and discarded; the second section is transferred to another sample container or vial. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of the eluent is pipetted into each sample container. For the internal standard method a 0.1 percent solution of internal standard in the eluent is used. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period.

If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization.

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

1. 30 ml/min (80 psig) nitrogen carrier gas flow.
2. 30 ml/min (50 psig) hydrogen gas flow to detector.
3. 300 ml/min (50 psig) air flow to detector.
4. 200 C injector temperature.
5. 300 C manifold temperature (detector).

6. 120 C column temperature.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-µl syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 µl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-µl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 µl to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 µl in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique. In this case 2-µl injections are satisfactory.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below (see Section 9).

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided that the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.0-ml sample container. This charcoal must be from

the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. A known amount of the analyte is injected directly into the activated charcoal with a 10-µl syringe, and the container is capped. The amount injected is equivalent to that present in a 10-liter sample at the selected level.

At least six tubes at each of three levels (0.5X, 1X, and 2X the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete absorption of the analyte onto the charcoal. These six tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

The weight of analyte found in each tube is determined from the standard curve (Section 9). Desorption efficiency is determined by the following equation:

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/ml of eluent. To minimize error due to the volatility of the eluent, one can add 10 times the weight to 10 ml of the eluent. (For the internal standard method use eluent containing 0.1 percent of the internal standard.) A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentrations in mg/ml versus peak area. In the case of the internal standard method plot the concentration versus the ratio of peak area of analyte to peak area of internal standard.

Note: Whether the absolute area of internal standard method is used standard solutions should be analyzed at the same time that the sample analysis is done. This will minimize the effect variations of FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area (area ratio in case of the internal standard method) from the standard curve. No volume corrections are needed, because the standard curve is based on mg/ml eluent and the volume of sample injected is identical to the volume of the standards injected.

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

$$mg = mg_s - mg_b$$

where:

mg_s = mg found in front section of sample tube

mg_b = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

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

10.4 Read the desorption efficiency from the curve (Section 8.5.2) for the amount of analyte found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

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

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm:

$$\text{ppm} = \text{mg/cu. m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (C) of air sampled
24.45 = molar volume (liter/mole) at 25 C and 760 mm Hg
MW = molecular weight (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (K)

11. References

11.1 White L. D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 "Documentation of NIOSH Validation Tests", Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract No. HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes, September 15, 1972."

ETHYL BUTYL KETONE

Analyte:	Ethyl butyl ketone (3-heptanone)	Method No.: S16
Matrix:	Air	Range: 100-460 mg/cu m
OSHA Standard:	50 ppm (230 mg/cu m)	Precision (CV_T): 0.0864
Procedure:	Adsorption on charcoal, desorption with eluent, GC	Validation Date: 10/11/74

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide containing 1% methanol.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 100-460 mg/cu m at an atmospheric temperature and pressure of 25 C and 758 mm Hg, using a nominal 10 liter sample. Under the conditions of sample size (10 liters) the probable range of this method is 25-700 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 4.6 mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of the analyte and other substances in the air. The first section of the charcoal tube was found to hold at least 11 mg of the analyte when a test atmosphere of 460 mg/cu m of the analyte in dry air was sampled at 0.2 liters per minute.

After 24 liters of the test atmosphere was sampled, the concentration of the analyte in the effluent was less than 1% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2.) If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments indicate that high humidity severely decreases the breakthrough volume.

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

3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 100 to 460 mg/cu m was 0.0864. The standard deviation at the OSHA standard level was 26.2 mg/cu m. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 The average values obtained using the overall sampling and analytical method were 7% higher than the "true" value at the OSHA standard level.

4.3 The above data are based on validation experiments using the internal standard method. (Reference 11.2)

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more compounds suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 An approved and calibrated personal sampling pump whose flow can be determined accurately (±5%) at the recommended flow rate. (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600 C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10 ft x 1/8 in. stainless steel) packed with 10% FFAP on 80/100 Chromosorb W-AW.

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

6.6 Two-milliliter glass sample containers with glass stoppers or Teflon®-lined caps. If an automatic sample injector is used, the sample injector vials can be used.

6.7 Microliter syringes: 10-µl, and other convenient sizes for making standards.

6.8 Pipets: 1.0-ml delivery type.

6.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Eluent: Carbon disulfide (chromatographic grade) containing 1% methanol (reagent grade).

7.2 Ethyl butyl ketone (3-heptanone) (reagent grade).

7.3 Internal Standard: n-Tridecane (99+%).

7.4 n-Heptane (reagent grade).

7.5 Purified nitrogen.

7.6 Prepurified hydrogen.

7.7 Filtered compressed air.

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 10 liters is recommended. This can be accomplished by sampling for 50 minutes at a rate of 0.20 liters per minute. The flow rate should be known with an accuracy of at least ±5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available the elevation should be recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

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

8.3.10 A sample of the suspected compound should be submitted to the laboratory in glass containers with Teflon®-lined caps. These liquid bulk samples should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container or automatic sample injector vial. The separating section of foam is removed and discarded; the second section is transferred to another sample container or vial. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of the eluant is pipetted into each sample container. For the internal standard method a 0.1 percent solution of internal standard in the eluent is used. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period.

If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization.

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

1. 30 ml/min (80 psig) nitrogen carrier gas flow.
2. 30 ml/min (50 psig) hydrogen gas flow to detector.
3. 300 ml/min (50 psig) air flow to detector.
4. 200 C injector temperature.
5. 300 C manifold temperature (detector).

6. 120 C column temperature.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-µl syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 µl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-µl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 µl to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 µl in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique. In this case 2-µl injections are satisfactory.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below (see Section 9).

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided that the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.0-ml sample container. This charcoal must be from

the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. A 5.75 percent stock solution of the analyte in n-heptane is prepared. A known amount of this solution is injected directly into the activated charcoal with a 10-µl syringe, and the container is capped. The amount injected is equivalent to that present in a 10-liter sample at the selected level. It is not practical to inject the neat liquid directly because the amounts to be added would be too small to measure accurately.

At least six tubes at each of three levels (0.5X, 1X, and 2X the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete absorption of the analyte onto the charcoal. These six tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

The weight of analyte found in each tube is determined from the standard curve (Section 9). Desorption efficiency is determined by the following equation:

$$\text{D.E.} = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/ml of eluent. To minimize error due to the volatility of the eluent, one can add 10 times the weight to 10 ml of the eluent. (For the internal standard method use eluent containing 0.1 percent of the internal standard.) A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentrations in mg/ml versus peak area. In the case of the internal standard method plot the concentration versus the ratio of peak area of analyte to peak area of internal standard.

Note: Whether the absolute area of internal standard method is used standard solutions should be analyzed at the same time that the sample analysis is done. This will minimize the effect variations of FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area (area ratio in case of the internal standard method) from the standard curve. No volume corrections are needed, because the standard curve is based on mg/ml eluent and the volume of sample injected is identical to the volume of the standards injected.

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

$$mg = mg_s - mg_b$$

where:

mg_s = mg found in front section of sample tube

mg_b = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

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

10.4 Read the desorption efficiency from the curve (Section 8.5.2) for the amount of analyte found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

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

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm:

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (C) of air sampled
24.45 = molar volume (liter/mole) at 25 C and 760 mm Hg
MW = molecular weight (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (K)

11. References

11.1 White L. D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 "Documentation of NIOSH Validation Tests", Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract No. HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes, September 15, 1972."

Hexone
(Methyl Isobutyl Ketone)

Analyte:	Hexone	Method No.: S18
Matrix:	Air	Range: 208-836 mg/cu m
OSHA Standard:	100 ppm (409 mg/cu m)	Precision (CV_T): 0.064
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 11/8/74

1. Principle of the Method

   1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

   1.2 The charcoal in the tube is transferred to a small, stoppered sample container and desorbed with carbon disulfide.

   1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

   2.1 This method was validated over the range of 208-836 mg/cu m at an atmospheric temperature and pressure 23°C and 754 mm Hg, using a 10 liter sample. Under the conditions of sample size (10 liters) the probable useful range of this method is 40-1230 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for the 12 mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency decreases with decreasing loading of hexone on activated charcoal.

   2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of hexone and other substances in the air. The first section of the charcoal tube was found to hold no more than 20 mg of hexone when a test atmosphere of 1145 mg/cu m

of hexone in air was sampled at 0.19 liter per minute. Under these experimental conditions, after 91.7 minutes a 5% breakthrough was observed, i.e. the concentration of hexone in the effluent was 5% (57 mg/cu m) of that in the influent (1145 mg/cu m). (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample, since, with differences in polarity, one may displace another from the charcoal.

3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Hence, retention time data on a single column, or even on a number of columns, cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 208-836 mg/cu m is 0.064. The standard deviation at the OSHA standard level is 17 mg/cu m. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 4.8% lower than the "true" values at the OSHA standard level.

5. Advantages and Disadvantages of the Method

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

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 An approved and calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10 ft x 1/8 in) packed with 10% FFAP stationary phase on 80/100 mesh, acid washed DMCS Chromosorb W solid support.

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

6.6 One-milliliter sample containers with glass stoppers or Teflon®-lined caps.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 0.5-ml delivery pipets or 1.0-ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 Hexone, reagent grade.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 10 liters is recommended. This can be accomplished by sampling for 50 minutes at a rate of 0.20 liters per minute. The flow rate should be known with an accuracy of at least $\pm$5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon®-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 0.50 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period.

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

1. 50 cc/min. (60 psig) nitrogen carrier gas flow
2. 65 cc/min. (24 psig) hydrogen gas flow to detector
3. 500 cc/min. (50 psig) air flow to detector
4. 260°C injector temperature
5. 193°C manifold temperature (detector)
6. 65°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation

within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

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

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process for a given compound, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

For this validation study, the amount injected is equivalent to that present in a 10-liter sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete absorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 0.5 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for absorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/0.5 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

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

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

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

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the total mg/sample.

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$mg/cu\ m = \frac{\text{total mg (Section 10.4) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

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

where:

P	= pressure (mm Hg) of air sampled
T	= temperature (°C) of air sampled
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	= molecular weight
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Cyclohexanone

Analyte:	Cyclohexanone.	Method No.: S19
Matrix:	Air	Range: 98-392 mg/cu m
OSHA Standard:	50 ppm (200 mg/cu m)	Precision (CV_T): 0.062
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 11/8/74

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 98-392 mg/cu m at an atmospheric temperature and pressure of 22°C and 764 mm Hg, using a 40 liter sample. Under the conditions of sample size (40 liters) the probable useful range of this method is 10- 500 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for the 20 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of cyclohexanone and other substances in the air. The first section of the charcoal tube was found to hold no more than 26 mg of cyclohexanone when a test atmosphere of 392 mg/cu m of cyclohexanone in air was sampled at

0.94 liter per minute. Under these experimental conditions, after 69 minutes a 5% breakthrough was observed, i.e., the concentration of cyclohexanone in the effluent was 5% (20 mg/cu m) of that in the influent (392 mg/cu m). (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample, since, with differences in polarity, one may displace another from the charcoal.

3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Hence, retention time data on a single column, or even on a number of columns, cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 98-392 mg/cu m is 0.062. The standard deviation at the OSHA standard level is 7.4 mg/cu m. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 6.5% lower than the "true" values at the OSHA standard level.

5. Advantages and Disadvantages of the Method

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

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 An approved and calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10 ft x 1/8 in) packed with 10% FFAP stationary phase on 80/100 mesh, acid washed DMCS Chromosorb W solid support.

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

6.6 One-milliliter sample containers with glass stoppers or Teflon®-lined caps.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 0.5-ml delivery pipets or 1.0-ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 Cyclohexanone, reagent grade.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 40 liters is recommended. This can be accomplished by sampling for 40 minutes at a rate of 1 liter per minute. The flow rate should be known with an accuracy of at least $\pm$5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon®-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 0.50 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period.

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

1. 50 cc/min. (60 psig) nitrogen carrier gas flow
2. 65 cc/min. (24 psig) hydrogen gas flow to detector
3. 500 cc/min. (50 psig) air flow to detector
4. 220°C injector temperature
5. 255°C manifold temperature (detector)
6. 110°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation

within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

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

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process for a given compound, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

For this validation study, the amount injected is equivalent to that present in a 40-liter sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete absorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 0.5 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for absorption losses.

Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/0.5 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

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

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

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

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the total mg/sample.

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$mg/cu\ m = \frac{\text{total mg (Section 10.4) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

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

where:

P	= pressure (mm Hg) of air sampled
T	= temperature (°C) of air sampled
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	= molecular weight
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

2-Pentanone

Analyte:	2-Pentanone	Method No.:	S20
Matrix:	Air	Range:	395-1570 mg/cu m
OSHA Standard:	200 ppm (705 mg/cu m)	Precision (CV_T):	0.063
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	11/8/74

1. Principle of the Method

   1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

   1.2 The charcoal in the tube is transferred to a small, stoppered sample container and desorbed with carbon disulfide.

   1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

   2.1 This method was validated over the range of 395-1570 mg/cu m at an atmospheric temperature and pressure of 24°C and 762 mm Hg, using a 10 liter sample. Under the conditions of sample size (10 liters) the probable useful range of this method is 70-2100 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for the 21 mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency decreases with decreasing loading of 2-pentanone on activated charcoal.

   2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of 2-pentanone and other substances in the air. The first section of the charcoal tube was found to hold no more than 27 mg of 2-pentanone when a test atmosphere

of 1450 mg/cu m of 2-pentanone in the air was sampled at 0.19 liter per minute. Under these experimental conditions, after 100 minutes a breakthrough was observed, i.e., the concentration of 2-pentanone in the effluent was 5% (72.5 mg/cu m) of that in the influent (1450 mg/cu m). (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2.) If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample, since, with differences in polarity, one may displace another from the charcoal.

3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Hence, retention time data on a single column, or even on a number of columns, cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 395-1570 mg/cu m is 0.063. The standard deviation at the OSHA standard level is 21 mg/cu m. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 1.3% lower than the "true" values at the OSHA standard level.

5. Advantages and Disadvantages of the Method

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

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 An approved and calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10 ft x 1/8 in) packed with 10% FFAP stationary phase on 80/100 mesh, acid washed DMCS Chromosorb W solid support.

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

6.6 One-milliliter sample containers with glass stoppers or Teflon®-lined caps.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 0.5-ml delivery pipets or 1.0-ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 2-Pentanone, reagent grade.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 10 liters is recommended. This can be accomplished by sampling for 50 minutes at a rate of 0.20 liters per minute. The flow rate should be known with an accuracy of at least $\pm$5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon®-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 0.50 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period.

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

1. 50 cc/min. (60 psig) nitrogen carrier gas flow
2. 65 cc/min. (24 psig) hydrogen gas flow to detector
3. 500 cc/min. (50 psig) air flow to detector
4. 190°C injector temperature
5. 250°C manifold temperature (detector)
6. 60°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation

within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

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

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process for a given compound, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

For this validation study, the amount injected is equivalent to that present in a 10-liter sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete absorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 0.5 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for absorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0:5 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/0.5 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

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

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

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

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the total mg/sample.

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$mg/cu\ m = \frac{\text{total mg (Section 10.4) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

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

where:

P	= pressure (mm Hg) of air sampled
T	= temperature (°C) of air sampled
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	= molecular weight
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

p-tert-Butyltoluene

Analyte:	p-tert-Butyltoluene	Method No.: S22
Matrix:	Air	Range: 29-119 mg/cu m
OSHA Standard:	10 ppm (60 mg/cu m)	Precision (CV_T): 0.067
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 11/8/74

1. Principle of the Method

   1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

   1.2 The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with carbon disulfide.

   1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

   2.1 This method was validated over the range of 29-119 mg/cu m at an atmospheric temperature and pressure of 22°C and 765 mm Hg, using a 10 liter sample. Under the conditions of sample size (10 liters) the probable useful range of this method is 6-180 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder a 2 mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

   2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of p-tert-butyltoluene and other substances in the air. The first section of the charcoal tube was found to hold 5 mg of p-tert-butyltoluene when a test atmosphere

containing 112 mg/cu m of p-tert-butyltoluene in air was sampled at 0.19 liter per minute for 231 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments indicate that high humidity severely decreases the breakthrough volume.

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

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

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 29-119 mg/cu m was 0.067. The standard deviation at the OSHA standard level was 2.9 mg/cu m. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 10.4% lower than the "true" values at the OSHA standard level.

5. Advantages and Disadvantages of the Method

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

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 An approved and calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10 ft x 1/8 in stainless steel) packed with 10% FFAP on 80/100 mesh, acid washed DMCS Chromosorb W.

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

6.6 One-milliliter sample containers with glass stoppers or Teflon®-lined caps.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 0.5-ml delivery pipets or 1.0-ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 p-Tert-Butyltoluene, reagent grade.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a flow of 0.20 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm$5%.

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

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

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

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon®-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 0.5 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period.

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

1. 50 cc/min. (60 psig) nitrogen carrier gas flow
2. 65 cc/min. (24 psig) hydrogen gas flow to detector
3. 500 cc/min. (50 psig) air flow to detector
4. 195°C injector temperature
5. 260°C manifold temperature (detector)
6. 115°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation

within the syringe needle, one should employ the solvent flush injection technique. The 10 microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5 microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

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

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of a hexane solution of p-tert-butyl-toluene is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

For this validation study, the amount injected is equivalent to that present in a 10-liter sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete absorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 0.5 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for absorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/0.5 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

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

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

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

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{corrected mg (Section 10.4) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
M.W. = molecular weight (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Cumene

Analyte:	Cumene	Method No.:	S23
Matrix:	Air	Range:	120-480 mg/cu m
OSHA Standard:	50 ppm (245 mg/cu m)	Precision (CV_T):	0.059
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	11/8/74

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 120-480 mg/cu m at an atmospheric temperature and pressure of 23°C and 763 mm Hg, using a 10 liter sample. Under the conditions of sample size (10 liters) the probable useful range of this method is 25-750 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 7.5 mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of cumene and other substances in the air. The first section of the charcoal tube was found to hold

at least 22 mg of cumene when a test atmosphere containing 480 mg/cu m of cumene in air was sampled at 0.19 liter per minute for 240 minutes; at that time the concentration of analyte in the effluent was less than 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments indicate that high humidity severely decreases the breakthrough volume.

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

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

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 120-480 mg/cu m was 0.059. The standard deviation at the OSHA standard level was 6.3 mg/cu m. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 4.6% higher than the "true" values at the OSHA standard level.

5. Advantages and Disadvantages of the Method

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

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 An approved and calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10 ft x 1/8 in stainless steel) packed with 10% FFAP on 80/100 mesh, acid washed DMCS Chromosorb W.

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

6.6 One-milliliter sample containers with glass stoppers or Teflon®-lined caps.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 0.5-ml delivery pipets or 1.0-ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 Cumene, reagent grade.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal

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

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a flow of 0.20 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm$5%.

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

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

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

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon®-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 0.5 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period.

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

1. 50 cc/min. (60 psig) nitrogen carrier gas flow
2. 65 cc/min. (24 psig) hydrogen gas flow to detector
3. 500 cc/min. (50 psig) air flow to detector
4. 195°C injector temperature
5. 255°C manifold temperature (detector)
6. 99°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation

within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

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

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of hexane solution of cumene containing 247 mg/ml is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

For this validation study, the amount injected is equivalent to that present in a 10-liter sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete absorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 0.5 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for absorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/0.5 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

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

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

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

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{corrected mg (Section 10.4) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	= pressure (mm Hg) of air sampled
T	= temperature (°C) of air sampled
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	= molecular weight (g/mole) of analyte
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Vinyl Toluene

Analyte:	Vinyl Toluene	Method No.:	S25
Matrix:	Air	Range:	256-970 mg/cu m
OSHA Standard:	100 ppm (480 mg/cu m)	Precision (CV_T):	0.058
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	11/8/74

1. Principle of the Method

   1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

   1.2 The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with carbon disulfide.

   1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

   2.1 This method was validated over the range of 256-970 mg/cu m at an atmospheric temperature and pressure of 20°C and 755 mm Hg, using a 10 liter sample. Under the conditions of sample size (10 liters) the probable useful range of this method is 45-1450 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 14.5 mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

   2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of vinyl toluene and other substances in the air. The first section of the charcoal tube was found to hold 34 mg of vinyl toluene when a test atmosphere containing

952 mg/cu m of vinyl toluene in air was sampled at 0.19 liter per minute for 188 minutes; breakthrough was observed at this time; i.e. the concentration of analyte in the effluent was 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments indicate that high humidity severely decreases the breakthrough volume.

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

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

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 256-970 mg/cu m was 0.058. The standard deviation at the OSHA standard level was 20 mg/cu m. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 9.5% lower than the "true" values at the OSHA standard level.

5. Advantages and Disadvantages of the Method

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

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 An approved and calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10 ft x 1/8 in stainless steel) packed with 10% FFAP on 80/100 mesh, acid washed DMCS Chromosorb W.

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

6.6 One-milliliter sample containers with glass stoppers or Teflon®-lined caps.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 0.5-ml delivery pipets or 1.0-ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 Vinyl toluene (60% meta, 40% para).

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a flow of 0.20 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm$5%.

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

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

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

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon®-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 0.5 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period.

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

1. 50 cc/min. (60 psig) nitrogen carrier gas flow
2. 65 cc/min. (24 psig) hydrogen gas flow to detector
3. 500 cc/min. (50 psig) air flow to detector
4. 195°C injector temperature
5. 255°C manifold temperature (detector)
6. 120°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation

within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

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

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

For this validation study, the amount injected is equivalent to that present in a 10-liter sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete absorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 0.5 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for absorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/0.5 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

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

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

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

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{corrected mg (Section 10.4) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	= pressure (mm Hg) of air sampled
T	= temperature (°C) of air sampled
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	= molecular weight (g/mole) of analyte
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Alpha-Methyl Styrene

Analyte:	Alpha-Methyl Styrene	Method No.: S26	
Matrix:	Air	Range: 236-943 mg/cu m	
OSHA Standard:	100 ppm (480 mg/cu m)-Ceiling	Precision (CV_T):	0.054
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	11/8/74

1. Principle of the Method

   1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

   1.2 The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with carbon disulfide.

   1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

   2.1 This method was validated over the range of 236-943 mg/cu m at an atmospheric temperature and pressure of 24°C and 765 mm Hg, using a 3 liter sample. Under the conditions of sample size (3 liters) the probable useful range of this method is 45-1450 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 14.5 mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

   2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of alpha-methyl styrene and other substances in the air. The first section of the charcoal tube was found to hold at least 42 mg of alpha-methyl styrene when a test

atmosphere containing 940 mg/cu m of alpha-methyl styrene in air was sampled at 0.19 liter per minute for 240 minutes; at that time the concentration of analyte in the effluent was less than 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments indicate that high humidity severely decreases the breakthrough volume.

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

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

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 236-943 mg/cu m was 0.054. The standard deviation at the OSHA standard level was 20 mg/cu m. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 10.8% lower than the "true" values at the OSHA standard level.

5. Advantages and Disadvantages of the Method

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

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 An approved and calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10 ft x 1/8 in stainless-steel) packed with 10% FFAP on 80/100 mesh, acid washed DMCS Chromosorb W.

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

6.6 One-milliliter sample containers with glass stoppers or Teflon®-lined caps.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 0.5-ml delivery pipets or 1.0-ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 Alpha-methyl styrene, reagent grade.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 3 liters is recommended. This can be accomplished by sampling for 15 minutes at a rate of 0.20 liters per minute. The flow rate should be known with an accuracy of at least $\pm$5%.

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

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

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

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon®-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 0.5 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period.

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

1. 50 cc/min. (60 psig) nitrogen carrier gas flow
2. 65 cc/min. (24 psig) hydrogen gas flow to detector
3. 500 cc/min. (50 psig) air flow to detector
4. 195°C injector temperature
5. 250°C manifold temperature (detector)
6. 115°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation

within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

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

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

For this validation study, the amount injected is equivalent to that present in a 3-liter sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete absorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 0.5 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for absorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/0.5 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

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

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

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

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{corrected mg (Section 10.4) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	= pressure (mm Hg) of air sampled
T	= temperature (°C) of air sampled
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	= molecular weight (g/mole) of analyte
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Terphenyls
(Ortho-terphenyl)

Analyte:	Terphenyls	Method No.:	S27
Matrix:	Air	Range:	4.5-20 mg/cu m
OSHA Standard:	1 ppm (10 mg/cu m)-Ceiling	Precision ($\overline{CV}_T$):	0.097
Procedure:	Filter collection, carbon disulfide extraction, GC	Validation Date:	11/8/74

1. Principle of the Method

1.1 A known volume of air is drawn through a cellulose membrane filter to collect particulate matter.

1.2 The filter is transferred to a screw cap bottle and extracted with carbon disulfide.

1.3 An aliquot of the extract is analyzed by flame ionization gas chromatography.

1.4 The area of the sample peak is determined and compared with areas obtained from standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 4.5-20 mg/cu m at an atmospheric temperature and pressure of 22°C and 760 mm Hg, using a 15-liter sample. The probable useful range of this method is 1-30 mg/cu m for 15-liter samples.

2.2 The upper limit of the range of the method is dependent on the collection efficiency of the cellulose membrane filter. If higher concentrations than those tested are to be sampled, smaller sample volumes should be used. The collection efficiency for o-terphenyl was determined to be 1.00 $\pm$ 0.01 when sampled for 15 minutes at 1 liter per minute from a test atmosphere containing 18.82 mg/cu m.

3. Interference

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

3.2 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 4.5-20 mg/cu m was 0.097. This value corresponds to a standard deviation of 0.97 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.1.

4.2 A collection efficiency of 1.00 $\pm$ 0.01 was determined for the collection medium; thus, no bias was introduced in the sample collection step. There was no apparent bias in the sampling and analytical method for which an analytical method recovery correction was made. Thus $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

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

5.2 Other volatile compounds which give a flame ionization response that are dispersed as particulates may interfere.

6. Apparatus

6.1 The sampling unit for the collection of personal air samples for the determination of organic aerosol has the following components:

6.1.1 The filter unit consisting of the filter media (Section 6.2) and a polystyrene 37-mm 3-piece cassette filter holder. Do not use tenite filter holders.

6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of $\pm$ 5% (Reference 11.1) at the recommended flow rate. The pump must be calibrated with a representative filter holder and filter in the line.

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

6.3 Screw cap bottles. Within 1 hour after the sample has been collected, the filter is transferred to a clean screw cap bottle (a 45-mm tissue sample holder is satisfactory) for shipping.

6.4 Gas chromatograph equipped with a flame ionization detector.

6.5 Column (10-ft X 1/8-in stainless steel) packed with 5% SE-30 on 80/100 mesh Gas Chrom W.

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

6.7 Sample extraction equipment.

6.7.1 Beakers, 50 ml.

6.7.2 Volumetric flasks, 1 ml for use in making GC standards.

6.7.3 Graduated ampoule, 10 ml.

6.7.4 Tweezers.

6.8 Microliter syringes: 10-microliter and other convenient sizes for making standard solutions.

6.9 Volumetric flasks: 1-ml and other convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 Ortho-terphenyl, reagent grade.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis as well as the screw cap bottles should be detergent washed and thoroughly rinsed with tap water and distilled water, dried, and then rinsed with carbon disulfide.

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

8.3 Collection and Shipping of Samples

8.3.1 Assemble the filter in the three piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad.

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

8.3.3 Air being sampled should not pass through any hose or tubing before entering the filter cassette.

8.3.4 A sample size of 15 liters is recommended. Sample at a flow rate of 1.0 liter per minute for 15 minutes. The flow rate should be known with an accuracy of $\pm$ 5%.

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

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

8.3.7 The cellulose filter should be removed from the cassette filter holder and the cellulose backup pad within 1 hour of sampling and placed in a clean screw cap bottle. Care must be taken to handle the filter only with clean tweezers.

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

8.3.9 With each batch of samples submit one filter which is subjected to exactly the same handling as for the samples except that no air is drawn through it. Label this as a blank.

8.3.10 The screw cap bottles in which the samples are stored should be shipped in a suitable container, designed to prevent damage in transit.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. Care must be taken to handle the filter only with clean tweezers. Open the screw cap bottle, remove the filter, and place the filter in a 50-ml beaker. Rinse the screw cap bottle with 1 ml carbon disulfide. Extract the filter three times with 1 ml carbon disulfide. (Total solvent should be 4 ml carbon disulfide.) Use a disposable pipet to transfer the extract into an ampoule which can accurately measure 0.5 ml. Gently evaporate the solvent to 0.5 ml under a nitrogen stream. Mix the sample thoroughly.

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

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 230°C detector temperature
5. 220°C injector temperature
6. 185°C column temperature

8.4.3 Injection. The first step in the analysis is the injection of an aliquot of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

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

8.5 Determination of Analytical Method Recovery

8.5.1 Need for determination. It is anticipated that the extraction scheme is dependent on operator skill and perhaps on the formulation used to disperse the analyte. Thus, it is necessary to determine the recovery of the analyte.

8.5.2 Procedure for determining analytical method recovery. A known amount of a hexane solution containing 13.55 mg/ml of o-terphenyl, preferably equivalent to the sample concentration expected, is added to a representative cellulose membrane filter and air-dried. The analyte is then extracted from the filter and analyzed as described in Section 8.4. An amount of the analyte equivalent to that present in a 15-liter sample at the selected level is used for the extraction studies. Six filters at each of the three levels (0.5X, 1X, and 2X the OSHA standard) are dosed accordingly. A parallel blank filter is also treated in the same manner except that no sample is added to it. All filters are then extracted and analyzed as described in Section 8.4.

Three standards are prepared by injecting the same amount of analyte into 0.5 ml of carbon disulfide with the same syringe used in the preparation of the dosed filters and are analyzed at the same time.

Analytical method recovery (A.M.R.) equals the weight in mg found divided by the weight in mg added to the filter, or

$$\text{A.M.R.} = \frac{\text{Weight found (mg)}}{\text{Weight added (mg)}}$$

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml carbon disulfide, because samples are extracted in this amount of carbon disulfide. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the flame ionization response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/0.5 ml of carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

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

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

where:

mg sample = mg found in sample filter
mg blank = mg found in blank filter

10.3 Divide the total weight by the analytical method recovery (A.M.R.) to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{A.M.R.}}$$

10.4 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.3) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

11. Reference

11.1 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Cyclohexane

Analyte:	Cyclohexane	Method No.:	S28
Matrix:	Air	Range:	510-2010 mg/cu m
OSHA Standard:	300 ppm (1030 mg/cu m)	Precision (CV_T):	0.066
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	11/8/74

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 510-2010 mg/cu m at an atmospheric temperature and pressure of 21°C and 765 mm Hg, using a 2.5 liter sample. Under the conditions of sample size (2.5 liters) the probable useful range of this method is 100-3000 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 7.5 mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of cyclohexane and other substances in the air. The first section of the charcoal tube was found to hold 12.5 mg of cyclohexane when a test atmosphere containing

1650 mg/cu m of cyclohexane in air was sampled at 0.19 liter per minute for 40 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments indicate that high humidity severely decreases the breakthrough volume.

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

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

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 510-2010 mg/cu m was 0.066. The standard deviation at the OSHA standard level was 29 mg/cu m. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 5.4% higher than the "true" values at the OSHA standard level.

5. Advantages and Disadvantages of the Method

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

The method can also be used for the simultaneous analysis of two or more solvents suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 An approved and calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (4 ft x 1/4 in stainless steel) packed with 50/80 mesh Porapak, Type Q.

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

6.6 One-milliliter sample containers with glass stoppers or Teflon®-lined caps.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 0.5-ml delivery pipets or 1.0-ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 Cyclohexane, reagent grade.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 2.5 liters is recommended. Sample at a flow of 0.20 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm$5%.

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

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

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

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon®-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 0.5 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period.

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

1. 50 cc/min. (60 psig) nitrogen carrier gas flow
2. 65 cc/min. (24 psig) hydrogen gas flow to detector
3. 400 cc/min. (40 psig) air flow to detector
4. 185°C injector temperature
5. 255°C manifold temperature (detector)
6. 210°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation

within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

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

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

For this validation study, the amount injected is equivalent to that present in a 2.5-liter sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete absorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 0.5 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for absorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/0.5 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

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

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

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

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{corrected mg (Section 10.4) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	= pressure (mm Hg) of air sampled
T	= temperature (°C) of air sampled
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	= molecular weight (g/mole) of analyte
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Analyte:	Ethyl Benzene	Method No.: S29
Matrix:	Air	Range: 222-884 mg/cu m
OSHA Standard:	100 ppm (435 mg/cu m)	Precision (CV_T): 0.041
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 11/8/74

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 222-884 mg/cu m at an atmospheric temperature and pressure of 22°C and 762 mm Hg, using a 10 liter sample. Under the conditions of sample size (10 liters) the probable useful range of this method is 40-1300 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 13 mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of ethyl benzene and other substances in the air. The first section of the charcoal tube was found to hold 32 mg of ethyl benzene when a test atmosphere containing

917 mg/cu m of ethyl benzene in air was sampled at 0.19 liter per minute for 186 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments indicate that high humidity severely decreases the breakthrough volume.

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

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

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 222-884 mg/cu m was 0.041. The standard deviation at the OSHA standard level was 17 mg/cu m. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 8.1% lower than the "true" values at the OSHA standard level.

5. Advantages and Disadvantages of the Method

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

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 An approved and calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10 ft x 1/8 in stainless steel) packed with 10% FFAP on 80/100 mesh, acid washed DMCS Chromosorb W.

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

6.6 One-milliliter sample containers with glass stoppers or Teflon®-lined caps.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 0.5-ml delivery pipets or 1.0-ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 Ethyl Benzene, reagent grade.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a flow of 0.20 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm$5%.

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

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

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

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon®-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 0.5 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period.

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

1. 50 cc/min. (60 psig) nitrogen carrier gas flow
2. 65 cc/min. (24 psig) hydrogen gas flow to detector
3. 500 cc/min. (50 psig) air flow to detector
4. 195°C injector temperature
5. 250°C manifold temperature (detector)
6. 85°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation

within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

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

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

For this validation study, the amount injected is equivalent to that present in a 10-liter sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete absorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 0.5 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for absorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/0.5 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

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

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

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

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{corrected mg (Section 10.4) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	= pressure (mm Hg) of air sampled
T	= temperature (°C) of air sampled
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	= molecular weight (g/mole) of analyte
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Analyte:	Styrene	Method No.: S30
Matrix:	Air	Range: 426-1710 mg/cu m
OSHA Standard:	200 ppm (850 mg/cu m)-Ceiling 100 ppm (425 mg/cu m)-T.W.A.	Precision (CV_T): 0.057
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 11/8/74

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 426-1710 mg/cu m at an atmospheric temperature and pressure of 23°C and 754 mm Hg, using a 5 liter sample. Under the conditions of sample size (5 liters) the probable useful range of this method is 85-2560 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 13 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of styrene and other substances in the air. The first section of the charcoal tube was found to hold

36 mg of styrene when a test atmosphere containing 1710 mg/cu m of styrene in air was sampled at 0.19 liter per minute for 111 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments indicate that high humidity severely decreases the breakthrough volume.

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

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

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 426-1710 mg/cu m was 0.057. The standard deviation at the OSHA standard level was 3.0 mg/cu m. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 10.7% lower than the "true" values at the OSHA standard level.

5. Advantages and Disadvantages of the Method

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

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 An approved and calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10 ft x 1/8 in stainless steel) packed with 10% FFAP on 80/100 mesh, acid washed DMCS Chromosorb W.

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

6.6 One-milliliter sample containers with glass stoppers or Teflon®-lined caps.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 0.5-ml delivery pipets or 1.0-ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 Styrene, reagent grade.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 5 liters is recommended. This can be accomplished by sampling for 5 minutes at a rate of 1 liter per minute. The flow rate should be known with an accuracy of at least $\pm 5\%$.

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

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

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

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon®-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 0.5 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period.

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

1. 50 cc/min. (60 psig) nitrogen carrier gas flow
2. 65 cc/min. (24 psig) hydrogen gas flow to detector
3. 500 cc/min. (50 psig) air flow to detector
4. 195°C injector temperature
5. 255°C manifold temperature (detector)
6. 109°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation

within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

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

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

For this validation study, the amount injected is equivalent to that present in a 5-liter sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete absorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 0.5 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for absorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/0.5 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

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

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

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

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{corrected mg (Section 10.4) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	= pressure (mm Hg) of air sampled
T	= temperature (°C) of air sampled
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	= molecular weight (g/mole) of analyte
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

sec-Amyl Acetate
(2-Pentyl Acetate)

Analyte:	sec -Amyl Acetate	Method No:	S31
Matrix:	Air	Range:	349-1460 mg/cu m
OSHA Standard:	125 ppm (650 mg/cu m)	Precision (CV_T):	0.0710
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	12/6/74

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 349-1460 mg/cu m at an atmospheric temperature and pressure of 22°C and 762 mm Hg, using a 10 liter sample. Under the conditions of sample size (10 liters) the probable useful range of this method is 65-1950 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 19.5 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 31 mg of analyte when a test atmosphere containing 1460 mg/cu m of analyte in air was sampled at 0.19 liters per minute for 110 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

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

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

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 349-1460 mg/cu m was 0.0710. This value corresponds to a 46.0 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 7.0% lower than the "true" value at the OSHA standard level.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

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

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 An approved and calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3).

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in stainless steel) packed with 5% FFAP stationary phase on 100/120 mesh Supelcoport.

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

6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide

7.2 sec -Amyl Acetate , reagent grade

7.3 Tridecane, internal standard

7.4 Purified helium

7.5 Prepurified hydrogen

7.6 Filtered compressed air

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a rate of 0.2 liter per minute or less. The flow rate should be known with an accuracy of at least ±5%.

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

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

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

1. 30 cc/min. (60 psig) Helium carrier gas flow
2. 35 cc/min. (25 psig) hydrogen gas flow to detector
3. 400 cc/min. (60 psig) air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 95°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

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

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once for a given batch of charcoal the percentage of the specific compound that is removed in the desorption process.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

When using an automatic sample injector, the vials associated with that equipment may be used in place of the glass tube. These vials are capped with the Teflon faced septa.

For this validation study, the amount injected is equivalent to that present in a 10 liter sample at the selected level. Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into a 1 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. It is suggested that the internal standard concentration be approximately 70% of the highest concentration to be analyzed. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

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

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

where:

mg sample = mg found in front section of sample tube
mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

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

$$\text{ppm} = \frac{\text{mg}}{\text{cu m}} \times \frac{24.45}{\text{MW}} \times \frac{760}{\text{P}} \times \frac{(\text{T} + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Analyte:	tert -Butyl Acetate	Method No:	S32
Matrix:	Air	Range:	424-1780 mg/cu m
OSHA Standard:	200 ppm (950 mg/cu m)	Precision (CV_T):	0.0909
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	12/6/74

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 424-1780 mg/cu m at an atmospheric temperature and pressure of 24°C and 761 mm Hg, using a 10 liter sample. Under the conditions of sample size (10 liters) the probable useful range of this method is 95-2850 mg/cu m at a detector sensitivity that gives nearly fxll deflection on the strip chart recorder for a 28.5 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 25 mg of analyte when a test atmosphere containing 1780 mg/cu m of analyte in air was sampled at 0.19 liters per minute for 75 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

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

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

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 424-1780 mg/cu m was 0.0909. This value corresponds to a 86.4 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 8.6% lower than the "true" value at the OSHA standard level.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

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

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 An approved and calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3).

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in stainless steel) packed with 5% FFAP stationary phase on 100/120 mesh Supelcoport.

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

6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide

7.2 tert.-Butyl Acetate , reagent grade

7.3 Undecane , internal standard

7.4 Purified helium

7.5 Prepurified hydrogen

7.6 Filtered compressed air

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a rate of 0.2 liter per minute or less. The flow rate should be known with an accuracy of at least ±5%.

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

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

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

1. 30 cc/min. (60 psig) Helium carrier gas flow
2. 35 cc/min. (25 psig) hydrogen gas flow to detector
3. 400 cc/min. (60 psig) air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 70 °C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

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

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once for a given batch of charcoal the percentage of the specific compound that is removed in the desorption process.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

When using an automatic sample injector, the vials associated with that equipment may be used in place of the glass tube. These vials are capped with the Teflon faced septa.

For this validation study, the amount injected is equivalent to that present in a 10 liter sample at the selected level. Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into a 1 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. It is suggested that the internal standard concentration be approximately 70% of the highest concentration to be analyzed. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

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

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

where:

mg sample = mg found in front section of sample tube
mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

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

$$\text{ppm} = \frac{\text{mg}}{\text{cu m}} \times \frac{24.45}{\text{MW}} \times \frac{760}{\text{P}} \times \frac{(\text{T} + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Dibutyl Phthalate

Analyte:	Dibutyl Phthalate	Method No.:	S33
Matrix:	Air	Range:	1.82 - 9.78 mg/cu m
OSHA Standard:	5 mg/cu m	Precision: ($\overline{CV}_T$):	0.059
Procedure:	Filter collection extraction with carbon disulfide, GC	Validation Date:	1/17/75

1. Principle of the Method

1.1 A known volume of air is drawn through a cellulose membrane filter to trap the organic aerosol present.

1.2 The filter in the cassette is transferred into a disposable glass pipet and eluted with carbon disulfide.

1.3 An aliquot of the eluted sample is injected into a gas chromatograph.

1.4 The area of the sample peak is determined and the concentration is determined from the calibration curve.

2. Range and Sensitivity

2.1 This method was validated over the range of 1.82 - 9.78 mg/cu m at an atmospheric temperature and pressure of 23° and 769 mm Hg using a 30-liter sample. Under the conditions of sample size (30 liters), the probable useful range of this method is 0.5 - 15 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for the 0.45 mg sample.

2.2 The upper limit of the range of the method is dependent on the filtration efficiency of the cellulose membrane filter. If higher concentrations than those tested are to be sampled, smaller sample volumes should be used. The filtration efficiency for dibutyl phthalate aerosol is greater than 95% when sampled for 30 minutes at 1 liter per minute from a test atmosphere containing 10 mg/cu m.

3. Interference

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

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

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 1.82 - 9.78 mg/cu m was 0.059. This value corresponds to a standard deviation of 0.29 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.1.

4.2 On the average the values obtained using the overall sampling and analytical method were 8.6% lower than the "true" values at the OSHA standard level.

These data are based on the validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

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

6. Apparatus

6.1 Sampling equipment - The sampling unit for the collection of personal air samples for the determination of organic aerosol has the following components:

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

6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of $\pm$ 5% (reference 11.2) at the recommended flow rate. The pump must be calibrated with a representative filter holder and filter in the lines.

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

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (6-ft x 1/8-in stainless steel) packed with 5% OV-101 on 100/120 mesh Supelcoport.

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

6.6 Assembly for sample elution.

6.6.1 Extraction tube, Fisher brand disposable Paster pipet (Cat. No. 13-678-5A) modified as follows: cut off the upper 1-inch portion, i.e., just below the notch to eliminate the constricted portion, and flame seal the lower tapered end.

6.6.2 Dumont No. 5 precision watchmakers tweezers, rustproof.

6.6.3 Volumetric flask, 1 ml.

6.6.4 Ultrasonic cleaner.

6.6.5 Triangular file.

6.7 Microliter syringes: 10-microliter and other convenient sizes for making standard solutions.

6.8 Volumetric flasks: 10-ml and other convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide

7.2 Dibutyl Phthalate, reagent grade

7.3 Heneicosane or other suitable internal standard

7.4 Purified helium

7.5 Prepurified hydrogen

7.6 Filtered compressed air

8. Procedure

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

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

8.3 Collection and Shipping of Samples

8.3.1 Assemble the filter in the three piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad.

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

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

8.3.4 A maximum sample size of 30 liters is recommended. Sample at a flow rate of 1.0 liter per minute. The flow rate should be known with an accuracy of at least $\pm$ 5%.

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

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

8.3.7 Collected sample cassette should be firmly sealed with the plugs in both the inlet and outlet.

8.3.8 Carefully record sample identity and all relevant sample data.

8.3.9 Blank: With each batch of samples submit one filter which is subjected to exactly the same handling as for the samples except that no air is drawn through it. Label this as a blank.

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

8.4 Analysis of Samples

8.4.1 Preparation of Samples

1. Open the cassette filter holder and carefully remove the cellulose membrane filter from the holder and cellulose backup pad.

2. With the aid of the Dumont tweezers, carefully roll the filter into a narrow cylinder. To do so, place the filter (sample side upwards) on a clean surface such as a watch glass and imagine a tangent to any edge of the circular filter. Pinch the filter with the long, sharp prongs of the tweezers along a line parallel to the imaginary tangent and about 1 cm inwards from the tangential point and start rolling the filter by gradually and carefully turning the tweezers' handle.

3. Insert the rolled filter into the modified pipet.

4. Add a known aliquot of the internal standard solution in carbon disulfide (ca. 100 microliters only) to the filter.

   Note: If the external standard method is used, this last step should be eliminated.

8.4.2 Extraction of Samples

1. Position pipets upright and add ca. 1 ml of carbon disulfide to the filter in the disposable pipet. Be sure that the entire filter is submerged in carbon disulfide and that there are no air bubbles trapped.

2. Seal the top of the pipet with a wad of glass wool to avoid sample contamination and loss during the next step.

3. Arrange the sample-containing pipets upright in a beaker and place the beaker in the ultrasonic vibrator for 30 minutes.

4. With a sharp file, very carefully score the tip (about 1 cm above the sealed end) of the pipet and break the tip inside the 1 ml volumetric flask. Allow the carbon disulfide eluent to drain completely into the flask. Apply air pressure, if necessary, to aid draining.

5. Rinse the filter inside the pipet with more carbon disulfide by dropwise addition of solvent until the total volume of eluent collected is 1.0 ml. If the 1.0 ml mark is overshot, concentrate sample to 1.0 ml by using a slow nitrogen flush.

6. If an automatic sample injector is used, transfer the sample extracts into the automatic sample injector vials prior to analysis.

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

1. 30 ml/min (60 psig) helium carrier gas flow
2. 35 ml/min (25 psig) hydrogen gas flow to detector
3. 400 ml/min (60 psig) air flow to detector
4. 300°C injector temperature
5. 300°C manifold temperature (detector)
6. 210°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10 microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9 - 5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

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

8.5 Determination of Sample Recovery

8.5.1 Need for determination. Since the extraction scheme may be dependent on operator skill, it is necessary to determine the recovery of the compound. The sample recovery should be determined in duplicates and should cover the concentration ranges of interest. If the recovery is less than 95%, the appropriate correction factor should be used to calculate the "true" value.

8.5.2 Procedure for determining extraction efficiency. A known amount of the analyte, preferably equivalent to the sample concentration expected, is added to a representative cellulose membrane filter and air-dried. The analyte is then extracted from the filter and analyzed as described in Section 8.4. Duplicate determinations should agree within 5%.

For this validation study, an amount of the analyte equivalent to that present in a 30-liter sample at the selected level has been used for the extraction studies. Six filters at each of the three levels (0.5X, 1X, and 2X the OSHA standard) have been dosed accordingly and a known amount of internal standard was added to each filter prior to extraction. A parallel blank filter was also treated in the same manner except that no sample was added to it. All filters were then extracted and analyzed as described in Section 8.4. The recovery values obtained were at least 95% and as such no correction factor has been used in the determination of the "true" values.

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

$$\text{Recovery} = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

Reproduced from best available copy.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration of 2X the OSHA standard level. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

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

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

where:

mg sample = mg found in sample filter
mg blank = mg found in blank filter

10.3 Divide the total weight by the extraction efficiency to obtain the corrected mg/sample

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{Recovery}}$$

10.4 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg(Section 10.3)} \times 1000 \text{ (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

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

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

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.2 Final Report, NIOSH Contract HSM-99-71-31. "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Analyte:	Ethyl Acrylate	Method No.:	S35
Matrix:	Air	Range:	50-210 mg/cu m
OSHA Standard:	25 ppm (100 mg/cu m)	Precision (CV_T):	0.0542
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	12/6/74

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 50-210 mg/cu m at an atmospheric temperature and pressure of 19°C and 770 mm Hg, using a 10 liter sample. Under the conditions of sample size (10 liters) the probable useful range of this method is 10-300 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 3.0 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold at least 10 mg of analyte when a test atmosphere containing 210 mg/cu m of analyte in air was sampled at 0.19 liters per minute for 240 minutes; at that time, the concentration of analyte in the effluent was less than 5% of that in the influent.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

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

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

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 11-210 mg/cu m was 0.0542. This value corresponds to a 5.4 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 6.3% lower than the "true" value at the OSHA standard level.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

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

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 An approved and calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3).

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in stainless steel) packed with 5% FFAP stationary phase on 100/120 mesh Supelcoport.

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

6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide

7.2 Ethyl Acrylate, reagent grade

7.3 Undecane, internal standard

7.4 Purified helium

7.5 Prepurified hydrogen

7.6 Filtered compressed air

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a rate of 0.2 liter per minute or less. The flow rate should be known with an accuracy of at least ±5%.

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

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml. of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is stirred occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

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

1. 30 ml/min (60 psig) Helium carrier gas flow
2. 35 ml/min (25 psig) hydrogen gas flow to detector
3. 400 ml/min (60 psig) air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 70°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

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

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

When using an automatic sample injector, the vials associated with that equipment may be used in place of the glass tube. These vials are capped with the Teflon faced septa.

For this validation study, the amount injected is equivalent to that present in a 10 liter sample at the selected level. Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1 ml. of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. It is suggested that the internal standard concentration be approximately 70% of the highest concentration to be analyzed. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

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

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

where:

mg sample = mg found in front section of sample tube
mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

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

$$\text{ppm} = \frac{\text{mg}}{\text{cu m}} \times \frac{24.45}{\text{MW}} \times \frac{760}{\text{P}} \times \frac{(\text{T} + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Ethyl Formate

Analyte:	Ethyl Formate	Method No:	S36
Matrix:	Air	Range:	171-666 mg/cu m
OSHA Standard:	100 ppm (300 mg/cu m)	Precision (CV_T):	0.0782
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	12/6/74

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 171-666 mg/cu m at an atmospheric temperature and pressure of 23°C and 766 mm Hg, using a 10 liter sample. Under the conditions of sample size (10 liters) the probable useful range of this method is 30-900 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 9 mg. sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 9.5 mg of analyte when a test atmosphere containing 666 mg/cu m of analyte in air was sampled at 0.19 liters per minute for 75 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

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

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

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 171-666 mg/cu m was 0.0782. This value corresponds to a 23.5 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 4.0% higher than the "true" value at the OSHA standard level.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

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

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 An approved and calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3).

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (20-ft x 1/8-in stainless steel) packed with 10% FFAP on 80/100 mesh Chromosorb W AW-DMCS.

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

6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide

7.2 Ethyl Formate, reagent grade

7.3 Nonane, internal standard

7.4 Purified helium

7.5 Prepurified hydrogen

7.6 Filtered compressed air

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a rate of 0.2 liter per minute or less. The flow rate should be known with an accuracy of at least ±5%.

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

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml.of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is stirred occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

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

1. 30 ml/min (60 psig) Helium carrier gas flow
2. 35 ml/min (25 psig) hydrogen gas flow to detector
3. 400 ml/min (60 psig) air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 65°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

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

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once for a given batch of charcoal the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

When using an automatic sample injector, the vials associated with that equipment may be used in place of the glass tube. These vials are capped with the Teflon faced septa.

For this validation study, the amount injected is equivalent to that present in a 10 liter sample at the selected level. Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1 ml. of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. It is suggested that the internal standard concentration be approximately 70% of the highest concentration to be analyzed. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

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

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

where:

mg sample = mg found in front section of sample tube
mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

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

$$\text{ppm} = \frac{\text{mg}}{\text{cu m}} \times \frac{24.45}{\text{MW}} \times \frac{760}{\text{P}} \times \frac{(\text{T} + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Methyl Isoamyl Acetate*
(4-Methyl-2-pentyl acetate)

Analyte:	Methyl Isoamyl Acetate*	Method No. S37
Matrix:	Air	Range: 143-601 mg/cu m
OSHA Standard:	50 ppm (300 mg/cu m)	Precision (CV_T): 0.0577
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 12/6/74

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from injection of standards

2. Range and Sensitivity

2.1 This method was validated over the range of 143-601 mg/cu m at an atmospheric temperature and pressure of 23°C and 758 mm Hg, using a 10 liter sample. Under the conditions of sample size (10 liters) the probable useful range of this method is 30-900 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 9 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold at least 27 mg of analyte when a test atmosphere containing 601 mg/cu m of analyte in air was sampled at 0.19 liters per minute for 240 minutes; at that time, the concentration of analyte in the effluent was less than 5% of that in the influent.

*Listed incorrectly as sec-Hexyl Acetate in 29 CFR 1910.93

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

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

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

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 143-601 mg/cu m was 0.0577. This value corresponds to a 17.3 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 4.5% lower than the "true" value at the OSHA standard level.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

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

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 An approved and calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3).

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in stainless steel) packed with 5% FFAP stationary phase on 100/120 mesh Supelcoport.

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

6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide

7.2 Methyl Isoamyl Acetate, reagent grade

7.3 Dodecane, internal standard

7.4 Purified helium

7.5 Prepurified hydrogen

7.6 Filtered compressed air

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a rate of 0.2 liter per minute or less. The flow rate should be known with an accuracy of at least ±5%.

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

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml. of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is stirred occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

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

1. 30 ml/min (60 psig) Helium carrier gas flow
2. 35 ml/min (25 psig) hydrogen gas flow to detector
3. 400 ml/min (60 psig) air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 90°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

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

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

When using an automatic sample injector, the vials associated with that equipment may be used in place of the glass tube. These vials are capped with the Teflon faced septa.

For this validation study, the amount injected is equivalent to that present in a 10 liter sample at the selected level. Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1 ml. of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. It is suggested that the internal standard concentration be approximately 70% of the highest concentration to be analyzed. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

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

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

where:

mg sample = mg found in front section of sample tube
mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

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

$$\text{ppm} = \frac{\text{mg}}{\text{cu m}} \times \frac{24.45}{\text{MW}} \times \frac{760}{\text{P}} \times \frac{(\text{T} + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

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

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

where:

mg sample = mg found in front section of sample tube
mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liters/cu m)}}{\text{Air Volume Sampled (liters)}}$$

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

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

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

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

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

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 11-214 mg/cu m was 0.0675. This value corresponds to an 8.1 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 0.5% lower than the "true" value at the OSHA standard level.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

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

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 An approved and calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10 ft x 1/8 in stainless steel) packed with 5% FFAP stationary phase on 100/120 mesh Supelcoport.

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

6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide

7.2 Methyl Cellosolve Acetate, reagent grade

7.3 Undecane , internal standard

7.4 Purified helium

7.5 Prepurified hydrogen

7.6 Filtered compressed air

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 20 liters is recommended. Sample at a rate of 0.2 liter per minute or less. The flow rate should be known with an accuracy of at least ±5%.

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

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml. of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is stirred occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

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

1. 30 ml/min (60 psig) Helium carrier gas flow
2. 35 ml/min (25 psig) hydrogen gas flow to detector
3. 400 ml/min (60 psig) air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 90 °C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

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

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

When using an automatic sample injector, the vials associated with that equipment may be used in place of the glass tube. These vials are capped with the Teflon faced septa.

For this validation study, the amount injected is equivalent to that present in a 20 liter sample at the selected level. Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1 ml. of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. It is suggested that the internal standard concentration be approximately 70% of the highest concentration to be analyzed. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

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

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

where:

mg sample = mg found in front section of sample tube
mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

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

$$\text{ppm} = \frac{\text{mg}}{\text{cu m}} \times \frac{24.45}{\text{MW}} \times \frac{760}{\text{P}} \times \frac{(\text{T} + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Methyl Acrylate

Analyte:	Methyl Acrylate	Method No.:	S38
Matrix:	Air	Range:	13.9-58.4 mg/cu m
OSHA Standard:	10 ppm (35 mg/cu m)	Precision ($\overline{CV}_T$):	0.066
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	12/6/74

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 13.9-58.4 mg/cu m at an atmospheric temperature and pressure of 23°C and 764 mm Hg, using a 6-liter sample. Under the conditions of sample size (5 liters) the probable useful range of this method is 7-70 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 0.35 mg sample.

2.2 The upper limit of the range of the method may be dependent on the absorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold at least 2.7 mg of analyte when a test atmosphere containing 59 mg/cu m of analyte in air was sampled at 0.19 liters per minute for 240 minutes; at that time, the concentration of analyte in the effluent was less than 5% of that in the influent. In this case, the upper range is limited by the reactivity of the monomer on charcoal. It is recommended that this method not be used outside the range stated in Section 2.1.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

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

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

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 13.9-58.4 mg/cu m was 0.066. This value corresponds to a 2.3 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 12.9% lower than the "true" value at the OSHA standard level.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

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

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3).

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in stainless steel) packed with 5% FFAP stationary phase on 100/120 mesh Supelcoport.

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

6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide

7.2 Methyl Acrylate, reagent grade

7.3 Undecane, or other suitable internal standard

7.4 Purified helium

7.5 Prepurified hydrogen

7.6 Filtered compressed air

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 5 liters is recommended. Sample at a rate of 0.2 liter per minute or less. The flow rate should be known with an accuracy of at least ±5%.

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

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

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

1. 30 ml/min (60 psig) Helium carrier gas flow
2. 35 ml/min (25 psig) Hydrogen gas flow to detector
3. 400 ml/min (60 psig) Air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 70°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

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

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample injector vials, capped with Teflon-faced septa, may be used in place of the glass tubes.

Six tubes at each of three concentration levels (0.5X,1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 5-liter sample at the selected level. The tubes are allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Methyl Cellosolve Acetate

Analyte:	Methyl Cellosolve Acetate	Method No.:	S39
Matrix:	Air	Range:	51-214 mg/cu m
OSHA Standard:	25 ppm (120 mg/cu m)	Precision (CV_T):	0.0675
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	12/6/74

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 51-214 mg/cu m at an atmospheric temperature and pressure of 23°C and 762 mm. Hg, using a 20 liter sample. Under the conditions of sample size (20 liters) the probable useful range of this method is 12-360 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 7.2 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 10 mg of analyte when a test atmosphere containing 214 mg/cu m of analyte in air was sampled at 0.19 liters per minute for 240 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

Di-2-Ethylhexyl Phthalate*

Analyte:	Di-2-ethylhexyl phthalate	Method No.:	S40
Matrix:	Air	Range:	2.03 - 10.9 mg/cu m
OSHA Standard:	5 mg/cu m	Precision: ($\overline{CV}_T$):	0.057
Procedure:	Filter collection extraction with carbon disulfide, GC	Validation Date:	1/17/75

1. Principle of the Method

1.1 A known volume of air is drawn through a cellulose membrane filter to trap the organic aerosol present.

1.2 The filter in the cassette is transferred into a disposable glass pipet and eluted with carbon disulfide.

1.3 An aliquot of the eluted sample is injected into a gas chromatograph.

1.4 The area of the sample peak is determined and the concentration is determined from the calibration curve.

2. Range and Sensitivity

2.1 This method was validated over the range of 2.03 - 10.9 mg/cu m at an atmospheric temperature and pressure of 23°C and 761 mm Hg, using a 32-liter sample. Under the conditions of sample size (30 liters), the probable useful range of this method is 0.5 - 15 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for the 0.45 mg sample.

2.2 The upper limit of the range of the method is dependent on the filtration efficiency of the cellulose membrane filter. If higher concentrations than those tested are to be sampled, smaller sample volumes should be used. The filtration efficiency for di-2-ethylhexyl phthalate aerosol is greater than 95% when sampled for 30 minutes at 1 liter per minute from a test atmosphere containing 10 mg/cu m.

* Listed incorrectly as di-sec-octyl phthalate in 29 CFR 1910.93.

3. Interference

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

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

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 2.03 - 10.9 mg/cu m is 0.057. This value corresponds to a standard deviation of 0.29 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.1.

4.2 On the average the values obtained using the overall sampling and analytical method were 8% higher than the "true" values at the OSHA standard level.

These data are based on the validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

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

6. Apparatus

6.1 Sampling equipment - The sampling unit for the collection of personal air samples for the determination of organic aerosol has the following components:

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

6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of $\pm$ 5% (reference 11.2) at the recommended flow rate. The pump must be calibrated with a representative filter holder and filter in the line.

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

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (6-ft x 1/8-in stainless steel) packed with 5% OV-101 on 100/120 mesh Supelcoport.

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

6.6 Assembly for sample elution.

6.6.1 Extraction tube, Fisher brand disposable Pasteur pipet (Cat. No. 13-678-5A) modified as follows: cut off the upper 1-inch portion, i.e., just below the notch to eliminate the constricted portion, and flame seal the lower tapered end.

6.6.2 Dumont No. 5 precision watchmakers tweezers, rustproof.

6.6.3 Volumetric flask, 1 ml.

6.6.4 Ultrasonic cleaner.

6.6.5 Triangular file.

6.7 Microliter syringes: 10-microliter and other convenient sizes for making standard solutions.

6.8 Volumetric flasks: 10-ml and other convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 Di-2-ethylhexyl phthalate, reagent grade.

7.3 Tricosane, or other suitable internal standard.

7.4 Purified helium.

7.5 Prepurified hydrogen.

7.6 Filtered compressed air.

8. Procedure

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

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

8.3 Collection and Shipping of Samples

8.3.1 Assemble the filter in the three piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad.

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

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

8.3.4 A maximum sample size of 30 liters is recommended. Sample at a flow rate of 1.0 liter per minute. The flow rate should be known with an accuracy of at least $\pm$ 5%.

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

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

8.3.7 Collected sample cassette should be firmly sealed with the plugs in both the inlet and outlet.

8.3.8 Carefully record sample identity and all relevant sample data.

8.3.9 Blank: With each batch of samples submit one filter which is subjected to exactly the same handling as for the samples except that no air is drawn through it. Label this as a blank.

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

8.4 Analysis of Samples

8.4.1 Preparation of Samples

1. Open the cassette filter holder and carefully remove the cellulose membrane filter from the holder and cellulose backup pad.

2. With the aid of the Dumont tweezers, carefully roll the filter into a narrow cylinder. To do so, place the filter (sample side upwards) on a clean surface such as a watch glass and imagine a tangent to any edge of the circular filter. Pinch the filter with the long, sharp prongs of the tweezers along a line parallel to the imaginary tangent and about 1 cm inwards from the tangential point and start rolling the filter by gradually and carefully turning the tweezers' handle.

3. Insert the rolled filter into the modified pipet.

4. Add a known aliquot of the internal standard solution in carbon disulfide (ca. 100 microliters only) to the filter.

Note: If the external standard method is used, this last step should be eliminated.

8.4.2 Extraction of Samples

1. Position pipets upright and add ca. 1 ml of carbon disulfide to the filter in the disposable pipet. Be sure that the entire filter is submerged in carbon disulfide and that there are no air bubbles trapped.

2. Seal the top of the pipet with a wad of glass wool to avoid sample contamination and loss during the next step.

3. Arrange the sample-containing pipets upright in a beaker and place the beaker in the ultrasonic vibrator for 30 minutes.

4. With a sharp file, very carefully score the tip (about 1 cm above the sealed end) of the pipet and break the tip inside the 1 ml volumetric flask. Allow the carbon disulfide eluent to drain completely into the flask. Apply air pressure, if necessary, to aid draining.

5. Rinse the filter inside the pipet with more carbon disulfide by dropwise addition of solvent until the total volume of eluent collected is 1.0 ml. If the 1.0 ml mark is overshot, concentrate sample to 1.0 ml by using a slow nitrogen flush.

6. If an automatic sample injector is used, transfer the sample extracts into the automatic sample injector vials prior to analysis.

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

1. 30 ml/min (60 psig) helium carrier gas flow
2. 35 ml/min (25 psig) hydrogen gas flow to detector
3. 400 ml/min (60 psig) air flow to detector
4. 300°C injector temperature
5. 300°C manifold temperature (detector)
6. 230°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10 microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9 - 5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

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

8.5 Determination of Sample Recovery

8.5.1 Need for determination. Since the extraction scheme may be dependent on operator skill, it is necessary to determine the recovery of the compound. The sample recovery should be determined in duplicates and should cover the concentration ranges of interest. If the recovery is less than 95%, the appropriate correction factor should be used to calculate the "true" value.

8.5.2 Procedure for determining extraction efficiency. A known amount of the analyte, preferably equivalent to the sample concentration expected, is added to a representative cellulose membrane filter and air-dried. The analyte is then extracted from the filter and analyzed as described in Section 8.4. Duplicate determinations should agree within 5%.

For this validation study, an amount of the analyte equivalent to that present in a 30-liter sample at the selected level has been used for the extraction studies. Six filters at each of the three levels (0.5X, 1X, and 2X the OSHA standard) have been dosed accordingly and a known amount of internal standard was added to each filter prior to extraction. A parallel blank filter was also treated in the same manner except that no sample was added to it. All filters were then extracted and analyzed as described in Section 8.4. The recovery values obtained were at least 95% and as such no correction factor has been used in the determination of the "true" values.

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

$$\text{Recovery} = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same conditions
under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the OSHA standard level. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

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

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

where:

mg sample = mg found in sample filter
mg blank = mg found in blank filter

10.3 Divide the total weight by the extraction efficiency to obtain the corrected mg/sample

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{Recovery}}$$

10.4 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg(Section 10.3) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

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

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

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.2 Final Report, NIOSH Contract HSM-99-71-31. "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Analyte:	2-Ethoxyethyl Acetate	Method No:	S41
Matrix:	Air	Range:	262-1100 mg/cu m
OSHA Standard:	100 ppm (540 mg/cu m)	Precision (CV_T):	0.0624
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	12/6/74

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 262-1100 mg/cu m at an atmospheric temperature and pressure of 23°C and 764 mm Hg, using a 10 liter sample. Under the conditions of sample size (10 liters) the probable useful range of this method is 54-1620 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 16.2 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 38 mg of analyte when a test atmosphere containing 1100 mg/cu m of analyte in air was sampled at 0.19 liters per minute for 182 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

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

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

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 262-1100 mg/cu m was 0.0624. This value corresponds to a 33.7 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 7.0% higher than the "true" value at the OSHA standard level.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

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

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 An approved and calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3).

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in stainless steel) packed with 5% FFAP stationary phase on 100/120 mesh Supelcoport.

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

6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide

7.2 2-Ethoxyethyl Acetate, reagent grade

7.3 Dodecane, internal standard

7.4 Purified helium

7.5 Prepurified hydrogen

7.6 Filtered compressed air

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a rate of 0.2 liter per minute or less. The flow rate should be known with an accuracy of at least ±5%.

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

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

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

1. 30 cc/min. (60 psig) Helium carrier gas flow
2. 35 cc/min. (25 psig) hydrogen gas flow to detector
3. 400 cc/min. (60 psig) air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 100°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

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

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once for a given batch of charcoal the percentage of the specific compound that is removed in the desorption process.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

When using an automatic sample injector, the vials associated with that equipment may be used in place of the glass tube. These vials are capped with the Teflon faced septa.

For this validation study, the amount injected is equivalent to that present in a 10 liter sample at the selected level. Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into a 1 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. It is suggested that the internal standard concentration be approximately 70% of the highest concentration to be analyzed. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

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

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

where:

mg sample = mg found in front section of sample tube
mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

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

$$\text{ppm} = \frac{\text{mg}}{\text{cu m}} \times \frac{24.45}{\text{MW}} \times \frac{760}{\text{P}} \times \frac{(\text{T} + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Methyl Acetate

Analyte:	Methyl Acetate	Method No.:	S42
Matrix:	Air	Range:	343-1330 mg/cu m
OSHA Standard:	200 ppm (610 mg/cu m)	Precision (CV_T):	0.0547
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	12/6/74

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 343-1330 mg/cu m at an atmospheric temperature and pressure of 24°C and 761 mm Hg, using a 7 liter sample. Under the conditions of sample size (7 liters) the probable useful range of this method is 61-1830 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 12.8 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 14 mg of analyte when a test atmosphere containing 1330 mg/cu m of analyte in air was sampled at 0.19 liters per minute for 54 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

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

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

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 343-1330 mg/cu m was 0.0547. This value corresponds to a 33.4 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 8.0% higher than the "true" value at the OSHA standard level.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

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

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 An approved and calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3).

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (20-ft x 1/8-in stainless steel) packed with 10% FFAP on 80/100 mesh Chromosorb W AW-DMCS.

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

6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide

7.2 Methyl Acetate, reagent grade

7.3 Decane, internal standard

7.4 Purified helium

7.5 Prepurified hydrogen

7.6 Filtered compressed air

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 7 liters is recommended. Sample at a rate of 0.2 liter per minute or less. The flow rate should be known with an accuracy of at least ±5%.

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

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml. of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is stirred occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

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

1. 30 ml/min (60 psig) Helium carrier gas flow
2. 35 ml/min (25 psig) hydrogen gas flow to detector
3. 400 ml/min (60 psig) air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 70°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

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

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

When using an automatic sample injector, the vials associated with that equipment may be used in place of the glass tube. These vials are capped with the Teflon faced septa.

For this validation study, the amount injected is equivalent to that present in a 7 liter sample at the selected level. Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1 ml. of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. It is suggested that the internal standard concentration be approximately 70% of the highest concentration to be analyzed. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

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

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

where:

mg sample = mg found in front section of sample tube
mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

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

$$\text{ppm} = \frac{\text{mg}}{\text{cu m}} \times \frac{24.45}{\text{MW}} \times \frac{760}{\text{P}} \times \frac{(\text{T} + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Isobutyl Acetate

Analyte:	Isobutyl Acetate	Method No:	S44
Matrix:	Air	Range:	306-1280 mg/cu m
OSHA Standard:	150 ppm (700 mg/cu m)	Precision (CV_T):	0.0654
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	12/6/74

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 306-1280 mg/cu m at an atmospheric temperature and pressure of 24°C and 768 mm Hg, using a 10 liter sample. Under the conditions of sample size (10 liters) the probable useful range of this method is 70-2100 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 21 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 28 mg of analyte when a test atmosphere containing 1280 mg/cu m of analyte in air was sampled at 0.19 liters per minute for 113 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

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

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

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 306-1280 mg/cu m was 0.0654. This value corresponds to a 45.8 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 4.0% higher than the "true" value at the OSHA standard level.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

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

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 An approved and calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3).

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in stainless steel) packed with 5% FFAP stationary phase on 100/120 mesh Supelcoport.

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

6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide

7.2 Isobutyl Acetate , reagent grade

7.3 Undecane , internal standard

7.4 Purified helium

7.5 Prepurified hydrogen

7.6 Filtered compressed air

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a rate of 0.2 liter per minute or less. The flow rate should be known with an accuracy of at least ±5%.

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

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

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

1. 30 cc/min. (60 psig) Helium carrier gas flow
2. 35 cc/min. (25 psig) hydrogen gas flow to detector
3. 400 cc/min. (60 psig) air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 70°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

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

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once for a given batch of charcoal the percentage of the specific compound that is removed in the desorption process.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

When using an automatic sample injector, the vials associated with that equipment may be used in place of the glass tube. These vials are capped with the Teflon faced septa.

For this validation study, the amount injected is equivalent to that present in a 10 liter sample at the selected level. Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into a 1 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. It is suggested that the internal standard concentration be approximately 70% of the highest concentration to be analyzed. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

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

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

where:

mg sample = mg found in front section of sample tube
mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

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

$$\text{ppm} = \frac{\text{mg}}{\text{cu m}} \times \frac{24.45}{\text{MW}} \times \frac{760}{\text{P}} \times \frac{(\text{T} + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Isoamyl Acetate

Analyte:	Isoamyl Acetate	Method No.:	S45
Matrix:	Air	Range:	208-874 mg/cu m
OSHA Standard:	100 ppm (525 mg/cu m)	Precision (CV_T):	0.0557
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	12/6/74

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 208-874 mg/cu m at an atmospheric temperature and pressure of 21°C and 767 mm Hg, using a 10 liter sample. Under the conditions of sample size (10 liters)the probable useful range of this method is 50 -1575 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 16 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 33 mg of analyte when a test atmosphere containing 1010 mg/cu m of analyte in air was sampled at 0.19 liters per minute for 170 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

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

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

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 208-874 mg/cu m was 0.0557. This value corresponds to a 29.2 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 8.6% lower than the "true" value at the OSHA standard level.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

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

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 An approved and calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3).

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in stainless steel) packed with 5% FFAP stationary phase on 100/120 mesh Supelcoport.

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

6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide

7.2 Isoamyl Acetate, reagent grade

7.3 Tridecane, internal standard

7.4 Purified helium

7.5 Prepurified hydrogen

7.6 Filtered compressed air

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a rate of 0.2 liter per minute or less. The flow rate should be known with an accuracy of at least ±5%.

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

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml. of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is stirred occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

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

1. 30 ml/min (60 psig) Helium carrier gas flow
2. 35 ml/min (25 psig) hydrogen gas flow to detector
3. 400 ml/min (60 psig) air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 90°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

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

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

When using an automatic sample injector, the vials associated with that equipment may be used in place of the glass tube. These vials are capped with the Teflon faced septa.

For this validation study, the amount injected is equivalent to that present in a 10 liter sample at the selected level. Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1 ml. of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. It is suggested that the internal standard concentration be approximately 70% of the highest concentration to be analyzed. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

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

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

where:

mg sample = mg found in front section of sample tube
mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

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

$$\text{ppm} = \frac{\text{mg}}{\text{cu m}} \times \frac{24.45}{\text{MW}} \times \frac{760}{\text{P}} \times \frac{(\text{T} + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

sec-Butyl Acetate

Analyte:	sec-Butyl Acetate	Method No.:	S46
Matrix:	Air	Range:	478-2005 mg/cu m
OSHA Standard:	200 ppm (950 mg/cu m)	Precision (CV_T):	0.0540
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	12/6/74

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 478-2005 mg/cu m at an atmospheric temperature and pressure of 23 °C and 770 mm Hg, using a 9 liter sample. Under the conditions of sample size (10 liters) the probable useful range of this method is 95-2850 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 29 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 30 mg of analyte when a test atmosphere containing 1800 mg/cu m of analyte in air was sampled at 0.19 liters per minute for 87 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

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

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

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 478-2005 mg/cu m was 0.0540. This value corresponds to a 51.3 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 1.6% lower than the "true" value at the OSHA standard level.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

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

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 An approved and calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3).

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in stainless steel) packed with 5% FFAP stationary phase on 100/120 mesh Supelcoport.

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

6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide

7.2 sec.-Butyl Acetate , reagent grade

7.3 Undecane , internal standard

7.4 Purified helium

7.5 Prepurified hydrogen

7.6 Filtered compressed air

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a rate of 0.2 liter per minute or less. The flow rate should be known with an accuracy of at least ±5%.

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

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

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

1. 30 cc/min. (60 psig) Helium carrier gas flow
2. 35 cc/min. (25 psig) hydrogen gas flow to detector
3. 400 cc/min. (60 psig) air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 60°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

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

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once for a given batch of charcoal the percentage of the specific compound that is removed in the desorption process.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

When using an automatic sample injector, the vials associated with that equipment may be used in place of the glass tube. These vials are capped with the Teflon faced septa.

For this validation study, the amount injected is equivalent to that present in a 10 liter sample at the selected level. Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into a 1 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. It is suggested that the internal standard concentration be approximately 70% of the highest concentration to be analyzed. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

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

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

where:

mg sample = mg found in front section of sample tube
mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

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

$$\text{ppm} = \frac{\text{mg}}{\text{cu m}} \times \frac{24.45}{\text{MW}} \times \frac{760}{\text{P}} \times \frac{(\text{T} + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Butyl Acetate

Analyte:	Butyl Acetate	Method No.:	S47
Matrix:	Air	Range:	352-1475 mg/cu m
OSHA Standard:	150 ppm (710 mg/cu m)	Precision (CV_T):	0.0690
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	12/6/74

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 352-1475 mg/cu m at an atmospheric temperature and pressure of 23°C and 762 mm Hg using a 10 liter sample. Under the conditions of sample size (10 liters)the probable useful range of this method is 71-2130 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 21.3 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 30 mg of analyte when a test atmosphere containing 1475 mg/cu m of analyte in air was sampled at 0.19 liters per minute for 108 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

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

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

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 352-1475 mg/cu m was 0.0690. This value corresponds to a 49.0 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were the same as the "true" value at the OSHA standard level.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

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

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 An approved and calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3).

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in stainless steel) packed with 5% FFAP stationary phase on 100/120 mesh Supelcoport.

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

6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide

7.2 Butyl Acetate, reagent grade

7.3 Dodecane, internal standard

7.4 Purified helium

7.5 Prepurified hydrogen

7.6 Filtered compressed air

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a rate of 0.2 liter per minute or less. The flow rate should be known with an accuracy of at least ±5%.

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

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml. of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is stirred occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

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

1. 30 ml/min (60 psig) Helium carrier gas flow
2. 35 ml/min (25 psig) hydrogen gas flow to detector
3. 400 ml/min (60 psig) air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 90°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

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

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once for a given batch of charcoal the percentage of the specific compound that is removed in the desorption process.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

When using an automatic sample injector, the vials associated with that equipment may be used in place of the glass tube. These vials are capped with the Teflon faced septa.

For this validation study, the amount injected is equivalent to that present in a 10 liter sample at the selected level. Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into a 1 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. It is suggested that the internal standard concentration be approximately 70% of the highest concentration to be analyzed. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

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

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

where:

mg sample = mg found in front section of sample tube
mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

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

$$\text{ppm} = \frac{\text{mg}}{\text{cu m}} \times \frac{24.45}{\text{MW}} \times \frac{760}{\text{P}} \times \frac{(\text{T} + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

n-Propyl Acetate

Analyte:	n-Propyl Acetate	Method No.:	S48
Matrix:	Air	Range:	384-1610 mg/cu m
OSHA Standard:	200 ppm (840 mg/cu m)	Precision (CV_T):	0.0563
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	12/6/74

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 384-1610 mg/cu m at an atmospheric temperature and pressure of 22°C and 765 mm Hg, using a 10 liter sample. Under the conditions of sample size (10 liters) the probable useful range of this method is 84-2520 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 25.2 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 29 mg of analyte when a test atmosphere containing 1610 mg/cu m of analyte in air was sampled at 0.19 liters per minute for 94 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

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

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

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 384-1610 mg/ cu m was 0.0563. This value corresponds to a 47.3 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 8.0% higher than the "true" value at the OSHA standard level.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

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

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 An approved and calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3).

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in stainless steel) packed with 5% FFAP stationary phase on 100/120 mesh Supelcoport.

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

6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide

7.2 n-Propyl Acetate, reagent grade

7.3 Undecane, internal standard

7.4 Purified helium

7.5 Prepurified hydrogen

7.6 Filtered compressed air

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a rate of 0.2 liter per minute or less. The flow rate should be known with an accuracy of at least ±5%.

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

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml. of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is stirred occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

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

1. 30 ml/min (60 psig) Helium carrier gas flow
2. 35 ml/min (25 psig) hydrogen gas flow to detector
3. 400 ml/min (60 psig) air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 70°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

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

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

When using an automatic sample injector, the vials associated with that equipment may be used in place of the glass tube. These vials are capped with the Teflon faced septa.

For this validation study, the amount injected is equivalent to that present in a 10 liter sample at the selected level. Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1 ml. of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. It is suggested that the internal standard concentration be approximately 70% of the highest concentration to be analyzed. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

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

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

where:

mg sample = mg found in front section of sample tube
mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

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

$$\text{ppm} = \frac{\text{mg}}{\text{cu m}} \times \frac{24.45}{\text{MW}} \times \frac{760}{\text{P}} \times \frac{(\text{T} + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Ethyl Acetate

Analyte:	Ethyl Acetate	Method No.:	S49
Matrix:	Air	Range:	704-2950 mg/cu m
OSHA Standard:	400 ppm (1400 mg/cu m)	Precision ($\overline{CV}_T$):	0.058
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	1/17/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 704-2950 mg/cu m at an atmospheric temperature and pressure of 23 °C and 759 mm Hg, using a 6 liter sample. Under the conditions of sample size (6 liters) the probable useful range of this method is 140-4200 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 25 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 25 mg of analyte when a test atmosphere containing 2950 mg/cu m of analyte in air was sampled at 0.19 liters per minute for 45 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

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

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

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 704-2950 mg/cu m was 0.058. This value corresponds to an 81 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 1.4% lower than the "true" value at the OSHA standard level.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

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

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3).

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in stainless steel) packed with 5% FFAP stationary phase on 100/120 mesh Supelcoport.

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

6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide

7.2 Ethyl Acetate, reagent grade

7.3 Undecane, or other suitable internal standard

7.4 Purified helium

7.5 Prepurified hydrogen

7.6 Filtered compressed air

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 6 liters is recommended. Sample at a rate of 0.2 liter per minute or less. The flow rate should be known with an accuracy of at least ±5%.

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

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

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

1. 30 ml/min (60 psig) Helium carrier gas flow
2. 35 ml/min (25 psig) Hydrogen gas flow to detector
3. 400 ml/min (60 psig) Air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 60°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

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

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample injector vials, capped with Teflon-faced septa, may be used in place of the glass tubes.

Six tubes at each of three concentration levels (0.5X,1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 6 liter sample at the selected level. The tubes are allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

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

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

where:

mg sample = mg found in front section of sample tube
mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liters/cu m)}}{\text{Air Volume Sampled (liters)}}$$

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

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

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Isopropyl Acetate

Analyte:	Isopropyl Acetate	Method No.: S50	
Matrix:	Air	Range: 446-1870 mg/cu m	
OSHA Standard:	250 ppm (950 mg/cu m)	Precision ($\overline{CV}_T$):	0.067
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	1/17/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 446-1870 mg/cu m at an atmospheric temperature and pressure of 23°C and 770 mm Hg, using an 8 liter sample. Under the conditions of sample size (8 liters) the probable useful range of this method is 95-2850 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 23 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 26 mg of analyte when a test atmosphere containing 1870 mg/cu m of analyte in air was sampled at 0.19 liters per minute for 72 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

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

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

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 446-1870 mg/cu m was 0.067. This value corresponds to a 63.6 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 0.4% lower than the "true" value at the OSHA standard level.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

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

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3).

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in stainless steel) packed with 5% FFAP stationary phase on 100/120 mesh Supelcoport.

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

6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide

7.2 Isopropyl Acetate, reagent grade

7.3 Undecane, or other suitable internal standard

7.4 Purified helium

7.5 Prepurified hydrogen

7.6 Filtered compressed air

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 9 liters is recommended. Sample at a rate of 0.2 liter per minute or less. The flow rate should be known with an accuracy of at least ±5%.

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

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

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

1. 30 ml/min (60 psig) Helium carrier gas flow
2. 35 ml/min (25 psig) Hydrogen gas flow to detector
3. 400 ml/min (60 psig) Air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 60°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

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

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample injector vials, capped with Teflon-faced septa, may be used in place of the glass tubes.

Six tubes at each of three concentration levels (0.5X,1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 9 liter sample at the selected level. The tubes are allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

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

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

where:

mg sample = mg found in front section of sample tube
mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liters/cu m)}}{\text{Air Volume Sampled (liters)}}$$

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

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

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

n-Amyl Acetate

Analyte:	n-Amyl Acetate	Method No.: S51
Matrix:	Air	Range: 208-871 mg/cu m
OSHA Standard:	100 ppm (525 mg/cu m)	Precision ($\overline{CV}_T$): 0.051
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 1/17/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 208-871 mg/cu m at an atmospheric temperature and pressure of 23°C and 767 mm Hg, using an 11 liter sample. Under the conditions of sample size (10 liters) the probable useful range of this method is 50-1575 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 16 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 30 mg of analyte when a test atmosphere containing 871 mg/cu m of analyte in air was sampled at 0.19 liters per minute for 180 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

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

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

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 208-871 mg/cu m was 0.051. This value corresponds to a 27 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 1.2% lower than the "true" value at the OSHA standard level.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

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

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3).

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in stainless steel) packed with 5% FFAP stationary phase on 100/120 mesh Supelcoport.

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

6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide

7.2 n-Amyl Acetate, reagent grade

7.3 Tridecane, or other suitable internal standard

7.4 Purified helium

7.5 Prepurified hydrogen

7.6 Filtered compressed air

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a rate of 0.2 liter per minute or less. The flow rate should be known with an accuracy of at least ±5%.

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

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

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

1. 30 ml/min (60 psig) Helium carrier gas flow
2. 35 ml/min (25 psig) Hydrogen gas flow to detector
3. 400 ml/min (60 psig) Air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 90°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

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

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample injector vials, capped with Teflon-faced septa, may be used in place of the glass tubes.

Six tubes at each of three concentration levels (0.5X,1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 10 liter sample at the selected level. The tubes are allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

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

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

where:

mg sample = mg found in front section of sample tube
mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liters/cu m)}}{\text{Air Volume Sampled (liters)}}$$

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

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

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Allyl Alcohol

Analyte:	Allyl Alcohol	Method No.:	S52
Matrix:	Air	Range:	1.8-8.4 mg/cu m
OSHA Standard:	2 ppm (4.8 mg/cu m)	Precision ($\overline{CV}_T$):	0.111
Procedure:	Adsorption on charcoal, desorption with eluent, GC	Validation Date:	1/17/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide containing 5% 2-propanol.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 1.8-8.4 mg/cu m at an atmospheric temperature and pressure of 25 C and 747 mm Hg, using a 10 liter sample. Under the conditions of sample size (10 liters) the probable range of this method is 0.5-15 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 0.1-mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of the analyte and other substances in the air. The first section of the charcoal tube was found to hold at least 0.38 mg of the analyte when a test atmosphere of 8 mg/cu m of the analyte in dry air was sampled at 0.2 liters per minute for 240 minutes. Breakthrough did not occur at this time, i.e., no allyl alcohol was found on the backup section

of the charcoal tubes. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2.) If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments with toluene indicate that high humidity severely decreases the breakthrough volume.

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

3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 1.8-8.4 mg/cu m was 0.111. This value corresponds to a standard deviation of 0.52 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 The average values obtained using the overall sampling and analytical method were 1.2% lower than the "true" value at the OSHA standard level.

4.3 The above data are based on validation experiments using the internal standard method. (Reference 11.2)

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more compounds suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined accurately (±5%) at the recommended flow rate, (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600 C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in. stainless steel) packed with 10% FFAP on 80/100 Chromosorb W-AW.

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

6.6 Two-milliliter glass sample containers with glass stoppers or Teflon®-lined caps. If an automatic sample injector is used, the sample injector vials can be used.

6.7 Microliter syringes: 10-µl, and other convenient sizes for making standards.

6.8 Pipets: 1.0-ml delivery type.

6.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Eluent: Carbon disulfide (chromatographic grade) containing 5% 2-propanol (reagent grade).

7.2 Allyl Alcohol (reagent grade).

7.3 Internal Standard: n-Dodecane (99+%) or other suitable standard.

7.4 n-Heptane (reagent grade).

7.5 Purified nitrogen.

7.6 Prepurified hydrogen.

7.7 Filtered compressed air.

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a flow of 0.20 liters per minute. The flow rate should be known with an accuracy of at least ±5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available the elevation should be recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

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

8.3.10 A sample of the suspected compound should be submitted to the laboratory in glass containers with Teflon®-lined caps. These liquid bulk samples should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container or automatic sample injector vial. The separating section of foam is removed and discarded; the second section is transferred to another sample container or vial. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of the eluent is pipetted into each sample container. For the internal standard method a 0.005 percent solution of internal standard in the eluent is used. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. The sample vials should be capped as soon as the solvent is added to minimize volatilization.

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

1. 30 ml/min (80 psig) nitrogen carrier gas flow.
2. 30 ml/min (50 psig) hydrogen gas flow to detector.
3. 300 ml/min (50 psig) air flow to detector.
4. 200 C injector temperature.
5. 300 C manifold temperature (detector).
6. 80 C column temperature.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-µl syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 µl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-µl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 µl to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 µl in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique. In this case 2-µl injections are satisfactory.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below (see Section 9).

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided that the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.0-ml sample container. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. A

12 mg/ml stock solution of the analyte in n-heptane is prepared. A known amount of this solution is injected directly into the activated charcoal with a 10-µl syringe, and the container is capped. The amount injected is equivalent to that present in a 10-liter sample at the selected level. It is not practical to inject the neat liquid directly because the amounts to be added would be too small to measure accurately.

At least six tubes at each of three levels (0.5X, 1X, and 2X the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These six tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

The weight of analyte found in each tube is determined from the standard curve (Section 9). Desorption efficiency is determined by the following equation:

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/ml of eluent. To minimize error due to the volatility of the eluent, one can add 10 times the weight to 10 ml of the eluent. (For the internal standard method use eluent containing 0.005 percent of the internal standard.) A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentrations in mg/ml versus peak area. In the case of the internal standard method plot the concentration versus the ratio of peak area of analyte to peak area of internal standard.

Note: Whether the absolute area or internal standard method is used standard solutions should be analyzed at the same time that the sample analysis is done. This will minimize the effect variations of FID response.

10. Calculations

10.1 Read the weights, in mg, corresponding to each peak area (area ratio in case of the internal standard method) from the standard curve. No volume corrections are needed, because the standard curve is based on mg/ml eluent and the volume of sample injected is identical to the volume of the standards injected.

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

mg = mg sample - mg blank

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

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

10.4 Read the desorption efficiency from the curve (Section 8.5.2) for the amount of analyte found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

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

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm:

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (C) of air sampled
24.45 = molar volume (liter/mole) at 25 C and 760 mm Hg
MW = molecular weight (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (K)

11. References

11.1 White L. D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 "Documentation of NIOSH Validation Tests", Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract No. HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes, September 15, 1972".

sec-Butyl Alcohol

Analyte:	sec-Butyl Alcohol	Method No.:	S53
Matrix:	Air	Range:	270-850 mg/cu m
OSHA Standard:	150 ppm (455 mg/cu m)	Precision (CV_T):	0.066
Procedure:	Adsorption on charcoal, desorption with eluent, GC	Validation Date:	1/17/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide containing 1% 2-propanol.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 270-850 mg/cu m at an atmospheric temperature and pressure of 25 C and 751 mm Hg, using a 10-liter sample. Under the conditions of sample size (10 liters) the probable useful range of this method is 45-850 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 6-mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of the analyte and other substances in the air. The first section of the charcoal tube was found to hold 12.3 mg of the analyte when a test atmosphere of 823 mg/cu m of the analyte in dry air was sampled at 0.2 liters per minute for 75 minutes; breakthrough was observed at that

i.e., the concentration of the analyte in the effluent was 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2.) If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments with toluene indicate that high humidity severely decreases the breakthrough volume.

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

3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 270 to 850 mg/cu m was 0.066. This value corresponds to a standard deviation of 30 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 The average values obtained using the overall sampling and analytical method were 7.2% higher than the "true" value at the OSHA standard level.

4.3 The above data are based on validation experiments using the internal standard method. (Reference 11.2)

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more compounds suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined accurately (±5%) at the recommended flow rate, (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600 C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in. stainless steel) packed with 10% FFAP on 80/100 Chromosorb W-AW.

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

6.6 Two-milliliter glass sample containers with glass stoppers or Teflon®-lined caps. If an automatic sample injector is used, the sample injector vials can be used.

6.7 Microliter syringes: 10-µl, and other convenient sizes for making standards.

6.8 Pipets: 1.0-ml delivery type.

6.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Eluent: Carbon disulfide (chromatographic grade) containing 1% 2-propanol (reagent grade).

7.2 2-Butanol (reagent grade).

7.3 Internal Standard: n-Undecane (99+%) or other suitable standard.

7.4 Purified nitrogen.

7.5 Prepurified hydrogen.

7.6 Filtered compressed air.

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a flow of 0.20 liters per minute or less. The flow rate should be known with an accuracy of at least ±5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available the elevation should be recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

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

8.3.10 A sample of the suspected compound should be submitted to the laboratory in glass containers with Teflon®-lined caps. These liquid bulk samples should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container or automatic sample injector vial. The separating section of foam is removed and discarded; the second section is transferred to another sample container or vial. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of the eluent is pipetted into each sample container. For the internal standard method a 0.4 percent solution of internal standard in the eluent is used. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. The sample vials should be capped as soon as the solvent is added to minimize volatilization.

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

1. 30 ml/min (80 psig) nitrogen carrier gas flow.
2. 30 ml/min (50 psig) hydrogen gas flow to detector.
3. 300 ml/min (50 psig) air flow to detector.
4. 200 C injector temperature.
5. 300 C manifold temperature (detector).
6. 70 C column temperature.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-µl syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 µl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-µl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 µl to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 µl in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique. In this case 2-µl injections are satisfactory.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below (see Section 9).

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided that the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.0-ml sample container. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes.

A known amount of the analyte is injected directly into the activated charcoal with a 10-µl syringe, and the container is capped. The amount injected is equivalent to that present in a 10-liter sample at the selected level.

At least six tubes at each of three levels (0.5X, 1X, and 2X the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These six tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

The weight of analyte found in each tube is determined from the standard curve (Section 9). Desorption efficiency is determined by the following equation:

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/ml of eluent. To minimize error due to the volatility of the eluent, one can add 10 times the weight to 10 ml of the eluent. (For the internal standard method use eluent containing 0.4 percent of the internal standard.) A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentrations in mg/ml versus peak area. In the case of the internal standard method plot the concentration versus the ratio of peak area of analyte to peak area of internal standard.

Note: Whether the absolute area or internal standard method is used standard solutions should be analyzed at the same time that the sample analysis is done. This will minimize the effect variations of FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area (area ratio in case of the internal standard method) from the

standard curve. No volume corrections are needed, because the standard curve is based on mg/ml eluent and the volume of sample injected is identical to the volume of the standards injected.

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

mg = mg sample - mg blank

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

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

10.4 Read the desorption efficiency from the curve (Section 8.5.2) for the amount of analyte found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

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

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm:

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (C) of air sampled
24.45 = molar volume (liter/mole) at 25 C and 760 mm Hg
MW = molecular weight (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (K)

11. References

11.1 White L. D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 "Documentation of NIOSH Validation Tests", Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract No. HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes, September 15, 1972."

Cyclohexanol

Analyte:	Cyclohexanol	Method No.: S54
Matrix:	Air	Range: 95-380 mg/cu m
OSHA Standard:	50 ppm (205 mg/cu m)	Precision ($\overline{CV_T}$): 0.080
Procedure:	Adsorption on charcoal, desorption with eluent, GC	Validation Date: 1/17/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide containing 5% 2-propanol.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 95-380 mg/cu m at an atmospheric temperature and pressure of 25 C and 742 mm Hg, using a 10-liter sample. Under the conditions of sample size (10 liters) the probable range of this method is 20-600 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 6-mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of the analyte and other substances in the air. The first section of the charcoal tube was found to hold at least 19.8 mg of the analyte when a test atmosphere of 414 mg/cu m of the analyte in dry air was sampled at 0.2 liters per minute for 4 hours. Breakthrough did not occur, i.e.,

the concentration of the analyte in the effluent was less than 2% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section or urethane foam. See Section 6.2.) If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments with toluene indicate that high humidity severely decreases the breakthrough volume.

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

3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 95 to 380 mg/cu m was 0.080. This value corresponds to a standard deviation of 16.4 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 The average values obtained using the overall sampling and analytical method were 1.1% lower than the "true" value at the OSHA standard level.

4.3 The above data are based on validation experiments using the internal standard method. (Reference 11.2)

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more compounds suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined accurately (±5%) at the recommended flow rate, (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600 C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in. stainless steel) packed with 10% FFAP on 80/100 Chromosorb W-AW.

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

6.6 Two-milliliter glass sample containers with glass stoppers or Teflon®-lined caps. If an automatic sample injector is used, the sample injector vials can be used.

6.7 Microliter syringes: 10-µl, and other convenient sizes for making standards.

6.8 Pipets: 1.0-ml delivery type.

6.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Eluent: Carbon disulfide (chromatographic grade) containing 5% 2-propanol (reagent grade).

7.2 Cyclohexanol (reagent grade).

7.3 Internal Standard: n-Pentadecane (99+%) or other suitable standard.

7.4 n-Heptane (reagent grade).

7.5 Purified nitrogen.

7.6 Prepurified hydrogen.

7.7 Filtered compressed air.

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a flow of 0.20 liters per minute or less. The flow rate should be known with an accuracy of at least ±5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available the elevation should be recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

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

8.3.10 A sample of the suspected compound should be submitted to the laboratory in glass containers with Teflon®-lined caps. These liquid bulk samples should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container or automatic sample injector vial. The separating section of foam is removed and discarded; the second section is transferred to another sample container or vial. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of the eluent is pipetted into each sample container. For the internal standard method a 0.2 percent solution of internal standard in the eluent is used. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. The sample vials should be capped as soon as the solvent is added to minimize volatilization.

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

1. 30 ml/min (80 psig) nitrogen carrier gas flow.
2. 30 ml/min (50 psig) hydrogen gas flow to detector.
3. 300 ml/min (50 psig) air flow to detector.
4. 200 C injector temperature.
5. 300 C manifold temperature (detector).
6. 120 C column temperature.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-µl syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 µl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-µl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 µl to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 µl in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique. In this case 2-µl injections are satisfactory.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below (see Section 9).

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided that the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.0-ml sample container. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. A

500 mg/ml stock solution of the analyte in n-heptane is prepared. A known amount of this solution is injected directly into the activated charcoal with a 10-µl syringe, and the container is capped. The amount injected is equivalent to that present in a 10-liter sample at the selected level. It is not practical to inject the neat liquid directly because the amounts to be added would be too small to measure accurately.

At least six tubes at each of three levels (0.5X, 1X, and 2X the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These six tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

The weight of analyte found in each tube is determined from the standard curve (Section 9). Desorption efficiency is determined by the following equation:

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/ml of eluent. To minimize error due to the volatility of the eluent, one can add 10 times the weight to 10 ml of the eluent. (For the internal standard method use eluent containing 0.2 percent of the internal standard.) A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentrations in mg/ml versus peak area. In the case of the internal standard method plot the concentration versus the ratio of peak area of analyte to peak area of internal standard.

Note: Whether the absolute area or internal standard method is used standard solutions should be analyzed at the same time that the sample analysis is done. This will minimize the effect variations of FID response.

10. Calculations

10.1 Read the weights, in mg, corresponding to each peak area (area ratio in case of the internal standard method) from the standard curve. No volume corrections are needed, because the standard curve is based on mg/ml eluent and the volume of sample injected is identical to the volume of the standards injected.

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

mg = mg sample - mg blank

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

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

10.4 Read the desorption efficiency from the curve (Section 8.5.2) for the amount of analyte found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

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

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm:

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (C) of air sampled
24.45 = molar volume (liter/mole) at 25 C and 760 mm Hg
MW = molecular weight (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (K)

11. References

11.1 White L. D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 "Documentation of NIOSH Validation Tests", Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract No. HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes, September 15, 1972."

Diacetone Alcohol

Analyte:	Diacetone Alcohol	Method No.:	S55
Matrix:	Air	Range:	140-510 mg/cu m
OSHA Standard:	50 ppm (240 mg/cu m)	Precision ($\overline{CV}_T$):	0.104
Procedure:	Adsorption on charcoal, desorption with eluent, GC	Validation Date:	1/17/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide containing 5% 2-propanol.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 140-510 mg/cu m at an atmospheric temperature and pressure of 25 C and 746 mm Hg, using a 10-liter sample. Under the conditions of sample size (10 liters) the probable range of this method is 24-750 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 6-mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of the analyte and other substances in the air. The first section of the charcoal tube was found to hold at least 24 mg of the analyte when a test atmosphere of 507 mg/cu m of the analyte in dry air was sampled at 0.2 liters per minute for 4 hours. Breakthrough did not occur at this time;

the concentration of the analyte in the effluent was less than 2% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2.) If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments with toluene indicate that high humidity severely decreases the breakthrough volume.

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

3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 140 to 510 mg/cu m was 0.104. This value corresponds to a standard deviation of 24.1 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 The average values obtained using the overall sampling and analytical method were 11.9% lower than the "true" value at the OSHA standard level.

4.3 The above data are based on validation experiments using the internal standard method. (Reference 11.2)

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more compounds suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined accurately (±5%) at the recommended flow rate, (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600 C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in. stainless steel) packed with 10% FFAP on 80/100 Chromosorb W-AW.

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

6.6 Two-milliliter glass sample containers with glass stoppers or Teflon®-lined caps. If an automatic sample injector is used, the sample injector vials can be used.

6.7 Microliter syringes: 10-µl, and other convenient sizes for making standards.

6.8 Pipets: 1.0-ml delivery type.

6.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Eluent: Carbon disulfide (chromatographic grade) containing 5% 2-propanol (reagent grade).

7.2 Diacetone Alcohol (reagent grade).

7.3 Internal Standard: n-Pentadecane (99+%) or other suitable standard.

7.4 n-Heptane (reagent grade).

7.5 Purified nitrogen.

7.6 Prepurified hydrogen.

7.7 Filtered compressed air.

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a flow of 0.20 liters per minute or less. The flow rate should be known with an accuracy of at least ±5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available the elevation should be recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

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

8.3.10 A sample of the suspected compound should be submitted to the laboratory in glass containers with Teflon®-lined caps. These liquid bulk samples should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container or automatic sample injector vial. The separating section of foam is removed and discarded; the second section is transferred to another sample container or vial. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of the eluent is pipetted into each sample container. For the internal standard method a 0.2 percent solution of internal standard in the eluent is used. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. The sample vials should be capped as soon as the solvent is added to minimize volatilization.

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

1. 30 ml/min (80 psig) nitrogen carrier gas flow.
2. 30 ml/min (50 psig) hydrogen gas flow to detector.
3. 300 ml/min (50 psig) air flow to detector.
4. 200 C injector temperature.
5. 300 C manifold temperature (detector).
6. 120 C column temperature.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-µl syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 µl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-µl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 µl to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 µl in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique. In this case 2-µl injections are satisfactory.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below (see Section 9).

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided that the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.0-ml sample container. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. A

600 mg/ml stock solution of the analyte in n-heptane is prepared. A known amount of this solution is injected directly into the activated charcoal with a 10-µl syringe, and the container is capped. The amount injected is equivalent to that present in a 10-liter sample at the selected level. It is not practical to inject the neat liquid directly because the amounts to be added would be too small to measure accurately.

At least six tubes at each of three levels (0.5X, 1X, and 2X the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These six tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

The weight of analyte found in each tube is determined from the standard curve (Section 9). Desorption efficiency is determined by the following equation:

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/ml of eluent. To minimize error due to the volatility of the eluent, one can add 10 times the weight to 10 ml of the eluent. (For the internal standard method use eluent containing 0.2 percent of the internal standard.) A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentrations in mg/ml versus peak area. In the case of the internal standard method plot the concentration versus the ratio of peak area of analyte to peak area of internal standard.

Note: Whether the absolute area or internal standard method is used standard solutions should be analyzed at the same time that the sample analysis is done. This will minimize the effect variations of FID response.

10. Calculations

10.1 Read the weights, in mg, corresponding to each peak area (area ratio in case of the internal standard method) from the standard curve. No volume corrections are needed, because the standard curve is based on mg/ml eluent and the volume of sample injected is identical to the volume of the standards injected.

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

mg = mg sample - mg blank

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

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

10.4 Read the desorption efficiency from the curve (Section 8.5.2) for the amount of analyte found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

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

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm:

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (C) of air sampled
24.45 = molar volume (liter/mole) at 25 C and 760 mm Hg
MW = molecular weight (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (K)

11. References

11.1 White L. D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 "Documentation of NIOSH Validation Tests", Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract No. HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes, September 15, 1972".

Ethyl Alcohol

Analyte:	Ethyl Alcohol	Method No.:	S56
Matrix:	Air	Range:	900-3300 mg/cu m
OSHA Standard:	1000 ppm (1885 mg/cu m)	Precision ($\overline{CV}_T$):	0.065
Procedure:	Adsorption on charcoal, desorption with eluent, GC	Validation Date:	1/17/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide containing 1% 2-butanol.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 900-3300 mg/cu m at an atmospheric temperature and pressure of 25 C and 742 mm Hg, using a 1-liter sample. Under the conditions of sample size (1 liter) the probable range of this method is 180-3500 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 3-mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of the analyte and other substances in the air. The first section of the charcoal tube was found to hold 5.2 mg of the analyte when a test atmosphere of 3275 mg/cu m of the analyte in dry air was sampled at 0.2 liters per minute for 8 minutes. Breakthrough occurred at this time, i.e., the concentration of

the analyte in the effluent was 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2.) If a particular atmosphere is suspected of containing a large amount of contaminants, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments with toluene indicate that high humidity severely decreases the breakthrough volume.

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

3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 900 to 3300 mg/cu m was 0.065. This value corresponds to a standard deviation of 126 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 The average values obtained using the overall sampling and analytical method were 2.2% less than the "true" value at the OSHA standard level.

4.3 The above data are based on validation experiments using the internal standard method. (Reference 11.2)

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more compounds suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined accurately (±5%) at the recommended flow rate, (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600 C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in. stainless steel) packed with 10% FFAP on 80/100 Chromosorb W-AW.

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

6.6 Two-milliliter glass sample containers with glass stoppers or Teflon®-lined caps. If an automatic sample injector is used, the sample injector vials can be used.

6.7 Microliter syringes: 10-µl, and other convenient sizes for making standards.

6.8 Pipets: 1.0-ml delivery type.

6.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Eluent: Carbon disulfide (chromatographic grade) containing 1% 2-butanol (reagent grade).

7.2 Ethanol (reagent grade).

7.3 Internal Standard: n-Undecane (99+%) or other suitable standard.

7.4 Purified nitrogen.

7.5 Prepurified hydrogen.

7.6 Filtered compressed air.

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 1 liter is recommended. Sample for 20 minutes at a flow of 0.05 liters per minute. The flow rate should be known with an accuracy of at least ±5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available the elevation should be recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

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

8.3.10 A sample of the suspected compound should be submitted to the laboratory in glass containers with Teflon®-lined caps. These liquid bulk samples should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container or automatic sample injector vial. The separating section of foam is removed and discarded; the second section is transferred to another sample container or vial. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of the eluent is pipetted into each sample container. For the internal standard method a 0.2 percent solution of internal standard in the eluent is used. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. The sample vials should be capped as soon as the solvent is added to minimize volatilization.

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

1. 30 ml/min (80 psig) nitrogen carrier gas flow.
2. 30 ml/min (50 psig) hydrogen gas flow to detector.
3. 300 ml/min (50 psig) air flow to detector.
4. 200 C injector temperature.
5. 300 C manifold temperature (detector).
6. 70 C column temperature.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-µl syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 µl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-µl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 µl to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 µl in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique. In this case 2-µl injections are satisfactory.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below (see Section 9).

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided that the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.0-ml sample container. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes.

A known amount of the analyte is injected directly into the activated charcoal with a 10-µl syringe, and the container is capped. The amount injected is equivalent to that present in a 1-liter sample at the selected level.

At least six tubes at each of three levels (0.5X, 1X, and 2X the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These six tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

The weight of analyte found in each tube is determined from the standard curve (Section 9). Desorption efficiency is determined by the following equation:

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/ml of eluent. To minimize error due to the volatility of the eluent, one can add 10 times the weight to 10 ml of the eluent. (For the internal standard method use eluent containing 0.2 percent of the internal standard.) A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentrations in mg/ml versus peak area. In the case of the internal standard method plot the concentration versus the ratio of peak area of analyte to peak area of internal standard.

Note: Whether the absolute area or internal standard method is used standard solutions should be analyzed at the same time that the sample analysis is done. This will minimize the effect variations of FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area (area ratio in case of the internal standard method) from the

standard curve. No volume corrections are needed, because the standard curve is based on mg/ml eluent and the volume of sample injected is identical to the volume of the standards injected.

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

mg = mg sample - mg blank

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

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

10.4 Read the desorption efficiency from the curve (Section 8.5.2) for the amount of analyte found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

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

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm:

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (C) of air sampled
24.45 = molar volume (liter/mole) at 25 C and 760 mm Hg
MW = molecular weight (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (K)

11. References

11.1 White L. D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 "Documentation of NIOSH Validation Tests", Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract No. HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes, September 15, 1972."

Hydroquinone

Analyte:	Hydroquinone	Method No:	S57
Matrix:	Air	Range:	0.84 - 4.05 mg/cu m
OSHA Standard:	2 mg/cu m	Precision ($\overline{CV}_T$):	0.061
Procedure:	Filter collection, extraction with aqueous acetic acid, HPLC	Validation Date:	11/26/76

1. Principle of the Method

1.1 A known volume of air is drawn through a mixed cellulose ester membrane filter to trap the hydroquinone aerosol present. This method is not applicable for sampling environments where significant hydroquinone vapor may be present.

1.2 Immediately after sample collection, the filter in the cassette is transferred into a jar and treated with aqueous acetic acid. Samples are stored and shipped in jars containing acetic acid solution.

1.3 An aliquot of the sample is injected into a high performance liquid chromatograph (HPLC) equipped with a variable wavelength UV detector set at 290 nm.

1.4 The area of the resulting sample peak is used as a measure of analyte concentration by comparison with corresponding areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 0.84 - 4.05 mg/cu m at an atmospheric temperature and pressure of 20°C and 762 mm Hg, using a 90 liter sample. For a sample size of 90 liters the working range of the method is estimated to be 0.4 - 8.0 mg/cu m.

2.2 The method may be extended to higher values by further dilution of the sample solution. The sensitivity of the analytical method is estimated to be at least 1.5 µg per ml.

3. Interference

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

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

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.84 - 4.05 mg/cu m was 0.061. This value corresponds to a 0.12 mg/cu m standard deviation at the OSHA standard level. Statistical information can be found in Reference 11.2. Details of the test procedure are found in Reference 11.3.

4.2 A collection efficiency of at least 96% was determined for the collection medium; thus, no significant bias was introduced in the sample collection step. There was also no bias in the analytical method--the average recovery from the filters was 99.4%. In addition, the samples were found to be stable when stored in the dilute acetic acid solution for seven days. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

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

5.2 One disadvantage is that some sample workup is required in the field to insure the stability of the sample. This step involves the transfer of the sample filter into a jar and addition of an aqueous solution of acetic acid.

6. Apparatus

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

6.1.1 Filter. The filter unit consists of the filter medium (Section 6.2) and 37-mm 3-piece cassette filter holder.

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

6.1.3 Ointment jars. Use squat form with Teflon film gaskets and screw cap for sample storage.

6.1.4 Graduated cylinder, 10 ml.

6.1.5 1% Aqueous acetic acid. Prepare a sufficient quantity for extraction and storage of samples.

6.1.6 Thermometer.

6.1.7 Barometer.

6.1.8 Stopwatch.

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

6.3 High Pressure Liquid Chromatograph equipped with a detector capable of UV detection at 290 nm.

6.4 Column (25 cm x 4.6 mm I.D. stainless steel) packed with Partisil™ 10-ODS, or equivalent.

6.5 Syringe, 100 µl, for HPLC injection.

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

6.7 Microliter syringes, 10-microliter and other convenient sizes for making standard solution.

6.8 Volumetric flasks, 25-milliliter and other convenient sizes for making standard solutions and sample dilutions.

7. Reagents

7.1 Hydroquinone, reagent grade.

7.2 Distilled water.

7.3 Glacial Acetic acid.

7.4 Acetic acid in distilled water, 1%. Prepare by diluting

10 ml of glacial acetic acid to 1000 ml with distilled water. This solution is used for sample extraction and all dilutions and also as the mobile phase for the HPLC analysis.

8. Procedure

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

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

8.3 Collection and shipping of samples

8.3.1 Assemble the filter in the three-piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad and the filter holder is held together by plastic tape or a shrinkable cellulose band. If the middle piece of the filter holder does not fit snugly into the bottom piece of the filter holder, sample leakage will occur around the filter. A piece of flexible tubing is used to connect the filter holder to the pump.

8.3.2 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 90 liters is recommended. Sample at a flow rate of 1.5 liter per minute. The flow rate should be known with an accuracy of at least $\pm$ 5%.

8.3.4 Turn the pump on and begin sample collection. Since it is possible for filters to become plugged by heavy 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 after the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation.

8.3.6 Open the cassette filter holder. Carefully remove the cellulose membrane filter from the holder and cellulose backup pad with the aid of appropriate tweezers and transfer filter to the 2-oz. ointment jar.

8.3.7 Add 10-ml of 1% acetic acid into the jar and properly cap unit. Gently swirl the jar to ensure that the filter is thoroughly wetted.

8.3.8 Shipping. The ointment jars should be shipped in a suitable container, designed to prevent damage and leakage in transit.

8.3.9 Blank. With each batch of samples, submit one filter which is subjected to exactly the same handling as for the samples except that no air is drawn through it. Label this as a blank. Submit one blank for every ten samples.

8.3.10 Bulk Sample. A bulk sample of the suspected material should be submitted to the laboratory in a glass container lined with a Teflon cap. Label of the bulk sample should match air samples for identification purposes.

8.4 Analysis of Samples

8.4.1 Preparation of samples:

1. Transfer the sample solution to a 25 ml volumetric flask.

2. Rinse at least twice with 5 ml of 1% acetic acid and add the washings to the volumetric flask.

3. Make volume up to 25 ml with 1% acetic acid.

8.4.2 Analysis by high pressure liquid chromatograph. The mobile phase is 1% acetic acid. The typical operating conditions for the liquid chromatograph are:

1. 1.0 ml/min solvent flow rate

2. Ambient column temperature

3. 400-600 psi system pressure

8.4.3 Injection. The first step in the analysis is the injection of the sample into the liquid chromatograph.

A 100 µl-sample aliquot is recommended for this analysis. The sample may be injected either by using an appropriate syringe or by filling a fixed volume sample loop provided that reproducibility requirements are satisfied. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

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

8.5 Determination of Analytical Method Recovery

8.5.1 Need for determination. To eliminate any bias in the analytical method, it is necessary to determine the recovery of the compound. The sample recovery should be determined in duplicate and should cover the concentration ranges of interest. If the recovery is less than 95%, the appropriate correction factor should be used to calculate the "true" value.

8.5.2 Procedure for determining recovery. A known amount of the analyte, preferably equivalent to the sample concentration expected, is added to a representative cellulose membrane filter and air-dried. The analyte is then extracted from the filter with 10-ml of 1% acetic acid in a jar, and analyzed as described in Section 8.4 Duplicate determinations should agree within $\pm$ 5%.

For the validation studies conducted to determine the precision and accuracy of the method, an amount of the analyte equivalent to that present in a 90-liter sample at the selected level was used to determine the analytical method recovery. Six filters at each of the three levels (0.5X, 1X and 2X the OSHA standard) were spiked. A parallel blank filter is also prepared except that no sample is added to it. All filters were then extracted and analyzed as described in Sections 8.3.7 and 8.4.

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

$$\text{Recovery} = \frac{\text{Average Weight (µg) recovered}}{\text{Weight (µg) added}}$$

The recovery value is used in Section 10.3 if the recovery is less than 95%.

9. Calibration and Standards

9.1 Hydroquinone stock solution, 90 µg/25 µl. Dissolve 0.0900 g of hydroquinone in 25 ml of 1% acetic acid. Prepare a fresh solution daily.

9.2 From the stock standard solution, prepare at least 6 working standards to cover the concentration range of 90-360 µg/25 ml. Transfer 25 to 100 µl aliquots of the stock standard into 25-ml volumetric flasks and dilute to volume with 1% acetic acid.

9.3 These series of standards are analyzed under the same HPLC conditions and during the same time period as the unknown samples. Curves are established by plotting concentrations in micrograms per 25.0 ml versus peak area.

NOTE: To minimize effect of variations in LC conditions and detector response due to sample cell conditions, frequent standardization should be practiced.

10. Calculations

10.1 Read the concentration, in µg/25 ml, corresponding to the peak area from the standard curve. No volume corrections for sample aliquots analyzed are needed, because the standard curve is based on µg per 25.0 ml and the volume of sample injected is identical to the volume of the standards injected.

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

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

where:

μg sample = μg found in 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 For personal sampling pumps with rotameters only, the following correction should be made.

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

where:

f = sampling flow rate
t = sampling time
P_1 = pressure during calibration of sampling pump (mm Hg)
P_2 = pressure of air sampled (mm Hg)
T_1 = temperature during calibration of sampling pump (^{o}K)
T_2 = temperature of air sampled (^{o}K)

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m (µg per liter = mg per cu m).

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

11. References

11.1 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.2 Memoranda, Kenneth A. Busch (Chief, Statistical Services, DLCD), to Deputy Director, DLCD, dated 1/6/76, 11/8/74, subject: Statistical Protocol for Analysis of Data from Contract CDC-99-74-45."

11.3 S57 Backup Data Report for Hydroquinone, prepared under NIOSH Contract No. 210-76-0123, 11/26/76.

Isoamyl Alcohol

Analyte:	Isoamyl Alcohol	Method No.: S58
Matrix:	Air	Range: 195-680 mg/cu m
OSHA Standard:	100 ppm (360 mg/cu m)	Precision ($\overline{CV}_T$): 0.077
Procedure:	Adsorption on charcoal, desorption with eluent, GC	Validation Date: 1/17/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide containing 5% 2-propanol.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 195-680 mg/cu m at an atmospheric temperature and pressure of 25 C and 743 mm Hg, using a 10-liter sample. Under the conditions of sample size (10 liters) the probable range of this method is 35-1100 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 10-mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of the analyte and other substances in the air. The first section of the charcoal tube was found to hold 20 mg of the analyte when a test atmosphere of 595 mg/cu m of the analyte in dry air was sampled at 0.2 liters per minute for 2 hours, 50 minutes. Breakthrough occurred at this time,

i.e., the concentration of the analyte in the effluent was 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2.) If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments with toluene indicate that high humidity severely decreases the breakthrough volume.

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

3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 195 to 680 mg/cu m was 0.077. This value corresponds to a standard deviation of 28 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 The average values obtained using the overall sampling and analytical method were 4.1% higher than the "true" value at the OSHA standard level.

4.3 The above data are based on validation experiments using the internal standard method. (Reference 11.2)

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more compounds suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined accurately (±5%) at the recommended flow rate, (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600 C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in. stainless steel) packed with 10% FFAP on 80/100 Chromosorb W-AW.

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

6.6 Two-milliliter glass sample containers with glass stoppers or Teflon®-lined caps. If an automatic sample injector is used, the sample injector vials can be used.

6.7 Microliter syringes: 10-µl, and other convenient sizes for making standards.

6.8 Pipets: 1.0-ml delivery type.

6.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Eluent: Carbon disulfide (chromatographic grade) containing 5% 2-propanol (reagent grade)

7.2 3-Methyl-1-butanol (reagent grade).

7.3 Internal Standard: n-Tetradecane (99+%) or other suitable standard.

7.4 Purified nitrogen.

7.5 Prepurified hydrogen.

7.6 Filtered compressed air.

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a flow of 0.20 liters per minute or less. The flow rate should be known with an accuracy of at least ±5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available the elevation should be recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

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

8.3.10 A sample of the suspected compound should be submitted to the laboratory in glass containers with Teflon®-lined caps. These liquid bulk samples should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container or automatic sample injector vial. The separating section of foam is removed and discarded; the second section is transferred to another sample container or vial. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of the eluent is pipetted into each sample container. For the internal standard method a 0.4 percent solution of internal standard in the eluent is used. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. The sample vials should be capped as soon as the solvent is added to minimize volatilization.

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

1. 30 ml/min (80 psig) nitrogen carrier gas flow.
2. 30 ml/min (50 psig) hydrogen gas flow to detector.
3. 300 ml/min (50 psig) air flow to detector.
4. 200 C injector temperature.
5. 300 C manifold temperature (detector).
6. 110 C column temperature.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-µl syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 µl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-µl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 µl to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 µl in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique. In this case 2-µl injections are satisfactory.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below (see Section 9).

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided that the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.0-ml sample container. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes.

A known amount of the analyte is injected directly into the activated charcoal with a 10-µl syringe, and the container is capped. The amount injected is equivalent to that present in a 10-liter sample at the selected level.

At least six tubes at each of three levels (0.5X, 1X, and 2X the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These six tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

The weight of analyte found in each tube is determined from the standard curve (Section 9). Desorption efficiency is determined by the following equation:

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/ml of eluent. To minimize error due to the volatility of the eluent, one can add 10 times the weight to 10 ml of the eluent. (For the internal standard method use eluent containing 0.2 percent of the internal standard.) A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentrations in mg/ml versus peak area. In the case of the internal standard method plot the concentration versus the ratio of peak area of analyte to peak area of internal standard.

Note: Whether the absolute area or internal standard method is used standard solutions should be analyzed at the same time that the sample analysis is done. This will minimize the effect variations of FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area (area ratio in case of the internal standard method) from the

standard curve. No volume corrections are needed, because the standard curve is based on mg/ml eluent and the volume of sample injected is identical to the volume of the standards injected.

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

mg = mg sample - mg blank

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

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

10.4 Read the desorption efficiency from the curve (Section 8.5.2) for the amount of analyte found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

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

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm:

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (C) of air sampled
24.45 = molar volume (liter/mole) at 25 C and 760 mm Hg
MW = molecular weight (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (K)

11. References

11.1 White L. D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 "Documentation of NIOSH Validation Tests", Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract No. HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes, September 15, 1972."

Methyl Alcohol

Analyte:	Methyl Alcohol	Method No.:	S59
Matrix:	Air	Range:	140-540 mg/cu m
OSHA Standard:	200 ppm (260 mg/cu m)	Precision ($\overline{CV_T}$):	0.070
Procedure:	Adsorption on silica gel, desorption with water, GC	Validation Date:	1/17/75

1. Principle of the Method

1.1 A known volume of air is drawn through a silica gel tube to trap the organic vapors present.

1.2 The silica gel in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with water.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 140-540 mg/cu m at an atmospheric temperature and pressure of 25 C and 748 mm Hg, using a nominal 5-liter sample. Under the conditions of sample size (5 liters) the probable range of this method is 25-900 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 4-mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the silica gel tube. This capacity varies with the concentration of the analyte and other substances in the air. The first section of the silica gel tube was found to hold 5.6 mg of the analyte when a test atmosphere of 540 mg/cu m of the analyte in dry air was sampled at 0.2 liters per minute for 52 minutes. Breakthrough occurred at this time,

i.e., the concentration of the analyte in the effluent was 5% of that in the influent. (The silica gel tube consists of two sections of silica gel separated by a section of urethane foam. See Section 6.2.) If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently.

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

3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 140 to 540 mg/cu m was 0.063. This value corresponds to a standard deviation of 16.5 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 The average values obtained using the overall sampling and analytical method were 8.9% lower than the "true" value at the OSHA standard level.

4.3 The above data are based on validation experiments using the internal standard method. (Reference 11.2)

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more compounds suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the silica gel tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined accurately (±5%) at the recommended flow rate, (Reference 11.3)

6.2 Silica gel tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh silica gel separated by a 2-mm portion of urethane foam. The absorbing section contains 100 mg of silica gel, the backup section 50 mg. A 3-mm portion of urethane form is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in. stainless steel) packed with 10% FFAP on 80/100 Chromosorb W-AW.

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

6.6 Two-milliliter glass sample containers with glass stoppers or Teflon®-lined caps. If an automatic sample injector is used, the sample injector vials can be used.

6.7 Microliter syringes: 10-µl, and other convenient sizes for making standards.

6.8 Pipets: 1.0-ml delivery type.

6.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Eluent: Distilled water.

7.2 Methyl Alcohol (reagent grade).

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of silica gel is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The silica gel tube should be placed in a vertical direction during sampling to minimize channeling through the silica gel.

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

8.3.5 A maximum sample size of 5 liters is recommended. Sample at a flow of 0.20 liters per minute or less. The flow rate should be known with an accuracy of at least ±5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available the elevation should be recorded.

8.3.7 The silica gel tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

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

8.3.10 A sample of the suspected compound should be submitted to the laboratory in glass containers with Teflon®-lined caps. These liquid bulk samples should not be transported in the same container as the silica gel tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each silica gel tube is scored with a file in front of the first section of silica gel and broken open. The glass wool is removed and discarded. The silica gel in the first (larger) section is transferred to a 2-ml stoppered sample container or automatic sample injector vial. The separating section of foam is removed and discarded; the second section is transferred to another sample container or vial. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of distilled water is pipetted into each sample container. Desorption should be done for 4 hours. Tests indicate that this is adequate if the sample is agitated occasionally during this period. The sample vials should be capped as soon as the water is added to minimize evaporation.

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

1. 30 ml/min (80 psig) nitrogen carrier gas flow.
2. 30 ml/min (50 psig) hydrogen gas flow to detector.
3. 300 ml/min (50 psig) air flow to detector.
4. 200 C injector temperature.
5. 300 C manifold temperature (detector).
6. 80 C column temperature.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-µl syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 µl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-µl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 µl to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 µl in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below (see Section 9).

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of silica gel to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process.

8.5.2 Procedure for determining desorption efficiency. Silica gel equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.0-ml sample container. This silica gel must be the same

type as that used in obtaining the samples and can be obtained from unused silica gel tubes. A known amount of the analyte is injected directly into the silica gel with a 10-µl syringe, and the container is capped. The amount injected is equivalent to that present in a 5-liter sample at the selected level.

At least six tubes at each of three levels (0.5X, 1X, and 2X the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the silica gel. These six tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

The weight of analyte found in each tube is determined from the standard curve (Section 9). Desorption efficiency is determined by the following equation:

$$\text{D.E.} = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the silica gel. Plot the desorption efficiency versus the weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/ml of eluent. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentrations in mg/ml versus peak area.

Note: Standard solutions should be analyzed at the same time that the sample analysis is done. This will minimize the effect variations of FID response.

10. Calculations

10.1 Read the weights, in mg, corresponding to each peak area (area ratio in case of the internal standard method) from the

standard curve. No volume corrections are needed, because the standard curve is based on mg/ml eluent and the volume of sample injected is identical to the volume of the standards injected.

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

mg = mg sample - mg blank

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

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

10.4 Read the desorption efficiency from the curve (Section 8.5.2) for the amount of analyte found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

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

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm:

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (C) of air sampled
24.45 = molar volume (liter/mole) at 25 C and 760 mm Hg
MW = molecular weight (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (K)

11. References

11.1 White L. D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 "Documentation of NIOSH Validation Tests", Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract No. HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes, September 15, 1972."

Methyl Isobutyl Carbinol

Analyte:	Methyl Isobutyl Carbinol	Method No.:	S60
Matrix:	Air	Range:	45-175 mg/cu m
OSHA Standard:	25 ppm (105 mg/cu m)	Precision ($\overline{CV_T}$):	0.080
Procedure:	Adsorption on charcoal, desorption with eluent, GC	Validation Date:	1/17/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide containing 5% 2-propanol.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 45-175 mg/cu m at an atmospheric temperature and pressure of 25 C and 743 mm Hg, using a 10-liter sample. Under the conditions of sample size (10 liters) the probable range of this method is 10-300 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 2.5-mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of the analyte and other substances in the air. The first section of the charcoal tube was found to hold at least 11.3 mg of the analyte when a test atmosphere of 237 mg/cu m of the analyte in dry air was sampled at 0.2 liters per minute for 4 hours. At that time the concentration of the

analyte in the effluent was less than 1% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2.) If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments with toluene indicate that high humidity severely decreases the breakthrough volume.

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

3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 45 to 175 mg/cu m was 0.080. This value corresponds to a standard deviation of 28.4 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 The average values obtained using the overall sampling and analytical method were 1.8% higher than the "true" value at the OSHA standard level.

4.3 The above data are based on validation experiments using the internal standard method. (Reference 11.2)

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more compounds suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined accurately (±5%) at the recommended flow rate, (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600 C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in. stainless steel) packed with 10% FFAP on 80/100 Chromosorb W-AW.

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

6.6 Two-milliliter glass sample containers with glass stoppers or Teflon®-lined caps. If an automatic sample injector is used, the sample injector vials can be used.

6.7 Microliter syringes: 10-µl, and other convenient sizes for making standards.

6.8 Pipets: 1.0-ml delivery type.

6.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Eluent: Carbon disulfide (chromatographic grade) containing 5% 2-propanol (reagent grade).

7.2 4-Methyl-2-pentanol (reagent grade).

7.3 Internal Standard: n-Tetradecane (99+%) or other suitable standard.

7.4 n-Heptane (reagent grade).

7.5 Purified nitrogen.

7.6 Prepurified hydrogen.

7.7 Filtered compressed air.

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a flow of 0.20 liters per minute or less. The flow rate should be known with an accuracy of at least ±5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available the elevation should be recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

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

8.3.10 A sample of the suspected compound should be submitted to the laboratory in glass containers with Teflon®-lined caps. These liquid bulk samples should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container or automatic sample injector vial. The separating section of foam is removed and discarded; the second section is transferred to another sample container or vial. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of the eluent is pipetted into each sample container. For the internal standard method a 0.1 percent solution of internal standard in the eluent is used. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. The sample vials should be capped as soon as the solvent is added to minimize volatilization.

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

1. 30 ml/min (80 psig) nitrogen carrier gas flow.
2. 30 ml/min (50 psig) hydrogen gas flow to detector.
3. 300 ml/min (50 psig) air flow to detector.
4. 200 C injector temperature.
5. 300 C manifold temperature (detector).
6. 120 C column temperature.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-µl syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 µl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-µl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 µl to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 µl in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique. In this case 2-µl injections are satisfactory.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below (see Section 9).

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided that the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.0-ml sample container. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. A

250 mg/ml stock solution of the analyte in n-heptane is prepared. A known amount of this solution is injected directly intthe activated charcoal with a 10-µl syringe, and the container is capped. The amount injected is equivalent to that present in a 10-liter sample at the selected level. It is not practical to inject the neat liquid directly because the amounts to be added would be too small to measure accurately.

At least six tubes at each of three levels (0.5X, 1X, and 2X the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These six tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

The weight of analyte found in each tube is determined from the standard curve (Section 9). Desorption efficiency is determined by the following equation:

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/ml of eluent. To minimize error due to the volatility of the eluent, one can add 10 times the weight to 10 ml of the eluent. (For the internal standard method use eluent containing 0.1 percent of the internal standard.) A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentrations in mg/ml versus peak area. In the case of the internal standard method plot the concentration versus the ratio of peak area of analyte to peak area of internal standard.

Note: Whether the absolute area or internal standard method is used standard solutions should be analyzed at the same time that the sample analysis is done. This will minimize the effect variations of FID response.

10. Calculations

10.1 Read the weights, in mg, corresponding to each peak area (area ratio in case of the internal standard method) from the standard curve. No volume corrections are needed, because the standard curve is based on mg/ml eluent and the volume of sample injected is identical to the volume of the standards injected.

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

mg = mg sample - mg blank

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

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

10.4 Read the desorption efficiency from the curve (Section 8.5.2) for the amount of analyte found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

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

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm:

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (C) of air sampled
24.45 = molar volume (liter/mole) at 25 C and 760 mm Hg
MW = molecular weight (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (K)

11. References

11.1 White L. D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 "Documentation of NIOSH Validation Tests", Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract No. HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes, September 15, 1972".

Propyl Alcohol

Analyte:	Propyl Alcohol	Method No.:	S62
Matrix:	Air	Range:	225-835 mg/cu m
OSHA Standard:	200 ppm (490 mg/cu m)	Precision ($\overline{CV}_T$):	0.075
Procedure:	Adsorption on charcoal, desorption with eluent, GC	Validation Date:	1/17/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide containing 1% 2-propanol.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 225-835 mg/cu m at an atmospheric temperature and pressure of 25 C and 748 mm Hg, using a 10-liter sample. Under the conditions of sample size (10 liters) the probable range of this method is 50-1000 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 10-mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of the analyte and other substances in the air. The first section of the charcoal tube was found to hold 18 mg of the analyte when a test atmosphere of 946 mg/cu m of the analyte in dry air was sampled at 0.2 liters per minute for 1 hour, 35 minutes; breakthrough occurred at this time,

i.e., the concentration of the analyte in the effluent was 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2.) If a particular atmosphere is suspected of containing a large amount of contaminants, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments with toluene indicate that high humidity severely decreases the breakthrough volume.

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

3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 225 to 835 mg/cu m was 0.075. This value corresponds to a standard deviation of 37 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 The average values obtained using the overall sampling and analytical method were 0.3% lower than the "true" value at the OSHA standard level.

4.3 The above data are based on validation experiments using the internal standard method. (Reference 11.2)

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more compounds suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined accurately (±5%) at the recommended flow rate, (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600 C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in. stainless steel) packed with 10% FFAP on 80/100 Chromosorb W-AW.

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

6.6 Two-milliliter glass sample containers with glass stoppers or Teflon®-lined caps. If an automatic sample injector is used, the sample injector vials can be used.

6.7 Microliter syringes: 10-µl, and other convenient sizes for making standards.

6.8 Pipets: 1.0-ml delivery type.

6.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Eluent: Carbon disulfide (chromatographic grade) containing 1% 2-propanol (reagent grade).

7.2 1-Propanol (reagent grade).

7.3 Internal Standard: n-Undecane (99+%) or other suitable standard.

7.4 n-Heptane (reagent grade).

7.5 Purified nitrogen.

7.6 Prepurified hydrogen.

7.7 Filtered compressed air.

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a flow of 0.20 liters per minute or less. The flow rate should be known with an accuracy of at least ±5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available the elevation should be recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

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

8.3.10 A sample of the suspected compound should be submitted to the laboratory in glass containers with Teflon®-lined caps. These liquid bulk samples should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container or automatic sample injector vial. The separating section of foam is removed and discarded; the second section is transferred to another sample container or vial. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of the eluent is pipetted into each sample container. For the internal standard method a 0.2 percent solution of internal standard in the eluent is used. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. The sample vials should be capped as soon as the solvent is added to minimize volatilization.

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

1. 30 ml/min (80 psig) nitrogen carrier gas flow.
2. 30 ml/min (50 psig) hydrogen gas flow to detector.
3. 300 ml/min (50 psig) air flow to detector.
4. 200 C injector temperature.
5. 300 C manifold temperature (detector).
6. 70 C column temperature.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-µl syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 µl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-µl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 µl to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 µl in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique. In this case 2-µl injections are satisfactory.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below (see Section 9).

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided that the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.0-ml sample container. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. A

625 mg/ml stock solution of the analyte in n-heptane is prepared. A known amount of this solution is injected directly into the activated charcoal with a 10-µl syringe, and the container is capped. The amount injected is equivalent to that present in a 10-liter sample at the selected level. It is not practical to inject the neat liquid directly because the amounts to be added would be too small to measure accurately.

At least six tubes at each of three levels (0.5X, 1X, and 2X the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These six tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

The weight of analyte found in each tube is determined from the standard curve (Section 9). Desorption efficiency is determined by the following equation:

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/ml of eluent. To minimize error due to the volatility of the eluent, one can add 10 times the weight to 10 ml of the eluent. (For the internal standard method use eluent containing 0.2 percent of the internal standard.) A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentrations in mg/ml versus peak area. In the case of the internal standard method plot the concentration versus the ratio of peak area of analyte to peak area of internal standard.

Note: Whether the absolute area or internal standard method is used standard solutions should be analyzed at the same time that the sample analysis is done. This will minimize the effect variations of FID response.

10. Calculations

10.1 Read the weights, in mg, corresponding to each peak area (area ratio in case of the internal standard method) from the standard curve. No volume corrections are needed, because the standard curve is based on mg/ml eluent and the volume of sample injected is identical to the volume of the standards injected.

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

mg = mg sample - mg blank

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

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

10.4 Read the desorption efficiency from the curve (Section 8.5.2) for the amount of analyte found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

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

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm:

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (C) of air sampled
24.45 = molar volume (liter/mole) at 25 C and 760 mm Hg
MW = molecular weight (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (K)

11. References

11.1 White L. D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 "Documentation of NIOSH Validation Tests", Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract No. HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes, September 15, 1972".

tert-Butyl Alcohol

Analyte:	tert-Butyl Alcohol	Method No.: S63
Matrix:	Air	Range: 165-600 mg/cu m
OSHA Standard:	100 ppm (305 mg/cu m)	Precision ($\overline{CV}_T$): 0.075
Procedure:	Adsorption on charcoal, desorption with eluent, GC	Validation Date: 1/17/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide containing 1% 2-butanol.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 165-600 mg/cu m at an atmospheric temperature and pressure of 25 C and 740 mm Hg, using a 10-liter sample. Under the conditions of sample size (10 liters) the probable range of this method is 30-750 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 6-mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of the analyte and other substances in the air. The first section of the charcoal tube was found to hold 9.9 mg of the analyte when a test atmosphere of 580 mg/cu m of the analyte in dry air was sampled at 0.2 liters per minute for 1 hour, 25 minutes; breakthrough occurred at that time, i.e.,

the concentration of the analyte in the effluent was 5% of that in the influent. (The charcoal tubes consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2.) If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments with toluene indicate that high humidity severely decreases the breakthrough volume.

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

3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 165 to 600 mg/cu m was 0.075. This value corresponds to a standard deviation of 22.9 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 The average values obtained using the overall sampling and analytical method were 5.7% lower than the "true" value at the OSHA standard level.

4.3 The above data are based on validation experiments using the internal standard method. (Reference 11.2)

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more compounds suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined accurately (±5%) at the recommended flow rate, (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600 C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in. stainless steel) packed with 10% FFAP on 80/100 Chromosorb W-AW.

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

6.6 Two-milliliter glass sample containers with glass stoppers or Teflon®-lined caps. If an automatic sample injector is used, the sample injector vials can be used.

6.7 Microliter syringes: 10-µl, and other convenient sizes for making standards.

6.8 Pipets: 1.0-ml delivery type.

6.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Eluent: Carbon disulfide (chromatographic grade) containing 1% 2-butanol (reagent grade).

7.2 2-Methyl-2-propanol (reagent grade).

7.3 Internal Standard: n-Undecane (99+%) or other suitable standard.

7.4 n-Heptane (reagent grade).

7.5 Purified nitrogen.

7.6 Prepurified hydrogen.

7.7 Filtered compressed air.

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a flow of 0.20 liters per minute or less. The flow rate should be known with an accuracy of at least ±5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available the elevation should be recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

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

8.3.10 A sample of the suspected compound should be submitted to the laboratory in glass containers with Teflon®-lined caps. These liquid bulk samples should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container or automatic sample injector vial. The separating section of foam is removed and discarded; the second section is transferred to another sample container or vial. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of the eluent is pipetted into each sample container. For the internal standard method a 0.2 percent solution of internal standard in the eluent is used. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. The sample vials should be capped as soon as the solvent is added to minimize volatilization.

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

1. 30 ml/min (80 psig) nitrogen carrier gas flow.
2. 30 ml/min (50 psig) hydrogen gas flow to detector.
3. 300 ml/min (50 psig) air flow to detector.
4. 200 C injector temperature.
5. 300 C manifold temperature (detector).
6. 70 C column temperature.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-µl syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 µl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-µl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 µl to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 µl in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique. In this case 2-µl injections are satisfactory.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below (see Section 9).

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided that the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.0-ml sample container. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. A

750 mg/ml stock solution of the analyte in n-heptane is prepared. A known amount of this solution is injected directly into the activated charcoal with a 10-µl syringe, and the container is capped. The amount injected is equivalent to that present in a 10-liter sample at the selected level. It is not practical to inject the neat liquid directly because the amounts to be added would be too small to measure accurately.

At least six tubes at each of three levels (0.5X, 1X, and 2X the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These six tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

The weight of analyte found in each tube is determined from the standard curve (Section 9). Desorption efficiency is determined by the following equation:

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/ml of eluent. To minimize error due to the volatility of the eluent, one can add 10 times the weight to 10 ml of the eluent. (For the internal standard method use eluent containing 0.2 percent of the internal standard.) A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentrations in mg/ml versus peak area. In the case of the internal standard method plot the concentration versus the ratio of peak area of analyte to peak area of internal standard.

Note: Whether the absolute area or internal standard method is used standard solutions should be analyzed at the same time that the sample analysis is done. This will minimize the effect variations of FID response.

10. Calculations

10.1 Read the weights, in mg, corresponding to each peak area (area ratio in case of the internal standard method) from the standard curve. No volume corrections are needed, because the standard curve is based on mg/ml eluent and the volume of sample injected is identical to the volume of the standards injected.

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

mg = mg sample - mg blank

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

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

10.4 Read the desorption efficiency from the curve (Section 8.5.2) for the amount of analyte found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

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

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm:

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (C) of air sampled
24.45 = molar volume (liter/mole) at 25 C and 760 mm Hg
MW = molecular weight (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (K)

11. References

11.1 White L. D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 "Documentation of NIOSH Validation Tests", Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract No. HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes, September 15, 1972".

Isobutyl Alcohol

Analyte:	Isobutyl Alcohol	Method No.:	S64
Matrix:	Air	Range:	180-620 mg/cu m
OSHA Standard:	100 ppm (305 mg/cu m)	Precision ($\overline{CV}_T$):	0.073
Procedure:	Adsorption on charcoal, desorption with eluent, GC	Validation Date:	1/17/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide containing 1% 2-propanol.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 180-620 mg/cu m at an atmospheric temperature and pressure of 25 C and 749 mm Hg, using a 10-liter sample. Under the conditions of sample size (10 liters) the probable range of this method is 30-900 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 9-mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of the analyte and other substances in the air. The first section of the charcoal tube was found to hold 21 mg of the analyte when a test atmosphere of 669 mg/cu m of the analyte in dry air was sampled at 0.2 liters per minute for 2 hours, 35 minutes; breakthrough occurred at this time,

i.e., the concentration of the analyte in the effluent was 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2.) If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments with toluene indicate that high humidity severely decreases the breakthrough volume.

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

3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 180 to 620 mg/cu m was 0.073. This value corresponds to a standard deviation of 22.1 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 The average values obtained using the overall sampling and analytical method were 7% lower than the "true" value at the OSHA standard level.

4.3 The above data are based on validation experiments using the internal standard method. (Reference 11.2)

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more compounds suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined accurately (±5%) at the recommended flow rate, (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600 C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in. stainless steel) packed with 10% FFAP on 80/100 Chromosorb W-AW.

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

6.6 Two-milliliter glass sample containers with glass stoppers or Teflon®-lined caps. If an automatic sample injector is used, the sample injector vials can be used.

6.7 Microliter syringes: 10-µl, and other convenient sizes for making standards.

6.8 Pipets: 1.0-ml delivery type.

6.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Eluent: Carbon disulfide (chromatographic grade) containing 1% 2-propanol (reagent grade).

7.2 2-Methyl-1-propanol (reagent grade).

7.3 Internal Standard: n-Dodecane (99+%) or other suitable standard.

7.4 n-Heptane (reagent grade).

7.5 Purified nitrogen.

7.6 Prepurified hydrogen.

7.7 Filtered compressed air.

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a flow of 0.20 liters per minute or less. The flow rate should be known with an accuracy of at least ±5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available the elevation should be recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

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

8.3.10 A sample of the suspected compound should be submitted to the laboratory in glass containers with Teflon®-lined caps. These liquid bulk samples should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container or automatic sample injector vial. The separating section of foam is removed and discarded; the second section is transferred to another sample container or vial. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of the eluent is pipetted into each sample container. For the internal standard method a 0.2 percent solution of internal standard in the eluent is used. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. The sample vials should be capped as soon as the solvent is added to minimize volatilization.

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

1. 30 ml/min (80 psig) nitrogen carrier gas flow.
2. 30 ml/min (50 psig) hydrogen gas flow to detector.
3. 300 ml/min (50 psig) air flow to detector.
4. 200 C injector temperature.
5. 300 C manifold temperature (detector).
6. 80 C column temperature.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-µl syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 µl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-µl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 µl to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 µl in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique. In this case 2-µl injections are satisfactory.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below (see Section 9).

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided that the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.0-ml sample container. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. A

750 mg/ml stock solution of the analyte in n-heptane is prepared. A known amount of this solution is injected directly into the activated charcoal with a 10-µl syringe, and the container is capped. The amount injected is equivalent to that present in a 10-liter sample at the selected level. It is not practical to inject the neat liquid directly because the amounts to be added would be too small to measure accurately.

At least six tubes at each of three levels (0.5X, 1X, and 2X the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These six tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

The weight of analyte found in each tube is determined from the standard curve (Section 9). Desorption efficiency is determined by the following equation:

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/ml of eluent. To minimize error due to the volatility of the eluent, one can add 10 times the weight to 10 ml of the eluent. (For the internal standard method use eluent containing 0.2 percent of the internal standard.) A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentrations in mg/ml versus peak area. In the case of the internal standard method plot the concentration versus the ratio of peak area of analyte to peak area of internal standard.

Note: Whether the absolute area or internal standard method is used standard solutions should be analyzed at the same time that the sample analysis is done. This will minimize the effect variations of FID response.

10. Calculations

10.1 Read the weights, in mg, corresponding to each peak area (area ratio in case of the internal standard method) from the standard curve. No volume corrections are needed, because the standard curve is based on mg/ml eluent and the volume of sample injected is identical to the volume of the standards injected.

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

mg = mg sample - mg blank

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

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

10.4 Read the desorption efficiency from the curve (Section 8.5.2) for the amount of analyte found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

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

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm:

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (C) of air sampled
24.45 = molar volume (liter/mole) at 25 C and 760 mm Hg
MW = molecular weight (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (K)

11. References

11.1 White L. D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 "Documentation of NIOSH Validation Tests", Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract No. HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes, September 15, 1972".

A known amount of the analyte is injected directly into the activated charcoal with a 10-µl syringe, and the container is capped. The amount injected is equivalent to that present in a 3-liter sample at the selected level.

At least six tubes at each of three levels (0.5X, 1X, and 2X the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These six tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

The weight of analyte found in each tube is determined from the standard curve (Section 9). Desorption efficiency is determined by the following equation:

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/ml of eluent. To minimize error due to the volatility of the eluent, one can add 10 times the weight to 10 ml of the eluent. (For the internal standard method use eluent containing 0.5 percent of the internal standard.) A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentrations in mg/ml versus peak area. In the case of the internal standard method plot the concentration versus the ratio of peak area of analyte to peak area of internal standard.

Note: Whether the absolute area or internal standard method is used standard solutions should be analyzed at the same time that the sample analysis is done. This will minimize the effect variations of FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area (area ratio in case of the internal standard method) from the

standard curve. No volume corrections are needed, because the standard curve is based on mg/ml eluent and the volume of sample injected is identical to the volume of the standards injected.

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

mg = mg sample - mg blank

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

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

10.4 Read the desorption efficiency from the curve (Section 8.5.2) for the amount of analyte found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

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

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm:

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (C) of air sampled
24.45 = molar volume (liter/mole) at 25 C and 760 mm Hg
MW = molecular weight (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (K)

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

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

8.3.10 A sample of the suspected compound should be submitted to the laboratory in glass containers with Teflon®-lined caps. These liquid bulk samples should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container or automatic sample injector vial. The separating section of foam is removed and discarded; the second section is transferred to another sample container or vial. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of the eluent is pipetted into each sample container. For the internal standard method a 0.5 percent solution of internal standard in the eluent is used. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. The sample vials should be capped as soon as the solvent is added to minimize volatilization.

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

1. 30 ml/min (80 psig) nitrogen carrier gas flow.
2. 30 ml/min (50 psig) hydrogen gas flow to detector.
3. 300 ml/min (50 psig) air flow to detector.
4. 200 C injector temperature.
5. 300 C manifold temperature (detector).
6. 70 C column temperature.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-µl syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 µl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-µl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 µl to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 µl in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique. In this case 2-µl injections are satisfactory.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below (see Section 9).

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided that the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.0-ml sample container. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined accurately (±5%) at the recommended flow rate, (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600 C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in. stainless steel) packed with 10% FFAP on 80/100 Chromosorb W-AW.

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

6.6 Two-milliliter glass sample containers with glass stoppers or Teflon®-lined caps. If an automatic sample injector is used, the sample injector vials can be used.

6.7 Microliter syringes: 10-µl, and other convenient sizes for making standards.

6.8 Pipets: 1.0-ml delivery type.

6.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Eluent: Carbon disulfide (chromatographic grade) containing 1% 2-butanol (reagent grade).

7.2 2-Propanol (reagent grade).

7.3 Internal Standard: n-Undecane (99+%) or other suitable standard.

7.4 Purified nitrogen.

7.5 Prepurified hydrogen.

7.6 Filtered compressed air.

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 3 liters is recommended. Sample at a flow of 0.20 liters per minute or less. The flow rate should be known with an accuracy of at least ±5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available the elevation should be recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

Isopropyl Alcohol

Analyte:	Isopropyl Alcohol	Method No.:	S65
Matrix:	Air	Range:	505-1890 mg/cu m
OSHA Standard:	400 ppm (985 mg/cu m)	Precision ($\overline{CV}_T$):	0.064
Procedure:	Adsorption on charcoal, desorption with eluent, GC	Validation Date:	1/17/75

1. Principle of the Method

   1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

   1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide containing 1% 2-butanol.

   1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

   2.1 This method was validated over the range of 505-1890 mg/cu m at an atmospheric temperature and pressure of 25 C and 747 mm Hg, using a 3-liter sample. Under the conditions of sample size (3 liters) the probable range of this method is 100-2500 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 6-mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

   2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of the analyte and other substances in the air. The first section of the charcoal tube was found to hold 11.3 mg of the analyte when a test atmosphere of 1890 mg/cu m of the analyte in dry air was sampled at 0.2 liters per minute for 30 minutes. Breakthrough occurred at this time, i.e., the

concentration of the analyte in the effluent was 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2.) If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments with toluene indicate that high humidity severely decreases the breakthrough volume.

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

3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 505 to 1890 mg/cu m was 0.064. This value corresponds to a standard deviation of 63 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 The average values obtained using the overall sampling and analytical method were 7.2% less than the "true" value at the OSHA standard level.

4.3 The above data are based on validation experiments using the internal standard method. (Reference 11.2)

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more compounds suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

11. References

11.1 White L. D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 "Documentation of NIOSH Validation Tests", Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract No. HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes, September 15, 1972."

Butyl Alcohol

Analyte:	Butyl Alcohol	Method No.:	S66
Matrix:	Air	Range:	170-610 mg/cu m
OSHA Standard:	100 ppm (305 mg/cu m)	Precision ($\overline{CV}_T$):	0.065
Procedure:	Adsorption on charcoal, desorption with eluent, GC	Validation Date:	1/17/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide containing 1% 2-propanol.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

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

2. Range and Sensitivity

2.1 This method was validated over the range of 170-610 mg/cu m at an atmospheric temperature and pressure of 25 C and 751 mm Hg, using a 10-liter sample. Under the conditions of sample size (10 liters) the probable range of this method is 30-900 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 9-mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of the analyte and other substances in the air. The first section of the charcoal tube was found to hold 21 mg of the analyte when a test atmosphere of 600 mg/cu m of the analyte in dry air was sampled at 0.2 liters per minute for 2 hours, 55 minutes; breakthrough was observed at this time, i.e., the concentration of the analyte in the

the effluent was 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2.) If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments with toluene indicate that high humidity severely decreases the breakthrough volume.

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

3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 170 to 610 mg/cu m was 0.065. This value corresponds to a standard deviation of 20 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 The average values obtained using the overall sampling and analytical method were 6.2% lower than the "true" value at the OSHA standard level.

4.3 The above data are based on validation experiments using the internal standard method. (Reference 11.2)

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more compounds suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

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

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined accurately (±5%) at the recommended flow rate, (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600 C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in. stainless steel) packed with 10% FFAP on 80/100 Chromosorb W-AW.

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

6.6 Two-milliliter glass sample containers with glass stoppers or Teflon®-lined caps. If an automatic sample injector is used, the sample injector vials can be used.

6.7 Microliter syringes: 10-µl, and other convenient sizes for making standards.

6.8 Pipets: 1.0-ml delivery type.

6.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Eluent: Carbon disulfide (chromatographic grade) containing 1% 2-propanol (reagent grade).

7.2 1-Butanol (reagent grade).

7.3 Internal Standard: n-Dodecane (99+%) or other suitable standard.

7.4 n-Heptane (reagent grade).

7.5 Purified nitrogen.

7.6 Prepurified hydrogen.

7.7 Filtered compressed air.

8. Procedure

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

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

8.3 Collection and Shipping of Samples

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

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

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

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a flow of 0.20 liters per minute or less. The flow rate should be known with an accuracy of at least ±5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available the elevation should be recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

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

8.3.10 A sample of the suspected compound should be submitted to the laboratory in glass containers with Teflon®-lined caps. These liquid bulk samples should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container or automatic sample injector vial. The separating section of foam is removed and discarded; the second section is transferred to another sample container or vial. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of the eluent is pipetted into each sample container. For the internal standard method a 0.2 percent solution of internal standard in the eluent is used. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. The sample vials should be capped as soon as the solvent is added to minimize volatilization.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (80 psig) nitrogen carrier gas flow.
2. 30 ml/min (50 psig) hydrogen gas flow to detector.
3. 300 ml/min (50 psig) air flow to detector.
4. 200 C injector temperature.
5. 300 C manifold temperature (detector).
6. 80 C column temperature.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-µl syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 µl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-µl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 µl to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 µl in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique. In this case 2-µl injections are satisfactory.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below (see Section 9).

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided that the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.0-ml sample container. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. A

750 mg/ml stock solution of the analyte in n-heptane is prepared. A known amount of this solution is injected directly into the activated charcoal with a 10-µl syringe, and the container is capped. The amount injected is equivalent to that present in a 10-liter sample at the selected level. It is not practical to inject the neat liquid directly because the amounts to be added would be too small to measure accurately.

At least six tubes at each of three levels (0.5X, 1X, and 2X the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These six tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

The weight of analyte found in each tube is determined from the standard curve (Section 9). Desorption efficiency is determined by the following equation:

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus the weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/ml of eluent. To minimize error due to the volatility of the eluent, one can add 10 times the weight to 10 ml of the eluent. (For the internal standard method use eluent containing 0.2 percent of the internal standard.) A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentrations in mg/ml versus peak area. In the case of the internal standard method plot the concentration versus the ratio of peak area of analyte to peak area of internal standard.

Note: Whether the absolute area or internal standard method is used standard solutions should be analyzed at the same time that the sample analysis is done. This will minimize the effect variations of FID response.

10. Calculations

10.1 Read the weights, in mg, corresponding to each peak area (area ratio in case of the internal standard method) from the standard curve. No volume corrections are needed, because the standard curve is based on mg/ml eluent and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

mg = mg sample - mg blank

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (Section 8.5.2) for the amount of analyte found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

10.5 The concentration of analyte in the air sampled can be expressed in mg per cu m, which is numerically equal to µg per liter of air

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm:

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (C) of air sampled
24.45 = molar volume (liter/mole) at 25 C and 760 mm Hg
MW = molecular weight (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (K)

11. References

11.1 White L. D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 "Documentation of NIOSH Validation Tests", Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract No. HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes, September 15, 1972."

PB-276 624
PART 2 OF 2

Chlorinated Camphene
(Toxaphene)

Analyte:	Chlorinated Camphene	Method No.: S67
Matrix:	Air	Range: 0.225-1.155 mg/cu m
OSHA Standard:	0.5 mg/cu m	Precision ($\overline{CV}_T$): 0.076
Procedure:	Filter collection, petroleum ether extraction, GC	Validation Date: 2/14/75

1. Principle of the Method

1.1 A known volume of air is drawn through a cellulose membrane filter to collect particulate matter.

1.2 The filter is transferred to a screw cap bottle and extracted with petroleum ether.

1.3 An aliquot of the extract is analyzed by electron capture gas chromatography.

1.4 The area of the sample peaks is determined and compared with areas obtained from standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 0.225-1.155 mg/cu m at an atmospheric temperature and pressure of 22°C and 761 mm Hg, using a 15-liter sample. The probable useful range of this method is 0.05-1.5 mg/cu m for 15-liter samples.

2.2 The upper limit of the range of the method is dependent on the collection efficiency of the cellulose membrane filter. If higher concentrations than those tested are to be sampled, smaller sample volumes should be used. The collection efficiency for chlorinated camphene was considered to be 1.00 $\pm$ 0.01 when sampled for 15 minutes at 1 liter per minute from a test atmosphere containing 1 mg/cu m.

3. Interference

3.1 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method and a high electron capture cross section is an interference.

3.3 Chlorinated camphene is composed of a mixture of compounds, which chromatograph over a range of retention times. Any compound with an electron capture response in this retention time band will interfere. This would include pesticides, such as aldrin, parathion, dieldrin, DDT and its metabolites, and PCB's.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.225-1.155 mg/cu m was 0.076. This value corresponds to a standard deviation of 0.038 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.1.

4.2 A collection efficiency of 1.00 $\pm$ 0.01 was determined for the collection medium; thus, no bias was introduced in the sample collection step. There were no apparent biases in the sampling and analytical method for which analytical method recovery corrections were made. Thus $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Samples collected on filters are analyzed by means of a quick, instrumental method.

5.2 Other volatile compounds which give an electron capture response that are dispersed as particulates, are likely to interfere.

6. Apparatus

6.1 The sampling unit for the collection of personal air samples for the determination of organic aerosol has the following components:

6.1.1 The filter unit consisting of the filter media (Section 6.2) and a polystyrene 37-mm 3-piece cassette filter holder. Do not use tenite filter holders.

6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of $\pm$ 5% (Reference 11.1) at the recommended flow rate. The pump must be calibrated with a representative filter holder and filter in the line.

6.2 Mixed cellulose ester membrane filter, 0.8 micrometer pore size and 37 mm diameter. The filter is held in the three piece cassette supported by a cellulose backup pad.

6.3 Screw cap bottles. Within 1 hour after the sample has been collected, the filter is transferred to a clean screw cap bottle (a 45-mm tissue sample holder is satisfactory) for shipping.

6.4 Gas chromatograph equipped with an electron capture detector.

6.5 Column (6-ft X 1/4-in glass) packed with 3% OV-1 on 100/120 mesh Gas-Chrom Q.

6.6 An electronic integrator or some other suitable method for measuring peak areas.

6.7 Sample extraction equipment.

6.7.1 Beakers, 50 ml.

6.7.2 Volumetric flasks, 10 ml.

6.7.3 Tweezers and funnels.

6.8 Microliter syringes: 10-microliter and other convenient sizes for making standard solutions.

6.9 Volumetric flasks: 10-ml and other convenient sizes for making standard solutions.

7. Reagents

7.1 Petroleum ether, 30° to 60°C boiling range, suitable for pesticide residue analysis, Mallinckrodt Nanograde® or equivalent.

7.2 Chlorinated camphene (toxaphene), reagent grade.

7.3 Purified nitrogen.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis as well as the screw cap bottles should be detergent washed and thoroughly rinsed with tap water and distilled water, dried, and then rinsed with petroleum ether.

8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative filter cassette in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Assemble the filter in the three piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad.

8.3.2 Remove the cassette plugs and attach to the personal sampling pump tubing. Clip the cassette to the worker's lapel.

8.3.3 Air being sampled should not pass through any hose or tubing before entering the filter cassette.

8.3.4 A sample size of 15 liters is recommended. Sample at a flow of 1.0 liter per minute. The flow rate should be known with an accuracy of $\pm 5\%$.

8.3.5 Turn the pump on and begin sample collection. Since it is possible for a filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently, and the sampling should be terminated at any evidence of a problem.

8.3.6 Terminate sampling at the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation.

8.3.7 The cellulose filter should be removed from the cassette filter holder and the cellulose backup pad within 1 hour of sampling and placed in a clean screw cap bottle. Care must be taken to handle the filter only with clean tweezers.

8.3.8 Carefully record sample identity and all relevant sampling data.

8.3.9 With each batch of samples submit one filter which is subjected to exactly the same handling as for the samples except that no air is drawn through it. Label this as a blank.

8.3.10 The screw cap bottles in which the samples are stored should be shipped in a suitable container, designed to prevent damage in transit.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. Care must be taken to handle the filter only with clean tweezers. Open the screw cap

bottle, remove the filter, and place the filter in a 50-ml beaker. Rinse the screw cap bottle with 3 ml petroleum ether. Pour the solvent into the beaker. Swirl the solvent over the filter, then decant the extract into a 10-ml volumetric flask. Repeat this process two more times. Dilute the combined extracts to a total of 10 ml with petroleum ether, stopper, and mix.

8.4.2 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 250°C detector temperature
3. 230°C injector temperature
4. 205°C column temperature

8.4.3 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.4.4 Measurement of area. The areas of the sample peaks are measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed in Section 9. The peaks are not resolved, and therefore the total area of the envelope of peaks is measured as a single area.

8.5 Determination of Analytical Method Recovery

8.5.1 Need for determination. It is anticipated that the extraction scheme is dependent on operator skill and perhaps on the formulation used to disperse the analyte. Thus, it is necessary to determine the recovery of the analyte.

8.5.2 Procedure for determining analytical method recovery. A known amount of petroleum ether solution containing 1.74 mg/ml of chlorinated camphene, preferably equivalent to the sample concentration expected, is added to a representative cellulose membrane filter and air-dried. The analyte is then extracted from the filter and analyzed as described in Section 8.4. An amount of the analyte equivalent to that present in a 15 liter sample at the selected level is used for the extraction studies. Six filters at each of the three levels (0.5X, 1X, and 2X the OSHA standard) are dosed accordingly. A parallel blank filter is also treated in the same manner except that no sample is added to it. All filters are then extracted and analyzed as described in Section 8.4.

Three standards are prepared by injecting the same amount of analyte into 10 ml of petroleum ether with the same syringe used in the preparation of the dosed filters and are analyzed at the same time.

Analytical method recovery (A.M.R.) equals the weight in mg found divided by the weight in mg added to the filter, or

$$A.M.R. = \frac{\text{Weight found (mg)}}{\text{Weight added (mg)}}$$

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/10 ml petroleum ether, because samples are extracted in this amount of petroleum ether. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/10 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the electron capture response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each envelope of peak areas from the standard curve. No volume corrections are needed, because the standard curve is based on mg/10 ml of petroleum ether and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

mg sample = mg found in sample filter
mg blank = mg found in blank filter

10.3 Divide the total weight by the analytical method recovery (A.M.R.) to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{A.M.R.}}$$

10.4 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.3) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

11. Reference

11.1 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Dipropylene Glycol Methyl Ether

Analyte:	Dipropylene Glycol Methyl Ether	Method No.: S69
Matrix:	Air	Range: 314-1197 mg/cu m
OSHA Standard:	100 ppm (610 mg/cu m)	Precision ($\overline{CV}_T$): 0.064
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 2/14/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 314-1197 mg/cu m at an atmospheric temperature and pressure of 22°C and 765 mm Hg, using a 10 liter sample. Under the conditions of sample size (10 liters) the probable useful range of this method is 60-1830 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 18 mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of dipropylene glycol methyl ether and other substances in the air. The first section of the charcoal tube was found to hold 33 mg of dipropylene glycol methyl ether

when a test atmosphere containing 1219 mg/cu m of dipropylene glycol methyl ether in air was sampled at 0.185 liter per minute for 145 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 314-1197 mg/cu m was 0.064. This value corresponds to a 39 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 1.4% higher than the "true" values at the OSHA standard level.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in stainless steel) packed with 10% FFAP on 80/100 mesh, acid washed DMCS Chromosorb W.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 One-milliliter sample containers with glass stoppers or Teflon-lined caps.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 0.5-ml delivery pipets or 1.0-ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 Dipropylene Glycol Methyl Ether, reagent grade.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a flow of 0.20 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm$5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 0.5 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 210°C injector temperature
5. 270°C manifold temperature (detector)
6. 160°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation

within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

The amount injected is equivalent to that present in a 10 liter air sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 0.5 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/0.5 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to get the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	= pressure (mm Hg) of air sampled
T	= temperature (°C) of air sampled
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	= molecular weight (g/mole) of analyte
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Analyte:	Glycidol	Method No.: S70
Matrix:	Air	Range: 73-310 mg/cu m
OSHA Standard:	50 ppm (150 mg/cu m)	Precision ($\overline{CV}_T$): 0.080
Procedure:	Adsorption on charcoal, desorption with tetrahydrofuran, GC	Validation Date: 2/14/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present, and the charcoal tube is immediately refrigerated at 4°C and held at that temperature until the sample is desorbed with tetrahydrofuran.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with tetrahydrofuran.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 73-310 mg/cu m at an atmospheric temperature and pressure of 21°C and 768 mm Hg, using a 50 liter sample. Under the conditions of sample size (50 liters) the probable useful range of this method is 15-450 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 22 mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of glycidol and other substances in the air. The first section of the charcoal tube was found to hold 45 mg of glycidol when a test atmosphere containing

300 mg/cu m of glycidol in air was sampled at 0.93 liter per minute for 163 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample. Since tetrahydrofuran is used rather than carbon disulfide to desorb the glycidol from the charcoal, it would not be possible to measure tetrahydrofuran in the sample with this desorbing solvent. If it is suspected that tetrahydrofuran is present, a separate sample should be collected for tetrahydrofuran analysis.

3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 73-310 mg/cu m was 0.080. This value corresponds to a 12 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 3.1% lower than the "true" values at the OSHA standard level.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

5.4 A disadvantage of the method is that the sample must be kept refrigerated, or recoveries are poor.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.2)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in stainless steel) packed with 10% FFAP on 80/100 mesh, acid washed DMCS Chromosorb W.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 One-milliliter sample containers with glass stoppers or Teflon-lined caps.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 0.5-ml delivery pipets or 1.0-ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Eluent: Tetrahydrofuran, chromatographic quality.

7.2 Glycidol, reagent grade.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A maximum sample size of 50 liters is recommended. Sample at a flow of 1.0 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm$5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping. Capped tubes should be refrigerated during storage and shipping at 4°C.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 0.5 ml of tetrahydrofuran is pipetted into each sample container. Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 225°C injector temperature
5. 260°C manifold temperature (detector)
6. 155°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation

within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. These tubes must be refrigerated after injection of the analyte onto the charcoal. Previous studies have shown that the desorption efficiency decreases with time if the samples are stored at room temperature.

The amount injected is equivalent to that present in a 50 liter air sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. The tubes should be kept refrigerated, and they are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 0.5 ml of the eluent with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml tetrahydrofuran, because samples are desorbed in this amount of tetrahydrofuran. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/0.5 ml tetrahydrofuran and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to get the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	= pressure (mm Hg) of air sampled
T	= temperature (°C) of air sampled
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	= molecular weight (g/mole) of analyte
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Methylal
(Dimethoxymethane)

Analyte:	Methylal	Method No.: S71
Matrix:	Air	Range: 1684-6670 mg/cu m
OSHA Standard:	1000 ppm (3110 mg/cu m)	Precision ($\overline{CV}_T$): 0.060
Procedure:	Adsorption on charcoal, desorption with hexane, GC	Validation Date: 2/14/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with hexane.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 1684-6670 mg/cu m at an atmospheric temperature and pressure of 22°C and 771 mm Hg, using a 2 liter sample. Under the conditions of sample size (2 liters) the probable useful range of this method is 310-9330 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 19 mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of methylal and other substances in the air. The first section of the charcoal tube was found to hold 23 mg of methylal when a test atmosphere containing 6250 mg/cu m

of methylal in air was sample at 0.183 liter per minute for 20 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample. Since hexane is used rather than carbon disulfide to desorb the methylal from the charcoal, it would not be possible to measure hexane in the sample with this desorbing solvent. If it is suspected that hexane is present, a separate sample should be collected for hexane analysis.

3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 1684-6670 mg/cu m was 0.060. This value corresponds to a 187 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 4.6% higher than the "true" values at the OSHA standard level.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (4-ft x 1/4-in stainless steel) packed with 50/80 mesh Porapak, Type Q.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 One-milliliter sample containers with glass stoppers or Teflon-lined caps.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 0.5-ml delivery pipets or 1.0-ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Eluent: Hexane, reagent grade.

7.2 Methylal, reagent grade.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A maximum sample size of 2 liters is recommended. Sample at a flow of 0.20 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm$5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 0.5 ml of hexane is pipetted into each sample container. Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 190°C injector temperature
5. 250°C manifold temperature (detector)
6. 195°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation

within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

The amount injected is equivalent to that present in a 2 liter air sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 0.5 ml of hexane with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml hexane, because samples are desorbed in this amount of hexane. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same period as the unknown samples. Curves are established by plotting concentration in mg/0.5 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/0.5 ml hexane and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to get the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	= pressure (mm Hg) of air sampled
T	= temperature (°C) of air sampled
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	= molecular weight (g/mole) of analyte
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Phenyl Ether

Analyte:	Phenyl Ether (vapor)	Method No.: S72
Matrix:	Air	Range: 3-13 mg/cu m
OSHA Standard:	1 ppm (7 mg/cu m)	Precision ($\overline{CV}_T$): 0.070
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 2/14/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 3-13 mg/cu m at an atmospheric temperature and pressure of 24°C and 766 mm Hg, using a 10 liter sample. Under the conditions of sample size (10 liters) the probable useful range of this method is 0.70-21 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 0.2 mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of phenyl ether and other substances in the air. The first section of the charcoal tube was found to hold at least 0.6 mg of phenyl ether when a test atmosphere

containing 13.1 mg/cu m of phenyl ether in air was sampled at 0.185 liter per minute for 240 minutes; at that time the concentration of analyte in the effluent was less than 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 3-13 mg/cu m was 0.070. This value corresponds to a 0.49 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 Collection efficiency of the collecting medium was found to be 1.00 ± 0.01, so that no bias was introduced in the sample collection step. There were no apparent biases in the sampling and analytical method for which desorption efficiency corrections were made. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in stainless steel) packed with 10% FFAP on 80/100 mesh, acid washed DMCS Chromosorb W.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 One-milliliter sample containers with glass stoppers or Teflon-lined caps.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 0.5-ml delivery pipets or 1.0-ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 Phenyl Ether, reagent grade.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a flow of 0.20 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm$5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 0.5 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 230°C injector temperature
5. 265°C manifold temperature (detector)
6. 215°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation

within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of hexane solution of phenyl ether containing 17.3 mg/ml is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

The amount injected is equivalent to that present in a 10 liter air sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 0.5 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/0.5 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to get the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	= pressure (mm Hg) of air sampled
T	= temperature (°C) of air sampled
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	= molecular weight (g/mole) of analyte
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Phenyl Ether - Biphenyl Mixture
(vapor)

Analyte:	Phenyl Ether-Biphenyl Mixture	Method No.: S73
Matrix:	Air	Range: 3.86-15.7 mg/cu m
OSHA Standard:	1 ppm (7 mg/cu m)	Precision ($\overline{CV}_T$): 0.089
Procedure:	Adsorption on silica gel, desorption with benzene, GC	Validation Date: 2/14/75

1. Principle of the Method

1.1 A known volume of air is drawn through a silica gel tube to trap the organic vapors present.

1.2 The silica gel in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with benzene.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The areas of the resulting peaks are determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 3.86-15.7 mg/cu m at an atmospheric temperature and pressure of 23°C and 761 mm Hg, using a 10 liter sample. Under the conditions of sample size (10 liters) the probable useful range of this method is 0.7-21 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 0.2 mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the silica gel tube. This capacity varies with the concentrations of the analyte and other substances in the air. The first section of the silica gel tube was found to hold at least 0.7 mg of analyte when a test atmosphere containing

15.7 mg/cu m of analyte in air was sampled at 0.185 liter per minute for 240 minutes. (The silica gel tube consists of two sections of silica gel separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 Silica gel has a high affinity for water, so organic vapors will not be trapped efficiently in the presence of a high relative humidity. This effect may be important even though there is no visual evidence of condensed water in the silica gel tube.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample. Since benzene is used rather than carbon disulfide to desorb the analyte from the silica gel, it is not possible to measure benzene in the sample with this desorbing solvent. If it is suspected that benzene is present, a separate sample should be collected for benzene analysis.

3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 3.86-15.7 mg/cu m was 0.089. This value corresponds to a 0.62 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 Collection efficiency of the collecting medium was found to be 1.00 ± 0.01, so that no bias was introduced in the sample collection step. There were no apparent biases in the sampling and analytical method for which desorption efficiency corrections were made. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the silica gel tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3)

6.2 Silica gel tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh silica gel separated by a 2-mm portion of urethane foam. The adsorbing section contains approximately 150 mg of silica gel, the backup section, approximately 75 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in stainless steel) packed with 5% OV-17 on 80/100 mesh, acid washed DMCS Chromosorb W.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 One-milliliter sample containers with glass stoppers or Teflon-lined caps.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 0.5-ml delivery pipets or 1.0-ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality benzene.

7.2 Biphenyl, reagent grade.

7.3 Phenyl Ether, reagent grade.

7.4 Phenyl Ether-Biphenyl Mixture: Ten grams of phenyl ether-biphenyl mixture is prepared by dissolving 2.65 grams solid biphenyl in 7.35 grams melted phenyl ether. (Liquid eutectic)

7.5 Prepurified hydrogen.

7.6 Filtered compressed air.

7.7 Purified nitrogen.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative silica gel tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of silica gel is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The silica gel tube should be placed in a vertical direction during sampling to minimize channeling through the silica gel.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the silica gel tube.

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a flow of 0.20 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm$5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The silica gel tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the silica gel tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each silica gel tube is scored with a file in front of the first section of silica gel and broken open. The glass wool is removed and discarded. The silica gel in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 0.5 ml of benzene is pipetted into each sample container. (All work with benzene should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period.

8.4.3 GC Conditions. It is necessary to be able to measure the phenyl ether and biphenyl separately. Using the following operating conditions, biphenyl and phenyl ether are observed as separate chromatographic peaks.

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 200°C injector temperature
5. 250°C manifold temperature (detector)
6. 140°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of area. The areas of the sample peaks for both components are measured separately by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from standard curves prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of silica gel to another. Thus, it is necessary to determine at least once the percentage of the specific compounds that are removed in the desorption process, provided the same batch of silica gel is used.

8.5.2 Procedure for determining desorption efficiency. Silica gel equivalent to the amount in the first section of the sampling tube (approximately 150 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This silica gel must be from the same batch as that used in obtaining the samples and can be obtained from unused silica gel tubes. The open end is capped with Parafilm. A known amount of hexane solution of the phenyl ether-biphenyl mixture (Section 7.4) containing 17.5 mg/ml is injected directly into the silica gel with a microliter syringe, and the tube is capped with more Parafilm.

The amount injected is equivalent to that present in a 10 liter air sample at the selected level.

Six tubes at each of three levels (using 2 microliters, 4 microliters, and 8 microliters of hexane solution for the 0.5X, 1X, and 2X OSHA levels) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the silica gel. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 0.5 ml of benzene with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The weight (mg) added for each component is calculated from the amount of solution added and the weight percent of that component in the solution. For instance, addition of an 8-microliter aliquot of the hexane solution of 17.5 mg/ml to 0.5 ml benzene results in a standard containing 0.102 mg phenyl ether/0.5 ml benzene and 0.037 mg biphenyl/0.5 ml benzene.

The desorption efficiencies (D.E.) for phenyl ether and biphenyl are determined separately. For each compound, the desorption efficiency equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$\text{D.E.} = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the silica gel. Plot the desorption efficiency versus weight of analyte found for the two components separately. These curves are used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml benzene, because samples are desorbed in this amount of benzene. The mixture of phenyl ether-biphenyl described in Section 7.4 is used for the standards. The density of the mixture (1.06 g/ml at 25°C), as given in Reference 11.4, is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, are prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. A curve for each component is established by plotting concentration in mg/0.5 ml for that component versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the

sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

The concentration in mg/cu m in air is determined for phenyl ether and biphenyl separately. The concentration of the mixture is the sum of these two concentrations.

10.1 Read the weight, in mg, corresponding to the peak area for each component from the appropriate standard curve. No volume corrections are needed, because the standard curve is based on mg/0.5 ml benzene and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 For each component, add the weights found in the front and backup sections to get the total weight of that component in the sample.

10.4 For each component, read the desorption efficiency from the curve (See Section 8.5.2) for the amount of that component found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of each component in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

The concentration of the mixture in air is the sum of the concentrations of the two components:

$$\text{mg/cu m}_{\text{(mixture)}} = \text{mg/cu m}_{\text{(phenyl ether)}} + \text{mg/cu m}_{\text{(biphenyl)}}$$

10.6 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	= pressure (mm Hg) of air sampled
T	= temperature (°C) of air sampled
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	= molecular weight (g/mole) of analyte
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

11.4 Hake, C.L. and Rowe, V.K., "Phenyl Ether-Biphenyl Eutectic Mixture (Dowtherm A)," Industrial Hygiene & Toxicology, Volume II, 1701, (1962).

Phenyl Glycidyl Ether

Analyte:	Phenyl Glycidyl Ether	Method No.: S74
Matrix:	Air	Range: 31-121 mg/cu m
OSHA Standard:	10 ppm (60 mg/cu m)	Precision ($\overline{CV}_T$): 0.057
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 2/14/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 31-121 mg/cu m at an atmospheric temperature and pressure of 22°C and 766 mm Hg, using a 50 liter sample. Under the conditions of sample size (50 liters) the probable useful range of this method is 6-180 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 9 mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of phenyl glycidyl ether and other substances in the air. The first section of the charcoal tube was found to hold at least 25 mg of phenyl glycidyl ether when a

test atmosphere containing 112 mg/cu m of phenyl glycidyl ether in air was sampled at 0.93 liter per minute for 240 minutes; at that time the concentration of analyte in the effluent was less than 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 31-121 mg/cu m was 0.057. This value corresponds to a 3.4 mg/cu m standard deviation at the QSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 8.8% lower than the "true" values at the OSHA standard level.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.2)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in stainless steel) packed with 10% FFAP on 80/100 mesh, acid washed DMCS Chromosorb W.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 One-milliliter sample containers with glass stoppers or Teflon-lined caps.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 0.5-ml delivery pipets or 1.0-ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 Phenyl Glycidyl Ether, reagent grade.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A maximum sample size of 50 liters is recommended. Sample at a flow of 1.0 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm 5\%$.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 0.5 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 230°C injector temperature
5. 265°C manifold temperature (detector)
6. 90°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation

within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

The amount injected is equivalent to that present in a 50 liter air sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 0.5 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/0.5 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to get the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	= pressure (mm Hg) of air sampled
T	= temperature (°C) of air sampled
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	= molecular weight (g/mole) of analyte
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Propylene Oxide

Analyte:	Propylene Oxide	Method No.: S75
Matrix:	Air	Range: 121-482 mg/cu m
OSHA Standard:	100 ppm (240 mg/cu m)	Precision ($\overline{CV}_T$): 0.085
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 2/14/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 121-482 mg/cu m at an atmospheric temperature and pressure of 24°C and 766 mm Hg, using a 5 liter sample. Under the conditions of sample size (5 liters) the probable useful range of this method is 25-720 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 3.5 mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of propylene oxide and other substances in the air. The first section of the charcoal tube was found to hold 4 mg of propylene oxide when a test atmosphere containing

484 mg/cu m of propylene oxide in air was sampled at 0.185 liter per minute for 45 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 121-482 mg/cu m was 0.085. This value corresponds to a 20 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 5.6% lower than the "true" values at the OSHA standard level.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (4-ft x 1/4-in stainless steel) packed with 50/80 mesh Porapak, Type Q.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 One-milliliter sample containers with glass stoppers or Teflon-lined caps.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 0.5-ml delivery pipets or 1.0-ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 Propylene Oxide, reagent grade.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A maximum sample size of 5 liters is recommended. Sample at a flow of 0.20 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm$5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 0.5 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 190°C injector temperature
5. 255°C manifold temperature (detector)
6. 145°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation

within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of hexane solution of propylene oxide containing 300 mg/ml is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

The amount injected is equivalent to that present in a 5 liter air sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 0.5 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/0.5 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to get the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	= pressure (mm Hg) of air sampled
T	= temperature (°C) of air sampled
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	= molecular weight (g/mole) of analyte
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

2-Butoxy Ethanol
(Butyl Cellosolve)

Analyte:	2-Butoxy Ethanol	Method No.: S76
Matrix:	Air	Range: 124-490 mg/cu m
OSHA Standard:	50 ppm (240 mg/cu m)	Precision ($\overline{CV}_T$): 0.060
Procedure:	Adsorption on charcoal, desorption with 5% methanol in methylene chloride, GC	Validation Date: 2/14/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with 5% methanol in methylene chloride.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 124-490 mg/cu m at an atmospheric temperature and pressure of 21°C and 766 mm Hg, using a 10 liter sample. Under the conditions of sample size (10 liters) the probable useful range of this method is 25-720 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 7 mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of 2-butoxy ethanol and other substances in the air. The first section of the charcoal tube was found to hold at least 21 mg of 2-butoxy ethanol when a test atmosphere

containing 480 mg/cu m of 2-butoxy ethanol in air was sampled at 0.183 liter per minute for 240 minutes; at that time the concentration of analyte in the effluent was less than 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample. Since 5% methanol in methylene chloride is used rather than carbon disulfide to desorb the 2-butoxy ethanol from the charcoal, it would not be possible to measure methanol or methylene chloride in the sample with this desorbing solvent. If it is suspected that methanol or methylene chloride is present, a separate sample should be collected for methanol or methylene chloride analysis.

3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 124-490 mg/cu m was 0.060. This value corresponds to a 14 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 8% lower than the "true values at the OSHA standard level.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in stainless steel) packed with 10% FFAP on 80/100 mesh, acid washed DMCS Chromosorb W.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 One-milliliter sample containers with glass stoppers or Teflon-lined caps.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 0.5-ml delivery pipets or 1.0-ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Eluent: 5% methanol in methylene chloride (both reagent grade).

7.2 2-Butoxy Ethanol, reagent grade.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a flow of 0.20 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm$5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 0.5 ml of 5% methanol in methylene chloride is pipetted into each sample container. Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 215°C injector temperature
5. 263°C manifold temperature (detector)
6. 145°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation

within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

The amount injected is equivalent to that present in a 10 liter air sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 0.5 ml of the eluent with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml of the eluent, because samples are desorbed in this amount of eluent. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/0.5 ml of the eluent and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to get the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	= pressure (mm Hg) of air sampled
T	= temperature (°C) of air sampled
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	= molecular weight (g/mole) of analyte
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Isopropyl Glycidyl Ether

Analyte:	Isopropyl Glycidyl Ether	Method No.: S77
Matrix:	Air	Range: 121-484 mg/cu m
OSHA Standard:	50 ppm (240 mg/cu m)	Precision ($\overline{CV}_T$): 0.067
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 2/14/75

1. Principle of the Method

   1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

   1.2 The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with carbon disulfide.

   1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

   1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

   2.1 This method was validated over the range of 121-484 mg/cu m at an atmospheric temperature and pressure of 21°C and 763 mm Hg, using a 10 liter sample. Under the conditions of sample size (10 liters) the probable useful range of this method is 25-720 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 7 mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

   2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of isopropyl glycidyl ether and other substances in the air. The first section of the charcoal tube was found to hold at least 21 mg of isopropyl glycidyl ether

when a test atmosphere containing 480 mg/cu m of isopropyl glycidyl ether in air was sampled at 0.183 liter per minute for 240 minutes; at that time the concentration of analyte in the effluent was less than 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 121-484 mg/cu m was 0.067. This value corresponds to a 16 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 7% lower than the "true" values at the OSHA standard level.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in stainless steel) packed with 10% FFAP on 80/100 mesh, acid washed DMCS Chromosorb W.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 One-milliliter sample containers with glass stoppers or Teflon-lined caps.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 0.5-ml delivery pipets or 1.0-ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 Isopropyl Glycidyl Ether, reagent grade.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a flow of 0.20 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm$5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 0.5 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 205°C injector temperature
5. 270°C manifold temperature (detector)
6. 115°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation

within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

The amount injected is equivalent to that present in a 10 liter air sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 0.5 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/0.5 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to get the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
M.W. = molecular weight (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Tetrahydrofuran

Analyte:	Tetrahydrofuran	Method No.: S78
Matrix:	Air	Range: 323-1240 mg/cu m
OSHA Standard:	200 ppm (590 mg/cu m)	Precision ($\overline{CV}_T$): 0.055
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 2/14/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 323-1240 mg/cu m at an atmospheric temperature and pressure of 22.5°C and 763 mm Hg, using a 9 liter sample. Under the conditions of sample size (9 liters) the probable useful range of this method is 60-1480 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 13 mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of tetrahydrofuran and other substances in the air. The first section of the charcoal tube was found to hold 15 mg of tetrahydrofuran when a test atmosphere containing

1140 mg/cu m of tetrahydrofuran in air was sampled at 0.185 liter per minute for 72 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 323-1240 mg/cu m was 0.055. This value corresponds to a 32 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 1.3% lower than the "true" values at the OSHA standard level.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (4-ft X 1/4-in stainless steel) packed with 50/80 mesh Porapak, Type Q.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 One-milliliter sample containers with glass stoppers or Teflon-lined caps.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 0.5-ml delivery pipets or 1.0-ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 Tetrahydrofuran, reagent grade.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A maximum sample size of 9 liters is recommended. Sample at a flow of 0.20 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm$5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 0.5 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 190°C injector temperature
5. 250°C manifold temperature (detector)
6. 185°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation

within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

The amount injected is equivalent to that present in a 9 liter air sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 0.5 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/0.5 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to get the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	= pressure (mm Hg) of air sampled
T	= temperature (°C) of air sampled
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	= molecular weight (g/mole) of analyte
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Methyl Cellosolve

Analyte:	Methyl Cellosolve	Method No.: S79
Matrix:	Air	Range: 44-160 mg/cu m
OSHA Standard:	25 ppm (80 mg/cu m)	Precision ($\overline{CV}_T$): 0.068
Procedure:	Adsorption on charcoal, desorption with 5% methanol in methylene chloride, GC	Validation Date: 2/14/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with 5% methanol in methylene chloride.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 44-160 mg/cu m at an atmospheric temperature and pressure of 22°C and 768 mm Hg, using a 50 liter sample. Under the conditions of sample size (50 liters) the probable useful range of this method is 8-240 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 12 mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of methyl cellosolve and other substances in the air. The first section of the charcoal tube was found to hold 20 mg of methyl cellosolve when a test atmosphere containing

158 mg/cu m of methyl cellosolve in air was sampled at 0.93 liter per minute for 138 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample. Since 5% methanol in methylene chloride is used rather than carbon disulfide to desorb the methyl cellosolve from the charcoal, it would not be possible to measure methanol or methylene chloride in the sample with this desorbing solvent. If it is suspected that methanol or methylene chloride is present, a separate sample should be collected for methanol or methylene chloride analysis.

3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 44-160 mg/cu m was 0.068. This value corresponds to a 5.4 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 7.2% lower than the "true" values at the OSHA standard level.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.2)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in stainless steel) packed with 10% FFAP on 80/100 mesh, acid washed DMCS Chromosorb W.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 One-milliliter sample containers with glass stoppers or Teflon-lined caps.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 0.5-ml delivery pipets or 1.0-ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Eluent: 5% methanol in methylene chloride (both reagent grade).

7.2 Methyl Cellosolve, reagent grade.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A maximum sample size of 50 liters is recommended. Sample at a flow of 1.0 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm$5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 0.5 ml of 5% methanol in methylene chloride is pipetted into each sample container. Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 215°C injector temperature
5. 268°C manifold temperature (detector)
6. 95°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation

within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

The amount injected is equivalent to that present in a 50 liter air sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 0.5 ml of the eluent with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml of the eluent, because samples are desorbed in this amount of eluent. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/0.5 ml of the eluent and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to get the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	= pressure (mm Hg) of air sampled
T	= temperature (°C) of air sampled
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	= molecular weight (g/mole) of analyte
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Ethyl Ether

Analyte:	Ethyl Ether	Method No.: S80
Matrix:	Air	Range: 606-2400 mg/cu m
OSHA Standard:	400 ppm (1210 mg/cu m)	Precision ($\overline{CV}_T$): 0.053
Procedure:	Adsorption on charcoal, desorption with ethyl acetate, GC	Validation Date: 2/14/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with ethyl acetate.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 606-2400 mg/cu m at an atmospheric temperature and pressure of 22°C and 766 mm Hg, using a 3 liter sample. Under the conditions of sample size (3 liters) the probable useful range of this method is 120-3630 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 11 mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of ethyl ether and other substances in the air. The first section of the charcoal tube was found to hold 15 mg of ethyl ether when a test atmosphere containing

2470 mg/cu m of ethyl ether in air was sampled at 0.185 liter per minute for 33 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample. Since ethyl acetate is used rather than carbon disulfide to desorb the ethyl ether from the charcoal it would not be possible to measure ethyl acetate in the sample with this desorbing solvent. If it is suspected that ethyl acetate is present, a separate sample should be collected for ethyl acetate analysis.

3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 606-2400 mg/cu m was 0.053. This value corresponds to a 64 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 5.1% higher than the "true" values at the OSHA standard level.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (4-ft x 1/4-in stainless steel) packed with 50/80 mesh Porapak, Type Q.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 One-milliliter sample containers with glass stoppers or Teflon-lined caps.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 0.5-ml delivery pipets or 1.0-ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Eluent: Ethyl acetate, reagent grade

7.2 Ethyl ether, reagent grade

7.3 Purified nitrogen

7.4 Prepurified hydrogen

7.5 Filtered compressed air

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A maximum sample size of 3 liters is recommended. Sample at a flow of 0.20 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm$5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 0.5 ml of ethyl acetate is pipetted into each sample container. Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 195°C injector temperature
5. 250°C manifold temperature (detector)
6. 175°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation

within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

The amount injected is equivalent to that present in a 3 liter air sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 0.5 ml of ethyl acetate with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml ethyl acetate, because samples are desorbed in this amount of ethyl acetate. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/0.5 ml ethyl acetate and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to get the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	= pressure (mm Hg) of air sampled
T	= temperature (°C) of air sampled
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	= molecular weight (g/mole) of analyte
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

n-Butyl Glycidyl Ether

Analyte:	n-Butyl Glycidyl Ether	Method No.: S81
Matrix:	Air	Range: 133-542 mg/cu m
OSHA Standard:	50 ppm (270 mg/cu m)	Precision ($\overline{CV}_T$): 0.074
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 2/14/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 133-542 mg/cu m at an atmospheric temperature and pressure of 22°C and 767 mm Hg, using a 10 liter sample. Under the conditions of sample size (10 liters) the probable useful range of this method is 30-810 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 8 mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of n-butyl glycidyl ether and other substances in the air. The first section of the charcoal tube was found to hold at least 23 mg of n-butyl glycidyl ether when

a test atmosphere containing 530 mg/cu m of n-butyl glycidyl ether in air was sampled at 0.183 liter per minute for 240 minutes; at that time the concentration of analyte in the effluent was less than 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 133-542 mg/cu m was 0.074. This value corresponds to a 20 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 1.8% lower than the "true" values at the OSHA standard level.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in stainless steel) packed with 10% FFAP on 80/100 mesh, acid washed DMCS Chromosorb W.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 One-milliliter sample containers with glass stoppers or Teflon-lined caps.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 0.5-ml delivery pipets or 1.0-ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 n-Butyl Glycidyl Ether, reagent grade.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a flow of 0.20 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm$5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 0.5 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 180°C injector temperature
5. 275°C manifold temperature (detector)
6. 130°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation

within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

The amount injected is equivalent to that present in a 10 liter air sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 0.5 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/0.5 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to get the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	= pressure (mm Hg) of air sampled
T	= temperature (°C) of air sampled
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	= molecular weight (g/mole) of analyte
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Cyclohexene

Analyte:	Cyclohexene	Method No.: S82
Matrix:	Air	Range: 510-2030 mg/cu m
OSHA Standard:	300 ppm (1010 mg/cu m)	Precision ($\overline{CV}_T$): 0.073
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 2/14/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 510-2030 mg/cu m at an atmospheric temperature and pressure of 23.5°C and 768 mm Hg, using a 5 liter sample. Under the conditions of sample size (5 liters) the probable useful range of this method is 100-3030 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 15 mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of cyclohexene and other substances in the air. The first section of the charcoal tube was found to hold 21 mg of cyclohexene when a test atmosphere containing

2002 mg/cu m of cyclohexene in air was sampled at 0.185 liter per minute for 56 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 510-2030 mg/cu m was 0.073. This value corresponds to a 74 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 9% higher than the "true" values at the OSHA standard level.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (4-ft X 1/4-in stainless steel) packed with 50/80 mesh Porapak, Type Q.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 One-milliliter sample containers with glass stoppers or Teflon-lined caps.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 0.5-ml delivery pipets or 1.0-ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 Cyclohexene, reagent grade.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A maximum sample size of 5 liters is recommended. Sample at a flow of 0.20 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm$5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal, and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 0.5 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 195°C injector temperature
5. 260°C manifold temperature (detector)
6. 205°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation

within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

The amount injected is equivalent to that present in a 5 liter air sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 0.5 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/0.5 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to get the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	= pressure (mm Hg) of air sampled
T	= temperature (°C) of air sampled
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	= molecular weight (g/mole) of analyte
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Naphtha, Coal Tar

Analyte:	Naphtha, Coal Tar	Method No.:	S86
Matrix:	Air	Range:	193-809 mg/cu m
OSHA Standard:	100 ppm (400 mg/cu m)	Precision ($\overline{CV}_T$):	0.051
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	3/14/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The total area of the resulting peaks is determined and compared with corresponding areas obtained from injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 193-809 mg/cu m at an atmospheric temperature and pressure of 24°C and 761 mm Hg, using a 10-liter sample. Under the conditions of sample size (10 liters)the probable useful range of this method is 40-1200 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 12-mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 29.6 mg of analyte when a test atmosphere containing 809 mg/cu m of analyte in air was sampled at 0.19 liters per minute for 193 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 When analyzing solvent mixtures such as this analyte, search for differences in gas chromatographic patterns between field samples and bulk or head space samples as evidence of an interference. It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 193-809 mg/cu m was 0.051. This value corresponds to a 20.4 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2

4.2 On the average the values obtained using the overall sampling and analytical method were 4.5% higher than the "true" value at the OSHA standard level.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3).

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (6-ft x 1/8-in stainless steel) packed with 1.5% OV-101 on 100/120 mesh Chromosorb W.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide

7.2 Naphtha, Coal tar (Boiling range: 154-195 °C)

7.3 Undecane,or other suitable internal standard

7.4 Purified helium

7.5 Prepurified hydrogen

7.6 Filtered compressed air

8. Procedure

8.1 Cleaning of equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a rate of 0.2 liter per minute or less. The flow rate should be known with an accuracy of at least ±5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (60 psig) Helium carrier gas flow
2. 35 ml/min (25 psig) Hydrogen gas flow to detector
3. 400 ml/min (60 psig) Air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 80°C column temperature

Note: The GC conditions have been chosen such that the analyte-related peaks elute as a cluster of unresolved peaks. Watch for distinctive patterns in searching for interferences and adjust GC conditions accordingly.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

8.4.5 Measurement of area. The total area of the sample peaks is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample injector vials, capped with Teflon-faced septa, may be used in place of the glass tubes.

Six tubes at each of three concentration levels (0.5X,1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 10 liter sample at the selected level. The tubes are allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

Bulk samples of the analyte should be used for the calibration.

It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus total area of relevant peaks.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte peaks to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each total peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

mg sample = mg found in front section of sample tube
mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liters/cu m)}}{\text{Air Volume Sampled (liters)}}$$

10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Propane

Method No. S87

Substance

Propane

Standard

8-hour time-weighted average: 1000 ppm (1800 mg/cu m)

Reference: 29 CFR 1910.93

Analytical Method

The propane vapor present in the atmosphere is measured directly by drawing the air sample into a combustible gas meter properly calibrated with propane. The meter reading is recorded and the equivalent concentration in ppm is read off the calibration curve. The method has been validated over the range of 481-2016 ppm at 20.5°C and 760 mm Hg atmospheric temperature and pressure.

Sampling Equipment

Dual range explosive gas meter such as the MSA Model 40 is used. No sample is actually collected since the atmosphere to be analyzed is usually drawn into the meter using a rubber aspirator bulb. The air can also be drawn into the meter with a personal sampling pump.

Sampling Procedure

The instructions given in the manual for the appropriate combustible gas meter used must be followed carefully for proper results. Typically, the procedure will require the following steps:

1. The combustion chamber must be swept free of combustible gases and be filled with fresh air.

2. Batteries must be turned on, and the proper voltage applied to the bridge.

3. The bridge must be balanced to zero deflection on the meter with fresh air in the open chamber.

4. The sample is drawn into the meter, and the meter reading is recorded. Repeat at least three times and report average.

5. The concentration of propane in the air samples tested is determined from the calibration curve provided with the properly calibrated meter.

Special Consideration

1. Any hydrocarbon present in the atmosphere will interfere with the analysis. Where other hydrocarbons are known or suspected to be present in the air, such information, including their suspected identities, should be noted.

2. Water vapor will impair the proper functioning of the sensing filaments. When testing atmospheres of high humidity, use available cotton filters or special humidity conditioning sample probes to remove excessive dust and moisture from the sample under test.

Reference

Instrument Manual, MSA Combustible Gas Indicator, Model 40, Mine Safety Appliance Company, Pittsburgh, Pennsylvania.

Turpentine

Analyte:	Turpentine	Method No.:	S88
Matrix:	Air	Range:	264-1107 mg/cu m
OSHA Standard:	100 ppm (560 mg/cu m)	Precision ($\overline{CV}_T$):	0.055
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	3/14/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The total area of the resulting peaks is determined and compared with corresponding areas obtained from injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 264-1107 mg/cu m at an atmospheric temperature and pressure of 24°C and 766 mm Hg, using a 10-liter sample. Under the conditions of sample size (10 liters) the probable useful range of this method is 56-1680 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 16.8-mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 26.5 mg of analyte when a test atmosphere containing 1107 mg/cu m of analyte in air was sampled at 0.19 liters per minute for 126 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 When analyzing solvent mixtures such as this analyte, search for differences in gas chromatographic patterns between field samples and bulk or head space samples as evidence of an interference. It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV_T}$) for the total analytical and sampling method in the range of 264-1107 mg/cu m was 0.055. This value corresponds to a 30.8 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 0.4% higher than the "true" value at the OSHA standard level.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3).

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (6-ft x 1/8-in stainless steel) packed with 1.5% OV-101 on 100/120 mesh Chromosorb W.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide

7.2 Turpentine (Boiling range: 150-170 °C)

7.3 Undecane, or other suitable internal standard

7.4 Purified helium

7.5 Prepurified hydrogen

7.6 Filtered compressed air

8. Procedure

8.1 Cleaning of equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a rate of 0.2 liter per minute or less. The flow rate should be known with an accuracy of at least ±5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (60 psig) Helium carrier gas flow
2. 35 ml/min (25 psig) Hydrogen gas flow to detector
3. 400 ml/min (60 psig) Air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 70°C column temperature

Note: The GC conditions have been chosen such that the analyte-related peaks elute as a cluster of unresolved peaks. Watch for distinctive patterns in searching for interferences and adjust GC conditions accordingly.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

8.4.5 Measurement of area. The total area of the sample peaks is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample injector vials, capped with Teflon-faced septa, may be used in place of the glass tubes.

Six tubes at each of three concentration levels (0.5X,1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 10 liter sample at the selected level. The tubes are allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

Bulk samples of the analyte should be used for the calibration.

It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus total area of relevant peaks.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte peaks to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each total peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

mg sample = mg found in front section of sample tube
mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liters/cu m)}}{\text{Air Volume Sampled (liters)}}$$

10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Analyte:	Heptane	Method No.:	S89
Matrix:	Air	Range:	968-4060 mg/cu m
OSHA Standard:	500 ppm (2000 mg/cu m)	Precision ($\overline{CV}_T$):	0.056
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	3/14/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 968-4060 mg/cu m at an atmospheric temperature and pressure of 24°C and 748 mm Hg, using a 4 liter sample. Under the conditions of sample size (4 liters) the probable useful range of this method is 200-6000 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 24 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 24.7 mg of analyte when a test atmosphere containing 4060 mg/cu m of analyte in air was sampled at 0.19 liters per minute for 32 minutes; breakthrough was observed at this time, i.e., the concentration of analyte in the effluent was 5% of that in the influent.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 968-4060 mg/cu m was 0.056. This value corresponds to a 112 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 6.5% lower than the "true" value at the OSHA standard level.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3).

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in stainless steel) packed with 10% OV-101 on 100/120 mesh Supelcoport.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide

7.2 Heptane,reagent grade

7.3 Nonane,or other suitable internal standard

7.4 Purified helium

7.5 Prepurified hydrogen

7.6 Filtered compressed air

8. Procedure

8.1 Cleaning of equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A maximum sample size of 4 liters is recommended. Sample at a rate of 0.2 liter per minute or less. The flow rate should be known with an accuracy of at least ±5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (60 psig) Helium carrier gas flow
2. 35 ml/min (25 psig) Hydrogen gas flow to detector
3. 400 ml/min (60 psig) Air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 80°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample injector vials, capped with Teflon-faced septa, may be used in place of the glass tubes.

Six tubes at each of three concentration levels (0.5X,1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 4 liter sample at the selected level. The tubes are allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

mg sample = mg found in front section of sample tube
mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liters/cu m)}}{\text{Air Volume Sampled (liters)}}$$

10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Analyte:	Hexane	Method No.:	S90
Matrix:	Air	Range:	877 - 3679 mg/cu m
OSHA Standard:	500 ppm (1800 mg/cu m)	Precision ($\overline{CV}_T$):	0.062
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	3/14/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 877 - 3679 mg/cu m at an atmospheric temperature and pressure of 17°C and 764 mm Hg, using a 4-liter sample. Under the conditions of sample size (4 liters), the probable useful range of this method is 180 - 5400 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 22-mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 21.7 mg of analyte when a test atmosphere containing 3679 mg/cu m of analyte in air was sampled at 0.19 liters per minute for 31 minutes; breakthrough was observed at this time, i.e., the concentration of analyte in the effluent was 5% of that in the influent.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 877 - 3679 mg/cu m was 0.062. This value corresponds to a 112 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 3.8% lower than the "true" value at the OSHA standard level.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3).

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (20-ft x 1/8-in stainless steel) packed with 10% FFAP on 80/100 mesh Chromosorb W AW-DMCS.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide

7.2 n-Hexane, reagent grade

7.3 Nonane, or other suitable internal standard

7.4 Purified helium

7.5 Prepurified hydrogen

7.6 Filtered compressed air

8. Procedure

8.1 Cleaning of equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A maximum sample size of 4 liters is recommended. Sample at a rate of 0.2 liter per minute or less. The flow rate should be known with an accuracy of at least ±5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (60 psig) Helium carrier gas flow
2. 35 ml/min (25 psig) Hydrogen gas flow to detector
3. 400 ml/min (60 psig) Air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 52°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample injector vials, capped with Teflon-faced septa, may be used in place of the glass tubes.

Six tubes at each of three concentration levels (0.5X,1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 4 liter sample at the selected level. The tubes are allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

mg sample = mg found in front section of sample tube
mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{MW}} \times \frac{760}{\text{P}} \times \frac{(\text{T} + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Butadiene

Analyte:	Butadiene	Method No.:	S91
Matrix:	Air	Range:	1065-4590 mg/cu m
OSHA Standard:	1000 ppm (2200 mg/cu m)	Precision ($\overline{CV}_T$):	0.058
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	3/14/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 1065-4590 mg/cu m at an atmospheric temperature and pressure of 22°C and 768 mm Hg, using a 1-liter sample. Under the conditions of sample size (1 liter) the probable useful range of this method is 200-6600 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 7-mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 7.9 mg of analyte when a test atmosphere containing 4370 mg/cu m of analyte in air was sampled at 0.19 liters per minute for 9.5 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent. The breakthrough data were obtained under different operating conditions.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$)for the total analytical and sampling method in the range of 1065-4590 was 0.058. This value corresponds to a 130 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 1.8% lower than the "true" value at the OSHA standard level.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3).

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (20-ft x 1/8-in stainless steel) packed with 10% FFAP on 80/100 mesh Chromosorb W AW-DMCS.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide

7.2 Butadiene, reagent grade

7.3 Nonane or other suitable internal standard

7.4 Purified helium

7.5 Prepurified hydrogen

7.6 Filtered compressed air

8. Procedure

8.1 Cleaning of equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A maximum sample size of 1 liter is recommended. Sample at a rate of 0.05 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm$5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (60 psig) Helium carrier gas flow
2. 35 ml/min (25 psig) Hydrogen gas flow to detector
3. 400 ml/min (60 psig) Air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 52°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. An appropriate aliquot of a solution containing a known amount of butadiene in carbon disulfide is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample injector vials, capped with Teflon-faced septa, may be used in place of the glass tubes.

Six tubes at each of three concentration levels (0.5X,1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 1-liter sample at the selected level. The tubes are allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

Pentane may be used in place of butadiene gas for the GC calibration.

It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of pentane is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

mg sample = mg found in front section of sample tube
mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liters/cu m)}}{\text{Air Volume Sampled (liters)}}$$

10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Ketene

Analyte:	Ketene	Method No.:	S92
Matrix:	Air	Range:	0.40 - 1.74 mg/cu m
OSHA Standard:	0.9 mg/cu m	Precision ($\overline{CV}_T$):	0.064
Procedure:	Bubbler Collection, Complexation, Colorimetric	Validation Date:	3/14/75

1. Principle of the Method

1.1 Ketene is collected in alkaline hydroxylammonium chloride absorbing solution where it is hydrolyzed to acetohydroxamic acid.

1.2 The resulting product is subsequently reacted with ferric chloride to form the purple complex.

1.3 The absorbance of the resulting solution is determined at 540 nm and is used as a measure of the amount of ketene present.

1.4 Ethyl acetate, which is less toxic and more stable than ketene, also reacts with alkaline hydroxylammonium chloride and ferric chloride in a similar manner and is used in place of ketene for standards. One mole of ethyl acetate is equivalent to one mole of ketene.

2. Range and Sensitivity

2.1 This method has been validated over the range of 0.40 - 1.74 mg/cu m at an atmospheric temperature and pressure of 23°C and 757 mm Hg, using a 50-liter sample. The probable range of the method is 0.20 to 2.2 mg/cu m based on the range of standards used to prepare the standard curve. For samples of high concentration where absorbance is greater than the limits of the standard curve, the samples can be diluted with a mixture of equal amounts of the absorbing solution and the ferric chloride solution after the color development to extend the upper limit of the range.

2.2 A concentration of 0.20 mg/cu m of ketene can be determined in a 50-liter air sample based on a difference of 0.05 absorbance unit from the blank using a 5-cm cell.

3. Interferences

3.1 Any material containing an RCO group will interfere with this determination. Among such materials are esters, acid chlorides and acid anhydrides.

3.2 The substance most likely to coexist with ketene in air is acetic anhydride. Interferences due to acetic anhydride can be minimized by initially passing the air through an absorber containing toluene before the air is collected in the alkaline hydroxylammonium chloride absorbing solution. The method is described in References 11.1 and 11.2.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.40 - 1.74 mg/cu m was 0.064. This value corresponds to a standard deviation of 0.058 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.3.

4.2 A collection efficiency of 0.944 ± 0.041 was determined for the collection medium. The collection efficiency was used as a correction factor to determine the concentration of the air sampled to compensate for any bias in the sampling method. There was 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 of the Method

5.1 The method is simple and requires approximately 1.5 hours to complete.

5.2 The alkaline hydroxylammonium chloride solution can produce dermatitis if it comes in contact with the skin.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the bubbler collection method consists of the following components:

6.6.1 A glass standard midget bubbler with a fritted glass inlet. The fritted end should have porosity approximately equal to that of Corning EC (170 - 220 microns maximum pore diameter). The bubbler bottom holds the absorbing solution (Section 7.4).

6.1.2 A pump suitable for sampling for 1 liter per minute for at least 50 minutes. The sampling pump is protected from splashover or water condensation by a 2-inch glass tube loosely packed with a plug of glass wool and inserted between the exit arm of the bubbler and the pump.

6.1.3 An integrating 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 Scintillation vials, linear polyethylene 20-ml Fisher-brand with screw caps.

6.3 Scintillation vial support.

6.4 Spectrophotometer. This instrument should be capable of measuring the developed color at 540 nm.

6.5 Matched glass cells or curvettes, 5 cm path length.

6.6 Assorted laboratory glassware: pipets, volumetric flasks, graduated cylinders of appropriate capacities.

7. Reagents

All reagents must be ACS reagent grade or better.

7.1 Distilled water.

7.2 Hydroxylammonium chloride solution. Prepare a 10% (W/V) solution in water. Store the solution in a refrigerator and reject any solution when it is 2 weeks old.

7.3 Sodium hydroxide, 2.5M solution. Dissolve 100 grams of sodium hydroxide in water in a 1-liter volumetric flask. Cool the solution to room temperature and dilute to volume.

7.4 Absorbing solution. Mix equal volumes of the hydroxylammonium chloride solution and the sodium hydroxide solution. This mixture is stable for only about 2 hours and should be freshly prepared for use.

7.5 Ferric chloride solution. Prepare a 5% (W/V) solution of the hydrated salt ($FeCl_3.6H_2O$) in a mixture of equal volumes of water and concentrated hydrochloric acid.

7.6 Ethyl acetate standard solution. Dissolve 200 microliters of ethyl acetate in 1 liter of water.

1 ml of this solution = 0.180 mg ethyl acetate = 0.086 mg ketene

8. Procedure

8.1 Cleaning of Equipment. No specialized cleaning of glassware is required. However, since known interferences occur with esters and aldehydes, cleaning techniques should insure the absence of all organic materials.

8.2 Calibration of Personal Pump. Personal sampling pump should be calibrated using integrating volume meter (6.1.3) or other means.

8.3 Collection and Shipping of Samples

8.3.1 Pipet 10.0 ml of the alkaline hydroxylammonium chloride absorbing solution (Section 7.4) into each midget bubbler.

8.3.2 Connect the midget bubbler in series with the sampling pumps using a short piece of flexible tubing containing a glass wool plug to protect the pump. The air being sampled should not pass through any tubing or other equipment before entering the bubbler.

8.3.3 Turn on pump to begin sample collection. Care should be taken to measure the flow rate, time and/or volume as accurately as possible. Record atmospheric pressure and temperature. The sample should be taken at a flow rate of 1 liter per minute. Sample for 50 minutes making the final volume 50 liters.

8.3.4 After sampling, the bubbler stem can be removed and cleaned. Tap the stem gently against the inside wall of the bubbler bottle to recover as much of the sampling solution as possible. Wash the stem with 1.0 ml of unused absorbing solution and add the washing to the bubbler. Make up the solution volume in the bubbler to 10.0 ml using unused absorbing solution or distilled water. (Note: All subsequent dilutions and measurements are based on this sample volume of 10.0 ml)

8.3.5 Quantitatively transfer (avoiding any loss of sample solution) the total contents of the bubbler into a 20-ml polyethylene scintillation vial with screw cap. Close cap tightly and secure with plastic tape around edges to avoid sample loss during transit.

8.3.6 Care should be taken to minimize spillage or loss by evaporation at all times.

8.3.7 Whenever possible, hand delivery of the samples is recommended. Otherwise, special shipping cases should be used to ship the samples.

8.3.8 A "blank" bubbler should be handled as the other samples (fill, transfer, seal, and transport) except that no air is sampled through this bubbler.

8.4 Analysis of Samples

8.4.1 The sample in each vial is analyzed separately.

8.4.2 Pipet 2.5 ml of the 5% ferric chloride solution and 2.5 ml of distilled water into the bubbler. The purple complex is formed readily.

8.4.3 Mix thoroughly and let stand a few minutes to allow the gas bubbles formed to dissipate.

8.4.4 The aliquots of reagents added (2.5 ml of ferric chloride and distilled water respectively) are such that the final solution volume is 15.0 ml. If it is suspected that the level of the solution in the vial is less than 15.0 ml, the total volume of the resulting solution should be measured before absorbance readings are carried out and the appropriate volume correction factor must be used. Note that all calibration standards are based on a 15.0 ml solution volume.

8.4.5 Read the absorbance in a spectrophotometer at 540 nm against a blank prepared from the alkaline hydroxylammonium chloride and ferric chloride solution in the same fashion as the samples.

9. Calibration and Standards

9.1 Pipet into a series of tubes 0.1, 0.2, 0.3, 0.4, 0.5, 0.8, 1.0, 1.5, and 2.0 ml of the ethyl acetate standard solution containing the equivalent of 0.086 mg ketene per ml.

9.2 Pipet 10.0 ml of freshly prepared absorbing solution (Section 7.4) into each tube, followed by 2.5 ml of the 5% ferric chloride solution and sufficient distilled water to make up total volume to 15.0 ml.

9.3 Proceed as directed in Section 8.4.3 and Section 8.4.5.

9.4 Construct a calibration curve by plotting absorbance against the equivalent mg of ketene in the color developed solution.

10. Calculations

10.1 Determine from the calibration curve (Section 9.3) the mg concentration of ketene present in each sample.

10.2 Corrections for the "blank" sample, if any, must be made for each sample.

$$\text{Total mg} = \text{mg sample} - \text{mg blank}$$

where:

mg sample = mg found in sample bubbler

mg blank = mg found in blank bubbler

10.3 Divide the total weight by the collection efficiency in the single bubbler. (Note: the collection efficiency when sampling an atmosphere containing 1.74 mg/cu m at 1.0-lpm for 50 minutes was determined to be 94%.)

$$\text{Corrected mg} = \frac{\text{Total Weight}}{\text{Collection Efficiency}}$$

10.4 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

10.5 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \frac{\text{mg}}{\text{cu m}} \times \frac{24.45}{\text{MW}} \times \frac{760}{\text{P}} \times \frac{(\text{T} + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 Hanson, N.W., D.A. Reilly, H.E. Stagg, eds., The Determination of Toxic Substances in Air, Heffer & Sons Ltd., Cambridge, England, pp. 152-156, 1965.

11.2 Diggle, W.M., and J.C. Gage, Analyst 78, 473 (1953).

11.3 Documentation of NIOSH Validation Tests, NIOSH Contract No.CDC-99-74-45.

LPG (Liquefied Petroleum Gas)

Method No. S93

Substance

LPG (Liquefied Petroleum Gas)

Standard

8-hour time-weighted average: 1000 ppm (1800 mg/cu m)

Reference: 29 CFR 1910.93

Analytical Method

The LPG vapor present in the atmosphere is measured directly by drawing the air sample into a combustible gas meter properly calibrated with LPG. The meter reading is recorded and the equivalent concentration in ppm is read off the calibration curve. The method has been validated over the range of 478-2006 ppm at 23°C and 750 mm Hg atmospheric temperature and pressure.

Sampling Equipment

A dual range explosive gas meter of sufficient sensitivity, such as the Davis Vapotester Model M 6, must be used. No sample is actually collected since the atmosphere to be analyzed is usually drawn into the meter using a rubber aspirator bulb. The air can also be drawn into the meter with a personal sampling pump.

Sampling Procedure

The instructions given in the manual for the appropriate combustible gas meter used must be followed carefully for proper results. Typically, the procedure will require the following steps:

1. The combustion chamber must be swept free of combustible gases and be filled with fresh air.

2. Batteries must be turned on, and the proper voltage applied to the bridge.

3. The bridge must be balanced to zero deflection on the meter with fresh air in the open chamber.

4. The sample is drawn into the meter, and the meter reading is recorded. Repeat at least three times and report average.

5. The concentration of LPG in the air samples tested is determined from the calibration curve provided with the properly calibrated meter.

Special Consideration

1. Any hydrocarbon present in the atmosphere will interfere with the analysis. Where other hydrocarbons are known or suspected to be present in the air, such information, including their suspected identities, should be noted.

2. Water vapor will impair the proper functioning of the sensing filaments. When testing atmospheres of high humidity, use available cotton filters or special humidity conditioning sample probes to remove excessive dust and moisture from the sample under test.

Reference

Instruction Manual, Davis Vapotester Model M-6, Davis Instruments, 45 Halleck Street, Newark, New Jersey.

Methylcyclohexane

Analyte:	Methylcyclohexane	Method No.:	S94
Matrix:	Air	Range:	940 - 3941 mg/cu m
OSHA Standard:	500 ppm (2000 mg/cu m)	Precision ($\overline{CV}_T$):	0.052
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	3/14/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 940 - 3941 mg/cu m at an atmospheric temperature and pressure of 18.5°C and 760 mm Hg, using a 4-liter sample. Under the conditions of sample size (4 liters) the probable useful range of this method is 200 - 6000 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 24 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 24 mg of analyte when a test atmosphere containing 3941 mg/cu m of analyte in air was sampled at 0.19 liters per minute for 32 minutes; breakthrough was observed at this time, i.e., the concentration of analyte in the effluent was 5% of that in the influent.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 940 -3941 mg/cu m was 0.052. This value corresponds to a 104 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the values obtained using the overall sampling and analytical method were 5.5% higher than the "true" value at the OSHA standard level.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3).

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (20-ft x 1/8-in stainless steel) packed with 10% FFAP on 80/100 mesh Chromosorb W AW-DMCS.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide

7.2 Methylcyclohexane, reagent grade

7.3 Nonane, or other suitable internal standard

7.4 Purified helium

7.5 Prepurified hydrogen

7.6 Filtered compressed air

8. Procedure

8.1 Cleaning of equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A maximum sample size of 4 liters is recommended. Sample at a rate of 0.2 liter per minute or less. The flow rate should be known with an accuracy of at least ±5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (60 psig) Helium carrier gas flow
2. 35 ml/min (25 psig) Hydrogen gas flow to detector
3. 400 ml/min (60 psig) Air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 55°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample injector vials, capped with Teflon-faced septa, may be used in place of the glass tubes.

Six tubes at each of three concentration levels (0.5X,1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 4 liter sample at the selected level. The tubes are allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$\text{D.E.} = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

mg sample = mg found in front section of sample tube
mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liters/cu m)}}{\text{Air Volume Sampled (liters)}}$$

10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Propylene Dichloride

Analyte:	Propylene Dichloride	Method No.: S95
Matrix:	Air	Range: 135-665 mg/cu m
OSHA Standard:	75 ppm (350 mg/cu m)	Precision ($\overline{CV}_T$): 0.056
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 3/14/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 135-665 mg/cu m at an atmospheric temperature and pressure of 25°C and 737 mm Hg, using a 10-liter sample. Under the conditions of sample size (10 liters) the probable range of this method is 35-1050 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 6-mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of the analyte and other substances in the air. The first section of the charcoal tube was found to hold 10.5 mg of the analyte when a test atmosphere of 586 mg/cu m of the analyte in dry air was sampled at 0.2 liter per minute for 1 hour, 30 minutes; breakthrough occurred at this time, i.e., the concentration of the analyte in the effluent was 5% of

that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2.) If a particular atmosphere is suspected of containing a large number of contaminants, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments with toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 135 to 665 mg/cu m was 0.056. This value corresponds to a standard deviation of 19.6 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 The average values obtained using the overall sampling and analytical method were the same as "true" value at the OSHA standard level.

4.3 The above data are based on validation experiments using the internal standard method. (Reference 11.2)

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more compounds suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined accurately (±5%) at the recommended flow rate, (Reference 11.3).

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than 1 inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in. stainless steel) packed with 10% FFAP on 80/100 Chromosorb W-AW.

6.5 An electronic integrator or some other suitable method for determining peak size areas.

6.6 Two-milliliter glass sample containers with glass stoppers or Teflon®-lined caps. If an automatic sample injector is used, the sample injector vials can be used.

6.7 Microliter syringes: 10-µl, and other convenient sizes for making standards.

6.8 Pipets: 1.0-ml delivery type.

6.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Eluent: Carbon disulfide (chromatographic grade).

7.2 Propylene dichloride (chromatographic grade).

7.3 Internal Standard: n-Undecane (99+%) or other suitable standard.

7.4 n-Heptane (reagent grade).

7.5 Purified nitrogen.

7.6 Prepurified hydrogen.

7.7 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a backup and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a flow of 0.20 liter per minute or less. The flow rate should be known with an accuracy of at least ±5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available the elevation should be recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the suspected compound should be submitted to the laboratory in glass containers with Teflon®-lined caps. These liquid bulk samples should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container or automatic sample injector vial. The separating section of foam is removed and discarded; the second section is transferred to another sample container or vial. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of the eluent is pipetted into each sample container. For the internal standard method a 0.2 percent solution of internal standard in carbon disulfide is used. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. The sample vials should be capped as soon as the solvent is added to minimize volatilization.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (80 psig) nitrogen carrier gas flow.
2. 30 ml/min (50 psig) hydrogen gas flow to detector.
3. 300 ml/min (50 psig) air flow to detector.
4. 170°C injector temperature.
5. 210°C manifold temperature (detector).
6. 80°C column temperature.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-µl syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 µl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-µl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 µl to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 µl in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique. In this case 2-µl injections are satisfactory.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below (see Section 9).

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided that the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.0-ml sample container. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. A

875 mg/ml stock solution of the analyte in n-heptane is prepared. A known amount of this solution is injected directly into the activated charcoal with a 10-µl syringe, and the container is capped. The amount injected is equivalent to that present in a 10-liter sample at the selected level. It is not practical to inject the neat liquid directly because the amounts to be added would be too small to measure accurately.

At least six tubes at each of three levels (0.5X, 1X, and 2X the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These six tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

The weight of analyte found in each tube is determined from the standard curve (Section 9). Desorption efficiency is determined by the following equation:

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus the weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/ml of carbon disulfide. To minimize error due to the volatility of the carbon disulfide, one can add 10 times the weight to 10 ml of the carbon disulfide. (For the internal standard method use carbon disulfide containing 0.2 percent of the internal standard.) A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentrations in mg/ml versus peak area. In the case of the internal standard method plot the concentration versus the ratio of peak area of analyte to peak area of internal standard.

Note: Whether the absolute area or internal standard method is used standard solutions should be analyzed at the same time that the sample analysis is done. This will minimize the effect variations of FID response.

10. Calculations

10.1 Read the weights, in mg, corresponding to each peak area (area ratio in case of the internal standard method) from the standard curve. No volume corrections are needed, because the standard curve is based on mg/ml eluent and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

mg = mg sample - mg blank

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (Section 8.5.2) for the amount of analyte found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

10.5 The concentration of analyte in the air sampled can be expressed in mg per cu m, which is numerically equal to µg per liter of air

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm:

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (K)

11. References

11.1 White L. D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 "Documentation of NIOSH Validation Tests", Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract No. HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes, September 15, 1972".

Pentachloronaphthalene

Analyte:	Pentachloronaphthalene	Method No.: S96
Matrix:	Air	Range: 0.293-1.541 mg/cu m
OSHA Standard:	0.5 mg/cu m - skin	Precision ($\overline{CV}_T$): 0.067
Procedure:	Filter and bubbler collection, iso-octane extraction, GC	Validation Date: 3/14/75

1. Principle of the Method

1.1 A known volume of air is drawn through a glass fiber filter connected in series to a midget bubbler containing 15 ml of iso-octane to collect the analyte.

1.2 The filter and the contents in the midget bubbler are transferred to a 20-ml scintillation vial.

1.3 An aliquot from the scintillation vial is analyzed by gas chromatography.

1.4 The total area of the peaks from the sample is determined and compared with areas obtained from standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 0.293-1.541 mg/cu m at an atmospheric temperature and pressure of 23°C and 761 mm Hg, using a 250-liter sample. The probable useful range of this method is 0.05-1.5 mg/cu m.

2.2 The upper limit of the range of the method is dependent on the collection efficiency of the glass fiber filter connected in series to the midget bubbler and the collection efficiency of the bubbler. If higher concentrations than those tested are to be sampled, smaller sample volumes should be used.

3. Interferences

3.1 When interfering compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.293-1.541 mg/cu m was 0.067. This value corresponds to a standard deviation of 0.034 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.1.

4.2 A collection efficiency of 1.00 was determined for the collection medium, thus, no bias was introduced in the sample collection step and no correction for collection efficiency is necessary. There was also no bias in the sampling and analytical method for which no analytical method recovery correction was necessary. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

5.1 Collected samples are analyzed by means of a quick, instrumental method.

5.2 A disadvantage of the method is the evaporation of iso-octane in the midget bubbler. The bubbler must be refilled periodically whenever the liquid level is lowered by an appreciable amount.

5.3 Another disadvantage of the method is the awkwardness in using midget bubblers for collecting personal samples. If the worker's job performance requires much body movement, loss of the collection solution during sampling may occur.

5.4 Pentachloronaphthalene is a mixture of isomers. Under the gas chromatographic conditions used for validation, an "envelope" of peaks was analyzed. The quantitation of area is difficult unless an integrator is used.

5.5 The precision of the method is limited by the reproducibility of the pressure drop across the filter and bubbler. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one filter/bubbler combination only.

5.6 Scintillation vials are more difficult to ship than adsorption tubes or filters due to possible breakage and leakage of the vials during shipping.

6. Apparatus

6.1 The sampling unit for the collection of personal air samples for the determination of pentachloronaphthalene has the following components:

6.1.1 The filter unit consisting of the filter media (Section 6.2) and a polystyrene 37-mm two-piece cassette filter holder connected in series with a midget bubbler (Section 6.3). Do not use Tenite filter holders.

6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of ±5%. The sampling pump is protected from splashover or solvent condensation by a 5-cm long by 6-mm I.D. glass tube loosely packed with a plug of glass wool and inserted between the exit arm of the bubbler and the pump.

6.1.3 Thermometer.

6.1.4 Manometer.

6.2 Glass fiber filter, Type A with a 37-mm diameter. The filter is held in the two-piece cassette filter holder. A backup pad should not be used.

6.3 A glass midget bubbler containing 15 ml of the collection medium (Section 7.2).

6.4 Scintillation vials, 20 ml. Teflon cap liners (22-mm)should be used for proper seal. Add 15 ml of distilled water into each vial and mark the liquid level. Pour out the water and dry each vial.

6.5 Gas chromatograph equipped with an electrolytic conductivity detector (Tracor or equivalent). The system includes an in-line vent between the exhaust end of the GC column and the reduction furnace, a quartz furnace operated in the reductive mode, an electrolytic conductivity cell, and a conductivity bridge.

6.6 Column (5-ft long X 1/8-in O.D. glass) packed with 5% SE-30 on 80/100 mesh, acid washed DMCS Chromosorb W.

6.7 An electronic integrator or some other suitable method for measuring peak areas.

6.8 Microliter syringes: 10-microliter and other convenient sizes for making standard solutions, and 25-microliter for making GC injections.

6.9 Volumetric flasks: 15-ml, and other convenient sizes for making standard solutions.

6.10 Pipets of convenient sizes.

6.11 Tweezers.

7. Reagents

7.1 Pentachloronaphthalene, reagent grade.

7.2 Iso-octane, nanograde.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis as well as the scintillation vials should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Sampling Pump. Each personal sampling pump must be calibrated with a representative filter cassette and bubbler in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples.

8.3.1 Assemble the filter in the two-piece filter cassette holder and close firmly.

8.3.2 Pipet 15 ml of the collection medium (Section 7.2) into each midget bubbler and mark the liquid level. The liquid level in the bubbler must be checked frequently. If the liquid level is lowered by an appreciable amount (to less than 10 ml) from evaporation, the bubbler must be refilled with additional iso-octane. The final refilling of iso-octane into the bubbler should be done at approximately 15 minutes before the end of sampling. The final volume of the bubbler at the end of sampling should be 12 ml or less.

8.3.3 Remove the cassette plugs and attach the outlet of the filter cassette to the inlet arm of the midget bubbler using a short piece of flexible tubing. Connect the outlet arm of the midget bubbler with a 5-cm glass splashover tube (6-mm I.D.) containing the glass wool plug, then to the personal sampling pump, using short pieces of flexible tubing. The bubbler must be maintained in a vertical position during sampling.

8.3.4 Air being sampled should not pass through any hose or tubing before entering the filter cassette.

8.3.5 A sample size of 250 liters is recommended. Sample at a flow rate of 1.3 liters per minute. The flow rate should be known with an accuracy of ±5%.

8.3.6 Turn the pump on and begin sample collection. Since it is possible for a filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently, and the sampling should be terminated at any evidence of a problem.

8.3.7 Terminate sampling at the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation.

8.3.8 After sampling remove the bubbler stem and tap the stem gently against the inside wall of the bubbler bottle to recover as much of the sampling solution as possible. Rinse the bubbler stem with 1 ml of iso-octane into the midget bubbler.

8.3.9 Transfer the contents of the midget bubbler to the scintillation vial which has been marked at 15 ml. Rinse the bubbler with 2 ml of iso-octane, adding the rinse to the vial. Bring the volume in the vial to the 15-ml mark with iso-octane.

8.3.10 The glass fiber filter should be removed from the cassette filter holder and placed in the scintillation vial. Care must be taken to handle the filter only with clean tweezers. Cap the scintillation vials with appropriate caps with Teflon liners.

8.3.11 Carefully record the sample identity and all relevant sampling data.

8.3.12 With each batch of ten samples, submit one filter and bubbler from the same lot of filters and bubblers which was used for sample collection and which are subjected to exactly the same handling as the samples except that no air is drawn through it. Label this as a blank.

8.3.13 The scintillation vials in which the samples are stored should be shipped in a suitable container, designed to prevent damage in transit.

8.4 Analysis of Samples

8.4.1 Each sample is analyzed separately. Prior to injection of the sample into the GC, swirl the contents in the vial for five minutes.

8.4.2 Appropriate blanks must be analyzed at the same time as the samples.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 150 ml/min nitrogen carrier gas flow
2. 150 ml/min hydrogen gas flow to furnace
3. 760°C furnace temperature
4. 225°C transfer temperature
5. 250°C vent temperature
6. 185°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of an aliquot of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 25-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 1.0 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 15-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.0 microliter to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 14.9-15.0 microliters in the barrel of the syringe. The gas chromatograph is equipped with a valve to vent the solvent peak after it passes through the GC column, but before it enters a reduction furnace. Since a 15-microliter aliquot is likely to cause malfunction of the conductivity cell, the valve should be opened when injection is made and should be closed after the solvent (iso-octane) has been vented and before the analyte is eluted. Under the conditions above (Section 8.4.3), it was found that 20 seconds was adequate to elute the solvent. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of area. The areas of the sample peaks are measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed in Section 9. The peaks are not resolved, and therefore the total area of the envelope of peaks is measured as a single area.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/15 ml iso-octane, because samples are extracted in this amount of iso-octane. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/15 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of day-to-day variations and variations during the same day of the electrolytic conductivity detector response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each envelope of peak area from the standard curve. No volume correction is needed, because the standard curve is based on mg/15 ml of iso-octane, and the volume of sample injected is identical to the volume of the standards injected.

10.2 A correction for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

mg sample = mg found in sample filter and bubbler
mg blank = mg found in blank filter and bubbler

10.3 The concentration of the analyte in the air sample can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.2) X 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

11. Reference

11.1 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Octachloronaphthalene

Analyte:	Octachloronaphthalene	Method No.:	S97
Matrix:	Air	Range:	0.055 - 0.215 mg/cu m
OSHA Standard:	0.1 mg/cu m	Precision:	$(\overline{CV}_T)$: 0.067
Procedure:	Filter collection extraction with hexane, GC	Validation Date:	3/14/75

1. Principle of the Method

1.1 A known volume of air is drawn through a cellulose membrane filter to trap the organic aerosol present.

1.2 The filter in the cassette is transferred into a jar and extracted with hexane.

1.3 An aliquot of the eluted sample is injected into a gas chromatograph with an electron capture detector.

1.4 The total area of the resulting sample peaks is determined and compared with corresponding areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 0.055 - 0.215 mg/cu m at an atmospheric temperature and pressure of 26°C and 756 mm Hg, using a 30-liter sample. Under the conditions of sample size (30 liters), the probable useful range of this method is 0.02 - 0.30 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for the 9-microgram sample, provided the electron capture detector response is linear throughout that range.

2.2 The upper limit of the range of the method is dependent on the filtration capacity of the cellulose membrane filter. If higher concentrations than those tested are to be sampled, smaller sample volumes should be used. The filtration efficiency for octachloronaphthalene aerosol is greater than 95% when sampled for 30 minutes at 1 liter per minute from a test atmosphere containing 0.23 mg/cu m.

3. Interference

3.1 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV_T}$) for the total analytical and sampling method in the range of 0.055 - 0.25 mg/cu m is 0.067. This value corresponds to a standard deviation of 0.0067 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in reference 11.1.

4.2 A collection efficiency of 1.00 $\pm$ 0.01 was determined for the collecting medium; thus no bias was introduced in the sample collection step. Likewise, there was no bias in the analytical method - the average recovery for the filters was 99.4%. Thus, $\overline{CV_T}$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

These data are based on the validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

The sampling device is small, portable and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The filters are analyzed by means of a quick, instrumental method.

6. Apparatus

6.1 Sampling equipment - The sampling unit for the collection of personal air samples for the determination of organic aerosol has the following components:

6.1.1 The filter unit consisting of the filter media (Section 6.2) and appropriate 37 mm 3-piece cassette filter holder.

6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of $\pm$ 5% (Reference 11.2) at the recommended flow rate. The pump must be calibrated with a representative filter holder and filter in the line.

6.2 Mixed cellulose ester membrane filter, 0.8 micrometer pore size and 37 mm diameter. The filter is held in the three piece cassette supported by a cellulose backup pad.

6.3 Gas chromatograph equipped with an electron capture detector.

6.4 Column (6-ft x 1/8-in stainless steel) packed with 5% OV-101 on 100/120 mesh Supelcoport.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 Jars for sample extraction: 2 oz. ointment jars, squat form with aluminum lined screw caps.

6.7 Microliter syringes: 10-microliter and other convenient sizes for making standard solutions.

6.8 Volumetric flasks: 10-milliliter and other convenient sizes for making standard solutions.

6.9 Pipets: 10-milliliter and other convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality hexane

7.2 Octachloronaphthalene, technical grade

7.3 9, 10-dichloroanthracene or other suitable internal standard

7.4 Purified nitrogen

8. Procedure

8.1 Cleaning of equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of personal pumps, Each personal pump must be calibrated with a representative filter cassette in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and shipping of samples

8.3.1 Assemble the filter in the three piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad.

8.3.2 Remove the cassette plugs and attach to the personal sampling pump tubing. Clip the cassette to the worker's lapel.

8.3.3 Air being sampled should not be passed through any hose or tubing before entering the filter cassette.

8.3.4 A sample size of 30 liters is recommended. Sample at a flow rate of 1.0 liter per minute. The flow rate should be known with an accuracy of at least $\pm$ 5%.

8.3.5 Turn the pump on and begin 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.

8.3.6 Terminate sampling after the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation.

8.3.7 Collected sample cassette should be firmly sealed with the plugs in both the inlet and outlet.

8.3.8 Carefully record sample identity and all relevant sample data.

8.3.9 Blank: With each batch of samples submit one filter which is subjected to exactly the same handling as for the samples except that no air is drawn through it. Label this as a blank.

8.3.10 The cassettes in which the samples are collected should be shipped in a suitable container, designed to prevent damage in transit.

8.4 Analysis of Samples

8.4.1 Preparation and Extraction of Samples

1. Open the cassette filter holder and carefully remove the cellulose membrane filter from the holder and cellulose backup pad with the aid of Millipore filter tweezers.

2. Transfer filter to the jar and pipet into the jar 10.0 ml of hexane. Seal the jar immediately to minimize evaporation. If the internal standard method is used, use 10.0 ml of the internal standard solution.

3. Place the sample-containing jars in the ultrasonic vibrator for 30 minutes.

8.4.2 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 26 ml/min (40 psig) nitrogen carrier gas flow
2. 290°C injector temperature
3. 290°C manifold temperature (detector)
4. 240°C column temperature

8.4.3 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10 microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 2-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 1.9 - 2.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

8.4.4 Measurement of area. The total area of the sample peaks is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed in Section 9.

8.5 Determination of Sample Recovery

8.5.1 Need for determination. To eliminate any bias in the analytical method, it is necessary to determine the recovery of the compound. The sample recovery should be determined in duplicate and should cover the concentration ranges of interest. If the recovery is less than 95%, the appropriate correction factor should be used to calculate the "true" value.

8.5.2 Procedure for determining recovery. A known amount of the analyte, preferably equivalent to the sample concentration expected, is added to a representative cellulose membrane filter and air-dried. The analyte is then extracted from the filter and analyzed as described in Section 8.4. Duplicate determinations should agree within ±5%.

For this validation study, an amount of the analyte equivalent to that present in a 30-liter sample at the selected level has been used for the extraction studies. Six filters at each of the three levels (0.5X, 1X, and 2X the OSHA standard) have been dosed accordingly and a solution of the internal standard was used for extraction. A parallel blank filter was also treated in the same manner except that no sample was added to it. All filters were then extracted and analyzed as described in Section 8.4. The recovery values obtained were at least 99% and as such no correction factor has been used in the determination of the "true" values.

The sample recovery equals the average weight in mg recovered from the filter divided by the weight in mg added to the filter, or

$$\text{Recovery} = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

9. Calibration and Standards

It is convenient to express concentration of standards in terms of micrograms per 10.0 ml hexane, because samples are desorbed in this amount of hexane. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in micrograms per 10.0 ml versus peak area.

For the internal standard method, use hexane containing a predetermined amount of the internal standard. The internal standard concentration chosen must meet the requirements for sufficient sensitivity and linearity of the electron capture detector. The analyte concentration in micrograms per 10.0 ml is plotted versus the area ratio of the analyte peaks to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in ECD response. Moreover, since the ECD response is very sensitive to changes in detector standing current, frequent standardization should be practiced, particularly when the external standard method is used.

10. Calculations

10.1 Read the weight, in µg, corresponding to the total peak area from the standard curve. No volume corrections are needed, because the standard curve is based on µg per 10.0 ml hexane and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\mu g = \mu g \text{ sample} - \mu g \text{ blank}$$

where:

µg sample = µg found in 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 The concentration of the analyte in the air sampled can be expressed in mg per cu m (µg per liter = mg per cu m).

$$\text{mg/cu m} = \frac{\text{Corrected } \mu g \text{ (Section 10.3)}}{\text{Air Volume Sampled (liter)}}$$

10.5 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \quad \frac{760}{P} \quad \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.2 Final Report, NIOSH Contract HSM-99-71-31. "Personal Sampler Pump for Charcoal Tubes", September 15, 1972.

Methyl Iodide

Analyte:	Methyl Iodide	Method No.:	S98
Matrix:	Air	Range:	17-52 mg/cu m
OSHA Standard:	5 ppm (28 mg/cu m)	Precision ($\overline{CV}_T$):	0.070
Procedure:	Adsorption on charcoal, desorption with toluene, GC	Validation Date:	4/11/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with toluene.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 17-52 mg/cu m at an atmospheric temperature and pressure of 25°C and 735 mm Hg, using a 50-liter sample. Under the conditions of sample size (50 liters) the probable range of this method is 3-84 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 2-mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of the analyte and other substances in the air. The first section of the charcoal tube was found to hold 12.5 mg of the analyte when a test atmosphere of 52 mg/cu m of the analyte in dry air was sampled at 1 liter per minute for 4 hours. Breakthrough did not occur at this time, i.e., the concentration of the analyte in the effluent was less than 5% of that

in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2.) If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great the condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments with toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 17-52 mg/cu m was 0.070. This value corresponds to a standard deviation of 2.0 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 The average values obtained using the overall sampling and analytical method were 8.6% less than the "true" value at the OSHA standard level.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more compounds suspected to be present in the same sample

by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined accurately (±5%) at the recommended flow rate.

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than 1 inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in. stainless steel) packed with Chromosorb 101.

6.5 An electronic integrator or some other suitable method of determining peak size areas.

6.6 Two-milliliter glass sample containers with glass stoppers or Teflon®-lined caps. If an automatic sample injector is used, the sample injector vials can be used.

6.7 Microliter syringes: 10-µl, and other convenient sizes for making standards.

6.8 Pipets: 1.0-ml delivery type.

6.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Eluent: Toluene (chromatographic grade).

7.2 Methyl Iodide (99%).

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples.

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a backup and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A maximum sample size of 50 liters is recommended. Sample at a flow of 1 liter per minute or less. The flow rate should be known with an accuracy of at least ±5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available the elevation should be recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

Reproduced from best available copy.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the suspected compound should be submitted to the laboratory in glass containers with Teflon®-lined caps. These liquid bulk samples should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container or automatic sample injector vial. The separating section of foam is removed and discarded; the second section is transferred to another sample container or vial. These 2 sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of toluene is pipetted into each sample container. Desorption should be done overnight or for an equivalent period of time. The sample vials should be capped as soon as the solvent is added to minimize volatilization.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (80 psig) nitrogen carrier gas flow.
2. 30 ml/min (50 psig) hydrogen gas flow to detector.
3. 300 ml/min (50 psig) air flow to detector.
4. 200°C injector temperature.
5. 300°C manifold temperature (detector).
6. 190°C column temperature.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-µl syringe is first flushed with solvent several times to

wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 µl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-µl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 µl to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 µl in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique. In this case 2-µl injections are satisfactory.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below (see Section 9).

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided that the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.0-ml sample container. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. A 350 mg/ml stock solution of the analyte in toluene is prepared. A known amount of this solution is injected directly into the activated charcoal with a 10-µl syringe, and the container is capped. The amount injected is equivalent to that present in a 50-liter sample at the selected level. It is not practical to inject the neat liquid directly because the amounts to be added would be too small to measure accurately.

At least 6 tubes at each of 3 levels (0.5X, 1X, and 2X the standard) are prepared in this manner and allowed to stand overnight to assure complete adsorption of the analyte onto the charcoal. These 6 tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

The weight of analyte found in each tube is determined from the standard curve (Section 9). Desorption efficiency is determined by the following equation:

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus the weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/ml of eluent. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentrations in mg/ml versus peak area.

Note: Standard solutions should be analyzed at the same time that the sample analysis is done. This will minimize the effect variations of FID response.

10. Calculations

10.1 Read the weights, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/ml eluent and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

mg = mg sample - mg blank

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (Section 8.5.2) for the amount of analyte found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

10.5 The concentration of analyte in the air sampled can be expressed in mg per cu m, which is numerically equal to µg per liter of air

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm:

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L. D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 "Documentation of NIOSH Validation Tests", Contract No. CDC-99-74-45.

Hexachloronaphthalene

Analyte:	Hexachloronaphthalene	Method No.:	S100
Matrix:	Air	Range:	0.104-0.459 mg/cu m
OSHA Standard:	0.2 mg/cu m	Precision ($\overline{CV}_T$):	0.063
Procedure:	Filter collection, extraction with hexane, GC	Validation Date:	4/11/75

1. Principle of the Method

1.1 A known volume of air is drawn through a cellulose membrane filter to trap the organic aerosol present.

1.2 The filter in the cassette is transferred into a jar and extracted with hexane.

1.3 An aliquot of the eluted sample is injected into a gas chromatograph with an electron capture detector.

1.4 The total area of the resulting sample peaks is determined and compared with corresponding areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 0.104 - 0.459 mg/cu m at an atmospheric temperature and pressure of 26°C and 759 mm Hg, using a 30-liter sample. Under the conditions of sample size (30 liters), the probable useful range of this method is 0.04-0.60 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for the 18-microgram sample, provided the electron capture detector response is linear throughout that range.

2.2 The upper limit of the range of the method is dependent on the filtration capacity of the cellulose membrane filter. If higher concentrations than those tested are to be sampled, smaller sample volumes should be used. The filtration efficiency for hexachloronaphthalene aerosol is greater than 95% when sampled for 30 minutes at 1 liter per minute from a test atmosphere containing 0.33 mg/cu m.

3. Interference

3.1 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.104 - 0.459 mg/cu m is 0.063. This value corresponds to a standard deviation of 0.013 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.1.

4.2 A collection efficiency of 1.00 $\pm$ 0.01 was determined for the collecting medium; thus no bias was introduced in the sample collection step. Likewise, there was no bias in the analytical method - the average recovery for the filters was 98.8%. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

These data are based on the validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

The sampling device is small, portable and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The filters are analyzed by means of a quick, instrumental method.

6. Apparatus

6.1 Sampling equipment - The sampling unit for the collection of personal air samples for the determination of organic aerosol has the following components:

6.1.1 The filter unit consisting of the filter media (Section 6.2) and appropriate 37 mm 3-piece cassette filter holder.

6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of $\pm$ 5% (Reference 11.2) at the recommended flow rate. The pump must be calibrated with a representative filter holder and filter in the line.

6.2 Mixed cellulose ester membrane filter, 0.8 micrometer pore size and 37 mm diameter. The filter is held in the three piece cassette supported by a cellulose backup pad.

6.3 Gas chromatograph equipped with an electron capture detector.

6.4 Column (6-ft x 1/8-in stainless steel) packed with 5% OV-101 on 100/120 mesh Supelcoport.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 Jars for sample extraction: 2 oz. ointment jars, squat form with aluminum lined screw caps.

6.7 Microliter syringes: 10-microliter and other convenient sizes for making standard solutions.

6.8 Volumetric flasks: 10-milliliter and other convenient sizes for making standard solutions.

6.9 Pipets: 10-milliliter and other convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality hexane

7.2 Hexachloronaphthalene, technical grade

7.3 1,4, Bis-Hexachloroxylene, or other suitable internal standard

7.4 Purified nitrogen

8. Procedure

8.1 Cleaning of equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of personal pumps. Each personal pump must be calibrated with a representative filter cassette in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and shipping of samples

8.3.1 Assemble the filter in the three piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad.

8.3.2 Remove the cassette plugs and attach to the personal sampling pump tubing. Clip the cassette to the worker's lapel.

8.3.3 Air being sampled should not be passed through any hose or tubing before entering the filter cassette.

8.3.4 A sample size of 30 liters is recommended. Sample at a flow rate of 1.0 liter per minute. The flow rate should be known with an accuracy of at least $\pm$ 5%.

8.3.5 Turn the pump on and begin 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.

8.3.6 Terminate sampling after the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation.

8.3.7 Collected sample cassette should be firmly sealed with the plugs in both the inlet and outlet.

8.3.8 Carefully record sample identity and all relevant sample data.

8.3.9 Blank: With each batch of samples submit one filter which is subjected to exactly the same handling as for the samples except that no air is drawn through it. Label this as a blank.

8.3.10 The cassettes in which the samples are collected should be shipped in a suitable container, designed to prevent damage in transit.

8.4 Analysis of Samples

8.4.1 Preparation and Extraction of Samples

1. Open the cassette filter holder and carefully remove the cellulose membrane filter from the holder and cellulose backup pad with the aid of Millipore filter tweezers.

2. Transfer filter to the jar and pipet into the jar 10.0 ml of hexane. Seal the jar immediately to minimize evaporation. If the internal standard method is used, use 10.0 ml of the internal standard solution.

3. Place the sample containing jars in the ultrasonic vibrator for 30 minutes.

8.4.2 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 26 ml/min (40 psig) nitrogen carrier gas flow
2. 290°C injector temperature
3. 290°C manifold temperature (detector)
4. 240°C column temperature

8.4.3 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10 microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 2-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 1.9 - 2.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

8.4.4 Measurement of area. The total area of the sample peaks is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed in Section 9.

8.5 Determination of Sample Recovery

8.5.1 Need for determination. To eliminate any bias in the analytical method, it is necessary to determine the recovery of the compound. The sample recovery should be determined in duplicate and should cover the concentration ranges of interest. If the recovery is less than 95%, the appropriate correction factor should be used to calculate the "true" value.

8.5.2 Procedure for determining recovery. A known amount of the analyte, preferably equivalent to the sample concentration expected, is added to a representative cellulose membrane filter and air-dried. The analyte is then extracted from the filter and analyzed as described in Section 8.4. Duplicate determinations should agree within ±5%.

For this validation study, an amount of the analyte equivalent to that present in a 30-liter sample at the selected level has been used for the extraction studies. Six filters at each of the three levels (0.5X, 1X, and 2X the OSHA standard) have been dosed accordingly and a solution of the internal standard was used for extraction. A parallel blank filter was also treated in the same manner except that no sample was added to it. All filters were then extracted and analyzed as described in Section 8.4. The recovery values obtained were at least 99% and as such no correction factor has been used in the determination of the "true" values.

The sample recovery equals the average weight in mg recovered from the filter divided by the weight in mg added to the filter, or

$$\text{Recovery} = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

9. Calibration and Standards

It is convenient to express concentration of standards in terms of micrograms per 10.0 ml hexane, because samples are desorbed in this amount of hexane. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in micrograms per 10.0 ml versus peak area.

For the internal standard method, use hexane containing a predetermined amount of the internal standard. The internal standard concentration chosen must meet the requirements for sufficient sensitivity and linearity of the electron capture detector. The analyte concentration in micrograms per 10.0 ml is plotted versus the area ratio of the analyte peaks to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in ECD response. Moreover, since the ECD response is very sensitive to changes in detector standing current, frequent standardization should be practiced, particularly when the external standard method is used.

10. Calculations

10.1 Read the weight, in µg, corresponding to the total peak area from the standard curve. No volume corrections are needed, because the standard curve is based on µg per 10.0 ml hexane and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\mu g = \mu g \text{ sample} - \mu g \text{ blank}$$

where:

µg sample = µg found in 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 The concentration of the analyte in the air sampled can be expressed in mg per cu m (µg per liter = mg per cu m).

$$\text{mg/cu m} = \frac{\text{Corrected } \mu g \text{ (Section 10.3)}}{\text{Air Volume Sampled (liter)}}$$

10.5 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.2 Final Report, NIOSH Contract HSM-99-71-31. "Personal Sampler Pump for Charcoal Tubes", September 15, 1972.

Hexachloroethane

Analyte:	Hexachloroethane	Method No.: S101
Matrix:	Air	Range: 5-25 mg/cu m
OSHA Standard:	1 ppm (10 mg/cu m)	Precision ($\overline{CV}_T$): 0.121
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 4/11/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 5-25 mg/cu m at an atmospheric temperature and pressure of 25°C and 744 mm Hg, using a 10-liter sample. Under the conditions of sample size (10 liters) the probable range of this method is 1-30 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 0.05-mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of the analyte and other substances in the air. The first section of the charcoal tube was found to hold at least 1.1 mg of the analyte when a test atmosphere of 23.4 mg/cu m of the analyte in dry air was sampled at 0.2 liter per minute for 4 hours. Breakthrough did not occur at this time; the concentration of the analyte in the effluent was less than 2% of that

in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2.) If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great the condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments with toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 5 to 25 mg/cu m was 0.121. This value corresponds to a standard deviation of 1.21 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 The average values obtained using the overall sampling and analytical method were 2.8% less than the "true" value at the OSHA standard level.

4.3 The above data are based on validation experiments using the internal standard method. (Reference 11.2.)

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more compounds suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined accurately (±5%) at the recommended flow rate (Reference 11.3).

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than 1 inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in. glass) packed with 3% OV-17 on 100/120 Gas Chrom Q.

6.5 An electronic integrator or some other suitable method of determining peak size areas.

6.6 Two-milliliter glass sample containers with glass stoppers or Teflon®-lined caps. If an automatic sample injector is used, the sample injector vials can be used.

6.7 Microliter syringes: 10-µl, and other convenient sizes for making standards.

6.8 Pipets: 1.0-ml delivery type.

6.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

6.10 Balance: Suitable size for weighing analyte for stock standard solutions.

7. Reagents

7.1 Eluent: Carbon dislufide (chromatographic grade).

7.2 Hexachloroethane (reagent grade).

7.3 Internal Standard: n-Tridecane (99+%) or other suitable standard.

7.4 Carbon tetrachloride (reagent grade).

7.5 Purified nitrogen.

7.6 Prepurified hydrogen.

7.7 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples.

8.3.1 Immediately before sampling, break the ends of each tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a backup and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a flow of 0.20 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm$5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available the elevation should be recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the suspected compound should be submitted to the laboratory in glass containers with Teflon®-lined caps. These liquid bulk samples should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container or automatic sample injector vial. The separating section of foam is removed and discarded; the second section is transferred to another sample container or vial. These 2 sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. For the internal standard method a 0.2 percent solution of internal standard in the eluent is used. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. The sample vials should be capped as soon as the solvent is added to minimize volatilization.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (80 psig) nitrogen carrier gas flow.
2. 30 ml/min (50 psig) hydrogen gas flow to detector.
3. 300 ml/min (50 psig) air flow to detector.
4. 170°C injector temperature.
5. 210°C manifold temperature (detector).
6. 110°C column temperature.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-µl syringe is first flushed with solvent several times to

wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 µl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-µl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 µl to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 µl in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique. In this case 2-µl injections are satisfactory.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below (see Section 9).

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided that the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.0-ml sample container. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. A 12.5 mg/ml stock solution of the analyte in carbon tetrachloride is prepared. A known amount of this solution is injected directly into the activated charcoal with a 10-µl syringe, and the container is capped. The amount injected is equivalent to that present in a 10-liter sample at the selected level. A solution must be used because the analyte is a solid.

At least 6 tubes at each of 3 levels (0.5X, 1X, and 2X the standard) are prepared in this manner and allowed to stand overnight to assure complete adsorption of the analyte onto the charcoal. These 6 tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

The weight of analyte found in each tube is determined from the standard curve (Section 9). Desorption efficiency is determined by the following equation:

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus the weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/ml of carbon disulfide. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentrations in mg/ml versus peak area.

Note: Whether the absolute area or internal standard method is used standard solutions should be analyzed at the same time that the sample analysis is done. This will minimize the effect variations of FID response.

10. Calculations

10.1 Read the weights, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/ml eluent and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

mg = mg sample - mg blank

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (Section 8.5.2) for the amount of analyte found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

10.5 The concentration of analyte in the air sampled can be expressed in mg per cu m, which is numerically equal to µg per liter of air

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm:

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L. D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 "Documentation of NIOSH Validation Tests", Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract No. HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes", September 15, 1972.

Fluorotrichloromethane

Analyte:	Fluorotrichloromethane	Method No.:	S102
Matrix:	Air	Range:	2390-10500 mg/cu m
OSHA Standard:	1000 ppm (5600 mg/cu m)	Precision ($\overline{CV}_T$):	0.072
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	10/29/76

1. Principle of the Method (Reference 11.1)

   1.1 A known volume of air is drawn through a large charcoal tube to trap the organic vapors present. The sampling tube consists of a front adsorbing section and a backup section.

   1.2 The charcoal in each tube is transferred to a serum vial and sealed with a septum and aluminum lacquered seals. The fluorotrichloromethane is desorbed with carbon disulfide and analyzed by gas chromatography.

2. Range and Sensitivity

   2.1 This method was validated over the range of 2390-10520 mg/cu m at an atmospheric temperature of 25°C and atmospheric pressure of 752 mm Hg using a 4-liter sample volume. This sample volume is based on two-thirds of the 5% breakthrough capacity determined at 90% relative humidity. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

   2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of fluorotrichloromethane and other substances in the air. (see Section 5.2)

3. Interferences

   3.1 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

   3.2 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.3 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV_T}$) for the total analytical and sampling method in the range of 2390-10520 mg/cu m was 0.072. This value corresponds to a 400-mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in References 11.2 and 11.3.

4.2 On the average, the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 3.1% lower than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result.

The data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. The sample capacity of the charcoal tube is dependent on humidity as indicated by experimental results on sampling fluorotrichloromethane in dry and high humidity atmospheres using tubes packed with 400 mg of activated coconut charcoal and sampling at a flow rate of 0.187 liter per minute. When a dry atmosphere containing 10660 mg/cu m of fluorotrichloromethane was sampled, 5% breakthrough was observed after 56 minutes (capacity = 10.5 liters or 112 mg). On the other hand, when an atmosphere at 90% relative humidity containing 10170 mg/cu m of fluorotrichloromethane was sampled, 5% breakthrough was observed after 33 minutes (capacity = 6.2 liters or 63 mg). The sample size recommended is less than the 5% breakthrough capacity at 90% R.H. to minimize the probability of overloading the sampling tube.

5.3 The precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3)

6.2 Charcoal tubes: The sampling tube consists of a glass tube, 10-cm long with an 8-mm O.D. and a 6-mm I.D. packed with charcoal. It has two sections of 20/40 mesh activated coconut charcoal separated by a 2-mm portion of urethane foam. The front section contains 400 mg of charcoal; the backup section, 200 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than 25 mm of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph: The unit must be equipped with a flame ionization detector.

6.4 Column: (20-ft x 1/8 in stainless steel) packed with 10% FFAP stationary phase on 100/120 mesh Supelcoport.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 Glass serum vials for desorption, 10-ml, molded to take a 13-mm Teflon-faced rubber septum and 13-mm aluminum seal.

6.6.1 Teflon-faced rubber septa, 13 mm.

6.6.2 Lacquered aluminum seals or caps, 13 mm.

6.6.3 Hand crimper, 13 mm, or equivalent for properly sealing the vial assembly.

Note: Glass stoppered containers are not adequate because of significant sample losses during desorption.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Gas-tight syringes: 10-ml and other convenient sizes for making standards.

6.9 Syringe: 5- or 10-ml capacity for adding the carbon disulfide used for desorption.

6.10 Syringe needle: 1.5-inch, 22 gauge or other convenient size.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 Fluorotrichloromethane, 99%.

7.3 Nonane or other suitable internal standard. The appropriate solution of the internal standard is prepared in carbon disulfide.

7.4 Purified nitrogen.

7.5 Prepurified hydrogen.

7.6 Filtered compressed air.

8. Procedure

8.1 Cleaning of equipment: All glassware used for the laboratory analysis should be detergent-washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps: Each personal pump must be calibrated with a representative sampling tube series in the line; the tube is described in Section 6.2. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples:

8.3.1 Immediately before sampling, break the two ends of the charcoal tube to provide an opening at least one-half the internal diameter of the tube (3 mm).

8.3.2 The section containing 200 mg of charcoal is used as a backup and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube series should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A sample size of 4 liters is recommended. Sample at a flow rate of 0.05 to 0.01 liter per minute; a flow rate less than 0.01 liter per minute should not be used. The flow rate should be known with an accuracy of at least $\pm$ 5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The charcoal tube should be labeled appropriately and capped with the supplied plastic caps. Under no circumstances should rubber caps be used.

8.3.8 With each batch of 10 samples, submit one charcoal tube which has been handled in the same manner as the sample tubes (break, seal and transport), except that no air is sampled through this tube. This tube should be labeled as the blank.

8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file and broken open. The glass wool is removed and discarded. The charcoal in the larger front section is transferred to a 10-ml serum vial and the vial is sealed with the Teflon-faced septum and the aluminum cap with the aid of the crimper. The charcoal in the backup section is transferred to another serum vial and handled in a similar manner.

8.4.2 Desorption of Sample. Immediately before desorption, lift up or remove the removable portion of the aluminum cap to expose a portion of the septum without destroying the seal. Insert a syringe needle through the septum keeping the tip of the needle just below the surface of the septum in the vial. (This needle serves as a vent to prevent pressure buildup in the tube when carbon disulfide is added.) Add 5.0 ml of carbon disulfide or 5.0 ml of internal standard stock solution into the sample vial with the aid of a syringe. After the carbon disulfide addition, remove the needle being used as a vent. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period.

If an automatic sample injector is used, the sample transfer should be carried out as follows to avoid sample loss. Seal an empty sample injector vial with the Teflon-lined septum and screw cap. Insert a syringe needle as above

to serve as vent. Transfer the sample solution from the desorption vial into the automatic sample injector vial with the aid of a syringe. (A syringe needle can be used as vent in the desorption vial if necessary to avoid creating a partial vacuum in the desorption vial when withdrawing the sample solution.)

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (60 psig) Nitrogen carrier gas flow
2. 30 ml/min (25 psig) Hydrogen gas flow to detector
3. 300 ml/min (60 psig) Air flow to detector
4. 175°C injector temperature
5. 220°C manifold temperature (detector)
6. 65°C column temperature

A retention time of approximately 3.0 minutes is to be expected for the analyte using these conditions and the column recommended in Section 6.4. The fluorotrichloromethane elutes before the carbon disulfide.

8.4.4 A 5-microliter aliquot of the sample solution is injected into the gas chromatograph. The solvent flush method or other suitable alternative such as an automatic sample injector can be used provided that duplicate injections of a solution agree well. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed in Section 9.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine the percentage of the specific compound that is removed in the desorption process for the particular batch of charcoal used for sample collection and over the concentration range of interest.

8.5.2 Preparation of analytical samples for desorption efficiency determination. The desorption efficiency must be determined over the sample concentration range of interest. In order to determine the sample concentration range which should be tested, the samples are analyzed first and then the analytical samples are prepared based on the relative

amount of fluorotrichloromethane found in the samples. The desorption efficiency must be determined at least in duplicate for each concentration level of fluorotrichloromethane found in the sample.

The analytical samples are prepared as follows: Activated charcoal, equivalent to the amount in the front section (400 mg), is measured into a 10-ml serum vial. This charcoal must be from the same batch as that used in obtaining the samples. Alternatively, unused commercially available charcoal tubes can be used. The serum vial is sealed air-tight using a Teflon-faced septum and aluminum seal with the aid of a crimper. The amount of fluorotrichloromethane added into the charcoal is determined gravimetrically by weighing the sealed vial before and after adding controlled amounts of fluorotrichloromethane. Fluorotrichloromethane is a low boiling liquid (b.p. = 24°C) and the use of volumetric methods for delivering liquid aliquots can lead to erroneous results.

For the validation studies conducted to determine the precision and accuracy of this method, six analytical samples at each of the three concentration levels (0.5S, 1X and 2X of the OSHA standard) were prepared by adding an amount of fluorotrichloromethane equivalent to that present in a 4-liter sample at the selected level. This required the addition of approximately 7 to 30 µl of fluorotrichloromethane for the 0.5X, 1X and 2X of the OSHA standard level. The analytical samples were allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. A parallel blank tube was treated in the same manner except that no sample was added to it.

The procedure described can be used to prepare the analytical samples which are analyzed to determine desorption efficiency over the concentration range of interest.

8.5.3 Desorption and analysis experiments are done on the analytical samples as described in Sections 8.4.2 to 8.4.5.

To prepare the standards, 5 ml of carbon disulfide is added to the 10-ml serum vial. The vial is then immediately sealed air-tight, using a Teflon-faced septum and aluminum cap with the aid of a crimper. Immediately before adding the fluorotrichloromethane, weigh the sealed vial. Add the appropriate amount of fluorotrichloromethane into the carbon disulfide, and weigh the vial again. Standards should be prepared at the same time that the sample analysis is done and should be analyzed with the samples.

The weight (mg) of fluorotrichloromethane in each standard and sample is calculated based on the difference in weight before and after addition of fluorotrichloromethane.

If the internal standard method is used, prepare calibration standards by using 5.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is expected to be dependent on the amount of fluorotrichloromethane collected on the charcoal. Plot the desorption efficiency versus weight of fluorotrichloromethane found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

9.1 Add 5.0 ml of carbon disulfide (or 5.0 ml of internal standard solution in carbon disulfide) to a 10-ml serum vial. With the aid of a crimper, immediately seal the vial air-tight with the Teflon-faced septum and aluminum cap to avoid evaporation. Immediately before adding the fluorotrichloromethane, weigh the sealed vial. Add the appropriate amount of fluorotrichloromethane to the carbon disulfide and weigh sealed vial again.

Calculate the number of mg of fluorotrichloromethane in the standard solution based on the weight difference before and after addition of fluorotrichloromethane into the sealed vial. The concentration of standards can be expressed in terms of mg fluorotrichloromethane per 5 ml of carbon disulfide. This unit is convenient because samples are desorbed in 5 ml of carbon disulfide.

9.2 A series of standards, varying in concentration over the range of interest, is prepared as described above and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting peak area (ordinate) against sample concentration in mg/5 ml.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The area ratio of the analyte to that of the internal standard is plotted against the analyte concentration in mg/5.0 ml.

Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 5.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

mg sample = mg found in front (400-mg) sample section

mg blank = mg found in front (400-mg) blank section

A similar procedure is followed for the backup tube.

10.3 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section of the tube. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

10.4 Add the amounts present in the front and backup sections for the same sample to determine the total weight in the sample.

10.5 Determine the volume of air sampled at ambient conditions in liters based on the appropriate information, such as flow rate in liters per minute multiplied by sampling time. If a pump using a rotameter for flow rate control was used for sample collection, a pressure and temperature correction must be made for the indicated flow rate. The expression for this correction is:

$$\text{Corrected Volume} = f \times t\left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}}\right)$$

where:

f = flow rate sampled

t = sampling time

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump (°K)

T_2 = temperature of air sampled (°K)

10.6 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (see Section 10.4) x 1000 (liters/cu m)}}{\text{Air Volume Sampled (liters)}}$$

10.7 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31, 225 (1970).

11.2 Memoranda, Kenneth A. Busch, Chief, Statistical Services, DLCD, to Deputy Director, DLCD, dated 1/16/75, 11/8/74, subject: "Statistical Protocol for Analysis of Data from Contract CDC-99-74-45."

11.3 Backup Data Report for Fluorotrichloromethane, prepared under NIOSH Contract No. 210-76-0123.

11.4 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes", September 15, 1972.

Ethylene Chlorohydrin

Analyte:	Ethylene Chlorohydrin	Method No.:	S103
Matrix:	Air	Range:	7-30 mg/cu m
OSHA Standard:	5 ppm (16 mg/cu m)	Precision ($\overline{CV}_T$):	0.076
Procedure:	Adsorption on charcoal, desorption with eluent, GC	Validation Date:	4/11/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with 5% isopropyl alcohol in carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 7-30 mg/cu m at an atmospheric temperature and pressure of 25°C and 742 mm Hg, using a 20-liter sample. Under the conditions of sample size (20 liters) the probable range of this method is 1.6-48 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 0.5-mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of the analyte and other substances in the air. The first section of the charcoal tube was found to hold at least 1.5 mg of the analyte when a test atmosphere of 31.5 mg/cu m of the analyte in dry air was sampled at 0.2 liter per minute for 4 hours. Breakthrough did not occur at this time; the concentration of the analyte in the effluent was less than 2% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of

urethane foam. See Section 6.2.) If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great the condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments with toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 7 to 30 mg/cu m was 0.076. This value corresponds to a standard deviation of 1.22 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 The average values obtained using the overall sampling and analytical method were 5.8% greater than the "true" value at the OSHA standard level.

4.3 The above data are based on validation experiments using the internal standard method. (Reference 11.2.)

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more compounds suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined accurately (±5%) at the recommended flow rate (Reference 11.3).

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh petroleum-derived activated charcoal separated by a 2-mm portion of urethane foam. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than 1 inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in. stainless steel) packed with 10% FFAP on 80/100 Chromosorb W-AW.

6.5 An electronic integrator or some other suitable method of determining peak size areas.

6.6 Two-milliliter glass sample containers with glass stoppers or Teflon®-lined caps. If an automatic sample injector is used, the sample injector vials can be used.

6.7 Microliter syringes: 10-µl, and other convenient sizes for making standards.

6.8 Pipets: 1.0-ml delivery type.

6.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Eluent: Carbon disulfide (chromatographic grade) containing 5% 2-propanol (reagent grade).

7.2 Ethylene chlorohydrin (reagent grade).

7.3 Internal Standard: n-Pentadecane (99+%) or other suitable standard.

7.4 Isopropyl alcohol (reagent grade).

7.5 Purified nitrogen.

7.6 Prepurified hydrogen.

7.7 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples.

8.3.1 Immediately before sampling, break the ends of each tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a backup and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A maximum sample size of 20 liters is recommended. Sample at a flow of 0.20 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm$5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available the elevation should be recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the suspected compound should be submitted to the laboratory in glass containers with Teflon®-lined caps. These liquid bulk samples should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container or automatic sample injector vial. The separating section of foam is removed and discarded; the second section is transferred to another sample container or vial. These 2 sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of the eluent is pipetted into each sample container. For the internal standard method a 0.2 percent solution of internal standard in the eluent is used. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. The sample vials should be capped as soon as the solvent is added to minimize volatilization.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (80 psig) nitrogen carrier gas flow.
2. 30 ml/min (50 psig) hydrogen gas flow to detector.
3. 300 ml/min (50 psig) air flow to detector.
4. 170°C injector temperature.
5. 210°C manifold temperature (detector).
6. 130°C column temperature.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-µl syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 µl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-µl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 µl to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 µl in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique. In this case 2-µl injections are satisfactory.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below (see Section 9).

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided that the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.0-ml sample container. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. An 80 mg/ml stock solution of the analyte in isopropyl alcohol is prepared. A known amount of this solution

is injected directly into the activated charcoal with a 10-µl syringe, and the container is capped. The amount injected is equivalent to that present in a 20-liter sample at the selected level. It is not practical to inject the neat liquid directly because the amounts to be added would be too small to measure accurately.

At least 6 tubes at each of 3 levels (0.5X, 1X, and 2X the standard) are prepared in this manner and allowed to stand overnight to assure complete adsorption of the analyte onto the charcoal. These 6 tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

The weight of analyte found in each tube is determined from the standard curve (Section 9). Desorption efficiency is determined by the following equation:

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus the weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/ml of eluent. For the internal standard method use carbon disulfide containing 0.2 percent of the internal standard. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentrations in mg/ml versus peak area.

Note: Whether the absolute area or internal standard method is used standard solutions should be analyzed at the same time that the sample analysis is done. This will minimize the effect variations of FID response.

10. Calculations

10.1 Read the weights, in mg, corresponding to each peak area (area ratio in case of the internal standard method) from the standard curve. No volume corrections are needed, because the standard curve is based on mg/ml eluent and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

mg = mg sample - mg blank

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (Section 8.5.2) for the amount of analyte found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

10.5 The concentration of analyte in the air sampled can be expressed in mg per cu m, which is numerically equal to µg per liter of air

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm:

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L. D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 "Documentation of NIOSH Validation Tests", Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract No. HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes", September 15, 1972.

Ethylene Dibromide

Analyte:	Ethylene Dibromide	Method No.: S104
Matrix:	Air	Range: 110-470 mg/cu m
OSHA Standard:	30 ppm (230 mg/cu m)-Ceiling 20 ppm (155 mg/cu m)-T.W.A.	Precision ($\overline{CT}_T$): 0.077
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 4/11/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 110-470 mg/cu m at an atmospheric temperature and pressure of 25 C and 738 mm Hg, using a 1-liter sample. Under the conditions of sample size (1 liter) the probable range of this method is 22-660 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 0.7-mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentration of the analyte and other substances in the air. The first section of the charcoal tube was found to hold at least 21.4 mg of the analyte when a test atmosphere of 446 mg/cu m of the analyte in dry air was sampled at 0.2 liters per minute for 4 hours. Breakthrough did not occur at this time;

the concentration of the analyte in the effluent was less than 2% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2.) If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments with toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 110 to 470 mg/cu m was 0.077. This value corresponds to a standard deviation of 16.9 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 The average values obtained using the overall sampling and analytical method were 8.2% lower than the "true" value at the OSHA standard level.

4.3 The above data are based on validation experiments using the internal standard method. (Reference 11.2)

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more compounds suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined accurately (±5%) at the recommended flow rate, (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600 C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in. stainless steel) packed with 10% FFAP on 80/100 Chromosorb W-AW.

6.5 An electronic integrator or some other suitable method for determining peak size areas.

6.6 Two-milliliter glass sample containers with glass stoppers or Teflon®-lined caps. If an automatic sample injector is used, the sample injector vials can be used.

6.7 Microliter syringes: 10-µl, and other convenient sizes for making standards.

6.8 Pipets: 1.0-ml delivery type.

6.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Eluent: Carbon disulfide (chromatographic grade).

7.2 Ethylene Dibromide (reagent grade).

7.3 Internal Standard: n-Pentadecane (99+%) or other suitable standard.

7.4 n-Heptane (reagent grade).

7.5 Purified nitrogen.

7.6 Prepurified hydrogen.

7.7 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 At the T.W.A. concentration a sample size of 10 liters is recommended. Sample at a flow of 0.2 liter per minute. The flow rate should be known with an accuracy of at least ±5%.

At the ceiling and peak concentrations, a sample size of 1 liter is recommended. Sample for 5 minutes at a flow of 0.2 liter per minute.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available the elevation should be recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the suspected compound should be submitted to the laboratory in glass containers with Teflon®-lined caps. These liquid bulk samples should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container or automatic sample injector vial. The separating section of foam is removed and discarded; the second section is transferred to another sample container or vial. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of the eluent is pipetted into each sample container. For the internal standard method a 0.2 percent solution of internal standard in the eluent is used. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. The sample vials should be capped as soon as the solvent is added to minimize volatilization.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (80 psig) nitrogen carrier gas flow.
2. 30 ml/min (50 psig) hydrogen gas flow to detector.
3. 300 ml/min (50 psig) air flow to detector.
4. 170 C injector temperature.
5. 210 C manifold temperature (detector).
6. 130 C column temperature.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-µl syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 µl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-µl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 µl to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 µl in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique. In this case 2-µl injections are satisfactory.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below (see Section 9).

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided that the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.0-ml sample container. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. A

55 mg/ml stock solution of the analyte in n-heptane is prepared. A known amount of this solution is injected directly into the activated charcoal with a 10-µl syringe, and the container is capped. The amount injected is equivalent to that present in a 1-liter sample at the selected level. It is not practical to inject the neat liquid directly because the amounts to be added would be too small to measure accurately.

At least six tubes at each of three levels (0.5X, 1X, and 2X the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These six tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

The weight of analyte found in each tube is determined from the standard curve (Section 9). Desorption efficiency is determined by the following equation:

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus the weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/ml of carbon disulfide. To minimize error due to the volatility of the carbon disulfide, one can add 10 times the weight to 10 ml of the carbon disulfide. (For the internal standard method use carbon disulfide containing 0.2 percent of the internal standard.) A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentrations in mg/ml versus peak area. In the case of the internal standard method plot the concentration versus the ratio of peak area of analyte to peak area of internal standard.

Note: Whether the absolute area or internal standard method is used standard solutions should be analyzed at the same time that the sample analysis is done. This will minimize the effect variations of FID response.

10. Calculations

10.1 Read the weights, in mg, corresponding to each peak area (area ratio in case of the internal standard method) from the standard curve. No volume corrections are needed, because the standard curve is based on mg/ml eluent and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

mg = mg sample - mg blank

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (Section 8.5.2) for the amount of analyte found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

10.5 The concentration of analyte in the air sampled can be expressed in mg per cu m, which is numerically equal to µg per liter of air

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm:

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (C) of air sampled
24.45 = molar volume (liter/mole) at 25 C and 760 mm Hg
MW = molecular weight (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (K)

11. References

11.1 White L. D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 "Documentation of NIOSH Validation Tests", Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract No. HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes, September 15, 1972".

Ethyl Bromide

Analyte:	Ethyl Bromide	Method No.:	S106
Matrix:	Air	Range:	550-2200 mg/cu m
OSHA Standard:	200 ppm (890 mg/cu m)	Precision ($\overline{CV}_T$):	0.054
Procedure:	Adsorption on charcoal, desorption with isopropyl alcohol, GC	Validation Date:	4/11/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with isopropyl alcohol.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 550-2200 mg/cu m at an atmospheric temperature and pressure of 25°C and 744 mm Hg, using a 4-liter sample. Under the conditions of sample size (4 liters) the probable range of this method is 90-2670 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for an 8-mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of the analyte and other substances in the air. The first section of the charcoal tube was found to hold 14.2 mg of the analyte when a test atmosphere of 2213 mg/cu m of the analyte in dry air was sampled at 0.2 liter per minute for 32 minutes; breakthrough was observed at this time, i.e., the concentration of the analyte in the effluent was 5% of that

in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2.) If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great the condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments with toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 550 to 2200 mg/cu m was 0.054. This value corresponds to a standard deviation of 48.1 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 The average values obtained using the overall sampling and analytical method were 3.2% lower than the "true" value at the OSHA standard level.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more compounds suspected to be present in the same sample

by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined accurately (±5%) at the recommended flow rate (Reference 11.3).

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than 1 inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in. stainless steel) packed with 10% FFAP on 80/100 Chromosorb W-AW.

6.5 An electronic integrator or some other suitable method of determining peak size areas.

6.6 Two-milliliter glass sample containers with glass stoppers or Teflon®-lined caps. If an automatic sample injector is used, the sample injector vials can be used.

6.7 Microliter syringes: 10-µl, and other convenient sizes for making standards.

6.8 Pipets: 1.0-ml delivery type.

6.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Eluent: Isopropyl alcohol (chromatographic grade).

7.2 Ethyl bromide (reagent grade).

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples.

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a backup and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A maximum sample size of 4 liters is recommended. Sample at a flow of 0.20 liter per minute or less. The flow rate should be known with an accuracy of at least ±5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available the elevation should be recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the suspected compound should be submitted to the laboratory in glass containers with Teflon®-lined caps. These liquid bulk samples should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container or automatic sample injector vial. The separating section of foam is removed and discarded; the second section is transferred to another sample container or vial. These 2 sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of isopropyl alcohol is pipetted into each sample container. Desorption should be done overnight or for an equivalent period of time. The sample vials should be capped as soon as the solvent is added to minimize volatilization.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (80 psig) nitrogen carrier gas flow.
2. 30 ml/min (50 psig) hydrogen gas flow to detector.
3. 300 ml/min (50 psig) air flow to detector.
4. 200°C injector temperature.
5. 300°C manifold temperature (detector).
6. 60°C column temperature.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ

the solvent flush injection technique. The 10-µl syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 µl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-µl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 µl to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 µl in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique. In this case 2-µl injections are satisfactory.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below (see Section 9).

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided that the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.0-ml sample container. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. A known amount of ethyl bromide is injected directly into the activated charcoal with a 10-µl syringe, and the container is capped. The amount injected is equivalent to that present in a 4-liter sample at the selected level.

At least 6 tubes at each of 3 levels (0.5X, 1X, and 2X the standard) are prepared in this manner and allowed to stand overnight to assure complete adsorption of the analyte onto the charcoal. These 6 tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

The weight of analyte found in each tube is determined from the standard curve (Section 9). Desorption efficiency is determined by the following equation:

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus the weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/ml of eluent. To minimize error due to the volatility of the eluent, one can add 10 times the weight to 10 ml of the isopropyl alcohol. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentrations in mg/ml versus peak area.

Note: Standard solutions should be analyzed at the same time that the sample analysis is done. This will minimize the effect variations of FID response.

10. Calculations

10.1 Read the weights, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/ml eluent and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

mg = mg sample - mg blank

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (Section 8.5.2) for the amount of analyte found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

10.5 The concentration of analyte in the air sampled can be expressed in mg per cu m, which is numerically equal to µg per liter of air

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm:

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L. D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 "Documentation of NIOSH Validation Tests", Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract No. HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes, September 15, 1972."

Difluorodibromomethane

Analyte:	Difluorodibromomethane	Method No.:	S107
Matrix:	Air	Range:	470-1875 mg/cu m
OSHA Standard:	100 ppm (860 mg/cu m)	Precision ($\overline{CV}_T$):	0.090
Procedure:	Adsorption on charcoal, desorption with isopropyl alcohol, GC	Validation Date:	4/11/75

1. Principle of the Method

1.1 A known volume of air is drawn through two charcoal tubes in series to trap the organic vapors present.

1.2 The charcoal in the tubes is transferred to a small, stoppered sample container and the analyte is desorbed with isopropyl alcohol.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 470-1875 mg/cu m at an atmospheric temperature and pressure of 25°C and 745 mm Hg, using a 10-liter sample. Under the conditions of sample size (10 liters) the probable range of this method is 90-2580 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 19 mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of the analyte and other substances in the air. The first section of the charcoal tube was found to hold 29.3 mg of the analyte when a test atmosphere of 1875 mg/cu m of the analyte in dry air was sampled at 0.2 liter per minute for 1 hour, 18 minutes; breakthrough was observed at this time, i.e., the concentration of the analyte in the effluent was 5% of that

in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2.) If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great the condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments with toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 470 to 1875 mg/cu m was 0.090. This value corresponds to a standard deviation of 77.4 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 The average values obtained using the overall sampling and analytical method were 4.7% higher than the "true" value at the OSHA standard level.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more compounds suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup tube exceeds 25% of that found on the front tube, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined accurately (±5%) at the recommended flow rate (Reference 11.3).

6.2 Charcoal tubes: two glass tubes in series, each with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to backing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than 1 inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in. stainless steel) packed with 10% FFAP on 80/100 Chromosorb W-AW.

6.5 An electronic integrator or some other suitable method of determining peak size areas.

6.6 Two-milliliter glass sample containers with glass stoppers or Teflon®-lined caps. If an automatic sample injector is used, the sample injector vials will also be needed.

6.7 Microliter syringes: 10-µl, and other convenient sizes for making standards.

6.8 Gastight syringe: 10-ml, or other convenient size.

6.9 Pipets: 1.0-ml delivery type.

6.10 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

6.11 Cold room or cold box for preparing standards at 0°C or lower.

7. Reagents

7.1 Eluent: Isopropyl alcohol (chromatographic grade).

7.2 Difluorodibromomethane.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples.

8.3.1 Immediately before sampling, break the ends of the sample and backup tubes to provide an opening at least one-half the internal diameter of the tube (3 mm).

8.3.2 One of the charcoal tubes is used as a back-up and should be positioned nearest the sampling pump. This should be labeled as the backup tube before shipping.

8.3.3 The charcoal tubes should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tubes.

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a flow of 0.20 liter per minute or less. The flow rate should be known with an accuracy of at least ±5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available the elevation should be recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the suspected compound should be submitted to the laboratory in glass containers with Teflon®-lined caps. These liquid bulk samples should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal sampling and backup tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first tube is transferred to a 2-ml vial. The second tube is transferred to another vial. These two tubes are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of isopropyl alcohol is pipetted into each vial. Desorption should be done overnight. Tests indicate that this is adequate. The sample vials should be capped as soon as the solvent is added to minimize volatilization. If an automatic sampler is to be used, the samples can be transferred to automatic sample injector vials after desorption.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (80 psig) nitrogen carrier gas flow.
2. 30 ml/min (50 psig) hydrogen gas flow to detector.
3. 300 ml/min (50 psig) air flow to detector.
4. 200°C injector temperature.
5. 300°C manifold temperature (detector).
6. 60°C column temperature.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ

the solvent flush injection technique. The 10-µl syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 µl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-µl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 µl to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 µl in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique. In this case 2-µl injections are satisfactory.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below (see Section 9).

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided that the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.0-ml sample container. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. A known amount of difluorodibromomethane is injected directly into the activated charcoal with a 10-µl syringe, and the container is capped. The amount injected is equivalent to that present in a 10-liter sample at the selected level. This must be done in a cold room below the boiling point of difluorodibromomethane, 0°C or lower.

At least 6 tubes at each of 3 levels (0.5X, 1X, and 2X the standard) are prepared in this manner and allowed to stand overnight to assure complete adsorption of the analyte onto the charcoal. These 6 tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

The weight of analyte found in each tube is determined from the standard curve (Section 9). Desorption efficiency is determined by the following equation:

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus the weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/ml of isopropyl alcohol. A series of standards, varying in concentration over the range of interest, is prepared by injecting the liquid with a syringe in a cold room and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentrations in mg/ml versus peak area.

Note: Standard solutions should be analyzed at the same time that the sample analysis is done. This will minimize the effect variations of FID response.

10. Calculations

10.1 Read the weights, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/ml isopropyl alcohol and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

mg = mg sample - mg blank

where:

mg sample = mg found in front tube of sample

mg blank = mg found in blank tube

A similar procedure is followed for the backup tubes.

10.3 Add the weights present in the front and backup tubes of the same sample to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (Section 8.5.2) for the amount of analyte found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

10.5 The concentration of analyte in the air sampled can be expressed in mg per cu m, which is numerically equal to µg per liter of air

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm:

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L. D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 "Documentation of NIOSH Validation Tests", Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract No. HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes", September 15, 1972.

Dichlorotetrafluoroethane*

Analyte:	Dichlorotetrafluoroethane	Method No.: S108
Matrix:	Air	Range: 3500-14100 mg/cu m
OSHA Standard:	1000 ppm (7000 mg/cu m)	Precision ($\overline{CV}_T$): 0.064
Procedure:	Adsorption on charcoal, desorption with methylene chloride, GC	Validation Date: 10/29/76

1. Principle of the Method (Reference 11.1)

   1.1 A known volume of air is drawn through two tubes in series containing activated coconut charcoal to trap gaseous dichlorotetrafluoroethane.

   1.2 Dichlorotetrafluoroethane is desorbed from the charcoal with methylene chloride, and the sample is analyzed by gas chromatography.

2. Range and Sensitivity

   2.1 This method was validated over the range of 3540-14090 mg/cu m at an atmospheric temperature of 25°C and atmospheric pressure of 759 mm Hg, using a 3-liter sample. This maximum sample size is based on the capacity of the charcoal to collect vapors of dichlorotetrafluoroethane in air with 90% relative humidity. The method may be capable of measuring smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

   2.2 The upper limit of the range of the method depends on the adsorptive capacity of the charcoal. This capacity may vary with the concentrations of dichlorotetrafluoroethane and other substances in the air. Breakthrough is defined as the time that the effluent concentration from the collection tube

*Refrigerant 114

(containing 600 mg of charcoal) reaches 5% of the concentration in the test gas mixture. The criterion for acceptance is that the volume of air that has passed through the tube at the time of breakthrough must be greater than 1.5 times the volume of air that would be passed through the tube for a sample at 2X the OSHA standard level. At a temperature of 24°C and relative humidity of 90%, breakthrough occurred in 158 minutes when a test concentration of 14600 mg/cu m was sampled at a flow rate of 0.046 liter/minute.

3. Interferences

3.1 When interfering compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 Any compound that has the same retention time as dichlorotetrafluoroethane at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 3540-14090 mg/cu m was 0.064. This value corresponds to a 450 mg/cu m standard deviation at the OSHA standard level. Statistical information can be found in Reference 11.2. Details of the test procedures are found in Reference 11.3.

4.2 No recovery correction should be applied to the final result in Section 10.6. On the average the concentrations obtained in the laboratory validation study at 0.5X, 1X, and 2X the OSHA standard level were 0.2% lower than the "true" concentrations for 18 samples. Therefore, the method has no bias. The Coefficient of Variation is a good measure of the accuracy of the method since the recoveries and storage stability were good. Storage stability studies on samples collected from a test atmosphere at a concentration of 6900 mg/cu m indicate that collected samples are stable for at least 7 days.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those that occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

5.2 One disadvantage of the method is that the amount of sample that can be taken is limited by the number of milligrams that the tube will hold before overloading. When the amount of dichlorotetrafluoroethane found on the backup charcoal tube exceeds 12 mg, the probability of sample loss exists.

5.3 The precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 Personal Sampling Pump: A calibrated personal sampling pump whose flow rate can be determined within 5% at the recommended flow rate.

6.2 Two charcoal tubes are used in this method. One charcoal tube is used to collect the samples, and a smaller charcoal tube is used as a backup. The charcoal tubes are connected in series with Tygon tubing. The larger charcoal tube is a glass tube, 9-cm long with a 8-mm O.D. and a 6-mm I.D. It has two sections of 20/40 mesh activated coconut charcoal separated by a 2-mm portion of urethane foam. The front section contains 400 mg of charcoal, the back section 200 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than 25 mm of mercury at a flow rate of 0.05 liter per minute. The smaller charcoal tube is 7-cm long with a 6-mm O.D. and a 4-mm I.D. The smaller charcoal tube contains 100 mg of charcoal in the front section and 50 mg in the backup section.

6.3 Gas chromatograph equipped with a flame ionization detector using hydrogen and air for the detector.

6.4 Column (4-ft long x 1/4-in O.D. stainless steel) packed with 80/100 mesh Chromosorb 102.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 Microliter syringes: 10-microliter for injection of samples into the gas chromatograph.

6.7 Gas tight syringes: 1, 2, 5, and 10-ml sizes for preparing standards.

6.8 Pipets: 20.0-ml delivery pipets.

6.9 Serum bottles: 30-ml glass bottles with 20-mm O.D. mouth.
Septa: 20-mm rubber septa with Teflon lining.
Aluminum tear-away seals to fit serum bottles.

6.10 Hand crimper for sealing septa to serum bottles.

6.11 Stopwatch.

6.12 Manometer.

7. Reagents

7.1 Methylene chloride, chromatographic quality.

7.2 Dichlorotetrafluoroethane, 99% pure.

7.3 Nitrogen, purified.

7.4 Hydrogen, prepurified.

7.5 Air, filtered, compressed.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed, thoroughly rinsed with tap water and distilled water, and dried.

8.2 Calibration of Sampling Pumps. Each personal sampling pump must be calibrated with representative charcoal tubes in the line to minimize errors associated with uncertainties in the volume sampled. (Reference 11.4)

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the two charcoal tubes to provide an opening at least one-half the internal diameter of the tube.

8.3.2 Connect the larger charcoal tube in series with the smaller charcoal tube by connecting the backup section of the large charcoal tube to the front section of the small charcoal tube with Tygon tubing. The shortest length of tubing compatible with maintaining a leak-free connection should be used. The smaller charcoal tube is used as a backup and should be positioned nearer the pump. Air should flow through the large charcoal tube before entering the small charcoal tube.

8.3.3 Both charcoal tubes should be vertical during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tubes.

8.3.5 A maximum sample size of 3 liters is recommended. Sample at a flow rate between 0.01 and 0.05 liter per minute. The collection time and the flow rate with an accuracy of 5% or better should be recorded. Also record the type of pump that is used.

8.3.6 The temperature, pressure, and relative humidity of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The charcoal tubes should be separated and capped individually with plastic caps immediately after sampling. Under no circumstances should rubber caps be used. Each set of tubes should be marked to identify the large charcoal tube with the corresponding backup charcoal tube.

8.3.8 With each batch of ten samples, submit one set of tubes (a larger charcoal tube and a smaller backup tube) from the same lot of tubes used for sample collection. These tubes must be subjected to exactly the same handling as the samples except that no air is drawn through them. These tubes should be labeled as the blanks.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.4 Analysis of Samples

8.4.1 Desorption of Dichlorotetrafluoroethane. Pipet 20 ml of methylene chloride into the 30-ml serum bottle. Remove the plastic caps from both ends of the larger charcoal tube. Remove the plug of urethane foam from the outlet end of the tube. Transfer the 200-mg portion of charcoal to the serum bottle. Next, remove the glass wool plug from the inlet end of the tube and transfer the 400-mg section of charcoal to the same bottle. Place the Teflon-lined septum over the mouth of the bottle and seal the aluminum seal on with the crimper. It is important that the transfer of the charcoal be carried out as quickly as possible once the methylene chloride has been added to the bottle. The backup charcoal tube should be handled in a similar manner, using a separate serum bottle. The two samples are analyzed separately.

8.4.2 Gently shake the sample. The extract is now ready for analysis. Analyses should be completed within one day after the dichlorotetrafluoroethane is desorbed. Prepare standards as in Section 8.5.3. Fresh standards should be prepared daily.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psig) nitrogen carrier gas flow rate
2. 65 ml/min (24 psig) hydrogen gas flow rate to detector
3. 500 ml/min (50 psig) air flow rate to detector
4. 240°C injector temperature
5. 275°C detector temperature
6. 110°C column temperature

A retention time of approximately 1.7 minutes is to be expected for dichlorotetrafluoroethane under these conditions and using the column recommended in Section 6.4. The methylene chloride will elute from the column after the dichlorotetrafluoroethane.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or evaporation of solvent within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. It is not advisable to use an automatic sample injector for dichlorotetrafluoroethane in methylene chloride.

8.4.5 The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine the fraction of the specific compound that is removed in the desorption process for a particular batch of charcoal.

8.5.2 Known amounts of dichlorotetrafluoroethane are sorbed from the gas phase on the charcoal in the tubes as described below.

The apparatus to be used for spiking charcoal with known amounts of dichlorotetrafluoroethane consists of a union tee connected to a source of purified nitrogen, a charcoal tube, and a septum for introducing dichlorotetrafluoroethane from a gas tight syringe. A known amount of dichlorotetrafluoroethane is injected through the septum where nitrogen at a flow rate of approximately 20 ml/min carries the dichlorotetrafluoroethane into the charcoal tube. The nitrogen is allowed to flow through the tube for an additional 30 seconds after discharge of the contents of the syringe through the septum. The charcoal tube is capped with plastic caps.

The amount sorbed is equivalent to that present in a 3-liter air sample at the selected level. This requires 1.5, 3, and 6 ml of the dichlorotetrafluoroethane for 0.5X, 1X, and 2X the OSHA standard level, respectively. The atmospheric temperature, pressure, and relative humidity at which the tubes are prepared should be recorded.

Six tubes at each of the three levels are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of dichlorotetrafluoroethane onto the charcoal in the tube. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it.

8.5.3 Desorption and analysis experiments are done on the contents of the larger charcoal tube as described in Section 8.4.1.

In preparation of the standards, 20 ml of methylene chloride is added to a 30-ml serum bottle. The bottle is then sealed using a Teflon-lined septum and aluminum seal. An appropriate amount of dichlorotetrafluoroethane is bubbled slowly into the methylene chloride, using a gas tight syringe.

The syringe needle should be immersed in the methylene chloride during discharge of dichlorotetrafluoroethane from the syringe. The bottle should be shaken gently after removal of the syringe needle. Standards should be prepared at the same time that the sample analysis is done, and analyzed with the samples.

The weight (mg) of dichlorotetrafluoroethane in each standard and sample is calculated by the formula in Section 9.

The desorption efficiency (DE) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$DE = \frac{\text{Average weight recovered (mg)}}{\text{Weight added (mg)}}$$

The desorption efficiency is dependent on the amount of dichlorotetrafluoroethane collected on the charcoal. Plot the desorption efficiency versus weight of dichlorotetrafluoroethane found. This curve is used to correct for losses, as described in Section 10.4.

9. Calibration and Standards

A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. The standards are prepared as described in Section 8.5.3. Curves are established by plotting concentration in mg/20 ml versus peak area.

It is convenient to express concentration of standards in terms of mg/20 ml methylene chloride, because samples are desorbed in this amount of methylene chloride. The number of mg in the standard is calculated as follows:

$$mg = V \times \frac{M.W.}{24.45} \times \frac{298}{T + 273} \times \frac{P}{760}$$

where:

V	=	ml of dichlorotetrafluoroethane used to prepare the standard
T	=	temperature (°C) at which the sample was prepared
P	=	pressure (mm Hg) at which the sample was prepared
24.45	=	molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	=	molecular weight of dichlorotetrafluoroethane
298	=	standard temperature (°K)
760	=	standard pressure (mm Hg)

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed because the standard curve is based on mg/20 ml methylene chloride and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

mg sample = mg found in both sections of sample tube

mg blank = mg found in both sections of blank tube

A similar procedure is followed for the backup tubes.

10.3 Add the weights found in the front and backup tubes to get the total weight of the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.3) for the amount found in the first tube. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{DE}}$$

10.5 For personal sampling pumps with rotameters only, the following correction should be made.

$$\text{Corrected Volume} = f \times t\left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}}\right)$$

where:

f = flow rate sampled
t = sampling time
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 dichlorotetrafluoroethane in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liters/cu m)}}{\text{Corrected air volume sampled (liters) (Section 10.5)}}$$

10.7 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	=	pressure (mm Hg) of air sampled
T	=	temperature (°C) of air sampled
24.45	=	molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	=	molecular weight (g/mole) of dichlorotetrafluoroethane
760	=	standard pressure (mm Hg)
298	=	standard temperature (°K)

11. References

11.1 White, L. D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31, 225, (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

11.3 Backup Data Report for Dichlorotetrafluoroethane, prepared under NIOSH Contract No. 210-76-0123.

11.4 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Dichloromonofluoromethane

Analyte:	Dichloromonofluoromethane	Method No.:	S109
Matrix:	Air	Range:	1730-7600 mg/cu m
OSHA Standard:	1000 ppm (4200 mg/cu m)	Precision ($\overline{CV}_T$):	0.061
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	9/30/76

1. Principle of the Method (Reference 11.1)

   1.1 A known volume of air is drawn through a large charcoal tube to trap the organic vapors present. The sampling tube consists of two separate tubes--a front adsorbing tube and a backup tube; this sampling arrangement is necessary to prevent sample migration effects upon storage.

   1.2 The charcoal in each tube is transferred to a serum vial and sealed with septum and aluminum lacquered seals. The dichloromonofluoromethane is desorbed with carbon disulfide and analyzed by gas chromatography.

2. Range and Sensitivity

   2.1 This method was validated over the range of 1730-7640 mg/cu m at an atmospheric temperature of 24°C and atmospheric pressure of 760 mm Hg using a 3-liter sample volume. This sample volume is based on two-thirds of the 5% breakthrough capacity at the 2S test level determined at 90% relative humidity. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

   2.2 The upper limit of the range of the method is dependent on the absorptive capacity of the charcoal tube. This capacity varies with the concentrations of dichloromonofluoromethane and other substances in the air. (See Section 5.2)

3. Interferences

   3.1 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.3 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 1730-7640 mg/cu m was 0.061. This value corresponds to a 256-mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in References 11.2 and 11.3.

4.2 On the average, the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 3.9% higher than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result.

The data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. The sample capacity of the charcoal tube is dependent on humidity as indicated by experimental results on sampling dichloromonofluoromethane in dry and high humidity atmospheres using tubes packed with 400 mg of activated coconut charcoal and sampling at a flow rate of 0.187 liter per minute. When a dry atmosphere containing 8850 mg of dichloromonofluoromethane was sampled, 5% breakthrough was observed after 64 minutes (capacity = 12 liters or 102 mg). On the other hand, when an atmosphere at 90% relative humidity containing 9120 mg of dichloromonofluoromethane was sampled,5% breakthrough was observed after 23 minutes (capacity = 4.3 liters or 39 mg).

To minimize the probability of overloading the sampling tube, the sample size recommended is less than the 5% breakthrough capacity at 90% R.H. for a test atmosphere at 2X OSHA standard level.

5.3 The precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3)

6.2 Charcoal tubes: The sampling tube series consists of two separate large charcoal tubes. The tubes are glass tubes with both ends flame-sealed, 10 cm long with an 8-mm O.D. and a 6-mm I.D. Each tube contains the appropriate amount of 20/40 mesh activated coconut charcoal. The front tube contains 400 mg of charcoal; the backup tube, 200 mg. A plug of silylated glass wool is placed at each end of the charcoal tubes. The pressure drop across the tubes must be less than one inch of mercury at a flow rate of 1 liter per minute.

This tube series can be prepared by modifying commercially available large charcoal tubes as follows. For the front tube--break off exit end of a large tube and using pointed tweezers remove glass wool plug and the backup charcoal section; push in snugly remaining plug and charcoal to minimize channeling. For the backup tube--similarly break off inlet end of a second large tube and remove retaining plug and the front charcoal section; again push together remaining plug and charcoal. The front tube is connected to the backup tube with a minimal piece of plastic or rubber tubing.

Note that this sampling tube scheme is necessary to minimize observed sample migration effects upon storage.

6.3 Gas chromatograph: The unit must be equipped with a flame ionization detector.

6.4 Column: (20-ft x 1/8 in stainless steel) packed with 10% FFAP stationary phase on 100/120 mesh Supelcoport.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 Glass serum vials for desorption, 10 ml, molded to take a 13-mm Teflon-faced rubber septa and 13-mm aluminum seal.

6.6.1 Teflon-faced rubber septa, 13 mm.

6.6.2 Lacquered aluminum seals or caps, 13 mm.

6.6.3 Hand crimper, 13 mm, or equivalent for properly sealing the vial assembly.

Note: Glass stoppered containers are not adequate because of significant sample losses during desorption.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Gas-tight syringes: 10-ml and other convenient sizes for making standards.

6.9 Syringe: 5.0 or 10.0 ml capacity for adding the carbon disulfide used for desorption.

6.10 Syringe needle: 1-1/2 inch, 22 gauge or other convenient size.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 Dichloromonofluoromethane, 99%.

7.3 Pentane or other suitable internal standard. The appropriate solution of the internal standard is prepared in carbon disulfide.

7.4 Purified nitrogen.

7.5 Prepurified hydrogen.

7.6 Filtered compressed air.

8. Procedure

8.1 Cleaning of equipment: All glassware used for the laboratory analysis should be detergent-washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps: Each personal pump must be calibrated with a representative sampling tube series in the line assembled as noted in Section 6.2. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the two charcoal tubes to provide an opening at least one-half the internal diameter of the tube (3 mm). Prepare and assemble as described in Section 6.2. Connect the front 400-mg tube to the 200-mg backup tube with a short piece of tubing.

8.3.2 The tube containing 200 mg of charcoal is used as a backup and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube series should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the front charcoal tube.

8.3.5 A sample size of 3 liters is recommended. Sample at a flow rate of 0.05 to 0.01 liter per minute; a flow rate less than 0.01 liter per minute should not be used. The flow rate should be known with an accuracy of at least ±5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The front charcoal tube should be separated from the backup tube immediately after sampling. Both tubes must be labeled appropriately and capped with the supplied plastic caps. Under no circumstances should rubber caps be used.

8.3.8 With each batch of 10 samples, submit one set of tubes prepared as described in Section 6.2 and handled in the same manner as the sample tubes (break, seal and transport), except that no air is sampled through these tubes. These tubes should be labeled as the blank.

8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file and broken open. The glass wool is removed and discarded. The charcoal in the front tube is transferred to a 10-ml serum vial and the vial is sealed with the Teflon-faced septum and the aluminum cap with the aid of the crimper. The charcoal in the backup tube is transferred to another serum vial and handled in a similar manner.

8.4.2 Desorption of Sample. Immediately before desorption, lift up or remove the removable portion of the aluminum cap to expose a portion of the septum without destroying the seal.

Insert a syringe needle through the septum keeping the tip of the needle just below the surface of the septum in the vial. (This needle serves as a vent to prevent pressure buildup in the tube when carbon disulfide is added.) Add 5.0 ml of carbon disulfide or 5.0 ml of internal standard stock solution into the sample-containing vial with the aid of a syringe. After the carbon disulfide addition, remove the needle being used as a vent. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period.

If an automatic sample injector is used, the sample transfer should be carried out as follows to avoid sample loss. Seal an empty sample injector vial with the Teflon-lined septum and screw cap. Insert a syringe needle as above to serve as vent. Transfer the sample solution from the desorption vial into the automatic sample injector vial with the aid of a syringe. (A syringe needle can be used as vent in the desorption vial if necessary to avoid creating a partial vacuum in the desorption vial when withdrawing the sample solution.)

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (60 psig) Nitrogen carrier gas flow
2. 30 ml/min (25 psig) Hydrogen gas flow to detector
3. 300 ml/min (60 psig) Air flow to detector
4. 125°C injector temperature
5. 220°C manifold temperature (detector)
6. 55°C column temperature

A retention time of approximately 6.0 minutes is to be expected for the analyte using these conditions and the column recommended in Section 6.4. The dichloromonofluoromethane elutes after the carbon disulfide.

8.4.4 A 5-microliter aliquot of the sample solution is injected into the gas chromatograph. The solvent flush method or other suitable alternative such as an automatic sample injector can be used provided that duplicate injections of a solution agree well. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or someother suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine the percentage of the specific compound that is removed in the desorption process for the particular batch of charcoal used for sample collection and over the concentration range of interest.

8.5.2 Preparation of analytical samples for desorption efficiency determination. The desorption efficiency must be determined over the sample concentration range of interest. In order to determine the sample concentration range which should be tested, the samples are analyzed first and then the analytical samples are prepared based on the relative amount of dichloromonofluoromethane found in the samples. The desorption efficiency must be determined at least in duplicate for <u>each concentration level</u> of dichloromonofluoromethane found in the sample.

The analytical samples are prepared as follows: Activated charcoal equivalent to the amount in the front tube (400 mg) is sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples. Alternatively, unused commercially available charcoal tubes can be used. A known amount of dichloromonofluoromethane is slowly injected directly into the activated charcoal with a gas-tight syringe. If the commercially available charcoal tube (with the 400-mg front and 200-mg backup sections) is used, break off the seals at each end of the tube and slowly add the dichloromonofluoromethane into the front 400-mg section of the tube. Slow addition will allow adsorption of the dichloromonofluoromethane on the front section only. Immediately after addition of the dichloromonofluoromethane to the front section, remove the backup 200-mg section and transfer this 200-mg of charcoal into a separate serum vial, seal and code properly; this 200-mg charcoal can be analyzed later to test for complete adsorption of the dichloromonofluoromethane added to the front 400-mg section. The tube containing the 400-mg front section which has been spiked with dichloromonofluoromethane is capped with the plastic caps supplied with the commercial tubes.

For the validation studies conducted to determine the precision and accuracy of this method, six tubes at each of three concentration levels (0.5X, 1X and 2X of the OSHA standard) were prepared by adding an amount of dichloromonofluoromethane equivalent to that present in a 3-liter sample at the selected level. This required the addition of 1.5, 3 and 6 ml of dichloromonofluoromethane for the

0.5X, 1X and 2X of the OSHA standard level. The tubes were allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the analytical samples. A parallel blank tube was treated in the same manner except that no sample was added to it.

The procedure described can be used to prepare the analytical samples which are analyzed to determine desorption efficiency.

8.5.3 Desorption and analysis experiments are done on the analytical samples as described in Sections 8.4.2 to 8.4.5.

To prepare the standards, 5 ml of carbon disulfide is added to the 10-ml serum vial. (A 20-ml serum vial can be used to prepare the equivalent 2X calibration standard.) The vial is then sealed air-tight, using a Teflon-faced septum and aluminum cap with the aid of a crimper. Immediately before adding the dichloromonofluoromethane gas, withdraw an amount of air from the sealed vial equal to the volume of the gas to be added. An appropriate amount of dichloromonofluoromethane gas is bubbled slowly into the carbon disulfide, using a gas-tight syringe. The syringe needle should be immersed in the carbon disulfide during discharge of the dichloromonofluoromethane from the syringe. Standards should be prepared at the same time that the sample analysis is done and should be analyzed with the samples.

The weight (mg) of dichloromonofluoromethane in each standard and sample is calculated by the formula in Section 9.

If the internal standard method is used, prepare calibration standards by using 5.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$\text{D.E.} = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is expected to be dependent on the amount of dichloromonofluoromethane collected on the charcoal. Plot the desorption efficiency versus weight of dichloromonofluoromethane found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

9.1 Add 5.0 ml of carbon disulfide (or 5.0 ml of internal standard solution in carbon disulfide) to a 10-ml or 20-ml serum vial.

9.2 To avoid evaporation, immediately seal the vial air-tight with the Teflon-faced septum and aluminum cap and aided by the crimper.

9.3 Immediately before adding the dichloromonofluoromethane gas, withdraw an amount of air from the sealed vial equal to the volume of the gas to be adeed. An appropriate amount of dichloromonofluoromethane gas is bubbled slowly into the carbon disulfide, using a gas-tight syringe. The syringe needle should be immersed in the carbon disulfide during discharge of the dichloromonofluoromethane from the syringe.

9.4 Calculate the number of mg of dichloromonofluoromethane in the standard solution by using the equation:

$$mg = V \times \frac{MW}{22.4} \times \frac{273}{T + 273} \times \frac{P}{760}$$

where:

V = ml of dichloromonofluoromethane gas used,
MW = molecular weight, 102.9,
T = atmospheric temperature in °C when sample was prepared,
P = atmospheric pressure in mm of Hg when sample was prepared

9.5 The concentration of standards can be expressed in terms of mg dichloromonofluoromethane per 5 ml of carbon disulfide. This unit is convenient because samples are desorbed in 5 ml of carbon disulfide.

9.6 A series of standards, varying in concentration over the range of interest, is prepared as described above and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/5 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The analyte concentration in mg per 5.0 ml is plotted versus the area ratio of the analyte to that of the internal standard.

Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the the standard curve. No volume corrections are needed, because the standard curve is based on mg per 5.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

mg sample = mg found in front (400-mg) sample tube
mg blank = mg found in front (400-mg) blank tube

A similar procedure is followed for the backup tube.

10.3 Add the amounts present in the front and backup tubes for the same sample to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front tube. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (See Section 10.4) x 1000 (liters/cu m)}}{\text{Air Volume Sampled (liters)}}$$

10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg

MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31, 225 (1970).

11.2 Memoranda, Kenneth A. Busch, Chief, Statistical Services, DLCD, to Deputy Director, DLCD, dated 1/16/75, 11/8/74, subject: "Statistical Protocol for Analysis of Data from Contract CDC-99-74-45."

11.3 Backup Data Report for Dichloromonofluoromethane, prepared under NIOSH Contract No. 210-76-0123.

11.4 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes", September 15, 1972.

1,2-Dichloroethylene

Analyte:	1,2-Dichloroethylene	Method No.: S110
Matrix:	Air	Range: 475-1915 mg/cu m
OSHA Standard:	200 ppm (790 mg/cu m)	Precision ($\overline{CV}_T$): 0.052
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 4/11/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 475-1915 mg/cu m at an atmospheric temperature and pressure of 25°C and 745 mm Hg, using a 3-liter sample. Under the conditions of sample size (3 liters) the probable range of this method is 80-2370 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 6-mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentration of the analyte and other substances in the air. The first section of the charcoal tube was found to hold 10.3 mg of the analyte when a test atmosphere of 1913 mg/cu m of the analyte in dry air was sampled at 0.2 liter per minute. for 27 minutes; breakthrough occurred at this time, i.e., the

concentration of the analyte in the effluent was 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2.) If a particular atmosphere is suspected of containing a large number of contaminants, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments with toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 475 to 1915 mg/cu m was 0.052. This value corresponds to a standard deviation of 41.1 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 The average values obtained using the overall sampling and analytical method were 0.9% greater than the "true" value at the OSHA standard level.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more compounds suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined accurately (±5%) at the recommended flow rate (Reference 11.3).

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in. stainless steel) packed with 10% FFAP on 80/100 Chromosorb W-AW.

6.5 An electronic integrator or some other suitable method for determining peak size areas.

6.6 Two-milliliter glass sample containers with glass stoppers or Teflon®-lined caps. If an automatic sample injector is used, the sample injector vials can be used.

6.7 Microliter syringes: 10-µl, and other convenient sizes for making standards.

6.8 Pipets: 1.0-ml delivery type.

6.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Eluent: Carbon disulfide (chromatographic grade).

7.2 1,2-Dichloroethylene (reagent grade).

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a backup and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A maximum sample size of 3 liters is recommended. Sample at a flow of 0.20 liter per minute. The flow rate should be known with an accuracy of at least ±5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available the elevation should be recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the suspected compound should be submitted to the laboratory in glass containers with Teflon®-lined caps. These liquid bulk samples should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container or automatic sample injector vial. The separating section of foam is removed and discarded; the second section is transferred to another sample container or vial. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of the eluent is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. The sample vials should be capped as soon as the solvent is added to minimize volatilization.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (80 psig) nitrogen carrier gas flow.
2. 30 ml/min (50 psig) hydrogen gas flow to detector.
3. 300 ml/min (50 psig) air flow to detector.
4. 170°C injector temperature.
5. 210°C manifold temperature (detector).
6. 60°C column temperature.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-µl syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is

pulled back about 0.2 µl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-µl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 µl to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 µl in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique. In this case 2-µl injections are satisfactory.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below (see Section 9).

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided that the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.0-ml sample container. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. A known amount of 1,2-dichloroethylene is injected directly into the activated charcoal with a 10-µl syringe, and the container is capped. The amount injected is equivalent to that present in a 3-liter sample at the selected level.

At least six tubes at each of three levels (0.5X, 1X, and 2X the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These six tubes are referred to as the samples. A parallel blank tube

should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

The weight of analyte found in each tube is determined from the standard curve (Section 9). Desorption efficiency is determined by the following equation:

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus the weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/ml of carbon disulfide. To minimize error due to the volatility of the carbon disulfide, one can add 10 times the weight to 10 ml of the carbon disulfide. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentrations in mg/ml versus peak area.

The standard solutions should be analyzed at the same time that the sample analysis is done. This will minimize the effect variations of FID response.

10. Calculations

10.1 Read the weights, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/ml eluent and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

mg = mg sample - mg blank

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (Section 8.5.2) for the amount of analyte found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

10.5 The concentration of analyte in the air sampled can be expressed in mg per cu m, which is numerically equal to µg per liter of air

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm:

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White L. D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 "Documentation of NIOSH Validation Tests", Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract No. HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes, September 15, 1972".

Dichlorodifluoromethane*

Analyte:	Dichlorodifluoromethane	Method No.:	S111
Matrix:	Air	Range:	2940-10500 mg/cu m
OSHA Standard:	1000 ppm (4950 mg/cu m)	Precision ($\overline{CV}_T$):	0.064
Procedure:	Adsorption on charcoal, desorption with methylene chloride, GC	Validation Date:	9/30/76

1. Principle of the Method (Reference 11.1)

   1.1 A known volume of air is drawn through two tubes in series containing activated coconut charcoal to trap the gaseous dichlorodifluoromethane.

   1.2 Dichlorodifluoromethane is desorbed from the charcoal with methylene chloride, and the sample is analyzed by gas chromatography.

2. Range and Sensitivity

   2.1 This method was validated over the range of 2940-10500 mg/cu m at an atmospheric temperature of 25°C and atmospheric pressure of 760 mm Hg, using a 3-liter air sample. This maximum sample size is based on the capacity of the charcoal to collect vapors of dichlorodifluoromethane in air at 94% relative humidity. The method may be capable of measuring smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

   2.2 The upper limit of the range of the method depends on the adsorptive capacity of the charcoal. This capacity may vary with the concentrations of dichlorodifluoromethane and other substances in the air. Breakthrough is defined as the time that the effluent concentration from the collection tube (containing 600 mg of charcoal) reaches 5% of the concentration in the test gas mixture. The criterion for acceptance is that the volume of air that has passed through the tube at the time of breakthrough must be greater than 1.5 times the volume of air that would be passed through the tube for a sample at 2X the OSHA standard. At a temperature of 23°C and relative humidity of 12%, breakthrough occurred in 146 minutes when a test concentration of 9730 mg/cu m was sampled at a flow rate of 0.043 liter/minute. When the relative humidity was 94%, breakthrough occurred in 96 minutes when the test concentration was 10190 mg/cu m and the flow rate was 0.045 liter/minute.

*Refrigerant 12

3. Interferences

3.1 When interfering compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 Any compound that has the same retention time as dichlorodifluoromethane at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV_T}$) for the total analytical and sampling method in the range of 2940-10500 mg/cu m was 0.064. This value corresponds to a 317 mg/cu m standard deviation at the OSHA standard level. Statistical information can be found in Reference 11.2. Details of the test procedures are found in Reference 11.3.

4.2 No recovery correction should be applied to the final result in Section 10.6. On the average the concentrations obtained in the laboratory validation study at 0.5X, 1X, and 2X the OSHA standard level were 1.8% lower than the "true" concentrations for 18 samples. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, the method has no bias. The Coefficient of Variation is a good measure of the accuracy of the method since the recoveries and storage stability were good. Storage stability studies on samples collected from a test atmosphere at a concentration of 5650 mg/cu m indicate that collected samples are stable for at least 7 days.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those that occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

5.2 One disadvantage of the method is that the amount of sample that can be taken is limited by the number of milligrams that the tube will hold before overloading. When the amount of dichlorodifluoromethane found on the backup charcoal tube exceeds 6 mg, the probability of sample loss exists.

5.3 The precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 Personal sampling pump: A calibrated personal sampling pump whose

flow rate can be determined within 5% at the recommended flow rate.

6.2 Charcoal tubes: Two charcoal tubes are used in this method. One charcoal tube is used to collect the samples, and a smaller charcoal tube is used as a backup. The charcoal tubes are connected in series with Tygon tubing. The larger charcoal tube is a glass tube, approximately 10-cm long with a 8-mm O.D. and a 6-mm I.D. It has two sections of 20/40 mesh activated coconut charcoal separated by a 2-mm portion of urethane foam. The front section contains 400 mg of charcoal, the back section 200 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than 25 mm of mercury at a flow rate of 0.05 liter per minute. The smaller charcoal tube is 7-cm long with a 6-mm O.D. and a 4-mm I.D. The smaller charcoal tube contains 100 mg of charcoal in the front section and 50 mg in the backup section.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (4-ft long x 1/4-in O.D. stainless steel) packed with 80/100 mesh Chromosorb 102.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 Microliter syringes: 10-microliter for injection of samples into the gas chromatograph.

6.7 Gas tight syringes: 1, 2, 5, and 10-ml sizes for preparing standards.

6.8 Pipets: 20.0-ml delivery pipets.

6.9 Serum bottles: 30-ml glass bottles with 20-mm O.D. mouth.
Septa: 20-mm rubber septa with Teflon lining.
Aluminum tear-away seals to fit serum bottles.

6.10 Hand crimper for sealing septa to serum bottles.

6.11 Stopwatch.

6.12 Manometer.

7. Reagents

7.1 Methylene chloride, chromatographic quality.

7.2 Dichlorodifluoromethane, 99% pure.

7.3 Nitrogen, purified.

7.4 Hydrogen, prepurified.

7.5 Air, filtered, compressed.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed, thoroughly rinsed with tap water and distilled water, and dried.

8.2 Calibration of Sampling Pumps. Each personal sampling pump must be calibrated with representative charcoal tubes in the line to minimize errors associated with uncertainties in the volume sampled. (Reference 11.4)

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the two charcoal tubes to provide an opening at least one-half the internal diameter of the tube.

8.3.2 Connect the larger charcoal tube in series with the smaller charcoal tube by connecting the backup section of the large charcoal tube to the front section of the small charcoal tube with Tygon tubing. The shortest length of tubing compatible with maintaining a leak-free connection should be used. The smaller charcoal tube is used as a backup and should be positioned nearer the pump. Air should flow through the large charcoal tube before entering the small charcoal tube.

8.3.3 Both charcoal tubes should be vertical during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tubes.

8.3.5 A maximum sample size of 3 liters is recommended. Sample at a flow rate between 0.01 and 0.05 liter per minute. The flow rate should be known with an accuracy of 5% or better and should be recorded. Also record collection time and the type of sampling pump used.

8.3.6 The temperature, pressure, and relative humidity of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The charcoal tubes should be separated and capped individually with plastic caps immediately after sampling. Under no circumstances should rubber caps be used. Each set of tubes should be marked to identify the large charcoal tube with the corresponding backup charcoal tube.

8.3.8 With each batch of ten samples, submit one set of tubes (a larger charcoal tube and a smaller backup tube) from the same lot of tubes used for sample collection. These tubes must be subjected to exactly the same handling as the samples except that no air is drawn through them. These tubes should be labeled as the blanks.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.4 Analysis of Samples

8.4.1 Desorption of Dichlorodifluoromethane. Pipet 20 ml of methylene chloride into the 30-ml serum bottle. Remove the plastic caps from both ends of the larger charcoal tube. Remove the plug of urethane foam from the outlet end of the tube. Transfer the 200-mg portion of charcoal to the serum bottle. Next, remove the glass wool plug from the inlet end of the tube and transfer the 400-mg section of charcoal to the same bottle. Place the Teflon-lined septum over the mouth of the bottle and seal the aluminum seal on with the crimper. It is important that the transfer of the charcoal be carried out as quickly as possible once the methylene chloride has been added to the bottle. The backup charcoal tube should be handled in a similar manner, using a separate serum bottle. The two samples are analyzed separately.

8.4.2 Gently shake the sample. The extract is now ready for analysis. Analyses should be completed within one day after the dichlorodifluoromethane is desorbed. Prepare standards as in Section 8.5.3. Fresh standards should be prepared daily.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psig) nitrogen carrier gas flow rate
2. 65 ml/min (24 psig) hydrogen gas flow rate to detector
3. 500 ml/min (50 psig) air flow rate to detector
4. 200°C injector temperature
5. 260°C detector temperature
6. 110°C column temperature

A retention time of approximately 2.5 minutes is to be expected for the analyte under these conditions and using the column recommended in Section 6.4. The methylene chloride will elute from the column after the dichlorodifluoromethane.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or evaporation of solvent within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the

volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliter to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. It is not advisable to use an automatic sample injector for dichlorodifluoromethane in methylene chloride.

8.4.5 The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine the fraction of the specific compound that is removed in the desorption process for a particular batch of charcoal.

8.5.2 Known amounts of dichlorodifluoromethane are sorbed from the gas phase on the charcoal in the tubes as described below:

The apparatus to be used for spiking charcoal with known amounts of dichlorodifluoromethane consists of a union tee connected to a source of purified nitrogen, a charcoal tube, and a septum for introducing dichlorodifluoromethane from a gas tight syringe. A known amount of dichlorodifluoromethane is injected through the septum where nitrogen at a flow rate of approximately 20 ml/min carries dichlorodifluoromethane into the charcoal tube. The nitrogen is allowed to flow through the tube for an additional 30 seconds after discharge of the contents of the syringe through the septum. The charcoal tube is capped with plastic caps.

The amount sorbed is equivalent to that present in a 3-liter air sample at the selected level. This requires 1.5, 3, and 6 ml of dichlorodifluoromethane for 0.5X, 1X, and 2X the OSHA standard level, respectively. The atmospheric temperature, pressure, and relative humidity at which the tubes are prepared should be recorded.

Six tubes at each of the three levels are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of dichlorodifluoromethane onto the charcoal in the tube. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it.

8.5.3 Desorption and analysis experiments are done on the contents of the larger charcoal tube as described in Section 8.4.1.

In preparation of the standards, 20 ml of methylene chloride is added to a 30-ml serum bottle. The bottle is then sealed using a Teflon-lined septum and aluminum seal. An appropriate amount of dichlorodifluoromethane gas is bubbled slowly into the methylene chloride, using a gas tight syringe.

The syringe needle should be immersed in the methylene chloride during discharge of dichlorodifluoromethane from the syringe. The bottle should be shaken gently after removal of the syringe needle. Standards should be prepared at the same time that the sample analysis is done, and analyzed with the samples.

The weight (mg) of dichlorodifluoromethane in each standard and sample is calculated by the formula in Section 9.

The desorption efficiency (DE) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$DE = \frac{\text{Average weight recovered (mg)}}{\text{Weight added (mg)}}$$

The desorption efficiency is dependent on the amount of dichlorodifluoromethane collected on the charcoal. Plot the desorption efficiency versus weight of dichlorodifluoromethane found. This curve is used to correct for losses, as described in Section 10.4.

9. Calibration and Standards

A series of standards, varying in concentration over the range of interest, is prepared as described in Section 8.5.3 and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/20 ml versus peak area.

It is convenient to express concentration of standards in terms of mg/20 ml methylene chloride, because samples are desorbed in this amount of methylene chloride. The number of mg in the standard is calculated as follows:

$$mg = V \times \frac{M.W.}{24.45} \times \frac{298}{T + 273} \times \frac{P}{760}$$

where:

V	=	ml of dichlorodifluoromethane used to prepare the standard
T	=	temperature (°C) at which the sample was prepared
P	=	pressure (mm Hg) at which the sample was prepared
24.45	=	molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	=	molecular weight of dichlorodifluoromethane
298	=	standard temperature (°K)
760	=	standard pressure (mm Hg)

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed because the standard curve is based on mg/20 ml methylene chloride and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

mg sample = mg found in both sections of sample tube

mg blank = mg found in both sections of blank tube

A similar procedure is followed for the backup tubes.

10.3 Add the weights found in the front and backup tubes to get the total weight of the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.3) for the amount found in the first tube. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{DE}}$$

10.5 For personal sampling pumps with rotameters only, the following correction should be made.

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

f = flow rate sampled

t = sampling time

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 dichlorodifluoromethane in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liters/cu m)}}{\text{Corrected air volume sampled (liters) (Section 10.5)}}$$

10.7 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	=	pressure (mm Hg) of air sampled
T	=	temperature (°C) of air sampled
24.45	=	molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	=	molecular weight (g/mole) of dichlorodifluoromethane
760	=	standard pressure (mm Hg)
298	=	standard temperature (°K)

11. References

11.1 White, L. D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31, 225, (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

11.3 Backup Data Report for Dichlorodifluoromethane, prepared under NIOSH Contract No. 210-76-0123.

11.4 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes, September 15, 1972.

Chloroprene*

Analyte:	Chloroprene	Method No.:	S112
Matrix:	Air	Range:	44-174 mg/cu m
OSHA Standard:	25 ppm (90 mg/cu m) - skin	Precision ($\overline{CV}_T$):	0.071
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	10/29/76

1. Principle of the Method (Reference 11.1)

   1.1 A known volume of air is drawn through a charcoal tube containing activated coconut charcoal to trap chloroprene vapors.

   1.2 Chloroprene is desorbed from the charcoal with carbon disulfide, and the sample is analyzed by gas chromatography.

2. Range and Sensitivity

   2.1 This method was validated over the range of 44.2-173.9 mg/cu m at an atmospheric temperature of 21°C and atmospheric pressure of 760 mm Hg, using a 3-liter sample. This maximum sample size is based on the capacity of the charcoal to collect vapors of chloroprene in air. The method may be capable of measuring smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

   2.2 The upper limit of the range of the method depends on the adsorptive capacity of the charcoal. This capacity may vary with the concentrations of chloroprene and other substances in the air. Breakthrough is defined as the time that the effluent concentration from the collection tube (containing 100 mg of charcoal) reaches 5% of the concentration in the test gas mixture. The criterion for acceptance is that the volume of air that has passed through the tube at the time of breakthrough must be greater than 1.5 times the volume of air that would be passed through the tube for a sample at 2X the OSHA

*2-Chloro-1,3-butadiene

standard level. Breakthrough did not occur after sampling for four hours at an average sampling rate of 0.045 liter/minute and relative humidity of 91% and temperature of 25°C. The breakthrough test was conducted at a concentration of 197 mg/cu m.

3. Interferences

3.1 When other compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 Any compound that has the same retention time as chloroprene at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 44.2-173.9 mg/cu m was 0.071. This value corresponds to a 6.4 mg/cu m standard deviation at the OSHA standard level. Statistical information can be found in Reference 11.2. Details of the test procedures are found in Reference 11.3.

4.2 No recovery correction should be applied to the final result in Section 10.6. On the average the concentrations obtained in the laboratory validation study at 0.5X, 1X, and 2X the OSHA standard level were 1.2% lower than the "true" concentrations for 18 samples. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, the method has no bias. The Coefficient of Variation is a good measure of the accuracy of the method since the recoveries and storage stability were good. Storage stability studies on samples collected from a test atmosphere at a concentration of 86.0 mg/cu m indicate that collected samples are stable for at least 7 days.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those that occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

5.2 One disadvantage of the method is that the amount of sample that can be taken is limited by the number of milligrams that the tube will hold before overloading. When the amount of chloroprene found on the backup section of the charcoal tube exceeds 25% of that found on the front section, the probability of sample loss exists.

5.3 The precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 Personal Sampling Pump: A calibrated personal sampling pump whose flow rate can be determined within 5% at the recommended flow rate.

6.2 Charcoal tubes. Glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing two sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than 25 mm of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (4-ft long x 1/4-in O.D. stainless steel) packed with 50/80 mesh Porapak Q.

6.5 An electronic integrator or some other suitable method of determining peak areas.

6.6 Sample Containers: Two-milliliter glass sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the sample injector vials can be used.

6.7 Microliter syringes: 10-microliter and other convenient sizes for making standards.

6.8 Pipets: Delivery type, 1.0-ml and other convenient sizes.

6.9 Volumetric flasks: 10-ml and other convenient sizes for making standard solutions.

6.10 Micro-distillation apparatus with provision for vacuum fractional distillation of pure chloroprene for making standards.

6.11 Stopwatch.

6.12 Manometer.

7. Reagents

7.1 Carbon Disulfide, chromatographic quality.

7.2 Chloroprene, reagent grade in xylene solution.

7.3 n-Pentane, reagent grade.

7.4 n-Hexane, reagent grade.

7.5 Nitrogen, purified.

7.6 Hydrogen, prepurified.

7.7 Air, filtered, compressed.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed, thoroughly rinsed with tap water and distilled water, and dried.

8.2 Calibration of Sampling Pumps. Each personal sampling pump must be calibrated with a representative charcoal tube in the line to minimize errors associated with uncertainties in the volume sampled. (Reference 11.4)

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the charcoal tube to provide an opening at least one-half the internal diameter of the tube. All tubes must be from the same manufacturer's lot.

8.3.2 The smaller section of charcoal is used as a backup and should be positioned nearer the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A maximum sample size of 3 liters is recommended. Sample at a flow rate between 0.01 and 0.05 liter per minute. The collection time and the flow rate with an accuracy of 5% or better should be recorded. Do not sample at a flow rate less than 0.010 liter per minute.

8.3.6 The temperature, pressure, and relative humidity of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The charcoal tube should be capped with plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 With each batch of ten samples, submit one tube from the same lot of tubes used for sample collection. This tube must be subjected to exactly the same handling as the samples except that no air is drawn through it. This tube should be labeled as the blank.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container or automatic sample injector vial. The separating section of foam is removed and discarded; the second section is transferred to another sample container vial. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicated that this is adequate if the sample is agitated occasionally during this period. The sample vials should be capped as soon as the solvent is added to minimize volatilization.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 50 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 200°C injector temperature
5. 250°C detector manifold temperature
6. 125°C column temperature

A retention time of approximately 10 minutes is to be expected for chloroprene under these conditions and using

the column recommended in Section 6.4. The carbon disulfide will elute from the column before the chloroprene.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or evaporation of solvent within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

8.4.5 The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine the fraction of the specific compound that is removed in the desorption process for a particular batch of charcoal.

8.5.2 Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 64-mm, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of freshly prepared pentane solution of chloroprene

(Section 9) containing 67.9 μg/μl is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample vials, capped with Teflon-faced septa, may be used in place of the glass tubes. The amount injected is equivalent to that present in a 3-liter air sample at the selected level. It is not practical to inject the neat liquid directly onto the charcoal, because the amounts to be added would be too small to measure accurately.

Six tubes at each of three levels (0.5X, 1X, and 2X the OSHA standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the chloroprene onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of chloroprene into 1.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples. These standards are used to confirm the calibration of the gas chromatograph.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight recovered (mg)}}{\text{Weight added (mg)}}$$

The desorption efficiency is dependent on the amount of chloroprene collected on the charcoal. Plot the desorption efficiency versus weight of chloroprene found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

A series of standards, varying in concentration over the range is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/1.0 ml versus peak area. Note: Since no internal standard is used in this method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

Calculations are based on a molecular weight of 88.54 and a density of 0.958 for pure chloroprene and 25 ppm (90.53 mg/cu m) for the OSHA standard. Since chloroprene polymerizes readily, special precautions must be taken in the preparation and storage of standards.

9.1 Stock Standard Solution. Pure chloroprene is obtained by fractionally distilling commercially available 50% chloroprene in xylene solution under vacuum (Note 1). A stock standard solution is prepared from freshly distilled chloroprene. Exactly 1.0 ml (0.958 g at 20°C) of pure chloroprene is delivered from a delivery type pipet under the surface of pentane in a partially filled 10-ml volumetric flask and then the solution is made up to exactly 10 ml with pentane. This solution may be stable for one day or even longer if stored at -15°C (Note 2).

9.2 Working Standard Solutions. Aliquots of the stock standard solution are delivered below the surface of carbon disulfide in partially filled 10-ml volumetric flasks. Each solution is diluted to exactly 10 ml with carbon disulfide and carefully mixed. A calibration curve should be prepared for the concentration range representing 0.1 to 3 times the OSHA standard.

9.3 Solutions for Desorption Efficiency Tests. Exactly 0.71 ml of pure chloroprene or an appropriate aliquot of the stock standard solution is delivered from appropriate pipets below the surface of pentane in a partially filled 10-ml volumetric flask and the solution is made up to exactly 10 ml with pentane. Appropriate aliquots are used for desorption efficiency tests. For a 3-liter air sample, aliquots of 2, 4, and 8 microliters represent 0.5X, 1X, and 2X the OSHA standard.

Note 1. The chloroprene used in the laboratory validation study was distilled at 31°C at a pressure of 354 mm Hg.

Note 2. Since chloroprene tends to polymerize, even in solutions, it may be necessary to monitor its concentration in the standard solutions.

Standards should be prepared immediately from freshly distilled chloroprene and stored at -15°C when not in use. A reference standard of hexane in carbon disulfide in a sealed vial with septum cap can be used to monitor the stability of the chloroprene standards. The concentration of the hexane reference standard should be chosen so that its flame ionization detector response is close to that of the chloroprene standards. When the ratio of the concentration of chloroprene standards to reference standard appears to decrease, prepare new standards.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed because the standard curve is based on mg/1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to determine the total weight of the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.3) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{DE}$$

10.5 For personal sampling pumps with rotameters only, the following correction should be made.

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

f = flow rate sampled
t = sampling time
P_1 = pressure during calibration of sampling pump (mm Hg)
P_2 = pressure of air sampled (mm Hg)
T_1 = temperature during calibration of sampling pump (°K)
T_2 = temperature of air sampled (°K)

10.6 The concentration of chloroprene in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liters/cu m)}}{\text{Corrected air volume sampled (liters) (Section 10.5)}}$$

10.7 Another method of expressing concentration is ppm.

$$ppm = \text{mg/cu m} \times \frac{24.45}{M.W.} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
M.W. = molecular weight (g/mole) of chloroprene
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L. D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31, 225, (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

11.3 Backup Data Report for Chloroprene, prepared under NIOSH Contract No. 210-76-0123.

11.4 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Chlorobromomethane

Analyte:	Chlorobromomethane	Method No.: S113
Matrix:	Air	Range: 640-2655 mg/cu m
OSHA Standard:	200 ppm (1050 mg/cu m)	Precision ($\overline{CV}_T$): 0.061
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 4/11/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 640-2655 mg/cu m at an atmospheric temperature and pressure of 25°C and 755 mm Hg, using a 5-liter sample. Under the conditions of sample size (5 liters) the probable range of this method is 105-3150 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 10-mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentration of the analyte and other substances in the air. The first section of the charcoal tube was found to hold 18.5 mg of the analyte when a test atmosphere of 2315 mg/cu m of the analyte in dry air was sampled at 0.2 liter per minute for 40 minutes; breakthrough occurred at this time, i.e., the

concentration of the analyte in the effluent was 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2.) If a particular atmosphere is suspected of containing a large amount of contaminants, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments with toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 640 to 2655 mg/cu m was 0.061. This value corresponds to a standard deviation of 54.0 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 The average values obtained using the overall sampling and analytical method were 2.2% greater than the "true" value at the OSHA standard level.

4.3 The above data are based on validation experiments using the internal standard method. (Reference 11.2)

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more compounds suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined accurately (±5%) at the recommended flow rate (Reference 11.3).

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in. stainless steel) packed with 10% FFAP on 80/100 Chromosorb W-AW.

6.5 An electronic integrator or some other suitable method for determining peak size areas.

6.6 Two-milliliter glass sample containers with glass stoppers or Teflon®-lined caps. If an automatic sample injector is used, the sample injector vials can be used.

6.7 Microliter syringes: 10-µl, and other convenient sizes for making standards.

6.8 Pipets: 1.0-ml delivery type.

6.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Eluent: Carbon disulfide (chromatographic grade).

7.2 Chlorobromomethane (reagent grade).

7.3 Internal Standard: n-Undecane (99+%) or other suitable standard.

7.4 Purified nitrogen.

7.5 Prepurified hydrogen.

7.6 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a backup and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A maximum sample size of 5 liters is recommended. Sample at a flow of 0.20 liter per minute. The flow rate should be known with an accuracy of at least ±5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available the elevation should be recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the suspected compound should be submitted to the laboratory in glass containers with Teflon®-lined caps. These liquid bulk samples should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container or automatic sample injector vial. The separating section of foam is removed and discarded; the second section is transferred to another sample container or vial. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of the eluent is pipetted into each sample container. For the internal standard method a 0.2 percent solution of internal standard in the eluent is used. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. The sample vials should be capped as soon as the solvent is added to minimize volatilization.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (80 psig) nitrogen carrier gas flow.
2. 30 ml/min (50 psig) hydrogen gas flow to detector.
3. 300 ml/min (50 psig) air flow to detector.
4. 170°C injector temperature.
5. 210°C manifold temperature (detector).
6. 80°C column temperature.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-µl syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The

needle is removed from the solvent, and the plunger is pulled back about 0.2 µl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-µl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 µl to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 µl in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique. In this case 2-µl injections are satisfactory.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below (see Section 9).

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided that the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.0-ml sample container. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. A known amount of chlorobromomethane is injected directly into the activated charcoal with a 10-µl syringe, and the container is capped. The amount injected is equivalent to that present in a 5-liter sample at the selected level.

At least six tubes at each of three levels (0.5X, 1X, and 2X the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These six tubes are referred to as the samples. A parallel blank tube

should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

The weight of analyte found in each tube is determined from the standard curve (Section 9). Desorption efficiency is determined by the following equation:

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus the weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/ml of carbon disulfide. To minimize error due to the volatility of the carbon disulfide, one can add 10 times the weight to 10 ml of the carbon disulfide. (For the internal standard method use carbon disulfide containing 0.2 percent of the internal standard.) A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentrations in mg/ml versus peak area. In the case of the internal standard method plot the concentration versus the ratio of peak area of analyte to peak area of internal standard.

Note: Whether the absolute area or internal standard method is used standard solutions should be analyzed at the same time that the sample analysis is done. This will minimize the effect variations of FID response.

10. Calculations

10.1 Read the weights, in mg, corresponding to each peak area (area ratio in case of the internal standard method) from the standard curve. No volume corrections are needed, because the standard curve is based on mg/ml eluent and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

mg = mg sample - mg blank

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (Section 8.5.2) for the amount of analyte found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

10.5 The concentration of analyte in the air sampled can be expressed in mg per cu m, which is numerically equal to µg per liter of air

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm:

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm H
MW = molecular weight (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White L. D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 "Documentation of NIOSH Validation Tests", Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract No. HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes, September 15, 1972".

Bromoform

Analyte:	Bromoform	Method No.:	S114
Matrix:	Air	Range:	3-10 mg/cu m
OSHA Standard:	0.5 ppm (5 mg/cu m)	Precision ($\overline{CV}_T$):	0.071
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	4/11/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 3-10 mg/cu m at an atmospheric temperature and pressure of 25 C and 749 mm Hg, using a 10-liter sample. Under the conditions of sample size (10 liters) the probable range of this method is 0.5-15 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 0.1-mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentration of the analyte and other substances in the air. The first section of the charcoal tube was found to hold at least 0.5 mg of the analyte when a test atmosphere of 9.7 mg/cu m of the analyte in dry air was sampled at 0.2 liters per minute for 4 hours. Breakthrough did not occur at this time;

the concentration of the analyte in the effluent was less than 2% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2.) If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments with toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 3 to 10 mg/cu m was 0.071. This value corresponds to a standard deviation of 0.35 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 The average values obtained using the overall sampling and analytical method were 1.2% lower than the "true" value at the OSHA standard level.

4.3 The above data are based on validation experiments using the internal standard method. (Reference 11.2)

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more compounds suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined accurately (±5%) at the recommended flow rate, (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600 C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in. stainless steel) packed with 10% FFAP on 80/100 Chromosorb W-AW.

6.5 An electronic integrator or some other suitable method for determining peak size areas.

6.6 Two-milliliter glass sample containers with glass stoppers or Teflon®-lined caps. If an automatic sample injector is used, the sample injector vials can be used.

6.7 Microliter syringes: 10-µl, and other convenient sizes for making standards.

6.8 Pipets: 1.0-ml delivery type.

6.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Eluent: Carbon disulfide (chromatographic grade).

7.2 Bromoform (chromatographic grade).

7.3 Internal Standard: n-Pentadecane (99+%) or other suitable standard.

7.4 n-Hexane (reagent grade).

7.5 Purified nitrogen.

7.6 Prepurified hydrogen.

7.7 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a flow of 0.20 liters per minute. The flow rate should be known with an accuracy of at least ±5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available the elevation should be recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the suspected compound should be submitted to the laboratory in glass containers with Teflon®-lined caps. These liquid bulk samples should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container or automatic sample injector vial. The separating section of foam is removed and discarded; the second section is transferred to another sample container or vial. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of the eluent is pipetted into each sample container. For the internal standard method a 0.2 percent solution of internal standard in the eluent is used. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. The sample vials should be capped as soon as the solvent is added to minimize volatilization.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (80 psig) nitrogen carrier gas flow.
2. 30 ml/min (50 psig) hydrogen gas flow to detector.
3. 300 ml/min (50 psig) air flow to detector.
4. 170 C injector temperature.
5. 210 C manifold temperature (detector).
6. 130 C column temperature.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-µl syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 µl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-µl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 µl to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 µl in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique. In this case 2-µl injections are satisfactory.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below (see Section 9).

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided that the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.0-ml sample container. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. A

12.5 mg/ml stock solution of the analyte in n-hexane is prepared. A known amount of this solution is injected directly into the activated charcoal with a 10-µl syringe, and the container is capped. The amount injected is equivalent to that present in a 10-liter sample at the selected level. It is not practical to inject the neat liquid directly because the amounts to be added would be too small to measure accurately.

At least six tubes at each of three levels (0.5X, 1X, and 2X the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These six tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

The weight of analyte found in each tube is determined from the standard curve (Section 9). Desorption efficiency is determined by the following equation:

$$\text{D.E.} = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus the weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/ml of carbon disulfide. To minimize error due to the volatility of the carbon disulfide, one can add 10 times the weight to 10 ml of the carbon disulfide. (For the internal standard method use carbon disulfide containing 0.2 percent of the internal standard.) A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentrations in mg/ml versus peak area. In the case of the internal standard method plot the concentration versus the ratio of peak area of analyte to peak area of internal standard.

Note: Whether the absolute area or internal standard method is used standard solutions should be analyzed at the same time that the sample analysis is done. This will minimize the effect variations of FID response.

10. Calculations

10.1 Read the weights, in mg, corresponding to each peak area (area ratio in case of the internal standard method) from the standard curve. No volume corrections are needed, because the standard curve is based on mg/ml eluent and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

mg = mg sample - mg blank

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (Section 8.5.2) for the amount of analyte found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

10.5 The concentration of analyte in the air sampled can be expressed in mg per cu m, which is numerically equal to µg per liter of air

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm:

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (C) of air sampled
24.45 = molar volume (liter/mole) at 25 C and 760 mm Hg
MW = molecular weight (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (K)

11. References

11.1 White L. D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 "Documentation of NIOSH Validation Tests", Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract No. HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes, September 15, 1972".

Benzyl Chloride

Analyte:	Benzyl Chloride	Method No.:	S115
Matrix:	Air	Range:	2-8 mg/cu m
OSHA Standard:	1 ppm (5 mg/cu m)	Precision ($\overline{CV}_T$):	0.096
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	4/11/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 2-8 mg/cu m at an atmospheric temperature and pressure of 25°C and 744 mm Hg, using a 10-liter sample. Under the conditions of sample size (10 liters) the probable range of this method is 0.5-15 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a .05-mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of the analyte and other substances in the air. The first section of the charcoal tube was found to hold at least .39 mg of the analyte when a test atmosphere of 8.1 mg/cu m of the analyte in dry air was sampled at 0.2 liter per minute for 4 hours. Breakthrough did not occur at this time; the concentration of the analyte in the effluent was less than 2% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2.) If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great the condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments with toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 2-8 mg/cu m was 0.096. This value corresponds to a standard deviation of 0.48 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 The average values obtained using the overall sampling and analytical method were 6.3% less than the "true" value at the OSHA standard level.

4.3 The above data are based on validation experiments using the internal standard method. (Reference 11.2.)

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more compounds suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained

for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined accurately (±5%) at the recommended flow rate (Reference 11.3).

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than 1 inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in. stainless steel) packed with 10% FFAP on 80/100 Chromosorb W-AW.

6.5 An electronic integrator or some other suitable method of determining peak size areas.

6.6 Two-milliliter glass sample containers with glass stoppers or Teflon®-lined caps. If an automatic sample injector is used, the sample injector vials can be used.

6.7 Microliter syringes: 10-µl, and other convenient sizes for making standards.

6.8 Pipets: 1.0-ml delivery type.

6.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Eluent: Carbon disulfide (chromatographic grade).

7.2 Benzyl chloride (reagent grade).

7.3 Internal Standard: n-Heptadecane (99+%) or other suitable standard.

7.4 n-Heptane (reagent grade).

7.5 Purified nitrogen.

7.6 Prepurified hydrogen.

7.7 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples.

8.3.1 Immediately before sampling, break the ends of each tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a backup and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a flow of 0.20 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm$5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If the pressure reading is not available the elevation should be recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the suspected compound should be submitted to the laboratory in glass containers with Teflon®-lined caps. These liquid bulk samples should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container or automatic sample injector vial. The separating section of foam is removed and discarded; the second section is transferred to another sample container or vial. These 2 sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of the eluent is pipetted into each sample container. For the internal standard method a 0.2 percent solution of internal standard in carbon disulfide is used. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. The sample vials should be capped as soon as the solvent is added to minimize volatilization.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (80 psig) nitrogen carrier gas flow.
2. 30 ml/min (50 psig) hydrogen gas flow to detector.
3. 300 ml/min (50 psig) air flow to detector.
4. 170°C injector temperature.
5. 210°C manifold temperature (detector).
6. 160°C column temperature.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-µl syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and

reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 µl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-µl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 µl to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 µl in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique. In this case 2-µl injections are satisfactory.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below (see Section 9).

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided that the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.0-ml sample container. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. A 12.5 mg/ml stock solution of the analyte in n-heptane is prepared. A known amount of this solution is injected directly into the activated charcoal with a 10-µl syringe, and the container is capped. The amount injected is equivalent ot that present in a 10-liter sample at the selected level. It is not practical to inject the neat liquid directly because the amounts to be added would be too small to measure accurately.

At least 6 tubes at each of 3 levels (0.5X, 1X, and 2X the standard) are prepared in this manner and allowed to stand overnight to assure complete adsorption of the analyte onto the charcoal. These 6 tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

The weight of analyte found in each tube is determined from the standard curve (Section 9). Desorption efficiency is determined by the following equation:

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus the weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/ml of carbon disulfide. (For the internal standard method use carbon disulfide containing 0.2 percent of the internal standard.) A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentrations in mg/ml versus peak area. In the case of the internal standard method plot the concentration versus the ratio of peak area of analyte to peak area of internal standard.

Note: Whether the absolute area or internal standard method is used standard solutions should be analyzed at the same time that the sample analysis is done. This will minimize the effect variations of FID response.

10. Calculations

10.1 Read the weights, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/ml eluent and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

mg = mg sample - mg blank

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (Section 8.5.2) for the amount of analyte found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

10.5 The concentration of analyte in the air sampled can be expressed in mg per cu m, which is numerically equal to µg per liter of air

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm:

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L. D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 "Documentation of NIOSH Validation Tests", Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract No. HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes", September 15, 1972.

Allyl Chloride

Analyte:	Allyl Chloride	Method No.: S116
Matrix:	Air	Range: 1.80-7.19 mg/cu m
OSHA Standard:	1 ppm (3 mg/cu m)	Precision ($\overline{CV}_T$): 0.071
Procedure:	Adsorption on charcoal, desorption with benzene, GC	Validation Date: 5/9/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with benzene.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 1.80-7.19 mg/cu m at an atmospheric temperature and pressure of 24°C and 759 mm Hg, using a 100-liter sample. Under the conditions of sample size (100 liters) the probable useful range of this method is 0.5-10 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 1-mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of allyl chloride and other substances in the air. The first section of the charcoal tube was found to hold 1.5 mg of allyl chloride when a test atmosphere containing 7.56 mg/cu m of allyl chloride in air was sample at 0.945 liter

per minute for 210 minutes. At this time 3% of the total was found on the backup section of the charcoal tube. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample. Since benzene is used rather than carbon disulfide to desorb the allyl chloride from the charcoal, it would not be possible to measure benzene in the sample with this desorbing solvent. If it is suspected that benzene is present, a separate sample should be collected for benzene analysis.

3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 1.80-7.19 mg/cu m was 0.071. This value corresponds to a 0.21 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 0.3% lower than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate.

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (4-ft x 1/4-in stainless steel) packed with 50/80 mesh Porapak, Type Q.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 1.0-ml delivery pipets.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality benzene.

7.2 Allyl chloride, reagent grade.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A maximum sample size of 100 liters is recommended. Sample at a flow of 1.0 liter per minute or less. The flow should be known with an accuracy of at least $\pm$5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of benzene is pipetted into each sample container. (All work with benzene should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 185°C injector temperature
5. 250°C manifold temperature (detector)
6. 160°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush method.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of hexane solution containing 7.5 mg/ml is injected directly into the charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample injector vials, capped with Teflon-faced septa, may be used in place of the glass tubes.

The amount injected is equivalent to that present in a 100-liter air sample at the selected level. Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1.0 ml of benzene with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight recovered (mg)}}{\text{Weight added (mg)}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/1.0 ml benzene, because samples are desorbed in this amount of benzene. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/1.0 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/1.0 ml benzene and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to get the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
M.W. = molecular weight (g/mole) of analyte
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Acetylene Tetrabromide

Analyte:	Acetylene Tetrabromide	Method No.: S117
Matrix:	Air	Range: 7.04-28.1 mg/cu m
OSHA Standard:	1 ppm (14 mg/cu m)	Precision ($\overline{CV}_T$): 0.096
Procedure:	Adsorption on silica gel, desorption with tetrahydrofuran, GC	Validation Date: 5/9/75

1. Principle of the Method

1.1 A known volume of air is drawn through a silica gel tube to trap the organic vapors present.

1.2 The silica gel in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with tetrahydrofuran.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 7.04-28.1 mg/cu m at an atmospheric temperature and pressure of 22°C and 760 mm Hg, using a 100-liter sample. Under the conditions of sample size (100 liters) the probable useful range of this method is 1.5-40 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 4-mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the silica gel tube. This capacity varies with the concentrations of the analyte and other substances in the air. The first section of the silica gel tube was found to hold at least 6.32 mg of analyte when a test atmosphere containing

28.1 mg/cu m of analyte in air was sampled at 0.91 liter per minute for 247 minutes. (The silica gel tube consists of two sections of silica gel separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interferences

3.1 Silica gel has a high affinity for water, so organic vapors will not be trapped efficiently in the presence of a high relative humidity. This effect may be important even though there is no visual evidence of condensed water in the silica gel tube.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample. Since tetrahydrofuran is used rather than carbon disulfide to desorb the analyte from the silica gel, it is not possible to measure tetrahydrofuran in the sample with this desorbing solvent. If it is suspected that tetrahydrofuran is present, a separate sample should be collected for tetrahydrofuran analysis.

3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 7.04-28.1 mg/cu m was 0.096. This value corresponds to a 1.34 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 3.5% lower than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the silica gel tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within $\pm$5% at the recommended flow rate.

6.2 Silica gel tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh silica gel separated by a 2-mm portion of urethane foam. The adsorbing section contains approximately 150 mg of silica gel, the backup section, approximately 75 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (3-ft x 1/4-in glass) packed with 5% SE-30 on 80/100 mesh Gas Chrom W.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 1.0-ml delivery pipets.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality tetrahydrofuran.

7.2 Acetylene tetrabromide, 98% solution, reagent grade.

7.3 Prepurified hydrogen.

7.4 Filtered compressed air.

7.5 Purified nitrogen.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative silica gel tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of silica gel is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The silica gel tube should be placed in a vertical direction during sampling to minimize channeling through the silica gel.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the silica gel tube.

8.3.5 A sample size of 100 liters is recommended. Sample at a flow of 1.0 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm$5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The silica gel tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the silica gel tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each silica gel tube is scored with a file in front of the first section of silica gel and broken open. The glass wool is removed and discarded. The silica gel in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of tetrahydrofuran is pipetted into each sample container. Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 220°C injector temperature
5. 270°C manifold temperature (detector)
6. 105°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of silica gel to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of silica gel is used.

8.5.2 Procedure for determining desorption efficiency. Silica gel equivalent to the amount in the first section of the sampling tube (approximately 150 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This silica gel must be from the same batch as that used in obtaining the samples and can be obtained from unused silica gel tubes. The open end is capped with Parafilm. A known amount of hexane solution of acetylene tetrabromide containing 350 mg/ml is injected directly into the silica gel with a microliter syringe, and the tube is capped with more Parafilm.

The amount injected is equivalent to that present in a 100-liter air sample at the selected level. Six tubes at each of three levels (using 2 microliters, 4 microliters, and 8 microliters of hexane solution for the 0.5X, 1X, and 2X OSHA standard levels) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the silica gel. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1.0 ml of tetrahydrofuran with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) is dependent on the amount of analyte collected on the silica gel. The desorption efficiency equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight recovered (mg)}}{\text{Weight added (mg)}}$$

The desorption efficiency is dependent on the amount of analyte collected on the silica gel. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/1.0 ml tetrahydrofuran, because samples are desorbed in this amount of tetrahydrofuran. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, are prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/1.0 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/1.0 ml tetrahydrofuran and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to get the total weight in the sample.

10.4 Read the desorption efficiency from the curve (See Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	= pressure (mm Hg) of air sampled
T	= temperature (°C) of air sampled
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	= molecular weight (g/mole) of analyte
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Epichlorohydrin
(1-Chloro-2,3-epoxypropane)

Analyte:	Epichlorohydrin	Method No.: S118
Matrix:	Air	Range: 11.7-43.1 mg/cu m
OSHA Standard:	5 ppm (20 mg/cu m)	Precision ($\overline{CV}_T$): 0.057
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 5/9/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 11.7-43.1 mg/cu m at an atmospheric temperature and pressure of 23°C and 765 mm Hg, using a 20-liter sample. Under the conditions of sample size (20 liters) the probable useful range of this method is 2-60 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 1-mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of epichlorohydrin and other substances in the air. The first section of the charcoal tube was found to hold at least 2 mg of epichlorohydrin when a test atmosphere

containing 43.1 mg/cu m of epichlorohydrin in air was sampled at 0.185 liter per minute for 240 minutes; at that time the concentration of epichlorohydrin in the effluent was less than 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV_T}$) for the total analytical and sampling method in the range of 11.7-43.1 mg/cu m was 0.057. This value corresponds to a 1.1 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 0.7% lower than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in stainless steel) packed with 10% FFAP on 80/100 mesh, acid washed DMCS Chromosorb W.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 1.0-ml delivery pipets.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 Epichlorohydrin, reagent grade.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A sample size of 20 liters is recommended. Sample at a flow of 0.20 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm$5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately. Samples should be analyzed within one week after collection.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 175°C injector temperature
5. 215°C manifold temperature (detector)
6. 120°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation

within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush method.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of hexane solution containing 94.5 mg/ml is injected directly into the charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample injector vials, capped with Teflon-faced septa, may be used in place of the glass tubes.

The amount injected is equivalent to that present in a 20-liter air sample at the selected level. Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight recovered (mg)}}{\text{Weight added (mg)}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/1.0 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to get the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	= pressure (mm Hg) of air sampled
T	= temperature (°C) of air sampled
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	= molecular weight (g/mole) of analyte
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Analyte:	Chlorinated Diphenyl Oxide	Method No.:	S119
Matrix:	Air	Range:	0.1002-0.965 mg/cu m
OSHA Standard:	0.5 mg/cu m	Precision ($\overline{CV}_T$):	0.070
Procedure:	Filter collection, iso-octane extraction, GC	Validation Date:	5/9/75

1. Principle of the Method

1.1 A known volume of air is drawn through a cellulose membrane filter to collect particulate matter.

1.2 The filter is transferred to a screw cap bottle within one hour after sampling and stored for analysis.

1.3 The analyte is extracted from the filter with iso-octane. An aliquot of the extract is analyzed by gas chromatography.

1.4 The area of the resulting peak is determined and compared with the areas for standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 0.1002-0.965 mg/cu m at an atmospheric temperature and pressure of 22°C and 767 mm Hg, using a 90-liter sample. The probable useful range of this method is 0.05-1.5 mg/cu m for 90-liter samples.

2.2 The upper limit of the range of the method is dependent on the capacity of the cellulose membrane filter. If higher concentrations than those tested are to be sampled, smaller sample volumes should be used.

3. Interferences

3.1 When interfering compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.1002-0.965 mg/cu m was 0.070. This value corresponds to a standard deviation of 0.035 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.1.

4.2 A collection efficiency of 1.00 was determined for the collection medium, thus, no bias was introduced in the sample collection step, and no correction for collection efficiency is necessary. There was also no bias in the sampling and analytical method. Thus $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

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 The sampling unit for the collection of personal air samples for the determination of organic aerosol has the following components:

6.1.1 The filter unit consisting of the filter media (Section 6.2) and a polystyrene 37-mm 2-piece cassette filter holder. Do not use Tenite filter holders.

6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of $\pm$ 5% (Reference 11.1) at the recommended flow rate. The pump must be calibrated with a representative filter holder and filter in the line.

6.1.3 Manometer.

6.1.4 Thermometer.

6.2 Mixed cellulose ester membrane filter, 0.8-micrometer pore size and 37-mm diameter. The filter is held in the two-piece cassette filter holder.

6.3 Screw cap bottles. Within 1 hour after sample has been collected, the filter is transferred to a clean screw cap bottle (a 45-mm tissue sample holder is satisfactory) for shipping. The bottle caps should be lined with Teflon for proper seal.

6.4 Gas chromatograph equipped with an electrolytic conductivity detector (Tracor or equivalent). The system includes an in-line vent between the exhaust end of the GC column and the reduction furnace, a quartz furnace operated in the reductive mode, an electrolytic conductivity cell, and a conductivity bridge.

6.5 Column (5-ft long X 1/8-in. O.D. glass) packed with 5% SE-30 on 80/100 mesh, acid washed DMCS Chromosorb W.

6.6 An electronic integrator or some other suitable method for measuring peak areas.

6.7 Tweezers.

6.8 Microliter syringes: 10-microliter and other convenient sizes for making standard solutions, and 25-microliter for making GC injections.

6.9 Volumetric flasks: 10-ml, and other convenient sizes for making standard solutions.

6.10 Pipets of convenient sizes.

7. Reagents

7.1 Chlorinated diphenyl oxide, reagent grade.

7.2 Iso-octane, nanograde.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis as well as the screw cap bottles should be detergent washed and thoroughly rinsed with tap water and distilled water, and dried.

8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative filter cassette in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples.

8.3.1 Assemble the filter in the two-piece filter cassette holder and close firmly. The cellulose membrane filter is held in place by a cellulose backup pad. Secure the cassette with a shrinkable band.

8.3.2 Remove the cassette plugs and attach to the personal sampling pump tubing. Clip the cassette to the worker's lapel.

8.3.3 Air being sampled should not pass through any hose or tubing before entering the filter cassette.

8.3.4 A sample size of 90 liters is recommended. Sample at a flow rate of 1.5 liters per minute. The flow rate should be known with an accuracy of $\pm$ 5%.

8.3.5 Turn the pump on and begin sample collection. Since it is possible for a filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently, and the sampling should be terminated at any evidence of a problem.

8.3.6 Terminate sampling at the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation.

8.3.7 The cellulose filter should be removed from the cassette filter holder and the cellulose backup pad within 1 hour of sampling and placed in a clean screw cap bottle. Care must be taken to handle the filter only with clean tweezers.

8.3.8 Carefully record the sample identity and all relevant sampling data.

8.3.9 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 for the samples except that no air is drawn through it. Label this as a blank.

8.3.10 The screw cap bottles in which the samples are stored should be shipped in a suitable container, designed to prevent damage in transit.

8.4 Analysis of Samples

8.4.1 Each sample is analyzed separately.

8.4.2 Pipet 10 ml of iso-octane into each screw cap bottle.

8.4.3 Swirl the contents in each bottle and allow to stand for two hours.

8.4.4 Appropriate filter blanks must be analyzed at the same time as the samples.

8.4.5 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 150 ml/min nitrogen carrier gas flow
2. 150 ml/min hydrogen gas flow to furnace
3. 760°C furnace temperature
4. 225°C transfer temperature
5. 250°C vent temperature
6. 210°C column temperature

8.4.6 Injection. The first step in the analysis is the injection of an aliquot of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 25-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 1.0 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 15-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.0 microliter to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 14.9-15.0 microliters in the barrel of the syringe. The gas chromatograph is equipped with a valve to vent the solvent peak after it passes through the GC column, but before it enters a reduction furnace. Since a 15-microliter aliquot is likely to cause malfunction of the conductivity cell, the valve should be opened when injection is made and should be closed after the solvent (iso-octane) has been vented and before the analyte is eluted. Under the conditions above (Section 8.4.5), it was found that 20 seconds was adequate to elute the solvent. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.4.7 Measurement of area. The areas of the sample peaks are measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed in Section 9.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/10 ml iso-octane, because samples are extracted in this amount of iso-octane. A series of standards, varying in concentration over the range of interest, are prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/10 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of day-to-day variations and variations during the same day of the electrolytic conductivity detector response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume correction is needed, because the standard curve is based on mg/10 ml of iso-octane and the volume of sample injected is identical to the volume of the standards injected.

10.2 A correction for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

mg sample = mg found in sample filter
mg blank = mg found in blank filter

10.3 The concentration of the analyte in the air sample can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{mg (Section 10.2) X 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

11. Reference

11.1 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Analyte:	Chlorodiphenyl (54% Chlorine)	Method No.:	S121
Matrix:	Air	Range:	0.322-1.255 mg/cu m
OSHA Standard:	0.5 mg/cu m	Precision ($\overline{CV_T}$):	0.063
Procedure:	Filter collection, petroleum ether extraction, GC	Validation Date:	5/9/75

1. Principle of the Method

1.1 A known volume of air is drawn through a cellulose membrane filter to collect particulate matter.

1.2 The filter is transferred to a screw cap bottle within one hour after sampling and stored for analysis.

1.3 The analyte is extracted from the filter with petroleum ether. An aliquot of the extract is analyzed by electron capture gas chromatography.

1.4 The total area of the peaks from the sample is determined and compared with areas obtained from standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 0.322-1.255 mg/cu m at an atmospheric temperature and pressure of 22°C and 760 mm Hg, using a 100-liter sample. The probable useful range of this method is 0.05-1.5 mg/cu m for 100-liter samples.

2.2 The upper limit of the range of the method is dependent on the collection efficiency of the cellulose membrane filter. If higher concentrations than those tested are to be sampled, smaller sample volumes should be used. The collection efficiency for chlorodiphenyl (54% chlorine) was determined to be 0.976 $\pm$ 0.002 when sampled for 68 minutes at 1.5 liter per minute from a test atmosphere containing 1.255 mg/cu m.

3. Interferences

3.1 When compounds other than the analyte are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV_T}$) for the total analytical and sampling method in the range of 0.322-1.255 mg/cu.m was 0.063. This value corresponds to a standard deviation of 0.032 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.1.

4.2 A collection efficiency of 0.976 $\pm$ 0.002 was determined for the collecting medium. The collection efficiency was used as a correction factor to determine the concentration of the air and to compensate for bias in the sampling method.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Samples collected on filters are analyzed by means of a quick, instrumental method.

5.2 Other volatile compounds which give an electron capture response that are dispersed as particulates may interfere.

6. Apparatus

6.1 The sampling unit for the collection of personal air samples for the determination of organic aerosol has the following components:

6.1.1 The filter unit consisting of the filter media (Section 6.2) and a polystyrene 37-mm 3-piece cassette filter holder. Do not use Tenite filter holders.

6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of $\pm$5% (Reference 11.1) at the recommended flow rate. The pump must be calibrated with a representative filter holder and filter in the line.

6.2 Mixed cellulose ester membrane filter, 0.8 micrometer pore size and 37 mm diameter. The filter is held in the three piece cassette supported by a cellulose backup pad.

6.3 Screw cap bottles. Within 1 hour after sample has been collected, the filter is transferred to a clean screw cap bottle (a 45-mm tissue sample holder is satisfactory) for shipping. The bottle caps should be lined with Teflon for proper seal.

6.4 Gas chromatograph equipped with an electron capture detector.

6.5 Column (6-ft X 1/4-in glass) packed with 3% OV-1 on 100/120 mesh Gas Chrom Q.

6.6 An electronic integrator or some other suitable method for measuring peak areas.

6.7 Sample extraction equipment.

6.7.1 Beakers, 50 ml.

6.7.2 Volumetric flasks, 100 ml for use in making GC standards and 10 ml for preparation of samples.

6.7.3 Tweezers.

6.8 Microliter syringes: 10-microliter and other convenient sizes for making standard solutions.

6.9 Volumetric flasks: 100 ml, 10 ml, and other convenient sizes for making standard solutions.

7. Reagents

7.1 Petroleum ether, 30°C to 60°C boiling range, suitable for pesticide residue analysis, Mallinckrodt Nanaograde® or equivalent.

7.2 Chlorodiphenyl (54% Chlorine), reagent grade.

7.3 Purified nitrogen.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis as well as the screw cap bottles should be detergent washed and thoroughly rinsed with tap water and distilled water, dried, and then rinsed with petroleum ether.

8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative filter cassette in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples.

8.3.1 Assemble the filter in the three piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad.

8.3.2 Remove the cassette plugs and attach to the personal sampling pump tubing. Clip the cassette to the worker's lapel.

8.3.3 Air being sample should not pass through any hose or tubing before entering the filter cassette.

8.3.4 A sample size of 100 liters is recommended. Sample at a flow rate of 1.5 liters per minute. The flow rate should be known with an accuracy of $\pm 5\%$.

8.3.5 Turn the pump on and begin sample collection. Since it is possible for a filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently, and the sampling should be terminated at any evidence of a problem.

8.3.6 Terminate sampling at the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation.

8.3.7 The cellulose filter should be removed from the cassette filter holder and the cellulose backup pad within 1 hour of sampling and placed in a clean screw cap bottle. Care must be taken to handle the filter only with clean tweezers.

8.3.8 Carefully record the sample identity and all relevant sampling data.

8.3.9 With each batch of samples submit one filter which is subjected to exactly the same handling as for the samples except that no air is drawn through it. Label this as a blank.

8.3.10 The screw cap bottles in which the samples are stored should be shipped in a suitable container, designed to prevent damage in transit.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. Care must be taken to handle the filter only with clean tweezers. Open the screw cap bottle, remove the filter and place the filter in a 50-ml beaker. Rinse the screw cap bottle with 3 ml petroleum ether. Pour the solvent into the beaker. Swirl the solvent over the filter, then decant the extract into a 10-ml volumetric flask. Repeat this process two more times. Dilute the combined extracts to a total of 10 ml with petroleum ether, stopper, and mix. For gas chromatographic analysis use a 1 to 100 dilution in petroleum ether. Measure the area of the envelope of peaks given by the mixture of compounds in chlorodiphenyl (54% chlorine).

8.4.2 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 250°C detector temperature
3. 215°C injector temperature
4. 210°C column temperature

8.4.3 Injection. The first step in the analysis is the injection of an aliquot of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.4.4 Measurement of area. The areas of the sample peaks are measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed in Section 9. The peaks are not resolved, and therefore the total area of the envelope of peaks is measured as a single area.

8.5 Determination of Analytical Method Recovery

8.5.1 Need for determination. It is anticipated that the extraction scheme is dependent on operator skill and perhaps on the formulation used to disperse the analyte. Thus, it is necessary to determine the recovery of the analyte.

8.5.2 Procedure for determining analytical method recovery. A known amount of a petroleum ether solution containing 0.0125 mg/microliter of chlorodiphenyl (54% chlorine), preferably equivalent to the sample concentration expected, is added to a representative cellulose membrane filter and air-dried. The analyte is then extracted from the filter and analyzed as described in Section 8.4.
Six filters at each of the three levels (0.5X, 1X, and 2X the OSHA standard) are dosed accordingly. A parallel blank filter is also treated in the same manner except that no sample is added to it. All filters are then extracted and analyzed as described in Section 8.4.

Three stock standards are prepared by injecting the same amount of analyte into 10 ml of petroleum ether with the same syringe used in the preparation of the dosed filters and are analyzed at the same time. A 1 to 100 dilution of the stock standard is used for the GC analysis.

Analytical method recovery (A.M.R.) equals the weight in mg found divided by the weight in mg added to the filter, or

$$\text{A.M.R.} = \frac{\text{Weight found (mg)}}{\text{Weight added (mg)}}$$

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/10 ml petroleum ether, because samples are extracted in this amount of petroleum ether. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/10 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample

analysis is done. This will minimize the effect of day-to-day variations and variations during the same day of the electron capture response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each envelope of peak area from the standard curve. No volume correction is needed, because the standard curve is based on mg/10 ml of petroleum ether and the volume of sample injected is identical to the volume of the standards injected.

10.2 A correction for the blank must be made for each sample.

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in sample filter
mg blank = mg found in blank filter

10.3 Divide the total weight by the analytical method (A.M.R.) to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{A.M.R.}}$$

10.4 The concentration of the analyte in the air sample can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.3) X 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

11. Reference

11.1 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

Ethylene Dichloride
(1,2-Dichloroethane)

Analyte:	Ethylene Dichloride	Method No.: S122
Matrix:	Air	Range: 195-819 mg/cu m
OSHA Standard:	100 ppm (405 mg/cu m)-Ceiling 50 ppm (200 mg/cu m)-T.W.A.	Precision ($\overline{CV}_T$): 0.079
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 6/6/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 195-819 mg/cu m at an atmospheric temperature and pressure of 26°C and 760.4 mm Hg, using a 3-liter sample. Under the conditions of sample size (3 liters) the probable useful range of this method is 41-1215 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 3.6 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 23.7 mg of analyte when a test atmosphere containing 821 mg/cu m of analyte in air was sampled at 0.187 liters per minute for 155 minutes; breakthrough was observed at this time, i.e., the concentration of analyte in the effluent was 5% of that in the influent. The breakthrough data are based on a prior experiment.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 195-819 mg/cu m was 0.079. This value corresponds to a 32 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 2.2% lower than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3).

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in stainless steel) packed with 10% OV-101 stationary phase on 100/120 mesh Supelcoport.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide

7.2 1,2-Dichloroethane, reagent grade

7.3 Octane, or other suitable internal standard

7.4 Purified nitrogen

7.5 Prepurified hydrogen

7.6 Filtered compressed air

8. Procedure

8.1 Cleaning of equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 At the ceiling and peak concentrations, a sample size of 3 liters is recommended. Sample for 15 minutes at a flow of 0.2 liters per minute. At the T.W.A. concentration, a sample size of 10 liters is recommended. Sample at a flow of 0.2 liters per minute or less. The flow rates should be known with an accuracy of at least $\pm$5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (60 psig) Nitrogen carrier gas flow
2. 35 ml/min (25 psig) Hydrogen gas flow to detector
3. 400 ml/min (60 psig) Air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 70°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample injector vials, capped with Teflon-faced septa, may be used in place of the glass tubes.

Six tubes at each of three concentration levels (0.5X,1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 3-liter sample at the selected level. The tubes are allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube
mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liters/cu m)}}{\text{Air Volume Sampled (liters)}}$$

10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$ppm = mg/cu\ m \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

1,1-Dichloroethane
(Ethylidene Chloride)

Analyte:	1,1-Dichloroethane	Method No.: S123
Matrix:	Air	Range: 212-838 mg/cu m
OSHA Standard:	100 ppm (405 mg/cu m)	Precision ($\overline{CV}_T$): 0.057
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 5/9/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 212-838 mg/cu m at an atmospheric temperature and pressure of 22°C and 766 mm Hg, using a 10-liter sample. Under the conditions of sample size (10 liters) the probable useful range of this method is 40-1215 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 12-mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of 1,1-dichloroethane and other substances in the air. The first section of the charcoal tube was found to hold 15 mg of 1,1-dichloroethane when a test atmosphere containing

838 mg/cu m of 1,1-dichloroethane in air was sampled at 0.185 liter per minute for 99 minutes; breakthrough was observed at this time, i.e. the concentration of 1,1-dichloroethane in the effluent was 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 212-838 mg/cu m was 0.057. This value corresponds to a 23 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 3.6% higher than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in stainless steel) packed with 10% FFAP on 80/100 mesh, acid washed DMCS Chromosorb W.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 One-milliliter sample containers with glass stoppers or Teflon-lined caps.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 0.5-ml delivery pipets or 1.0-ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 1,1-Dichloroethane, reagent grade.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a flow of 0.20 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm$5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 0.5 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 100°C injector temperature
5. 175°C manifold temperature (detector)
6. 50 °C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation

within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

The amount injected is equivalent to that present in a 10-liter air sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 0.5 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight recovered (mg)}}{\text{Weight added (mg)}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/0.5 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to get the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	= pressure (mm Hg) of air sampled
T	= temperature (°C) of air sampled
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	= molecular weight (g/mole) of analyte
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

1,1,2,2-Tetrachloroethane

Analyte:	1,1,2,2-Tetrachloroethane	Method No.: S124
Matrix:	Air	Range: 16-70 mg/cu m
OSHA Standard:	5 ppm (35 mg/cu m)	Precision ($\overline{CV}_T$): 0.057
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 5/9/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 16-70 mg/cu m at an atmospheric temperature and pressure of 21.5°C and 761 mm Hg, using a 10-liter sample. Under the conditions of sample size (10 liters) the probable useful range of this method is 3.5-105 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 1-mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of 1,1,2,2-tetrachloroethane and other substances in the air. The first section of the charcoal tube was found to hold at least 4.5 mg of 1,1,2,2-tetrachloroethane

when a test atmosphere containing 101 mg/cu m of 1,1,2,2-tetrachloroethane in air was sampled at 0.185 liter per minute for 240 minutes; at that time the concentration of 1,1,2,2-tetrachloroethane in the effluent was less than 5% of that in the influent. (The charcoal tube consists of two sections of petroleum-based charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 16-70 mg/cu m was 0.057. This value corresponds to a 2 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 5.6% higher than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh petroleum-based charcoal (Lot 104, supplied by SKC, Inc. or equivalent*) separated by a 2-mm portion of urethane foam. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in stainless steel) packed with 10% FFAP on 80/100 mesh, acid washed DMCS Chromosorb W.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 1.0-ml delivery pipets.

---

* Lot 104 is a petroleum-based charcoal which is less active than Lot 105. The Lot 105 charcoal is prepared from coconut shells. A highly activated charcoal such as Lot 105 should not be used to collect 1,1,2,2-tetrachloroethane.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 1,1,2,2-Tetrachloroethane, reagent grade.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A sample size of 10 liters is recommended. Sample at a flow of 0.20 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm$5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 175°C injector temperature
5. 230°C manifold temperature (detector)
6. 160°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation

within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush method.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of hexane solution containing 79.8 mg/ml is injected directly into the charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample injector vials, capped with Teflon-septa, may be used in place of glass tubes.

The amount injected is equivalent to that present in a 10-liter air sample at the selected level. Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight recovered (mg)}}{\text{Weight added (mg)}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/1.0 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to get the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	= pressure (mm Hg) of air sampled
T	= temperature (°C) of air sampled
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	= molecular weight (g/mole) of analyte
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Analyte:	Trifluoromonobromomethane	Method No.: S125
Matrix:	Air	Range: 2,890-11,560 mg/cu m
OSHA Standard:	1000 ppm (6090 mg/cu m)	Precision ($\overline{CV}_T$): 0.065
Procedure:	Adsorption on charcoal, desorption with methylene chloride, GC	Validation Date: 5/9/75

1. Principle of the Method (Reference 11.1)

   1.1 A known volume of air is drawn through a charcoal tube which is connected in line to a smaller backup charcoal tube to trap the organic vapors present.

   1.2 The charcoal in the tube is transferred to a stoppered sample container, and the analyte is desorbed with methylene chloride.

   1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

   1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

   2.1 This method was validated over the range of 2,890-11,560 mg/cu m at an atmospheric temperature and pressure of 25°C and 760 mm Hg, using a 1-liter sample. Under the conditions of sample size (1 liter) the probable useful range of this method is 610-18,000 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for an 18-mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

   2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the large charcoal tube. This capacity varies with the concentrations of trifluoromonobromomethane and other substances in the air. The charcoal tube was found to hold 51 mg of trifluoromonobromomethane when a test atmosphere

containing 12,370 mg/cu m of analyte in air was sampled at 0.046 liter per minute for 90 minutes; breakthrough was observed at this time, i.e. the concentration of the analyte in the effluent was 5% of that in the influent. (Breakthrough tests were done using a large charcoal tube connected in line to a smaller backup charcoal tube). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample. Since methylene chloride is used rather than carbon disulfide to desorb the trifluoromonobromomethane from the charcoal, it would not be possible to measure methylene chloride in the sample with this desorbing solvent. If it is suspected that methylene chloride is present, a separate sample should be collected for methylene chloride analysis.

3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 2890-11,560 mg/cu m was 0.065. This value corresponds to a 395 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were equal to the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup charcoal tube exceeds 25% of that found on the large charcoal tube, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3)

6.2 Charcoal tubes: Two charcoal tubes are used in this method, because it was discovered that trifluoromonobromomethane migrates from the front section to the backup section in the charcoal tube. A large charcoal tube is used to collect the samples, and a smaller charcoal tube is used as a backup. The charcoal tubes are connected in line with tygon tubing. The large charcoal tube is a glass tube with both ends flame sealed. It is 9 cm long with a 8-mm O.D. and a 6-mm I.D. The charcoal tube has 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The front section contains 400 mg of charcoal, the back section 200 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The small charcoal tube is 7 cm long with a 6-mm O.D. and a 4-mm I.D. The front section of the small charcoal tube contains 100 mg of charcoal and the backup section has 50 mg. The pressure drop across both tubes must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (4-ft x 1/4-in stainless steel) packed with 50/80 mesh Porapak, Type Q.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 Microliter syringes: 10-microliter for injection of samples into the gas chromatograph.

6.7 Gas tight syringes: convenient sizes for making standards.

6.8 Pipets: 10.0-ml delivery pipets.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions and desorbing the samples.

7. Reagents

7.1 Chromatographic quality methylene chloride.

7.2 Trifluoromonobromomethane, 99% pure.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with two representative charcoal tubes in the line, a large tube followed by a small tube. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the two charcoal tubes to provide an opening at least one-half the internal diameter of the tube.

8.3.2 Connect the larger charcoal tube in line to the smaller charcoal tube with tygon tubing. The shortest length of tubing compatible with maintaining a leak-free connection should be used. The smaller charcoal tube is used as a backup and should be positioned nearest the sampling pump.

8.3.3 Both charcoal tubes should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tubes.

8.3.5 A maximum sample size of 1 liter is recommended. Sample at a flow of 0.050 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm$5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One set of tubes (a large charcoal tube and a smaller backup tube) should be handled in the same manner as the sample tubes (break, seal, and transport), except that no air is sampled through these tubes. These tubes should be labeled as the blank.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in both sections of the large charcoal tube is transferred to a 10-ml stoppered sample container. The separating section of foam is removed and discarded. The charcoal in both sections of the smaller charcoal tube is transferred to another stoppered container. These two charcoal tubes are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 5 ml of methylene chloride is pipetted into each sample container. Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. Samples should be analyzed immediately after desorption and should not be stored overnight.

Prepare standards as in Section 8.5.2 during this time period.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 225°C injector temperature
5. 260°C manifold temperature (detector)
6. 160°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Desorption efficiency tests are done using both sections of the large charcoal tubes described in Section 6.2. The charcoal in the tubes must be from the same batch as that used in obtaining the samples. A known amount of analyte is injected through a septum where nitrogen carries the analyte through a heated inlet directly into the charcoal tube at a flow of approximately 200 ml/min. The charcoal tube is capped with the supplied plastic caps.

The amount injected is equivalent to that present in a 1-liter air sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure comple adsorption of the analyte onto the charcoal in both sections of the tube. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

In preparation of the standards, 5 ml of methylene chloride is added to a 10-ml volumetric flask. An appropriate amount of trifluoromonobromomethane gas is bubbled slowly into the methylene chloride using a gas tight syringe. Caution should be taken to make sure that the syringe needle is as near as possible to the bottom of the volumetric flask so that the gas will be completely dissolved in the methylene chloride and no gas will escape. Additional caution should be taken to observe the disappearance of gas bubbles. If bubbles escape from the solution, this may be an indication that all of the analyte is not being dissolved in the solvent. Standards should be prepared at the same time the sample analysis is done and are analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight recovered (mg)}}{\text{Weight added (mg)}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/5.0 ml methylene chloride, because samples are desorbed in this amount of methylene chloride. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/5.0 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/5.0 ml methylene chloride and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

mg sample = mg found in both sections of sample tube

mg blank = mg found in both sections of blank tube

A similar procedure is followed for the backup tubes.

10.3 Add the weights found in the front and backup tubes to get the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front tube. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	= pressure (mm Hg) of air sampled
T	= temperature (°C) of air sampled
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	= molecular weight (g/mole) of analyte
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

1,2,3-Trichloropropane

Analyte:	1,2,3-Trichloropropane	Method No.: S126
Matrix:	Air	Range: 163-629 mg/cu m
OSHA Standard:	50 ppm (300 mg/cu m)	Precision ($\overline{CV}_T$): 0.068
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 5/9/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 163-629 mg/cu m at an atmospheric temperature and pressure of 21°C and 767 mm Hg, using a 10-liter sample. Under the conditions of sample size (10 liters) the probable useful range of this method is 30-900 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 9-mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of 1,2,3-trichloropropane and other substances in the air. The first section of the charcoal tube was found to hold at least 28 mg of 1,2,3-trichloropropane when a

test atmosphere containing 629 mg/cu m of 1,2,3-trichloropropane in air was sampled at 0.185 liter per minute for 240 minutes; at that time the concentration of 1,2,3-trichloropropane in the effluent was less than 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV_T}$) for the total analytical and sampling method in the range of 163-629 mg/cu m was 0.068. This value corresponds to a 20 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 8.2% higher than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in stainless steel) packed with 10% FFAP on 80/100 mesh, acid washed DMCS Chromosorb W.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 One-milliliter sample containers with glass stoppers or Teflon-lined caps.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 0.5-ml delivery pipets or 1.0-ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 1,2,3-Trichloropropane, reagent grade.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A sample size of 10 liters is recommended. Sample at a flow of 0.20 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm$5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 0.5 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 180°C injector temperature
5. 230°C manifold temperature (detector)
6. 160°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation

within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

The amount injected is equivalent to that present in a 10-liter air sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 0.5 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight recovered (mg)}}{\text{Weight added (mg)}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/0.5 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to get the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	= pressure (mm Hg) of air sampled
T	= temperature (°C) of air sampled
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	= molecular weight (g/mole) of analyte
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Trichloronaphthalene

Analyte:	Trichloronaphthalene	Method No.: S128
Matrix:	Air	Range: 1.647-8.79 mg/cu m
OSHA Standard:	5 mg/cu m - skin	Precision (CV_T): 0.117
Procedure:	Filter and bubbler collection, iso-octane extraction, GC	Validation Date: 5/9/75

1. Principle of the Method

1.1 A known volume of air is drawn through a glass fiber filter connected in series to a midget bubbler containing 15 ml of iso-octane to collect the analyte.

1.2 The filter and the contents in the midget bubbler are transferred to a 20-ml scintillation vial.

1.3 An aliquot from the scintillation vial is analyzed by gas chromatography.

1.4 The total area of the peaks from the sample is determined and compared with areas obtained from standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 1.647-8.79 mg/cu m at an atmospheric temperature and pressure of 22°C and 760 mm Hg, using a 100-liter sample. The probable useful range of this method is 0.5-15 mg/cu m.

2.2 The upper limit of the range of the method is dependent on the capacity of the glass fiber filter connected in series to the midget bubbler and the capacity of the midget bubbler. If higher concentrations than those tested are to be sampled, smaller sample volumes should be used.

3. Interferences

3.1 When interfering compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference.

4. Precision and Accuracy

4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 1.647-8.79 mg/cu m was 0.117. This value corresponds to a standard deviation of 0.58 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.1.

4.2 A collection efficiency of 1.00 was determined for the collection medium, thus, no bias was introduced in the sample collection step and no correction for collection efficiency is necessary. There was also no bias in the sampling and analytical method for which an analytical method recovery correction was made. Thus, CV_T is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

5.1 Collected samples are analyzed by means of a quick, instrumental method.

5.2 A disadvantage of the method is the evaporation of iso-octane in the midget bubbler. The bubbler must be refilled periodically whenever the liquid level is lowered by an appreciable amount.

5.3 Another disadvantage of the method is the awkwardness in using midget bubblers for collecting personal samples. If the worker's job performance requires much body movement, loss of the collection solution during sampling may occur.

5.4 Trichloronaphthalene is a mixture of isomers. Under the gas chromatographic conditions used for validation, an "envelope" of peaks was analyzed. The quantitation of area is difficult unless an integrator is used.

5.5 The precision of the method is limited by the reproducibility of the pressure drop across the filter and bubbler. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one filter/bubbler combination only.

5.6 Scintillation vials are more difficult to ship than adsorption tubes or filters due to possible breakage and leakage of the vials during shipping.

6. Apparatus

6.1 The sampling unit for the collection of personal air samples for the determination of trichloronaphthalene has the following components:

6.1.1 The filter unit consisting of the filter media (Section 6.2) and a polystyrene 37-mm two-piece cassette filter holder connected in series with a midget bubbler (Section 6.3). Do not use Tenite filter holders.

6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of ±5%. The sampling pump is protected from splashover or solvent condensation by a 5-cm long by 6-mm I.D. glass tube loosely packed with a plug of glass wool and inserted between the exit arm of the bubbler and the pump.

6.1.3 Thermometer.

6.1.4 Manometer.

6.2 Glass fiber filter, Type A with a 37-mm diameter. The filter is held in the two-piece cassette filter holder. A backup pad should not be used.

6.3 A glass midget bubbler containing 15 ml of the collection medium (Section 7.3).

6.4 Scintillation vials, 20 ml. Teflon cap liners (22 mm) should be used for proper seal. Add 15 ml of distilled water into each vial and mark the liquid level. Pour out the water and dry each vial.

6.5 Gas chromatograph equipped with an electrolytic conductivity detector (Tracor or equivalent). The system includes an in-line vent between the exhaust end of the GC column and the reduction furnace, a quartz furnace operated in the reductive mode, an electrolytic conductivity cell, and a conductivity bridge.

6.6 Column (5-ft long X 1/8-in O.D. glass) packed with 5% SE-30 on 80/100 mesh, acid washed DMCS Chromosorb W.

6.7 An electronic integrator or some other suitable method for measuring peak areas.

6.8 Microliter syringes: 10-microliter and other convenient sizes for making standard solutions, and 25-microliter for making GC injections.

6.9 Volumetric flasks: 15-ml, and other convenient sizes for making standard solutions.

6.10 Pipets of convenient sizes.

6.11 Tweezers.

7. Reagents

7.1 Trichloronaphthalene, reagent grade.

7.2 Benzene, reagent grade.

7.3 Iso-octane, nanograde.

7.4 Purified nitrogen.

7.5 Prepurified hydrogen.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis as well as the scintillation vials should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Sampling Pump. Each personal sampling pump must be calibrated with a representative filter cassette and bubbler in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples.

8.3.1 Assemble the filter in the two-piece filter cassette holder and close firmly.

8.3.2 Pipet 15 ml of the collection medium (Section 7.3) into each midget bubbler and mark the liquid level. The liquid level in the bubbler must be checked frequently. If the liquid level is lowered by an appreciable amount (to less than 10 ml) from evaporation, the bubbler must be refilled with additional iso-octane. The final refilling of iso-octane into the bubbler should be done at approximately 15 minutes before the end of sampling. The final volume of the solution at the end of sampling should be 12 ml or less.

8.3.3 Remove the cassette plugs and attach the outlet of the filter cassette to the inlet arm of the midget bubbler using a short piece of flexible tubing. Connect the outlet arm of the midget bubbler with a 5-cm glass splashover tube (6-mm I.D.) containing the glass wool

plug, then to the personal sampling pump, using short pieces of flexible tubing. The bubbler must be maintained in a vertical position during sampling.

8.3.4 Air being sampled should not pass through any hose or tubing before entering the filter cassette.

8.3.5 A sample size of 100 liters is recommended. Sample at a flow rate of 1.3 liters per minute. The flow rate should be known with an accuracy of $\pm$5%.

8.3.6 Turn the pump on and begin sample collection. Since it is possible for a filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently, and the sampling should be terminated at any evidence of a problem.

8.3.7 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.

8.3.8 After sampling remove the bubbler stem and tap the stem gently against the inside wall of the bubbler bottle to recover as much of the sampling solution as possible. Rinse the bubbler stem with 1 ml of iso-octane into the midget bubbler.

8.3.9 Transfer the contents of the midget bubbler to the scintillation vial which has been marked at 15 ml. Rinse the bubbler with 2 ml of iso-octane, adding the rinse to the vial. Bring the volume in the vial to the 15-ml mark with iso-octane.

8.3.10 The glass fiber filter should be removed from the cassette filter holder and placed in the scintillation vial. Care must be taken to handle the filter only with clean tweezers. Cap the scintillation vials with appropriate caps with Teflon liners.

8.3.11 Carefully record the sample identity and all relevant sampling data.

8.3.12 With each batch of ten samples, submit one filter and bubbler from the same lot of filters and bubblers which was used for sample collection and which are subjected to exactly the same handling as the samples except that no air is drawn through it. Label this as a blank.

8.3.13 The scintillation vials in which the samples are stored should be shipped in a suitable container, designed to prevent damage in transit.

8.4 Analysis of Samples

8.4.1 Each sample is analyzed separately. Before injection of the sample into the GC, swirl the contents in the vials for 5 minutes.

8.4.2 Appropriate blanks must be analyzed at the same time as the samples.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 150 ml/min nitrogen carrier gas flow
2. 150 ml/min hydrogen gas flow to furnace
3. 760°C furnace temperature
4. 225°C transfer temperature
5. 250°C vent temperature
6. 185°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of an aliquot of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 25-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 1.0 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 15-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.0 microliter to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 14.9-15.0 microliters in the barrel of the syringe. The gas chromatograph is equipped with a valve to vent the solvent peak after it passes through the GC column, but before it enters a reduction furnace. Since a 15-microliter aliquot is likely to cause malfunction of the electrolytic conductivity cell, the valve should be opened when injection is made and should be closed after the solvent (iso-octane) has been vented and before the analyte is eluted. Under the conditions above (Section 8.4.3), it was found that 20 seconds was adequate to elute the solvent. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of area. The areas of the sample peaks are measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed in Section 9. The peaks are not resolved, and therefore the total area of the envelope of peaks is measured as a single area.

8.5 Determination of Analytical Method Recovery

8.5.1 Need for Determination. To eliminate any bias in the analytical method, it is necessary to determine the recovery of the analyte. The analytical method recovery (A.M.R.) should be determined over the concentration range of interest.

8.5.2 Procedure for determining analytical method recovery. A known amount of benzene solution containing 1.25 g/ml of trichloronaphthalene is added to a representative glass fiber filter and allowed to air dry. The analyte is then extracted from the filter with 15 ml of iso-octane for one hour and analyzed as described in Section 8.4. Six filters at each of the three levels (0.5X, 1X, and 2X the OSHA standard) are dosed accordingly. A parallel blank filter is also treated in the same manner except that no sample is added to it. All filters are extracted in 15 ml iso-octane for one hour and analyzed as described in Section 8.4.

Three standards are prepared by injecting the same amount of analyte into 15 ml of iso-octane with the same syringe used in the preparation of the dosed filters and are analyzed at the same time.

Analytical method recovery (A.M.R.) equals the weight in mg found divided by the weight in mg added to the filter, or

$$\text{A.M.R.} = \frac{\text{Weight found (mg)}}{\text{Weight added (mg)}}$$

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/15 ml iso-octane, because samples are extracted in this amount of iso-octane. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/15 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of day-to-day variations and variations during the same day of the electrolytic conductivity detector response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each envelope of peak area from the standard curve. No volume correction is needed, because the standard curve is based on mg/15 ml of iso-octane, and the volume of sample injected is identical to the volume of the standards injected.

10.2 A correction for the blank must be made for each sample.

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in sample filter and bubbler
mg blank = mg found in blank filter and bubbler

10.3 Divide the total weight by the analytical method recovery (A.M.R.) to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{A.M.R.}}$$

10.4 The concentration of the analyte in the air sample can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.3) X 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

11. Reference

11.1 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

1,1,2-Trichloro-1,2,2-trifluoroethane
(Refrigerant 113)

Analyte:	1,1,2-Trichloro-1,2,2-trifluoroethane	Method No.: S129	
Matrix:	Air	Range: 3,300 - 14,200 mg/cu m	
OSHA Standard:	1000 ppm (7660 mg/cu m)	Precision ($\overline{CV}_T$): 0.070	
Procedure:	Adsorption on charcoal, desorption with carbon disulfide	Validation Date: 5/9/75	

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 3,300-14,200 mg/cu m at an atmospheric temperature and pressure of 22°C and 759 mm Hg, using a 1.5-liter sample. Under the conditions of sample size (1.5 liters) the probable useful range of this method is 760-23,000 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 34-mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of the analyte and other substances in the air. The first section of the charcoal tube was found to

hold 40 mg of the analyte when a test atmosphere containing 14,500 mg/cu m of the analyte in air was sampled at 0.046 liter per minute for 60 minutes; breakthrough was observed at this time, i.e. the concentration of the analyte in the effluent was 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 3,300-14,200 mg/cu m was 0.070. This value corresponds to a 540 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 0.3% higher than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (6-ft x 1/4-in stainless steel) packed with 50/80 mesh Porapak, Type Q.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 1.0-ml delivery pipets.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 1,1,2-Trichloro-1,2,2-trifluoroethane, reagent grade.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A maximum sample size of 1.5 liters is recommended. Sample at a flow of 0.050 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm$5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 200°C injector temperature
5. 200°C manifold temperature (detector)
6. 150°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation

within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush method.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample injector vials, capped with Teflon-faced septa, may be used in place of the glass tubes.

The amount injected is equivalent to that present in a 1.5-liter air sample at the selected level. Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight recovered (mg)}}{\text{Weight added (mg)}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/1.0 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to get the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	= pressure (mm Hg) of air sampled
T	= temperature (°C) of air sampled
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	= molecular weight (g/mole) of analyte
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Tetrachloronaphthalene

Analyte:	Tetrachloronaphthalene	Method No.: S130
Matrix:	Air	Range: 0.912-4.04 mg/cu m
OSHA Standard:	2 mg/cu m - skin	Precision ($\overline{CV}_T$): 0.097
Procedure:	Filter and bubbler collection, iso-octane extraction, GC	Validation Date: 5/9/75

1. Principle of the Method

1.1 A known volume of air is drawn through a glass fiber filter connected in series to a midget bubbler containing 15 ml of iso-octane to collect the analyte.

1.2 The filter and the contents in the midget bubbler are transferred to a 20-ml scintillation vial.

1.3 An aliquot from the scintillation vial is analyzed by gas chromatography.

1.4 The total area of the peaks from the sample is determined and compared with areas obtained from standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 0.912-4.04 mg/cu m at an atmospheric temperature and pressure of 22°C and 760 mm Hg, using a 100-liter sample. The probable useful range of this method is 0.2-6 mg/cu m.

2.2 The upper limit of the range of the method is dependent on the capacity of the glass fiber filter connected in series to the midget bubbler and the capacity of the midget bubbler. If higher concentrations than those tested are to be sampled, smaller sample volumes should be used.

3. Interferences

3.1 When interfering compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.912-4.04 mg/cu m was 0.097. This value corresponds to a standard deviation of 0.19 mg/cu m at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.1.

4.2 A collection efficiency of 1.00 was determined for the collection medium, thus, no bias was introduced in the sample collection step and no correction for collection efficiency is necessary. There was also no bias in the sampling and analytical method for which an analytical method recovery correction was made. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

5.1 Collected samples are analyzed by means of a quick, instrumental method.

5.2 A disadvantage of the method is the evaporation of iso-octane in the midget bubbler. The bubbler must be refilled periodically whenever the liquid level is lowered by an appreciable amount.

5.3 Another disadvantage of the method is the awkwardness in using midget bubblers for collecting personal samples. If the worker's job performance requires much body movement, loss of the collection solution during sampling may occur.

5.4 Tetrachloronaphthalene is a mixture of isomers. Under the gas chromatographic conditions used for validation, an "envelope" of peaks was analyzed. The quantitation of area is difficult unless an integrator is used.

5.5 The precision of the method is limited by the reproducibility of the pressure drop across the filter and bubbler. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one filter/bubbler combination only.

5.6 Scintillation vials are more difficult to ship than adsorption tubes or filters due to possible breakage and leakage of the vials during shipping.

6. Apparatus

6.1 The sampling unit for the collection of personal air samples for the determination of tetrachloronaphthalene has the following components:

6.1.1 The filter unit consisting of the filter media (Section 6.2) and a polystyrene 37-mm two-piece cassette filter holder connected in series with a midget bubbler (Section 6.3). Do not use Tenite filter holders.

6.1.2 Personal Sampling Pump: A calibrated personal sampling pump whose flow can be determined to an accuracy of ±5%. The sampling pump is protected from splashover or solvent condensation by a 5-cm long by 6-mm I.D. glass tube loosely packed with a plug of glass wool and inserted between the exit arm of the bubbler and the pump.

6.1.3 Thermometer.

6.1.4 Manometer.

6.2 Glass fiber filter, Type A with a 37-mm diameter. The filter is held in the two-piece cassette filter holder. A backup pad should not be used.

6.3 A glass midget bubbler containing 15 ml of the collection medium (Section 7.3).

6.4 Scintillation vials, 20 ml. Teflon cap liners (22-mm) should be used for proper seal. Add 15 ml of distilled water into each vial and mark the liquid level. Pour out the water and dry each vial.

6.5 Gas chromatograph equipped with an electrolytic conductivity detector (Tracor or equivalent). The system includes an in-line vent between the exhaust end of the GC column and the reduction furnace, a quartz furnace operated in the reductive mode, an electrolytic conductivity cell, and a conductivity bridge.

6.6 Column (5-ft long X 1/8-in O.D. glass) packed with 5% SE-30 on 80/100 mesh, acid washed DMCS Chromosorb W.

6.7 An electronic integrator or some other suitable method for measuring peak areas.

6.8 Microliter syringes: 10-microliter and other convenient sizes for making standard solutions, and 25-microliter for making GC injections.

6.9 Volumetric flasks: 15-ml, and other convenient sizes for making standard solutions.

6.10 Pipets of convenient sizes.

6.11 Tweezers.

7. Reagents

7.1 Tetrachloronaphthalene, reagent grade.

7.2 Benzene, reagent grade.

7.3 Iso-octane, nanograde.

7.4 Purified nitrogen.

7.5 Prepurified hydrogen.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis as well as the scintillation vials should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Sampling Pump. Each personal sampling pump must be calibrated with a representative filter cassette and bubbler in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples.

8.3.1 Assemble the filter in the two-piece filter cassette holder and close firmly.

8.3.2 Pipet 15 ml of the collection medium (Section 7.3) into each midget bubbler and mark the liquid level. The liquid level in the bubbler must be checked frequently. If the liquid level is lowered by an appreciable amount (to less than 10 ml) from evaporation, the bubbler must be refilled with additional iso-octane. The final refilling of iso-octane into the bubbler should be done at approximately 15 minutes before the end of sampling. The final volume of the solution at the end of sampling should be 12 ml or less.

8.3.3 Remove the cassette plugs and attach the outlet of the filter cassette to the inlet arm of the midget bubbler using a short piece of flexible tubing. Connect the outlet arm of the midget bubbler with a 5-cm glass splashover tube (6-mm I.D.) containing the glass wool plug, then to the personal sampling pump, using short pieces of flexible tubing. The bubbler must be maintained in a vertical position during sampling.

8.3.4 Air being sampled should not pass through any hose or tubing before entering the filter cassette.

8.3.5 A sample size of 100 liters is recommended. Sample at a flow rate of 1.3 liters per minute. The flow rate should be known with an accuracy of ±5%.

8.3.6 Turn the pump on and begin sample collection. Since it is possible for a filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently, and the sampling should be terminated at any evidence of a problem.

8.3.7 Terminate sampling at the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation.

8.3.8 After sampling remove the bubbler stem and tap the stem gently against the inside wall of the bubbler bottle to recover as much of the sampling solution as possible. Rinse the bubbler stem with 1 ml of iso-octane into the midget bubbler.

8.3.9 Transfer the contents of the midget bubbler to the scintillation vial which has been marked at 15 ml. Rinse the bubbler with 2 ml of iso-octane, adding the rinse to the vial. Bring the volume in the vial to the 15-ml mark with iso-octane.

8.3.10 The glass fiber filter should be removed from the cassette filter holder and placed in the scintillation vial. Care must be taken to handle the filter only with clean tweezers. Cap the scintillation vials with appropriate caps with Teflon liners.

8.3.11 Carefully record the sample identity and all relevant sampling data.

8.3.12 With each batch of ten samples submit one filter and bubbler from the same lot of filters and bubblers which was used for sample collection and which are subjected to exactly the same handling as the samples except that no air is drawn through it. Label this as a blank.

8.3.13 The scintillation vials in which the samples are stored should be shipped in a suitable container, designed to prevent damage in transit.

8.4 Analysis of Samples

8.4.1 Each sample is analyzed separately. Before injection of the sample into the GC, swirl the contents in the vials for 5 minutes.

8.4.2 Appropriate blanks must be analyzed at the same time as the samples.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 150 ml/min nitrogen carrier gas flow
2. 150 ml/min hydrogen gas flow to furnace
3. 760°C furnace temperature
4. 225°C transfer temperature
5. 250°C vent temperature
6. 185°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of an aliquot of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 25-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 1.0 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 15-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.0 microliter to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 14.9-15.0 microliters in the barrel of the syringe. The gas chromatograph is equipped with a valve to vent the solvent peak after it passes through the GC column, but before it enters a reduction furnace. Since a 15-microliter aliquot is likely to cause malfunction of the electrolytic conductivity cell, the valve should be opened when injection is made and should be closed after the solvent (iso-octane) has been vented and before the analyte is eluted. Under the conditions above (Section 8.4.3), it was found that 20 seconds was adequate to elute the solvent. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of area. The areas of the sample peaks are measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed in Section 9. The peaks are not resolved, and therefore the total area of the envelope of peaks is measured as a single area.

8.5 Determination of Analytical Method Recovery

8.5.1 Need for Determination. To eliminate any bias in the analytical method, it is necessary to determine the recovery of the analyte. The analytical method recovery (A.M.R.) should be determined over the concentration range of interest.

8.5.2 Procedure for determining analytical method recovery. A known amount of benzene solution containing 50 mg/ml of tetrachloronaphthalene is added to a representative glass fiber filter and allowed to air dry. The analyte is then extracted from the filter with 15 ml of iso-octane for one hour and analyzed as described in Section 8.4. Six filters at each of the three levels (0.5X, 1X, and 2X the OSHA standard) are dosed accordingly. A parallel blank filter is also treated in the same manner except that no sample is added to it. All filters are extracted in 15 ml iso-octane for one hour and analyzed as described in Section 8.4.

Three standards are prepared by injecting the same amount of analyte into 15 ml of iso-octane with the same syringe used in the preparation of the dosed filters and are analyzed at the same time.

Analytical method recovery (A.M.R.) equals the weight in mg found divided by the weight in mg added to the filter, or

$$A.\,M.\,R. = \frac{\text{Weight found (mg)}}{\text{Weight added (mg)}}$$

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/15 ml iso-octane, because samples are extracted in this amount of iso-octane. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/15 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of day-to-day variations and variations during the same day of the electrolytic conductivity detector response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each envelope of peak area from the standard curve. No volume correction is needed, because the standard curve is based on mg/15 ml of iso-octane, and the volume of sample injected is identical to the volume of the standards injected.

10.2 A correction for the blank must be made for each sample.

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in sample filter and bubbler
mg blank = mg found in blank filter and bubbler

10.3 Divide the total weight by the analytical method recovery (A.M.R.) to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{A.M.R.}}$$

10.4 The concentration of the analyte in the air sample can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.3) X 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

11. Reference

11.1 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

1,1,1,2-Tetrachloro-2,2-difluoroethane

Analyte:	1,1,1,2-Tetrachloro-2,2-difluoroethane	Method No.: S131
Matrix:	Air	Range: 2,160-9,020 mg/cu m
OSHA Standard:	500 ppm (4,170 mg/cu m)	Precision ($\overline{CV}_T$): 0.069
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 5/9/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 2,160-9,020 mg/cu m at an atmospheric temperature and pressure of 22°C and 763 mm Hg, using a 2-liter sample. Under the conditions of sample size (2 liters) the probable useful range of this method is 400-12,000 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 24-mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of the analyte and other substances in the air. The first section of the charcoal tube was found to hold 39 mg of analyte when a test atmosphere containing 14,300 mg/cu m

of the analyte in air was sampled at 0.035 liter per minute for 77 minutes; breakthrough was observed at this time, i.e. the concentration of the analyte in the effluent was 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 2,160-9,020 mg/cu m was 0.069. This value corresponds to a 290 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 1.3% higher than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in stainless steel) packed with 10% FFAP on 80/100 mesh, acid washed DMCS Chromosorb W.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 1.0-ml delivery pipets.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 1,1,1,2-Tetrachloro-2,2-difluoroethane, reagent grade.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A maximum sample size of 2 liters is recommended. Sample at a flow of 0.035 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm 5\%$.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 185°C injector temperature
5. 250°C manifold temperature (detector)
6. 50°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation

within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush method.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of hexane solution containing 1336 mg/ml is injected directly into the charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample vials, capped with Teflon-faced septa, may be used in place of the glass tubes.

The amount injected is equivalent to that present in a 2-liter air sample at the selected level. Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$\text{D.E.} = \frac{\text{Average Weight recovered (mg)}}{\text{Weight added (mg)}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/1.0 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to get the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	= pressure (mm Hg) of air sampled
T	= temperature (°C) of air sampled
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	= molecular weight (g/mole) of analyte
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

1,1,2,2-Tetrachloro-1,2-difluoroethane

Analyte:	1,1,2,2-Tetrachloro-1,2-difluoroethane	Method No.: S132
Matrix:	Air	Range: 1,883-8,060 mg/cu m
OSHA Standard:	500 ppm (4,170 mg/cu m)	Precision ($\overline{CV}_T$): 0.054
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 5/9/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 1,883-8,060 mg/cu m at an atmospheric temperature and pressure of 25°C and 763 mm Hg, using a 2-liter sample. Under the conditions of sample size (2 liters) the probable useful range of this method is 420-12,500 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 25-mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of the analyte and other substances in the air. The first section of the charcoal tube was found to

hold at least 52 mg of the analyte when a test atmosphere containing 6,990 mg/cu m of the analyte in air was sampled at 0.041 liter per minute for 183 minutes; at that time the concentration of the analyte in the effluent was less than 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 1,883-8,060 mg/cu m was 0.054. This value corresponds to a 225 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 2.6% higher than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in stainless steel) packed with 10% FFAP on 80/100 mesh, acid washed DMCS Chromosorb W.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 1.0-ml delivery pipets.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 1,1,2,2-Tetrachloro-1,2-difluoroethane, reagent grade.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A sample size of 2 liters is recommended. Sample at a flow of 0.05 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm$5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 50°C injector temperature
5. 240°C manifold temperature (detector)
6. 50°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation

within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush method.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of hexane solution containing 861 mg/ml is injected directly into the charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample vials, capped with Teflon-faced septa, may be used in place of the glass tubes.

The amount injected is equivalent to that present in a 2-liter air sample at the selected level. Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight recovered (mg)}}{\text{Weight added (mg)}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/1.0 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to get the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	= pressure (mm Hg) of air sampled
T	= temperature (°C) of air sampled
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	= molecular weight (g/mole) of analyte
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

Chlorobenzene
(Monochlorobenzene)

Analyte:	Chlorobenzene	Method No.: S133
Matrix:	Air	Range: 183-736 mg/cu m
OSHA Standard:	75 ppm (345 mg/cu m)	Precision ($\overline{CV}_T$): 0.056
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 5/9/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 183-736 mg/cu m at an atmospheric temperature and pressure of 25°C and 761 mm Hg, using a 10 liter sample. Under the conditions of sample size (10 liters) the probable useful range of this method is 35-1035 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 10-mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of chlorobenzene and other substances in the air. The first section of the charcoal tube was found to hold at least 31 mg of chlorobenzene when a test atmosphere

containing 704 mg/cu m of chlorobenzene in air was sampled at 0.185 liter per minute for 240 minutes; at that time the concentration of chlorobenzene in the effluent was less than 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 183-736 mg/cu m was 0.056. This value corresponds to a 19 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 3.3% higher than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3)

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in stainless steel) packed with 10% FFAP on 80/100 mesh, acid washed DMCS Chromosorb W.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 One-milliliter sample containers with glass stoppers or Teflon-lined caps.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 0.5-ml delivery pipets or 1.0-ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 Chlorobenzene, reagent grade.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A sample size of 10 liters is recommended. Sample at a flow of 0.20 liter per minute or less. The flow rate should be known with an accuracy of at least $\pm$5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 1-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 0.5 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 50 ml/min (60 psig) nitrogen carrier gas flow
2. 65 ml/min (24 psig) hydrogen gas flow to detector
3. 500 ml/min (50 psig) air flow to detector
4. 190°C injector temperature
5. 250°C manifold temperature (detector)
6. 105°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation

within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Descrption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm.

The amount injected is equivalent to that present in a 10 liter air sample at the selected level.

Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 0.5 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight recovered (mg)}}{\text{Weight added (mg)}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/0.5 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in front section of sample tube

mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to get the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) X 1000 (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	= pressure (mm Hg) of air sampled
T	= temperature (°C) of air sampled
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	= molecular weight (g/mole) of analyte
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

1,1,2-Trichloroethane

Analyte:	1,1,2-Trichloroethane	Method No.:	S134
Matrix:	Air	Range:	26-111 mg/cu m
OSHA Standard:	10 ppm (55 mg/cu m)	Precision ($\overline{CV}_T$):	0.057
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date:	6/6/75

1. Principle of the Method

1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.

1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

1.4 The area of the resulting peak is determined and compared with areas obtained from injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 26-111 mg/cu m at an atmospheric temperature and pressure of 26.5°C and 762 mm Hg, using a 10-liter sample. Under the conditions of sample size (10 liters) the probable useful range of this method is 5-165 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 1.6 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold at least 4.9 mg of analyte when a test atmosphere containing 108 mg/cu m of analyte in air was sampled at 0.19 liters per minute for 240 minutes; i.e., at that time, the concentration of analyte in the effluent was less than 5% of that in the influent.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.

3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 26-111 mg/cu m was 0.057. This value corresponds to a 3 mg/cu m standard deviation at the the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.

4.2 On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 7.7% lower than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3).

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (10-ft x 1/8-in stainless steel) packed with 10% OV-101 stationary phase on 100/120 mesh Supelcoport.

6.5 An electronic integrator or some other suitable method for measuring peak areas.

6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.

6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide

7.2 1,1,2-Trichloroethane, reagent grade

7.3 Octane, or other suitable internal standard

7.4 Purified nitrogen

7.5 Prepurified hydrogen

7.6 Filtered compressed air

8. Procedure

8.1 Cleaning of equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A maximum sample size of 10 liters is recommended. Sample at a rate of 0.2 liter per minute or less. The flow rate should be known with an accuracy of at least ±5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 ml/min (60 psig) Nitrogen carrier gas flow
2. 35 ml/min (25 psig) Hydrogen gas flow to detector
3. 400 ml/min (60 psig) Air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 70°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample injector vials, capped with Teflon-faced septa, may be used in place of the glass tubes.

Six tubes at each of three concentration levels (0.5X,1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 10-liter sample at the selected level. The tubes are allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$D.E. = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2X the standard. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

mg sample = mg found in front section of sample tube
mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liters/cu m)}}{\text{Air Volume Sampled (liters)}}$$

10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

INDEX

Volume 1, Methods 102-262
Volume 2, Methods S1-S134
Volume 3, Methods S135-S391

Acetic anhydride S170
Acetone 127, S1
Acetonitrile (Methyl cyanide) S165
Acetylene dichloride (see 1,2-Dichloroethylene)
Acetylene tetrabromide (Tetrabromoethane) S117
Acrolein 118, 211
Acrylonitrile 202, S156
Aldrin S275
Allyl alcohol S52
Allyl chloride S116
Aluminum 173
Amines, aliphatic 221
Amines, aromatic 168
Ammonia 205
n-Amyl acetate S51
sec-Amyl acetate (alpha-Methyl butyl acetate) S31
Aniline 168, S310
Anisidine 168
Anthanthrene 183, 184, 206
Anthracene 206
Antimony 107, 173, 189, 193, 197, S2
Arsenic 139, 140, 173, 180, 188, 192, 196, S309
Arsine S229
Asbestos 239, 245
Azelaic acid 256
Azo dyes 234
Barium 173, S198
Benz(c)acridine 183
Benz(a)anthracene 183
Benz(a,h)anthracene 183, 184
Benz(a)anthrone 183
Benzene 127, S311
Benzene-solubles 217
Benzidine 243
Benzo(b)fluoranthene 183
Benzo(j)fluoranthene 183
Benzo(k)fluoranthene 183, 184
Benzo(g,h,i)perylene 183
Benzo(a)pyrene 183, 184, 186, 206, 251
Benzo(e)pyrene 183, 184
Benzyl chloride S115
Beryllium 121, 173, S339
Bibenzyl 183
Biphenyl-phenyl ether mixture (see Phenyl ether-biphenyl vapor mixture)

Bis(chloromethyl) ether 213, 220
Bismuth 173
2,2-Bis(p-chlorophenyl)-1,1,1-trichloroethane (see DDT)
Boron oxide S349
Bromoform S114
Butadiene (1,3-Butadiene) S91
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
tert-Butyl alcohol S63
Butyl alcohol (n-Butyl alcohol) S66
Butyl cellosolve (see 2-Butoxy ethanol)
n-Butyl glycidyl ether S81
Butylamine 221
p-tert-Butyltoluene S22
Cadmium 173, 191, 223, 224, S312, S313
Calcium 173
Calcium arsenate 173
Calcium oxide 173, S205
Camphor S10
Carbaryl (Sevin) S273
Carbon black S262
Carbon dioxide S249
Carbon disulfide 179, S248
Carbon monoxide 112, 113
Carbon tetrachloride 127, S314
Carbonyl chloride (see Phosgene)
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)
Chlorobenzene (Monochlorobenzene) S133
Chlorobromomethane S113
Chlorodiphenyl (54% chlorine) S121
2-Chloroethanol (see Ethylene chlorohydrin)
Chloroform 127, S351
Chloromethyl methyl ether 220
Chloroprene (2-Chloro-1,3-butadiene) S112
Chromic acid 152, 169, S317
Chromium 152, 173, 182, S323, S352
Chrysene 183, 184, 206
Chrysotile 245
Coal tar naphtha (see Naphtha, coal tar)
Coal tar pitch volatiles 183, 184, 217
Cobalt 173
Copper dusts and mists 173, S186

Copper 173
Cresol, all isomers S167
Cristobalite 109, 259, S315
Cumene S23
Cyanide 116, S250
Cyclohexane S28
Cyclohexanol S54
Cyclohexanone S19
Cyclohexene S82
Cyclohexylamine 221
DBPC 226
DDT (2,2-Bis(p-chlorophenyl)-1,1,1-trichloroethane) S274
Diacetone alcohol (4-Hydroxy-4-methyl-2-pentanone) S55
Diazomethane S137
Diazonium salts 234
1,2-Dibromoethane (see Ethylene dibromide)
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)
Dichloroethyl ether S357
1,2-Dichloroethylene (Acetylene dichloride) S110
Dichloromethane (see Methylene chloride)
Dichloromonofluoromethane (Refrigerant 21) S109
Dichlorotetrafluoroethane (Refrigerant 114) S108
Dieldrin S283
Diethylamine 221, S139
Diethylene dioxide (see Dioxane)
Difluorodibromomethane S107
Difluorodichloromethane S111
Diisobutyl ketone (2,6-Dimethyl-4-heptanone) S358
Diisopropylamine 221
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)
Dimethylamine 221, S142
2,4-Dimethylaminobenzene (see Xylidine)
N,N-Dimethylaniline 168, S164
1,1-Dimethylhydrazine 248, S143
Dioxane 127, S360
p,p-Diphenylmethane diisocyanate 142
Dipropylene glycol methyl ether S69
2,6-Di-tert-butyl-p-cresol 226
Dowtherm A (see Phenyl ether-biphenyl vapor mixture)

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)
Ethanol (see Ethyl alcohol)
Ether S80
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 ether S80
Ethyl formate S36
Ethyl sec-amyl ketone (see 5-Methyl-3-heptanone)
Ethyl silicate S264
O-Ethyl-O-p-nitrophenyl thionobenzene phosphonate (see EPN)
Ethylamine 221, S144
Ethylene chloride (see Ethylene dichloride)
Ethylene chlorohydrin (2-Chloroethanol) S103
Ethylene dibromide (1,2-Dibromoethane) S104
Ethylene dichloride (1,2-Dichloroethane) 127, S122
Ethylene glycol dinitrate 203, S216
Ethylene oxide S286
di-2-Ethylhexylphthalate (see di-sec-Octyl phthalate)
Ethylidene chloride (see 1,1-Dichloroethane)
N-Ethylmorpholine S146
Fluoranthene 183, 184
Fluoride 114, 117, 212
Fluorotrichloromethane (Refrigerant 11) S102
Formaldehyde 125, 235
Formic acid 232
Gallium 177, 198
Glycidol (2,3-Epoxy-1-propanol) S70
Heptane S89
3-Heptanone (see Ethyl butyl ketone)
2-Heptanone (see Methyl (n-amyl) ketone)
Hexachloroethane S101
Hexachloronaphthalene S100
Hexane S90
2-Hexanone (Methyl butyl ketone or MBK) S178
Hexone (Methyl isobutyl ketone or MIBK) S18
sec-Hexyl acetate (1,3-Dimethyl butyl acetate) S37
Hydrazine 248, S237
Hydrogen bromide S175
Hydrogen chloride S246
Hydrogen cyanide 116
Hydrogen fluoride 117, 212, S176
Hydrogen sulfide 126, S4
Hydroquinone S57

4-Hydroxy-4-methyl-2-pentanone (see Diacetone alcohol)
Indium 173, 190, 194, 199
Iron 173
Isoamyl acetate S45
Isoamyl alcohol S58
Isobutyl acetate S44
Isobutyl alcohol S64
Isophorone S367
Isopropanol (see Isopropyl alcohol)
Isopropyl acetate S50
Isopropyl alcohol (Isopropanol) S65
Isopropyl benzene (see Cumene)
Isopropyl glycidyl ether S77
Isopropylamine 221, S147
Isopropylether S368
Kepone 225
Ketene S92
Lead 102, 173, 191, 195, 200, 208, 214, 262, S341
Lindane S290
Liquified petroleum gas (see LPG)
Lithium 173
LPG (Liquified petroleum gas) S93
Magnesium 173
Magnesium oxide fume S369
Malathion S370
Manganese 173, S5
MBK (see 2-Hexanone)
MDI (see Methylene bisphenyl isocyanate)
MEK (see 2-Butanone)
Mercury 145, 165, 167, 175
Mesityl oxide S12
Methanol (see Methyl alcohol)
2-Methoxyethanol (see Methyl cellosolve)
Methyl(n-amyl)ketone (2-Heptanone) S15
5-Methyl-3-heptanone S13
Methyl acetate S42
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
Methyl cellosolve acetate S39
Methyl chloride 201
Methyl chloroform (1,1,1-Trichloroethane) 127, S328
Methyl cyanide (see Acetonitrile)
Methyl ethyl ketone (see 2-Butanone)
Methyl iodide S98
Methyl isoamyl acetate S37
Methyl isobutyl carbinol S60
Methyl isobutyl ketone (see Hexone)

alpha-Methyl styrene S26
Methylal (Dimethoxymethane) S71
Methylamine 221
Methylcyclohexane S94
4,4'-Methylenebis(2-chloroaniline) 236
Methylene bisphenyl isocyanate (MDI) 142
Methylene chloride (Dichloromethane) 127, S329
Methylhydrazine 248, S149
MIBK (see Hexone)
MOCA 236
Molybdenum 173
Molybdenum insoluble compounds S376
Molybdenum soluble compounds S193
Monochlorobenzene (see Chlorobenzene)
Monomethyl aniline S153
Monomethyl hydrazine 248, S149
Morpholine S150
Naphtha, coal tar (Coal tar naphtha) S86
Naphthalene S292
Nickel 173, S206
Nicotine S293
Nitric oxide 231
p-Nitroaniline 168
Nitrobenzene S217
p-Nitrochlorobenzene S218
Nitrogen dioxide 108, 231
Nitroglycerin 203, S216
Nitroglycol 203
N-Nitrosodimethylamine 252
Nitrotoluene S223
Octachloronaphthalene S97
Octane S378
di-sec-Octyl phthalate (di-2-Ethylhexylphthalate) S40
Oil mist 159, S272
Organic solvents 127
Organo(alkyl) mercury 175
Ozone 153, 154, S8
Palladium 173
Parathion 158, S295
PCB 244, 253, S121
Pentachloronapthalene S96
Pentachlorophenol 230
Pentane S379
2-Pentanone S20
Perchloroethylene (see Tetrachloroethylene)
Perylene 184, 206
Petroleum distillates (Petroleum naphtha) S380
Petroleum naphtha (See Petroleum distillates)
Phenanthene 206
Phenol S330
Phenyl ether S72

Phenyl ether-biphenyl vapor mixture (Dowtherm A) S73
Phenyl ethylene (see Styrene)
Phenyl glycidyl ether S74
Phenylhydrazine 248, S160
Phosgene (Carbonyl chloride) 219
Phosphate 215
Phosphoric acid 216, S333
Phosphorus (white, yellow) 242, 257
Phthalic anhydride S179
Platinum, soluble salts S191
PNAs 183, 184, 186, 206
Polychlorinated biphenyl (PCB) 244, 253, S121
Polymethylsiloxane 227
Polynuclear aromatic hydrocarbons (PNAs) 183, 184, 186, 206
Potassium 173
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
Pyrene 183, 184
Pyridine S161
Quartz (see Silica, crystalline)
Refrigerant 11 (see Fluorotrichloromethane)
Refrigerant 113 (see 1,1,2-Trichloro-1,2,2-trifluoroethane)
Refrigerant 114 (see Dichlorotetrafluoroethane)
Refrigerant 12 (see Dichlorodifluoromethane)
Refrigerant 21 (see Dichloromonofluoromethane)
Rhodium, metal fume and dust S188
Rhodium, soluble salts S189
Rubidium 173
Selenium 124, 181, S190
Sevin (see Carbaryl)
Silica, crystalline 106, 109, 110, 259, S315
Silicon 173
Silver 173
Sodium 173
Sodium hydroxide 241
Stoddard solvent S382
Strontium 173
Styrene (Vinyl benzene) 127, S30
Sulfur dioxide 146, 160, 163, 204
Sulfuric acid 187, S174
TDI (see Toluene-2,4-diisocyanate)
Tellurium 173, S204
Tellurium hexafluoride S187
Terphenyl 183, S27
Tetrabromoethane (see Acetylene tetrabromide)

1,1,1,2-Tetrachloro-2,2-difluoroethane S131
1,1,2,2-Tetrachloro-1,2-difluoroethane S132
1,1,2,2-Tetrachloroethane S124
Tetrachloroethylene (Perchloroethylene) 127, S335
Tetrachloromethane (see Carbon tetrachloride)
Tetrachloronaphthalene S130
Tetrahydrofuran S78
Tetramethyl succinonitrile S155
Tetramethyl thiuram disulfide (see Thiram)
Tetranitromethane S224
Tetryl (2,4,6-Trinitrophenylmethylnitramine) S225
Thallium 173, S306
Thiophene 255
Thiram (Tetramethyl thiuram disulfide) 228
Tin 173, 176, S183
Tin, organic compounds 176
Tissue preparation 237
Titanium dioxide S385
Toluene 127, S343
Toluene-2,4-diisocyanate (TDI) 141
o-Toluidine 168, S168
Toxaphene (see Chlorinated camphene)
Tributyl phosphate S208
1,1,2-Trichloro-1,2,2-trifluoroethane (Refrigerant 113) S129
1,1,1-Trichloroethane (see Methyl chloroform)
1,1,2-Trichloroethane 127, S134
Trichloroethylene 127, S336
Trichloromonofluoromethane (see Fluorotrichloromethane)
Trichloronaphthalene S128
1,2,3-Trichloropropane S126
Tridymite 109, 259, S315
Triethylamine 221, S152
Trifluoromonobromomethane S125
2,4,6-Trinitrophenylmethylnitramine (see Tetryl)
Triorthocresyl phosphate S209
Triphenyl phosphate S210
Turpentine S88
Vanadium 173, S391
Vinyl benzene (see Styrene)
Vinyl chloride 178
Vinyl toluene S25
Xylene (Xylol or Dimethyl benzene) 127, S318
Xylidine (2,4-Dimethylaminobenzene) 168, S162
Xylol (see Xylene)
Yttrium S200
Zinc 173
Zinc oxide 222
Zirconium compounds S185

★ U.S. GOVERNMENT PRINTING OFFICE: 1977—757-057/6749

S 134-17