Although the specific details of the analytical methods have not been identified our current best judgment is that the personal monitoring procedure will be a charcoal tube sample collection and a gas chromatographic analysis similar to the enclosed NIOSH #178. Personal monitoring will be required for those employees working in areas where VCM can exceed the "Action Level" (0.5 ppm averaged over an 8 hour day). Personal monitoring must be repeated monthly for employees exposed in excess of the "Permissible Limit" (1.0 ppm for 8 hours or 5.0 ppm for 15 minutes). Continuous monitoring is required in areas where VCM levels may exceed the allowable concentration for "the devices in use". Our current inquiry to OSHA has included a request for clarification of this statement.

L. B. Crider

LBC/ch

Distribution
*A. W. Clements
*C. B. Cooper ← COPY FOR ←
A. M. Fairlie
*R. J. Fawcett
*C. R. Flynn
E. W. Harrington
*M. N. Johnson
*E. B. Katzenmeyer, Jr.
F. E. Krause
R. M. Kreager
*P. H. Lawrence
R. W. MacCuspie
J. F. Malone
J. L. Nelson
H. R. Rex
*R. N. Rylands
*G. D. Schaaf
E. G. Schwaegerle
R. D. Scott
*R. W. Strassburg
R. L. Toole
A. Vittone
*P. J. Weaver
*A. R. Webber
W. J. Wilcox
*C. L. Woods
*B. M. G. Zwicker
R. J. Coffey
W. M. Smith
*P. M. Zakriski
A. L. Schultz
C. H. Lufter
*J. A. Klupar
LBC/File

*Enclosures: (1) Index to NIOSH Manual
(2) NIOSH Procedure #127
(3) NIOSH Procedure #178

NIOSH

MANUAL OF ANALYTICAL METHODS

Physical and Chemical Analysis Branch
Division of Laboratories and Criteria Development
1014 Broadway, Cincinnati, Ohio 45202

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Center for Disease Control
National Institute for Occupational Safety and Health
1974

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

INDEX OF METHODS ARRANGED ACCORDING TO ANALYTE

Analyte	Matrix	Procedure		P & CAM No.
		Sampling	Analysis	
Acrolein	Air	Impinger	Colorimetric	118
Antimony	Urine		Colorimetric	107
Aromatic Amines	Air	Silica gel Adsorption	GC	168
Arsenic	Air, Urine	Membrane Filter	AA	139
Arsenic	Air, Urine	Membrane Filter	Colorimetric	140
Beryllium	Air, Settled Dust	Membrane Filter	AA	121
	Ore, Swipe Samples			
Beryllium	Air, Settled Dust	Membrane Filter	Emission Spectroscopy	123
	Ore, Swipe Samples			
Cadmium	Air	Membrane Filter	AA	151
Carbon Monoxide	Air	Grab-bag	IR	112
Chromic Acid Mist	Air	Membrane Filter	Colorimetric	169
Chromium (Particulate)	Air	Membrane Filter	AA	152
Cyanide	Air	Impinger	Ion-Specific Electrode	116
Diphenylmethane-diisocyanate	Air	Impinger	Colorimetric	142
Fluoride	Urine		Ion-Specific Electrode	114
Fluorides and Hydrogen Fluoride	Air	Impinger	Ion-Specific Electrode	117
Formaldehyde	Air	Impinger	Colorimetric	125

Analyte	Matrix	Procedure		P & CAM No.
		Sampling	Analysis	
Hydrogen Sulfide	Air	Impinger	Colorimetric	126
Lead	Air	Membrane Filter	AA	155
Lead	Blood, Urine	Vacutainers	AA	101
Lead	Blood, Urine	Vacutainers	Colorimetric	102
Mercury (Particulate, Metallic, Organic Vapor)	Air	Three Section Solid Phase Sampler	Flameless AA	175
Mercury	Blood	Vacutainers	Flameless AA	105
Mercury	Blood	Vacutainers	Flameless AA	167
Mercury	Urine		Flameless AA	103
Mercury	Urine		Flameless AA	165
Metals (General Procedure)	Industrial Hygiene Samples	Membrane Filter	AA	173
Nitrogen Dioxide	Air	Impinger	Colorimetric	108
Oil Mist	Air	Membrane Filter	Fluorescence	159
Organic Solvents	Air	Charcoal Adsorption	GC	127
Ozone	Air	Impinger	Colorimetric	153
Parathion	Air	Impinger	GC	158
Quartz	Coal Dust	Membrane Filter	Infrared	110
Silica (Quartz)	Air, Dust Biological Tissue	Membrane Filter	Colorimetric	106
Silica (Quartz, Cristobalite, Tridymite)	Air	Membrane Filter	X-Ray Diffraction	109
Sulfur Dioxide	Air	Impinger	Titration	146
Sulfur Dioxide	Air	Impinger	Colorimetric	160

Analyte	Matrix	Procedure		P & CAM No.
		Sampling	Analysis	
Sulfur Dioxide	Air	Impinger	Titration	163
2,4-Toluene-diisocyanate	Air	Impinger	Colorimetric	141

ORGANIC SOLVENTS IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Organic Solvents (See Table 1)	Method No:	P&CAM 127
Matrix:	Air	Range:	For the specific compound, refer to Tables I&II
Procedure:	Adsorption on charcoal desorption with carbon disulfide, GC		
Date Issued:	9/15/72	Precision:	10.5% RSD
Date Revised:	7/15/74	Classification:	See Table 1

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, graduated test tube 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

   The lower limit in mg/sample for the specific compound at 16 x 1 attenuation on a gas chromatograph fitted with a 10:1 splitter is shown in Table 1. This value can be lowered by reducing the attenuation or by eliminating the 10:1 splitter.

3. Interferences

   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. Preliminary experiments indicate that high humidity severely decreases the breakthrough volume.

   3.2 When two or more solvents 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 specific compound under study 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. For this reason it is important that a sample of the bulk solvent(s) be submitted at the same time so that identity(ies) can be established by other means.

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

4. Precision and Accuracy

4.1 The mean relative standard deviation of the analytical method is 8%. (Ref. 11.4).

4.2 The mean relative standard deviation of the analytical method plus field sampling using an approved personal sampling pump is 10% (Ref. 11.4). Part of the error associated with the method is related to uncertainties in the sample volume collected. If a more powerful vacuum pump with associated gas-volume integrating equipment is used, sampling precision can be improved.

4.3 The accuracy of the overall sampling and analytical method is 10% (NIOSH's unpublished data) when the personal sampling pump is calibrated with a charcoal tube in the line.

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. During sample storage the more volatile compounds will migrate throughout the tube until equilibrium is reached (33% of the sample on the backup section).

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 for personal samples. For an area sample any vacuum pump whose flow can be determined accurately at 1 liter per minute or less.

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 palced infront of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 ℓpm.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (20 ft x 1/8 in) with 10% FFAP stationary phase on 80/100 mesh, acid-washed DMCS Chromosorb W solid support. Other columns capable of performing the required separations may be used.

6.5 A mechanical or electronic integrator or a recorder and some method for determining peak area.

6.6 Glass stoppered micro tubes. The 2.5-mℓ graduated microcentrifuge tubes are recommended.

6.7 Hamilton syringes: 10 µl, and 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 Spectroquality carbon disulfide (Matheson Coleman and Bell)

7.2 Sample of the specific compound under study, preferably chromatoquality grade.

7.3 Bureau of Mines Grade A helium.

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, the ends of the tube should be broken to provide an opening at least one-half the internal diameter of the tube (2mm).

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 vertical during sampling.

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

8.3.5 The flow, time, and/or volume must be measured as accurately as possible. The sample should be taken at a flow rate of 1 ℓpm or less to attain the total sample volume required. The minimum and maximum sample volumes that should be collected for each solvent are shown in Table 1. The minimum volume quoted must be collected if the desired sensitivity is to be achieved.

8.3.6 The temperature and pressure of the atmosphere being sampled should be measured and 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 Samples of the suspected solvent(s) should be submitted to the laboratory in containers furnished by NIOSH for such purpose. These liquid bulk samples should not be transported in the same container as the samples or blank tube. If possible, a bulk air sample (at least 50ℓ air drawn through tube) should be shipped for qualitative identification purposes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In prepration 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 small stoppered test tube. The separating section of foam is removed and discarded; the second section is transferred to another test tube. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, one-half ml of carbon disulfide is pipetted into each test tube. (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. The use of graduated glass-stoppered, microcentrifuge tubes is recommended so that one can observe any apparent change in volume during the desorption process. Carbon disulfide is a very volatile solvent, so volume changes can occur during the desorption process depending on the surrounding temperature. The initial volume occupied by the charcoal plus the 0.5 mℓ CS_2 should be noted and corresponding volume adjustments should be made whenever necessary just before GC analysis.

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

1. 85 cc/min. (70 psig) helium 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. 200°C injector temperature.

5. 200°C manifold temperature (detector)

6. Isothermal oven or column temperature - refer to Table 1 for specific compounds.

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 blowback 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 a short distance to minimize evaporation of the sample from the tip of the needle. 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. The Physical and Chemical Analysis Branch of NIOSH has found that the desorption efficiencies for the compounds in Table 1 are between 81% and 100% and vary with each batch of charcoal.

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 5cm, 4-mm I.D. glass tube, flame-sealed at one end (similar to commercially available culture tubes). 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 compound is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. The amount injected is usually equivalent to that present in a 10-liter sample at a concentration equal to the federal standard.

At least five tubes are prepared in this manner and allowed to stand for at least overnight to assure complete abosrption of the specific compound onto the charcoal. These five tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.3.

Two or three standards are prepared by injecting the same volume of compound into 0.5 mℓ of CS_2 with the same syringe used in the preparation of the sample. These are analyzed with the samples.

The desorption efficiency equals the difference between the average peak area of the samples and the peak area of the blank divided by the average peak area of the standards, or

$$\text{desorption efficiency} = \frac{\text{Area sample} - \text{Area blank}}{\text{Area standard}}$$

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 mℓ CS_2 because samples are desorbed in this amount of CS_2. To minimize error due to the volatility of carbon disulfide, one can inject 20 times the weight into 10 mℓ of CS_2. For example, to prepare a 0.3 mg/0.5 mℓ standard, one would inject 6.0 mg into exactly 10 mℓ of CS_2 in a glass-stoppered flask. The density of the specific compound is used to convert 6.0 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/0.5mℓ 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 The weight, in mg, corresponding to each peak area is read from the standard curve for the particular compound. No volume corrections are needed, because the standard curve is based on mg/0.5 mℓ CS_2 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.

$$\text{Correct mg} = mg_s - mg_b$$

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 The corrected amounts present in the front and backup sections of the same sample tube are added to determine the total measured amount in the sample.

10.4 This total weight is divided by the determined desorption efficiency to obtain the total mg per sample.

10.5 The volume of air sampled is converted to standard conditions of of 25°C and 760 mm Hg.

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

where:

V_s = 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 degree centigrade

10.6 The concentration of the organic solvent in the air sampled can be expressed in mg per m^3, which is numerically equal to µg per liter of air

$$mg/m^3 = \mu g/\ell = \frac{\text{total mg (Section 10.4) x 1000 (µg/mg)}}{V_s}$$

10.7 Another method of expressing concentration is ppm, defined as µℓ of compounds per liter of air

$$\text{ppm} = \mu\ell \text{ of compound}/V_s$$

$$\text{ppm} = \frac{\mu\ell \text{ of compound}}{V_s} \times \frac{24.45}{MW}$$

where:

24.45 = molar volume at 25°C and 760 mm Hg

MW = molecular weight of the compound (Table 1)

11. References

11.1 White, L.D., D.G. Taylor, P.A. Mauer, and R.E. Kupel, "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 Young, D.M. and A.D. Crowell, Physical Adsorption of Gases, Butterworths, London, 1962, pp. 137-146.

11.3 Federal Register, 37 (#202), 22139-22142 (October 18, 1972).

11.4 NIOSH Contract HSM-99-72-98, Scott Research Laboratories, Inc., "Collaborative Testing of Activated Charcoal Sampling Tubes for Seven Organic Solvents," pp. 4-22, 4-27 (1973).

TABLE I

PARAMETERS ASSOCIATED WITH P&CAB ANALYTICAL METHOD NO. 127

Organic Solvent	Method Classification	Detection limit (mg/sample)	Sample Volume (ℓ) Minimum[a]	Maximum[b]	GC Column Temperature(°C)	Molecular Weight
Acetone	D	-	0.5	7.7	60	58.1
Benzene	A	0.01	0.5	55	90	78.1
Carbon tetrachloride	A	0.20	10	60	60	154.0
Chloroform	A	0.10	0.5	13	80	119
Dichloromethane	D	0.05	0.5	3.8	85	84.9
p-Dioxane	A	0.05	1	18	100	88.1
Ethylene dichloride	D	0.05	1	12	90	99.0
Methyl ethyl ketone	B	0.01	0.5	13	80	72.1
Styrene	D	0.10	1.5	34	150	104
Tetrachloroethylene	B	0.06	1	25	130	166
1,1,2-trichloroethane	B	0.05	10	97	150	133
1,1,1-trichloroethane (Methyl Chloroform)	B	0.05	0.5	13	150	133
Trichloroethylene	A	0.05	1	17	90	131
Toluene	B	0.01	0.5	22	120	92.1
Xylene	A	0.02	0.5	31	100	106

(a) Minimum volume, in liters, required to measure 0.1 times the OSHA standard

(b) These are breakthrough volumes calculated with data derived from a potential plot (reference 11.2) for activated coconut charcoal. Concentrations of vapor in air at 5 times the OSHA standard (reference 11.3) or 500 ppm, whichever is lower, 25°C, and 760 torr were assumed. These values will be as much as 50% lower for atmospheres of high humidity. The effects of multiple contaminants have not been investigated, but it is suspected that less volatile compounds may displace more volatile compounds (See 3.1 and 3.2)

TABLE II

CHEMICALS WHICH HAVE GREATER THAN 80% DESORPTION EFFICIENCY BUT HAVE NOT BEEN THOROUGHLY TESTED BY NIOSH

Class E (Proposed)

Acrylonitrile
Allyl glycidyl ether
n-Amyl acetate
2-Butoxyethanol
n-Butyl acetate
n-Butyl alcohol
n-Butylglycidyl ether
Chlorobenzene
Cyclohexane
Cyclohexanone
o-Dichlorobenzene
p-Dichlorobenzene
Diethyl ether
N,N-Dimethyl aniline
Epichlorohydrin
2-Ethoxylethyl acetate
Ethyl acetate
Ethylbenzene
Ethyl butyl ketone
Fufural
Heptane
Hexane
Isoamyl acetate
Isobutyl acetate
Isobutyl alcohol
Isoctane
Isophorone
Isopropyl acetate
Isopropyl glycidyl ether
2,6-Lutidine
Methyl acetate
Methyl acrylate
Methyl n-butyl ketone
Methyl ethyl ketone
Methyl isobutyl ketone
Methyl methacrylate
α-Methyl styrene
p-Methyl styrene
n-Octane
3-Octanone
Pentane
2-Pentanone
α-pinene
n-Propyl acetate
1,1,2,2-Tetrachloroethane
Tetrahydrofuran
Trichlorotrifluoroethane (Freon 113)

Recommended Sample Size = 10ℓ

VINYL CHLORIDE IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Vinyl Chloride (Chloroethene, Chloroethylene)	Method No.:	P&CAM #178
Matrix:	Air	Range:	0.2-1500 ng per injection
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC		
Date Issued:	9/3/74	Precision:	Unknown
Date Revised:		Classification:	D (Operational)

1. Principle of the Method

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

   1.2 The charcoal in the tube is transferred to a small vial containing carbon disulfide where the vinyl chloride is desorbed.

   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 The minimum detectable amount of vinyl chloride was found to be 0.2 nanograms per injection at a 1 x 1 attenuation on a gas chromatograph.

   2.2 At the recommended sampling flow rate of 50 ml/min, the total volume to be sampled should not exceed 5.0 liters. This value is the volume which the front section of the charcoal tube will hold at 200 ppm before a significant amount of vinyl chloride is found on the backup section. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethan foam. [See Section 6.2.]) If a particular atmosphere

is suspected of containing a high concentration of contaminants and/or a high humidity is suspected, the sampling volume should be reduced by 50%.

3. Interferences

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. Preliminary experiments indicate that high humidity severely decreases the capacity of the charcoal for organic vapors.

3.2 When two or more substances are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample since these compounds may interfere with the analysis for vinyl chloride.

3.3 It must be emphasized that any compound which has the same retention time as vinyl chloride at the operation 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. For this reason it is important that a sample of the bulk material be submitted at the same time so that identity(ies) can be established by other means.

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

The precision and accuracy of the total sampling and analytical method have not been determined.

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 components 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 20% of that found on the front section, the possibility of sample loss exists. During sample storage, volatile compounds such as vinyl chloride will migrate throughout the tube until equilibrium is reached. At this time ~33% of this compound will be found in the backup section. This may lead to some confusion as to whether breakthrough has occurred. This migration effect can be considerably decreased by shipping and storing the tubes at -20°.

5.3 The precision of the overall 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 for personal and area samples whose flow can be determined accurately at 50 milliliters per minute.

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 urethan foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing to remove material possibly absorbed on charcoal. The primary absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethan 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 ℓ/min.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (20 ft x 1/8 in) with 10% SE-30 stationary phase on 80/100 mesh, Chromosorb W, acid washed, silanized with dimethyldichlorosilane solid support. Other columns capable of performing the required separations may be used.

6.5 A mechanical or electronic integrator or a recorder and some method for determining peak area.

6.6 Two-ml vials which can be sealed with caps containing teflon-lined silicone rubber septa.

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

6.8 Gas-tight syringes: 1 mℓ, with open/close valve.

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

6.10 Volumetric flasks: 10-mℓ or convenient sizes for making standard solutions. It is preferable to have plastic stoppers for the volumetric flasks.

7. Reagents

7.1 Spectroquality carbon disulfide.

7.2 Vinyl chloride, lecture bottle, 99.9% minimum purity.

7.3 Toluene, chromatographic quality.

7.4 Bureau of Mines Grade A 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 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, the ends of the tube are broken 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 is positioned nearest the sampling pump.

8.3.3 The charcoal tube is placed in a vertical position during sampling, open end pointing upward, to prevent "channelling" of the charcoal.

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

8.3.5 Bulk air samples are taken along with personal samples, i.e. sample 10-20 liters of the air in the environment using a separate charcoal tube.

8.3.6 The flow, time, and/or volume must be measured as accurately as possible. The sample is taken at a flow rate of 50 ml/min. The maximum volume to be sampled should not exceed 5.0 liters (See Section 2.2).

8.3.7 The temperature and pressure of the atmosphere being sampled is measured and recorded.

8.3.8 The charcoal tubes are capped with the supplied plastic caps immediately after sampling. Under no circumstances are rubber caps to be used.

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

8.3.10 Capped tubes are packed tightly before they are shipped to minimize tube breakage during transport to the laboratory. If the samples will spend a day or more in transit, cooling (e.g., with dry ice) is necessary to minimize migration of vinyl chloride to the backup section.

8.3.11 Samples received at the laboratory are logged in and immediately stored in a freezer (--20°C) until time for analysis. Samples may be stored in this manner for long periods of time with no appreciable loss of vinyl chloride (2 months). It should be pointed out that during long periods of storage (more than 2 weeks), the vinyl chloride will equilibrate between the two sections of charcoal, i.e., will migrate to the backup section. This does not constitute breakthrough.

8.4 Analysis of Samples

8.4.1 Preparation and Desorption 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 small vial containing 1 ml of carbon disulfide. (Note the addition of the CS_2 is important.) The vial is topped with a

septum cap (See Section 6.6). The separating section of foam is removed and discarded; the second section is transferred to another small vial containing 1 ml of CS_2. These two sections are analyzed separately. Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period. In any case samples should be analyzed within 60 minutes after addition of CS_2.

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

1. 40 cc/min. (80 psig) helium carrier gas flow
2. 65 cc/min. (20 psig) hydrogen gas flow to detector
3. 500 cc/min. (50 psig) air flow to detector
4. 230°C injector temperature
5. 230°C manifold temperature (detector)
6. 60°C isothermal column temperature (oven).

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 blowback 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. Two microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent and the plunger is pulled back about 0.4 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 to the 7.4 µℓ mark (2 µℓ solvent + 0.4 µℓ air + 5 µℓ sample = 7.4 µℓ). After the needle is removed from the sample and prior to injection the plunger is pulled back a short distance to minimize evaporation of the sample from the tip of the needle. Duplicate injections of each sample and standard are 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 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 vinyl chloride that is removed in the

desorption process. Desorption efficiency should be determined on the same batch of charcoal tubes used in sampling. Results indicate that desorption efficiency varies with loading (total vinyl chloride on the tube) particularly at lower values, i.e., 2.5 µg.

8.5.2 Procedure for determining desorption efficiency. Charcoal tubes from the same batch as that used in obtaining samples are used in this determination. A known volume of vinyl chloride gas is injected into a bag containing a known volume of air. The bag is made of Tedlar (or a material which will retain the vinyl chloride and not absorb it) and should have a gas sampling valve and a septum injection port. The concentration of the bag may be calculated at room temperature and pressure. A known volume is then sampled through a charcoal tube with a calibrated sampling pump. At least five tubes are prepared in this manner. These tubes are desorbed and analyzed in the same manner as the samples (See Section 8.4). Samples taken with a gas tight syringe from the bag are also injected into the GC. The concentration in the bag is compared to the concentration obtained from the tubes.

The desorption efficiency equals the difference between the average weight of the samples and the weight of the blank divided by the average weight of the vinyl chloride standard gas mixture in the bag or

$$\text{Desorption efficiency} = \frac{\text{Weight on sample} - \text{Weight on blank}}{\text{Weight in standard gas mixture}}$$

9. Calibration and Standards

CAUTION: Laboratory Operations Involving Carcinogens

Vinyl chloride has been identified as a human carcinogen and appropriate precautions must be taken in handling this gas. Specifically, the Occupational Safety and Health Administration has promulgated regulations for the use and handling of vinyl chloride. The regulations currently serve as an emergency standard and may be found in 29 CFR 1910.93q (Section 1910.93q in Title 29 of the Code of Federal Regulations available in the Federal Register, Vol. 39, No. 125, Thursday, June 27, 1974.) Note that the above is an emergency standard (temporary) and will be replaced by a permanent standard in October of 1974.

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 µg/1.0 mℓ versus peak area. There are two methods of preparing standards and as long as highly purified vinyl chloride is used, both are comparable.