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from CPM*

File: NIOSH/Vinyl

VINYL CHLORIDE IN AIR

Physical and Chemical Analysis Branch

Analytical Method

In February 1974, shortly after NIOSH became aware of the carcinogenic hazard of vinyl chloride, a research program was implemented to develop sampling and analytical procedures for vinyl chloride. In response to an OSHA request and based upon a thorough literature search, NIOSH at that time recommended sampling vinyl chloride in gas collecting tubes and subsequent analysis by gas chromatography. While the glass tube is less susceptible to sampling errors, there are certain disadvantages which led NIOSH to investigate alternate methods of sampling. The result of our research effort has been a method in which vinyl chloride is collected on charcoal tubes, desorbed and determined by gas chromatography.

Enclosed is a copy of P&CAM No. 178

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

NIOSH CLASSIFICATION OF ANALYTICAL METHODS

Physical and Chemical Analysis Branch
Division of Laboratories and Criteria Development

Class A--Recommended---A method which has been fully evaluated and successfully collaboratively tested by a selected group of laboratories.

Class B--Accepted---A method which has been subjected to a thorough evaluation procedure in the NIOSH laboratory and found to be acceptable.

Class C--Tentative---A method which is in wide use and which has been adopted as a standard method or recommended by another Government agency or one of several professional societies such as ACGIH, AOAC, AIHA, ASTM or ISC.

Class D--Operational---A method in general use or approved by most professional industrial hygiene analysts but has not been thoroughly evaluated by NIOSH or any professional societies.

Class E--Proposed---A new, unproved or suggested method not previously used by industrial hygiene analysts but which gives promise of being suitable for the determination of a given substance.

December 17, 1973

R&S 141430

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:	10/15/74	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 of air containing 200 ppm of vinyl chloride which can be sampled 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 6.2.1) 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 these compounds will be found in the backup section. This may lead to some confusion as to whether sample loss 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 coconut 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 Stainless steel column (20 ft x 1/8 in) packed with 10% SE-30 on 80/100 mesh Chromosorb W (acid washed, silanized with dimethyldichlorosilane). 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 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.

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- 8.3.5 Bulk air samples (i.e., samples of 10-20 liters of the air in the environment) are taken along with personal samples.
- 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 (around -20°) 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). Even around -20°C, vinyl chloride will equilibrate between the two sections of charcoal, i.e., will migrate to the backup section. This phenomenon is observable after two weeks and may be confused with sample loss after 1 to 2 months.

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 to the CS₂ 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 CS₂. These two sections are analyzed separately. Tests indicate that desorption is complete in 30 minutes if the sample is agitated occasionally during this period. In any case samples should be analyzed within 60 minutes after addition to CS₂.

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- μ l 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 μ l 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- μ l aliquot is withdrawn to the 7.4 μ l mark (2 μ l solvent + 0.4 μ l air + 5 μ l sample = 7.4 μ l). 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

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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 measured volume of vinyl chloride gas is injected into a bag containing a measured 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 knowing room temperature and pressure. A measured 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 amount of vinyl chloride desorbed from the charcoal divided by the quantity of vinyl chloride contained in the volume of synthetic atmosphere sampled, or

$$\frac{\text{quantity vinyl chloride from charcoal}}{\text{concentration vinyl chloride in atmosphere} \times \text{volume atmosphere sampled}}$$

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. The Occupational Safety and Health Administration has promulgated regulations for the use and handling of vinyl chloride. They 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. 194, Friday, October 4, 1974, pp. 35890-35898).

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.

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 of the FID response.

9.1 Standard Preparation

Gravimetric Method - Vinyl chloride is slowly bubbled into a tared 10-ml volumetric flask containing approximately 5 ml of toluene. After 3 minutes, the flask is again weighed. A weight change of 100-300 mg is usually observed. The solution is diluted to exactly 10 ml with carbon disulfide and is used to prepare other standards by removal of aliquots with different sized syringes. Subsequent dilution of these aliquots with carbon disulfide results in a series of points that are linear from the range of 0.2 nanograms per injection, the minimum detectable amount of vinyl chloride, to 1.5 micrograms per injection.

Volumetric Method - A 1-ml gas sample of pure vinyl chloride is drawn into a gas-tight syringe and the tip of the needle is inserted into a 10-ml volumetric flask containing approximately 5 ml of CS₂. The plunger is withdrawn slightly to allow the CS₂ to enter the syringe. The action of the vinyl chloride dissolving in the CS₂ creates a vacuum and the syringe becomes filled with the solvent. An air bubble (~2%) is present and was found to be due to the void volume in the needle of the syringe. The solution is returned to the flask and the syringe is rinsed with clean CS₂ and the washings added to the volumetric. The volumetric is then filled to the mark with CS₂. Other standards are then prepared from this stock solution.

Standards are stored in a freezer at -20°C and are found to be stable at this temperature for three days. Tight-fitting plastic tops on the volumetrics seem to retain the vinyl chloride better than ground glass stoppers.

10. Calculations

10.1 The weight, in μg , corresponding to each peak area is read from the standard curve for vinyl chloride. No volume corrections are needed, because the standard curve is based on $\mu\text{g}/1.0\text{ ml}$ CS₂ and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank are made for each sample.

$$\mu\text{g} = \mu\text{g}_s - \mu\text{g}_b$$

where:

μg_s = μg found in front section of sample tube

μg = μg found in front section of blank tube

A similar procedure is followed for the backup sections.

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- 10.3 These values are further corrected for the desorption efficiency at the level of vinyl chloride measured.

$$\text{Corrected } \mu\text{g} = \frac{\mu\text{g}}{\text{desorption efficiency}}$$

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

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

$$\text{mg}/\text{m}^3 = \mu\text{g}/\text{l} = \frac{\text{total } \mu\text{g (Section 10.4)}}{V}$$

where:

V is the volume of air sampled

- 10.6 Another method of expressing concentration is ppm, defined as μl of vinyl chloride gas/liter of air

$$\text{ppm} = \mu\text{g}/\text{l} \times \frac{24.45}{62.5} \times \frac{760}{P} \times \frac{T+273}{298}$$

where:

P = pressure (mm Hg) of air sampled

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

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

62.5 = molecular weight (g/mole) of vinyl chloride

760 = standard pressure (mm Hg)

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

11. References

- 11.1 Hill, R.H., C.S. McCammon, A.T. Saalwaechter, A.W. Teass, and W.J. Woodfin, "Determination of Vinyl Chloride in Air," in preparation.
- 11.2 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," Am. Ind. Hyg. Assn. J., 31, 225 (1970).