

METHOD FOR THE DETERMINATION
OF
VINYLIDENE CHLORIDE (VDC) IN AIR

1. Principle of the Method

- 1.1 A known volume of air is drawn through a charcoal tube to trap VDC present.
- 1.2 The charcoal in the tube is transferred to a small vial where the VDC is desorbed by 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. Safety Precautions

Extended exposure to VDC may cause drowsiness and possible systemic injury. VDC liquid and vapors are flammable as are the other solvents used. The reagent solvents may also be hazardous from inhalation, eye, and skin contact. Handle with care. Avoid breathing vapors, avoid skin and eye contact. Keep the solvents away from open flames.

3. Range and Sensitivity

- 3.1 The minimum detectable amount of VDC was found to be 0.2 nanograms per injection at the maximum sensitivity of a gas chromatograph.
- 3.2 The sampling flow rate should not exceed 500 ml/min and the total volume sampled should not exceed 10.0 liters. This value is the volume of air containing 200 ppm of VDC which can be sampled before a significant breakthrough (0.1%) occurs.

4. Interferences

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

- 4.3 It must be emphasized that any compound which has the same retention time as VDC 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.
- 4.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

5. Precision and Accuracy

A statistical treatment of the round robin data indicated the "f" test shows no bias in analysis and the normal distribution observed can be attributed to variations among laboratories. The data may be summarized as follows:

<u>Level, ppm</u>	<u>Mean</u>	<u>Variance</u>	<u>Standard Deviation</u>
1.5	1.58	0.03	0.18
5	5.68	0.76	0.87
10	10.94	6.03	2.50
10*	10.02	1.02	1.01

*Two extremely high values (15 and 16.9) which may be discarded by usual statistical procedures were omitted from these calculations.

6. Advantages and Disadvantages of the Method

- 6.1 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.
- 6.2 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. During sample storage, volatile compounds such as VDC will migrate throughout the tube until equilibrium is reached. This migration effect can be considerably decreased by shipping and storing the tubes at -20°.

- 6.3 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.

7. Apparatus

- 7.1 An approved and calibrated personal sampling pump for personal and area samples whose flow can be determined accurately at the desired rate.
- 7.2 Charcoal tubes: 600 mg SKC charcoal tubes (available from Environmental Compliance Corporation, Venetia, Pennsylvania, Catalogue No. 226-09).

Sample holders may be made from 6 mm I.D. glass tubing, with both ends flame sealed shut or from Type 316 stainless steel tubing with Swagelok caps. Fill the tubes with 600 mg Pittsburgh PCB 12 X 30 activated carbon (Pittsburgh activated carbon, Division of Calgon Corporation, Calgon Center, P. O. Box 1346, Pittsburgh, Pennsylvania 15230). 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/min.

- 7.3 Gas chromatograph equipped with a flame ionization detector.
- 7.4 Stainless steel column (3 meters x 4 mm) packed with Durapak OPN chemically bonded to Porasil C (Waters Associates, Milford, Massachusetts 01757). Employing this column and the gas chromatographic conditions outlined below, carbon disulfide elutes in about 2 minutes and vinylidene chloride in 4 minutes. Any column demonstrated to be satisfactory, such as the following, may also be used:
- (a) 6.5 meters x 4 mm packed with 10% SP2100 on 100/120 mesh Chromosorb WAW.
- 7.5 A mechanical or electronic integrator or a recorder and some method for determining peak area.
- 7.6 Two-ml vials which can be sealed with caps containing Teflon-lined silicone rubber septa. Hycar or Viton septa are satisfactory.
- 7.7 Microliter syringes: 10- μ l, and convenient sizes (250- μ l) for making standards.
- 7.8 Syringe: 2.0-ml type graduated in 0.1 ml increments.
- 7.9 Hypo-vials: 15-ml and 6-ml hypo-vials for making standard solutions.

8. Reagents

- 8.1 Spectroquality carbon disulfide.
- 8.2 VDC, technical grade, keep refrigerated.
- 8.3 n-Heptane, Analytical Reagent Grade.
- 8.4 Prepurified nitrogen or helium.
- 8.5 Prepurified hydrogen.
- 8.6 Filtered compressed air.

9. Procedure

- 9.1 Cleaning of equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with distilled water.
- 9.2 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.
- 9.3 Collection and Shipping of Samples.
 - 9.3.1 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).
 - 9.3.2 The smaller section of charcoal is positioned nearest the sampling pump.
 - 9.3.3 The charcoal tube is placed in a vertical position during sampling to prevent "channelling" of the charcoal.
 - 9.3.4 Air being sampled is not to be passed through any hose or tubing before entering the charcoal tube.
 - 9.3.5 The flow, time, and/or volume must be measured as accurately as possible. The sample is taken at a maximum flow rate of 500 ml/min. The maximum volume to be sampled should not exceed 10.0 liters.
 - 9.3.6 The temperature and pressure of the atmosphere being sampled is measured and recorded.
 - 9.3.7 The charcoal tubes are capped with the supplied plastic caps immediately after sampling. Under no circumstances are rubber caps to be used.
 - 9.3.8 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.

9.3.9 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 recommended to minimize migration of VDC to the backup section.

9.3.10 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 VDC (2 months). Even around -20°C ., VDC will equilibrate between the two sections of charcoal, i.e., will migrate to the backup section.

9.4 Analysis of Samples

9.4.1 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 entire contents of the tube is transferred to a small vial. The vial is topped with a septum cap. Two-ml of carbon disulfide are added to the vial via a syringe using a second syringe needle as a vent. Place the vial in a freezer for 30 minutes. Tests indicate that desorption is complete in 30 minutes if the sample is agitated during this period. In any case samples should be analyzed within 60 minutes after addition to CS_2 .

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

1. 30 cc/min helium carrier gas flow.
2. 30 cc/min hydrogen gas flow to detector.
3. 300 cc/min air flow to detector.
4. 200°C . injector temperature.
5. 300°C . manifold temperature (detector).
6. 80°C . isothermal column temperature (oven)

9.4.3 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. Employing a 10 μl syringe inject a 2 μl aliquot of the carbon disulfide solutions. Duplicate injections of each sample and standard are made. (Note 1).

9.4.4 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.

9.5 Determination of Desorption Efficiency

9.5.1 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 VDC 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 VDC on the tube), particularly at lower values, i.e., 2.5 µg.

9.5.2 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 VDC is injected into a bag containing a measured volume of air. The bag is made of Tedlar[®] or saran 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. The standards should not be left in the bags longer than 24 hours. 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 9.4). 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 VDC desorbed from the charcoal divided by the quantity of VDC contained in the volume of synthetic atmosphere sampled, or

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

10. Calibration and Standards

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/2.0 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 day-to-day variations of the FID response.

10.1 Standard Preparation. Approximately 11 ml of CS₂ is weighed into a previously weighed 15 ml hypo-vial sealed with a Viton septum. Addition is by means of a hypodermic syringe using a second syringe needle as a vent. 150 µl of VDC are then injected into the hypo-vial and the vial is reweighed to obtain the weight of VDC added. Two serial dilutions are made using 4 ml of CS₂ in

6 ml hypo-vials, weighing as before. Approximately 0.6 ml of the first solution are used in the first dilution and 50 μ l of the second solution in the second dilution steps, the exact amount added being determined by weighing. The resulting solution will contain ~ 10 μ g/g CS_2 . The actual concentration is calculated by means of the following equation:

$$\frac{C}{\text{VDC}} = \frac{W}{C \times D \times E} \frac{\text{VDC} \times A \times B}{\text{C} \times \text{D} \times \text{E}} \times 10^6 \text{ ppm (w/w)}$$

Where:

W_{VDC} = Weight of VDC added to the first hypo-vial.

A = Weight of solution from first vial added to the second vial.

B = Weight of solution from second vial added to the third vial.

C = Total solution weight in first vial.

D = Total solution weight in second vial.

E = Total solution weight in third vial.

Standards are run daily, stored in a freezer at 0°C and are not kept for more than seven days.

11. Calculations

11.1 The weight, in μ g, corresponding to each peak area is read from the standard curve for VDC. No volume corrections are needed, because the standard curve is based on μ g/2.0 ml CS_2 and the volume of sample injected is identical to the volume of the standards injected.

If a calibration curve is not employed, concentrations may be calculated from the ratio of the peak heights of the standard and sample.

11.2 Corrections for the blank are made for each sample.

(Note 2).

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

Where:

μg_s = μ g found in sample tube

μg_b = μ g found in blank tube

11.3 These values are further corrected for the desorption efficiency at the level of VDC measured.

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

11.4 The concentration of the VDC in the air samples is expressed in mg/m^3 , which is numerically equal to $\mu\text{g}/\text{liter}$ of air.

$$\text{mg}/\text{m}^3 = \mu\text{g}/\text{l} = \frac{\text{Corrected } \mu\text{g (Section 11.3)}}{V}$$

Where

V is the volume of air sampled

11.5 Another method of expressing concentration is ppm, defined as μl of VDC/liter of air.

$$\text{ppm} = \mu\text{g}/\text{l} \times \frac{24.45}{96.94} \times \frac{760}{P} \times \frac{T+273}{298}$$

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.

96.94 = molecular weight (g/mole) of VDC.

760 = standard pressure (mm Hg).

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

NOTE 1: If difficulties arise 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 2- μl aliquot is withdrawn to the 4.4 μl mark (2 μl solvent + 0.4 μl air + 2 μl sample = 4.4 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.

NOTE 2: If high blank values are obtained from a specific lot of charcoal it is recommended that the charcoal be discarded rather than attempting to apply a correction.

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