



Designation: D4766 – 21

# Standard Test Method for Vinyl Chloride in Workplace Atmospheres (Charcoal Tube Method)<sup>1</sup>

This standard is issued under the fixed designation D4766; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method describes the determination of vinyl chloride monomer (VCM) in workplace atmospheres using a modified charcoal tube method (see Practice D3686).

1.2 This procedure is compatible with low-flow rate personal sampling equipment. It can be used for personal or stationary monitoring. It cannot be used to determine instantaneous fluctuations in concentration to detect maximum values. Alternative on-site procedures, such as gas chromatography or infrared spectrometry, are required to measure fast-changing concentrations.

1.3 The range of this test method is from the limit of quantitation approximately 0.03 to 100 ppm (v).

1.4 The sampling method provides a time-weighted average sample.

1.5 The values stated in SI units are to be regarded as standard. The values given in parentheses after SI units are provided for information only and are not considered standard.

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* For more specific precautionary statements, see Section 9, 10.2.3, and 11.1.3.

1.7 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D22 on Air Quality and is the direct responsibility of Subcommittee D22.04 on Workplace Air Quality.

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## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>2</sup>

D1356 Terminology Relating to Sampling and Analysis of Atmospheres

D3686 Practice for Sampling Atmospheres to Collect Organic Compound Vapors (Activated Charcoal Tube Adsorption Method)

E355 Practice for Gas Chromatography Terms and Relationships

## 3. Terminology

3.1 *Definitions*—For definitions of terms relating to this test method, refer to Terminology D1356 and Practice E355.

## 4. Summary of Test Method

4.1 Known volumes of sampled air are passed through glass or metal tubes packed with activated charcoal. Vinyl chloride is adsorbed on the charcoal and thus removed from the flowing gas stream (1-3).<sup>3</sup>

4.2 A two-section tube containing a front and a backup section of adsorbent is used to collect the sample.

4.3 The vinyl chloride is desorbed with carbon disulfide and analyzed with a gas chromatograph equipped with a flame ionization detector. Two or more different columns are to be used to reveal interferences that might otherwise not be detected.

4.4 Adsorption/desorption efficiencies are determined by the same techniques used for the atmospheric analysis applied to known standards. Instrument calibrations are made with prepared standard solutions of vinyl chloride in carbon disulfide.

## 5. Significance and Use

5.1 Vinyl chloride monomer (VCM) is the starting material for the manufacture of poly(vinyl chloride) (PVC), which is

<sup>2</sup> For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

<sup>3</sup> The boldface numbers in parentheses refer to a list of references at the end of this standard.

used extensively in construction, electronics, packaging, and other industries. The vinyl chloride gas can escape during manufacturing, transportation, and polymerization stages. Residual monomer can also escape during subsequent fabrication processes.

5.2 Vinyl chloride is a toxic and explosive hazardous material.

5.3 Vinyl chloride is suspected to be a carcinogenic agent (4), and occupational exposure limits (OELs) have been established for this agent. For instance, the present U.S. Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for VCM is 1.0 ppm (v) with a 0.5-ppm (v) action level; the maximum length of operator exposure at 5 ppm (v) is 15 min (5).

5.4 This test method is made selective for vinyl chloride by choosing chromatographic columns that will separate vinyl chloride from other organic compounds in the sample.

5.5 This test method meets requirements (for example, those of OSHA and NIOSH) for monitoring workplace atmospheres in vinyl chloride and poly(vinyl chloride) production and fabrication processes.

## 6. Interferences

6.1 Organic components that have the same or nearly the same retention time as vinyl chloride during gas-chromatographic analysis will potentially interfere. Other volatile organic compounds in the collected samples require consideration.

6.2 Such interferences can be minimized by proper selection of gas-chromatographic columns. A mass spectrometric detector can be used to confirm the presence of vinyl chloride.

6.3 Water mists and high humidity affect adsorption efficiencies by reducing the adsorptive capacity of the activated charcoal for vinyl chloride.

## 7. Apparatus

### 7.1 Charcoal Sampling Tube:

7.1.1 *Description*—A sampling tube consists of a length of glass tubing containing two sections of activated charcoal that are held in place by non-adsorbent material and sealed at each end.

7.1.2 Sampling tubes are commercially available and normally consist of a glass tube 110 mm long, 10 mm in outside diameter, and 8 mm in inside diameter. They contain two sections of 20/40 mesh activated charcoal, 800 and 200 mg, each separated by a 2-mm section of urethane foam. The front section is retained by a plug of glass wool and the back section is retained by a second 2-mm portion of urethane foam or other retainer, such as glass wool. The ends of the tube are flame sealed.

7.1.3 The back section of the sample tube (200 mg) adsorbs vapors that penetrate the front section and is used to determine whether the collection capacity of the tube has been exceeded. Instead of a single tube, two tubes in series may be used if breakthrough is observed (see 11.1.11).

7.1.4 The pressure drop across the charcoal tube should be no greater than 3.3 kPa (2.5 cm Hg) at a flowrate of 1000 mL/min.

7.1.5 Glass tubes shall be held in suitable protective holders to prevent breakage during sampling.

### 7.2 Syringes:

7.2.1 *Gas-Tight Syringe*, 1 to 2-mL capacity.

7.2.2 *Microlitre Syringes*, 10, 25, and 100- $\mu$ L or other convenient sizes for preparing standard solutions.

7.3 *Polyethylene End Caps*, for capping charcoal tubes. Caps must fit snugly to prevent leakage.

7.4 *Vials*, glass, approximately 12 mL (3-dram), for desorbing samples and holding standard solutions: polyethylene or TFE-fluorocarbon-lined screw cap or septum valve. A 30-mL (1-oz) vial with the same types of seal is needed for standard preparation.

7.5 *Plastic Bags*—Poly(vinylidene chloride) or poly(vinyl fluoride), 50 to 100 L, for preparing known concentrations of vinyl chloride. The significant solubility of vinyl chloride in polytetrafluorethylene renders bags made of this type of film unsuitable. Other equivalent containers for preparing known concentrations are also suitable.

7.6 *Sampling Equipment*—See Ref (6) for general information on air sampling instrumentation.

7.6.1 *Personal Sampling Pump*, with flow rate accurately determined to within  $\pm 5\%$  and set at the desired sampling rate. Pumps having stable low flow rates (10 to 200 mL/min) are preferable for long period sampling (up to 8 h) or for short periods when concentration of organic vapors are expected to be high. All sampling pumps must be carefully flow-rate adjusted with a charcoal tube in the proper sampling position. (See Practice D3686 and Annex A1.)

7.6.2 *Tubing*, rubber or plastic, 6-mm ( $\frac{1}{4}$  in.), bore about 0.9 m (3 ft) long, equipped with a spring clip to hold the tubing and charcoal tube in place on worker's lapel area. Sampling tubes shall not be used with plastic or rubber tubing upstream of the charcoal. Absorption by the tubing may introduce sampling errors.

### 7.7 Gas Chromatograph:

7.7.1 Gas chromatographs that employ either a flame ionization detector or a detector whose specifications are equivalent in sensitivity and selectivity shall be used. Detectors shall be capable of determining vinyl chloride concentrations of interest with a signal-to-noise ratio of at least 10 to 1. Suitable detectors are capable of detecting approximately  $5 \times 10^{-10}$  g of vinyl chloride per injection.

7.7.2 A gas-chromatographic column capable of separating vinyl chloride from other components is required. A number of suitable columns have been discussed in the literature (7). Table 1 lists 14 columns and the oven temperatures used for vinyl chloride determination. Table 2 lists the relative retention times of some potential interferences for four chromatographic columns. Column suitability must be verified by testing with two or more columns of dissimilar packings to ensure the absence of interferences. If the chromatographic peak for vinyl

**TABLE 1 Common Packings and Oven Temperatures for the Vinyl Chloride Analysis**

Column Packing	Oven Temperature, °C	Reference
3 to 6 m (10 to 20 ft) SE-30 on Chromosorb G, Chromosorb W, or Anakrom ABS	ambient to 90	<b>3, 8, 9</b>
6 m (20 ft) 10 % FFAP on Chromosorb W	65	<b>3</b>
1.8 m (6 ft) Poropak Q	100–135	<b>2, 10, 11</b>
1.5 to 1.8 m (5 to 6 ft) Poropak QS	70–120	<b>1, 12, 13</b>
1.8 m (6 ft) Chromosorb 101	90–100	<b>14, 15</b>
0.5 to 1.8 m (1.5 to 6 ft) Chromosorb 102 <sup>A</sup>	70–145	<b>16, 17, 18, 19</b>
1.8 m (6 ft) 10–20 % DC 200 on Chromosorb W or Supelcoport	80	<b>1, 17</b>
6 m (20 ft) Carbowax 4000 on Supelcoport	80	<b>1</b>
1.8 m (6 ft) 0.4 % Carbowax 1500 on Carbowax A	ambient	<b>17, 20</b>
1.8 m (6 ft) 5 % OV-101 on Chromosorb W	ambient	<b>11</b>
1.8 m (6 ft) 10 % Apiezon M on Chromosorb W	ambient	<b>11</b>
1.8 m (6 ft) silica gel	30	<b>21</b>
90 m (300 ft) open tubular column, coated with dibutyl maleate	0	<b>21</b>
4.8 m (16 ft) 16.7 % triscyano ethoxypropane on Chromosorb W	programmed from 50 to 170	<b>22</b>

**TABLE 2 Relative Retention Times of Potential Interferences to Vinyl Chloride**  
(Vinyl Chloride Retention = 1.0)

Compound	Chromosorb <sup>A</sup> 102	Chromosorb <sup>B</sup> 102	Poropak Q <sup>C</sup>	0.4 % Carbowax <sup>D</sup> 1500 on Carbowax A
Methane	0.15	...	0.05	0.20
Ethane	0.21	...	...	0.29
Ethene	0.21	0.33	...	0.26
1,1-Difluoroethylene	...	0.33	...	0.63
Propene	...	0.62	0.46	0.63
Propane	0.54	...	0.52	0.63
Methylacetylene	...	...	0.56	...
Methyl chloride	0.63	...	0.57	0.45
1,1-Difluoroethane	...	0.51	...	...
Chlorodifluoromethane	...	0.53	...	...
Cyclopropane	...	...	0.59	...
Formaldehyde	...	...	0.62	...
1-Chloro-1,1-difluoroethane	...	0.92	...	...
Acetylaldehyde	0.93	...	0.95	0.77
Dichlorotetrafluoroethane	...	1.21	...	...
Isobutane	1.22	...	...	...
Isobutylene	1.37	1.25	...	...
Methanol	...	...	...	1.38
1,3-Butadiene	1.57	1.27	...	...
1-Butene	1.43	1.30	...	...
Vinyl methyl ether	...	1.36	...	...
Trans-2-butene	1.57	1.38	...	2.92
Ethyl chloride	1.70	...	...	1.54
Cis-2-butene	1.73	1.43	...	...
Vinyl bromide	...	1.85	...	...
1,1-dichloroethylene	2.00	...	...	...

<sup>A</sup> 1.8 m by 3.2 mm (6 ft by 1/8 in.) Chromosorb 102 (80/100 mesh) at 100°C.

<sup>B</sup> 1.8 m by 3.2 mm (6 ft by 1/8 in.) Chromosorb 102 (80/100 mesh) at 145°C.

<sup>C</sup> 1.8 m by 3.2 mm (6 ft by 1/8 in.) Poropak Q (80/100 mesh) at 100°C.

<sup>D</sup> 1.8 m by 3.2 mm (6 ft by 1/8 in.) 0.4 % Carbowax 1500 on Carbowax A at ambient temperature.

7.7.3 Gas chromatographic operating conditions for the instrument being used should be optimized so that the separation required for a successful analysis can be obtained in a reasonable time.

## 8. Reagents

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise noted, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>4</sup> Other reagents may be used provided it can be demonstrated that they are of sufficiently high purity to permit their use without decreasing the accuracy of determination.

8.2 *Activated Coconut-Shell Charcoal*—Commercially available coconut charcoal (20/40 mesh) has been found to have adequate adsorption capacity.

8.3 *Calibration Standards*—Standard concentrations of vinyl chloride in air may be purchased or prepared in the laboratory. Laboratory standard concentrations are prepared by pressure dilution in stainless steel cylinders, atmospheric pressure dilution in plastic bags, or dynamically with permeation tubes (23). These standards are used to determine adsorption/desorption efficiencies of the activated charcoal (Annex A1).

8.4 *Carbon Disulfide (CS<sub>2</sub>)*, spectroquality.

8.5 *Vinyl Chloride (VCM)*, gas cylinder.

## 9. Safety Precautions

9.1 Carbon disulfide and vinyl chloride vapors are toxic and highly flammable. Usage should be restricted to a well-ventilated hood.

9.2 Small waste quantities of carbon disulfide shall be disposed of only in accordance with local regulations and accepted practices.

9.3 The vapors of vinyl chloride should not be inhaled since they have anesthetic properties and are suspected to be carcinogenic.

9.4 Avoid skin contact with carbon disulfide, solutions of vinyl chloride in CS<sub>2</sub>, and vinyl chloride liquid.

## 10. Calibration and Standardization

10.1 *Pump Flow Setting*—Set the sampling pump flow rate in accordance with Practice D3686 and Annex A1.

### 10.2 Standardization:

10.2.1 Prepare calibration standards as micrograms of vinyl chloride per 10 mL of carbon disulfide over range of interest.

10.2.2 Pipet 30 mL of carbon disulfide into a 30-mL (1-oz) bottle and seal.

chloride overlaps the peak for other components by no greater than 5 %, the separation is considered to be satisfactory.

<sup>4</sup> ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

10.2.3 Fill a 1.0-mL gas-tight syringe with pure vinyl chloride vapor from a cylinder of pure vinyl chloride. (**Warning**—Handle the pure vinyl chloride gas in a hood.)

10.2.4 Inject 1.0 mL of vinyl chloride vapor (through the septum) directly into the carbon disulfide in the vial. Mix thoroughly. This standard contains 852 µg of vinyl chloride per 10 mL of carbon disulfide and is equivalent to 13.3 ppm in air based on a 25-L sample. Prepare in duplicate (see **Note 1**).

**NOTE 1**—The concentration of the standard solution is based on injection of 1.0 mL of gas at 25°C and 1 atmosphere (101.3 kPa). For other conditions of temperature and pressure, the concentration should be multiplied by a correction factor, as follows:

$$\text{Correction Factor} = \frac{\text{barometric pressure (kPa)}}{101.3 \text{ kPa}} \times \frac{298}{T_C + 273} \quad (1)$$

10.2.5 Prepare a dilute standard by pipetting 1 mL of the above standard solution into a 12-mL (3-dram) vial containing 10 mL of carbon disulfide giving a total volume of 11 mL. Cap immediately with a septum valve. This standard contains 77.5 µg/10 mL of carbon disulfide and is equivalent to 1.18 ppm in air based on a 25-L sample.

10.2.6 Additional standards are prepared by dilution of the above standards with carbon disulfide. Care must be taken in the dilution steps to minimize the chance of vinyl chloride loss.

10.2.7 Analyze each vinyl chloride in carbon disulfide standard in duplicate by gas chromatography.

10.2.8 Draw 3 to 4 µL of the solution to be analyzed into a 10-µL syringe and make sure there are no bubbles in the syringe. Adjust the volume in the syringe to 2 µL. After the needle is removed from the sample and prior to injection, the plunger is pulled back approximately 1 µL to minimize evaporation of the sample from the tip of the needle.

10.2.9 An alternative injection procedure may be used. Before taking a sample from the standard solution, draw about 1 µL of carbon disulfide solvent into a 10-µL syringe. Draw a specified amount, up to 5 µL of the calibration mixture into a barrel of the syringe, leaving a 0.5-µL air space between the CS<sub>2</sub> and the calibration mixture. Draw the entire sample into the barrel of the syringe. Inject the sample plus the CS<sub>2</sub> (flushing plug) into the gas chromatograph.

10.2.10 Prepare a calibration curve by plotting micrograms of vinyl chloride per 10 mL of carbon disulfide versus peak height or peak area.

10.2.11 From the calibration curve, determine the linear range for the analysis. If the plot is linear over the range of the samples, a linear regression equation or an appropriate response factor may be used.

10.2.12 Analyze freshly prepared standards with each batch of samples.

## 11. Procedure

### 11.1 Sampling:

11.1.1 Break open both ends of the charcoal tube to be used for sampling, ensuring that each opening is at least one half the inside diameter of the tube.

11.1.2 Attach the previously flow adjusted sampling pump (10.1) to the activated charcoal tube with rubber or plastic tubing, placing the backup section nearest the pump.

11.1.3 For a breathing zone sample, fasten the sampling pump to the worker and attach the sampling tube as close to the worker's breathing zone as possible. Position the tube in a vertical position to avoid channeling of air through adsorber sections. (**Warning**—Ensure that the presence of the sampling equipment is not a safety hazard to the worker.)

11.1.4 Turn on the pump, which has previously been adjusted and calibrated to provide a sampling rate of 100 mL/min for a 4-h sample time or 50 mL/min for an 8-h sample time. Note and record the time, flow rate or pump register, temperature, and barometric pressure.

11.1.5 Sample volumes up to 25 L are sufficient for determining vinyl chloride concentrations for compliance purposes. Attempting to collect larger quantities at high concentrations, high flow rates, or long sampling times may result in breakthrough of vinyl chloride and loss of sample. The breakthrough volume is determined in accordance with **Annex A2**.

11.1.6 At the end of the sampling period, note the flow rate, turn the pump off, and note and record the time, temperature, barometric pressure, and pump register reading if appropriate.

11.1.7 Disconnect the sample tube and seal both ends with polyethylene end caps. Place identifying labels on each tube.

11.1.8 Present at least one charcoal sampling tube for analysis as a blank with every 20 samples, and for each specific inspection or field study. Break the sealed ends off the tube and cap it with the plastic caps. Do not draw air through the tube, but in all other ways treat it as an air sample.

11.1.9 Ship samples as soon as possible, store in a freezer (–20°C) until they are analyzed, and analyze within 3 weeks. If the sample tubes are shipped in dry ice, place them in leak proof vials. (Shipment of samples packed with dry ice may require special handling.)

11.1.10 Do not store samples at room temperature longer than 6 days. Migration or equilibration of the sampled material within the sampling tube during prolonged or adverse storage or handling could be confused with breakthrough.

11.1.11 If samples cannot be analyzed within 6 days or stored in a freezer, collect samples using a 1-g charcoal tube for the front section and a 150-mg charcoal tube connected in series for the back section. The tubes are separated immediately after sampling.

### 11.2 Analysis:

11.2.1 Prepare a set of 12-mL vials by placing appropriate labels on them, indicating the identification number and designating whether they are front (F) section of the sample tube or the backup (B) section.

11.2.2 Pipet exactly 10.0 mL of carbon disulfide into each vial, seal, and chill in dry ice for 10 min.

11.2.3 Remove the plastic cap from the front end of the sampling tubes or score and break the tubes just above the front retainer plug.

11.2.4 Remove the plug of glass wool that holds the front portion of charcoal and add it to the vial. Slowly add the charcoal to the chilled carbon disulfide in the vial. Reseal the vial.

11.2.5 Discard the foam spacer and pour the charcoal from the back section into a second vial containing chilled carbon disulfide.