Designation: D 4457 – 02

Standard Test Method for Determination of Dichloromethane and 1,1,1-Trichloroethane in Paints and Coatings by Direct Injection into a Gas Chromatograph[1]

This standard is issued under the fixed designation D 4457; 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 (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the determination of total amount of dichloromethane or 1,1,1-trichloroethane, or both, in paints and coatings. It has been evaluated for cellulose nitrate, alkyd, vinyl, and styrene-butadiene systems. It has not yet been evaluated for other formulations, but is believed to be applicable. The established working range of this test method is from 31 to 65 % for 1,1,1-trichloroethane and 32 to 78 % for dichloromethane. There is no reason to believe it will not work outside of these ranges. The presence of 1-propanol in paints and coatings requires the use of a different internal standard. (See also Practice E 260.)

1.2 The values stated in inch-pound units are to be regarded as the standard. The values given in parentheses are for information only.

1.3 *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 and health practices and determine the applicability of regulatory limitations prior to use.* Specific hazard statements are given in Section 7.

2. Referenced Documents

2.1 *ASTM Standards:*

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals[2]

E 260 Practice for Packed Column Gas Chromatography[3]

3. Summary of Test Method

3.1 Anhydrous 1-propanol (see 10.5) is added as an internal standard to suitable aliquot of the whole paint. The aliquot is then diluted with dimethylformamide and injected onto a gas chromatographic column containing a porous polymer packing that separates dichloromethane and 1,1,1-trichloroethane from other volatile compounds.

4. Significance and Use

4.1 Use of 1,1,1-trichloroethane and dichloromethane, which do not measurably contribute to the atmospheric oxidant level, is a way for industry to meet government or other regulations on volatile organic compounds. This test method is designed to determine the content of these halohydrocarbon solvents in paints and coatings. That content can subsequently be used in calculating the volatile organic compound content of a coating.

5. Apparatus

5.1 *Chromatograph*, any gas-liquid chromatographic instrument equipped with a thermal conductivity detector and capable of being temperature programmed (see Table 1). Optionally, a flame ionization detector may be used if the sample is diluted so that no more than 1000 ppm each of dichloromethane and 1,1,1-trichloroethane is present in the injected specimen.

5.2 *Recorder*, a recording potentiometer with a full-scale deflection of 10 mV, a full-scale response time of 2 s or less, and a maximum noise of ±0.03 % of full scale.

5.3 *Pre-Column*, 40 in. (100 mm) long by ⅛ in. (3.2 mm) outside diameter stainless steel, packed with glass wool, fitted on the entrance end of the column to retain any nonvolatile materials and minimize sludge buildup in the column.

5.4 *Column*, 4 ft (1.22 m) long by ⅛ in. (3.2 mm) outside diameter stainless steel, packed with 80/100 mesh (150 to 180 µm) porous polymer packing material,[4] or other suitable material.

5.5 *Liquid Charging Devices*, such as microsyringes of 5-µL or 10-µL capacity, cleaned with acetone or other suitable solvent. Visually inspect for plugs or cracks before and after each injection.

[1] This test method is under the jurisdiction of ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee D01.21 on Chemical Analysis of Paint and Paint Materials.

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[2] *Annual Book of ASTM Standards*, Vol 15.05.

[3] *Annual Book of ASTM Standards*, Vol 14.02.

[4] Porapak R®, available from Waters Associates, Inc., Milford, MA, has been found satisfactory for this purpose.

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TABLE 1 Typical Instrument Conditions

Detector	thermal conductivity
Column	4 ft (1.22 m) by ⅛in. (3.2 mm) outside diameter packed with 80–100 mesh porous polymer packing
Temperature, °C	
Injection port	200
Detector block	250
Column	
Initial	100
Final	230 (for 8 min)
°C/min	8
Carrier gas	helium
Flow rate, mL/min	30
Specimen size, µL	1

5.6 *Vials*, 25-mL to minimize head space, capable of being septum sealed.[5]

6. Reagents and Materials

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests, unless otherwise specified (as in 6.7). Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[6] Other grades may be used provided it is first ascertained that the reagent is of sufficient high purity to permit its use without lessening the accuracy of the determination.

6.2 *Carrier Gas*, helium of 99.995 % or higher purity. High purity nitrogen may also be used.

6.3 *Dimethylformamide (DMF)*, reagent grade.

6.4 *1-Propanol*, gas chromatography spectrophotometric quality (see 10.5).

6.5 *1,1,1-Trichloroethane* (see 6.7).

6.6 *Dichloromethane* (see 6.7).

6.7 *Halogenated Hydrocarbon Stabilizers*—All commercial grades of these halogenated hydrocarbons contain stabilizers. Either obtain the same solvent used in the coating for use as the standard, or find the type and quantity of stabilizer specified for use in the solvent of interest and add the appropriate quantity to the pure solvent.

7. Hazards

7.1 Dimethylformamide is harmful if inhaled or absorbed through skin. Use only with adequate ventilation. Avoid contact with skin, eyes, and clothing.

8. Preparation of Apparatus

8.1 *Column Conditioning*—The packed column is installed in the gas chromatographic unit leaving the exit end disconnected from the detector. This will prevent any contamination of the detector with the column bleed. Set the helium flow rate at 30 mL/min if a ⅛ in. (3.2 mm) outside diameter column is used. Purge the column 5 to 10 min before heating. Heat the column from room temperature to 200°C at 5°C/min and hold this temperature for at least 12 h (overnight). At the end of this period of time, heat the column to 240°C at a 5°C/min rate and hold this temperature for several hours. The maximum temperature for this packing is 250°C. Cool the column to 100°C and reheat to 240°C at 5°C/min to observe the column bleed. Optimum conditioning of this column may take several cycles of the heating program before a good recorder baseline is achieved. Conditioning of any column other than that suggested (5.4) should be in accordance with the manufacturer's recommendations.

8.2 Install the column in the chromatograph and use the information in Table 1 as a guide to establish the conditions required to give the desired separation. Allow sufficient time for the instrument to reach equilibrium as indicated by a stable recorder baseline. Adjust the carrier-gas flow to a constant rate. Before each calibration and series of determinations (or daily), condition the column at 200°C for 1 h with carrier-gas flow.

9. Calibration

9.1 *Preparation of Standards*—All standards, as well as samples and blanks, should be at a constant temperature. The given order of ingredient addition should be observed to minimize loss of volatile ingredients.

9.1.1 Weighing to 1.0 mg, add 16.0 g of dimethylformamide to a vial capable of being septum sealed. Add 2.0 g of 1,1,1-trichloroethane, 2.0 g of 1-propanol (see 10.5) and 2.0 g of dichloromethane. Seal the vial with a crimp-on or septum seal.

9.2 Determine the retention time of each component by injecting small amounts either separately or in known mixtures. The components should elute close to the typical retention times given in Table 1 and the chromatograms should closely approximate those shown in Fig. 1.

9.3 The area under each peak of the chromatogram is considered a quantitative measure of the corresponding compound. The relative area is proportional to concentration if the detector responds equally to all the sample components. The response to different components is generally significantly different for both flame ionization and thermal conductivity detectors and especially for flame ionization detectors. This difference in detector response may be corrected by use of relative response factors obtained by injecting and measuring the response of known blends. For precise and accurate determination of the halogenated hydrocarbons inject a 1 µL specimen of the standard in accordance with the preparation in 9.1. Calculate the response factors relative to unity for the halogenated hydrocarbons.

10. Procedure

10.1 Keep all samples, blanks, and standards at a constant temperature. Observe the given order of ingredient addition to minimize loss of volatile ingredients. Shake paints, then sample from the middle of the container.

10.2 Weighing to 1.0 mg, add 16.0 g of dimethylformamide

[5] Mininert valves, available from The Pierce Chemical Co., Box 117, Rockford, IL 61105, have been found satisfactory for this purpose.

[6] *Reagent Chemicals, American Chemical Society Specifications*, 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. American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, and the "United States Pharmacopeia."