Designation: D 5320 – 96

Standard Test Methods for Determination of 1,1,1-Trichloroethane and Methylene Chloride Content in Stabilized Trichloroethylene and Tetrachloroethylene[1]

This standard is issued under the fixed designation D 5320; 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 These test methods provide a means for determining low levels of 1,1,1-trichloroethane and methylene chloride in virgin or reclaimed trichloroethylene and tetrachloroethylene.

1.2 Two test methods are covered, as follows:

1.2.1 *Test Method A*—Capillary column gas chromatographic determination of 1,1,1-trichloroethane and methylene chloride in trichloroethylene and tetrachloroethylene.

1.2.2 *Test Method B*—Packed column gas chromatographic determination of 1,1,1-trichloroethane and methylene chloride in trichloroethylene and tetrachloroethylene.

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.*

2. Summary of Test Methods

2.1 Samples of trichloroethylene or tetrachloroethylene are introduced into a gas chromatography (GC) equipped with either a thermal conductivity detector (TCD) or a flame ionization detector (FID). Calibration mixtures containing known concentrations of methylene chloride, 1,1,1-trichloroethane, or other impurities of interest are introduced into the chromatograph in the same manner. The amount of these impurities in the samples is then calculated by comparing the peak areas of these compounds from sample chromatograms with the corresponding peak areas from calibration standard chromatograms. Instrumental parameters are provided to allow the use of either capillary or packed gas chromatography columns.

3. Significance and Use

3.1 These test methods can be used to determine the impurity levels of 1,1,1-trichloroethane and methylene chloride in both trichloroethylene and tetrachloroethylene.

3.2 These test methods can be used to determine the impurity levels of other components, such as stabilizers, found in trichloroethylene and tetrachloroethylene. The other components shall be able to be resolved by recommended GC columns and the gas chromatograph shall be calibrated with known concentration of these compounds.

4. Interferences

4.1 Compounds that co-elute with 1,1,1-trichloroethane, methylene chloride, or other components of interest can interfere with the accuracy of these test methods.

5. Apparatus

5.1 *Gas Chromatograph*, temperature programmable and having the following minimum capabilities:

5.1.1 *Chart Recorder or Electronic Integrator*—An electronic integrator is preferable.

5.1.2 *Flame Ionization Detector and Capillary Split/Splitless Injection Port* (for Test Method A).

5.1.3 *Thermal Conductivity Detector and Packed Column Injection Port* (for Test Method B).

NOTE 1—This procedure was tested using the combinations of capillary column with flame ionization detector and packed GC column with thermal conductivity detector. It should be possible, however, to perform this analysis with either column and detector combination.

5.2 *Gas Chromatography Columns*:

5.2.1 *Column for Test Method A*—30-m by 0.53-mm inner diameter fused silica capillary, internally coated to a 3-μm thickness with a cross-linked polymethyl silicone.[2]

5.2.2 *Column for Test Method B*—10-ft by ⅛-in. outer diameter stainless steel packed with 3 % SP1500 on 80/100 mesh Carbopack B, or equivalent.

5.3 *Syringe*, 10 μL.

5.4 *Microsyringes*, assorted sizes for preparing calibration standards.

5.5 *Volumetric Flasks*, 100 mL.

5.6 *Flow Meter*, soap bubble or electronic type.

5.7 *Analytical Balance*, capable of weighing to four decimal places.

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[1] These test methods are under the jurisdiction of ASTM Committee D-26 on Halogenated Organic Solvents and Fire Extinguishing Agents and are the direct responsibility of Subcommittee D26.04 on Test Methods.

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[2] J&W Scientific DB-1 fused silica capillary column (Cat# 125-1035) available from J&W Scientific, 91 Blue Ravine Rd., Folsom, CA 95630-4917, or Supelco (SPB-1 Cat# 2-5341M) available from Supelco, Inc., Supelco Park, Bellefonte, PA 16823-0048, have been found satisfactory for this purpose. Any equivalent may be used.

6. Reagents and Materials

6.1 *Carrier Gas*—Chromatographic-grade helium (minimum purity: 99.99 %).

6.2 *Hydrogen*—High purity, for use with flame ionization detectors.

6.3 *Air*—Chromatographic or zero grade, for use with flame ionization detectors.

6.4 *Trichloroethylene*, high-purity, for use as a base solvent for preparation of GC calibration standards.

6.5 *Tetrachloroethylene*, high-purity, for use as a base solvent for preparation of GC calibration standards.

6.6 *Methylene Chloride*, 1,1,1-trichloroethylene and other compounds of interest, high purity, for use in preparing GC calibration standards.

7. Preparation of Apparatus

7.1 Prior to use, gas chromatography columns should be conditioned according to the column manufacturer's recommendations.

7.2 After conditioning, set the operating conditions to obtain the desired separation (see Table 1). Since some gas flows such as air, hydrogen, and detector makeup gas vary with the make and model of GC, the manufacturer's recommended flows should be used. Gas flows should be verified with the use of an electronic- or soap- bubble-type flowmeter.

NOTE 2—The capillary column procedure (Test Method A) recommends the use of a capillary column split/splitless injector operated in the split mode. It may also be possible to use other injection techniques (direct or on-column) in conjunction with the capillary column technique, however, these sample introduction alternatives were not investigated.

8. Calibration

8.1 Determine the retention times of the components of interest by injecting small amounts of these compounds either separately or in known mixtures into the gas chromatograph.

8.2 Prepare a calibration standard mixture by adding known

amounts of the components of interest into the base solvent that is to be analyzed.

8.2.1 *Example*—To prepare a calibration mixture of tetrachloroethylene (PCE) containing 0.01 weight % methylene chloride (MEC) and 0.01 weight % 1,1,1 trichloroethane (1,1,1), add 0.010 g of MEC and 0.010 g of 1,1,1 to 99.98 g of PCE.

8.2.2 An alternative method of preparing these standards is to use an appropriately sized microsyringe to inject known volumes of the compounds into a weighed amount of base solvent and calculate the exact weight of the compound that was added by using the volume and density information for each component as well as the final weight of the solution.

8.2.3 It is recommended that at least three calibration mixtures be used. One standard should be below the expected concentration of the analytes of interest; one should be above the expected concentration, and the third should fall somewhere between these two.

8.3 Inject 1 μL of each mixture into the gas chromatograph using the appropriate instrumental parameters listed in Table 1. After chromatograms have been generated, use the peak area data from these chromatograms to calibrate the electronic integrator according to the manufacturer's instructions. If an integrator is not used, calculate the peak areas of the compounds of interest and retain this information for later use.

9. Procedure

9.1 Inject 1.0 μL of either trichloroethylene or tetrachloroethylene samples under the identical conditions as were used for the calibration standards (see Table 1). Determine the peak areas of methylene chloride, 1,1,1-trichloroethane, or other components of interest. Typical chromatograms are shown in Fig. 1 (Test Method A) and Fig. 2 (Test Method B).

10. Calculation

10.1 Calculate the weight percent of each component of interest, as follows:

$$C_1 = \frac{(A_1)(C_s)}{(A_s)} \quad (1)$$

where:
C_1 = concentration of Component 1 in sample, weight %,
A_1 = peak area of Component 1 from sample chromatogram,
A_s = peak area of Component 1 from standard chromatogram, and
C_s = concentration of Component 1 in standard, weight %.

10.2 If several calibration standards of an impurity have been chromatographed, the concentrations of impurity in the sample can be based upon values determined from a linear regression curve calculated from concentrations versus areas for that particular component.

11. Precision and Bias

11.1 Based on work done with standards made in perchloroethylene and trichloroethylene in two laboratories only, the relative standard deviation was found to average 9.5 ± 4.8 % for Test Method A. The bias was not determined.

TABLE 1 Instrument Parameters

	Test Method A	Test Method B
Column:		
Tubing	fused silica	stainless steel
Stationary phase	methyl silicone	3 % SP1500
Solid support	crosslinked	Carbopack B80/120
Film thickness	3 μm	...
Length	30 m	10 ft
Diameter	0.53-mm ID	⅛-in. OD
Oven:		
Initial temperature,° C	60	70
Initial hold time, min	8	5
Program rate, °C/min	15	6
Final temperature,° C/min	215	180
Final hold time, min	10	10
Detector	FID	TCD
Detector temperature, °C	275	220
Injector	split/splitless	packed
Injector mode	split	...
Injector temperature, °C	225	150
Split ratio	10:1	...
Carrier gas	helium	helium
Column flow, mL/min	5	35
Run time, min	29	33
Sample size, μL	1.0	1.0
Septum purge	helium at 3 mL/min	...
Makeup gas	helium at 30 mL/min	...