Designation: D 4509 – 96

Standard Test Methods for Determining the 24-Hour Gas (AIR) Space Acetaldehyde Content of Freshly Blown PET Bottles [1]

This standard is issued under the fixed designation D 4509; 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 cover the 24-h gas-space acetaldehyde (AA) content of freshly blown polyethylene terephthalate (PET) bottles.

1.2 These test methods, containing internal or external standard calibration, are applicable to all PET bottles.

1.3 The values stated in SI units are to be regarded as the standard.

NOTE 1—There is no similar or equivalent ISO standard.

1.4 *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. Referenced Documents

2.1 *ASTM Standards:*[2]

D 883 Terminology Relating to Plastics

D 1193 Specification for Reagent Water

D 1600 Terminology for Abbreviated Terms Relating to Plastics

E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

E 355 Practice for Gas Chromatography Terms and Relationships

E 380 Practice for Use of the International System of Units (SI) (the Modernized Metric System)

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

3.1 The gas chromatographic terms employed in these test methods are those recommended by Practice E 355E 355.

3.2 Units, symbols, and abbreviations used in these test methods are those recommended by Practice E 380E 380.

3.3 For further information on abbreviation, PET, refer to Terminology D 1600D 1600.

3.4 Additional terms relative to plastics are explained in Terminology D 883D 883.

4. Summary of Test Methods

4.1 A molded preform (any size) is blown into a bottle that is purged with nitrogen, capped, and aged. After 24 h, a headspace gas sample is taken from the bottle, and the gas sample is injected into a gas chromatograph for comparison with known external standards (Sections 9-11) or internal standards (Sections 12-14).

5. Significance and Use

5.1 Before proceeding with these test methods, reference should be made to the specification of the material being tested. Any test specimens preparation, conditioning, dimensions, and testing parameters covered in the materials specification, shall take precedence over those mentioned in these test methods. If there is no material specification, then the default conditions apply.

5.2 Acetaldehyde is a decomposition product of the polycondensation reaction and is a by-product of melt processing of polyethylene terephthalate (PET). It adds undesirable flavor to some beverages.

5.3 The level of acetaldehyde in PET blown containers is monitored by these test methods.

6. Apparatus

6.1 *Gas Chromatograph*, with flame ionization detector, equipped with a six-port gas-sampling valve and a 5-mL gas-sampling loop for sampling the headspace of the beverage bottle, as shown in Fig. 1.

6.2 Any suitable system of peak integration can be used for measurement of the acetaldehyde.

[1] These test methods are under the jurisdiction of ASTM Committee D20 on Plastics and are the direct responsibility of Subcommittee D20.70 on Analytical Methods (Section D20.70.03).

This standard has been reviewed and the following items added: an ISO equivalency statement; a material specification reference statement; and a Keywords Section.

Current edition approved August 10, 1996. Published February 1997.

[2] 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.

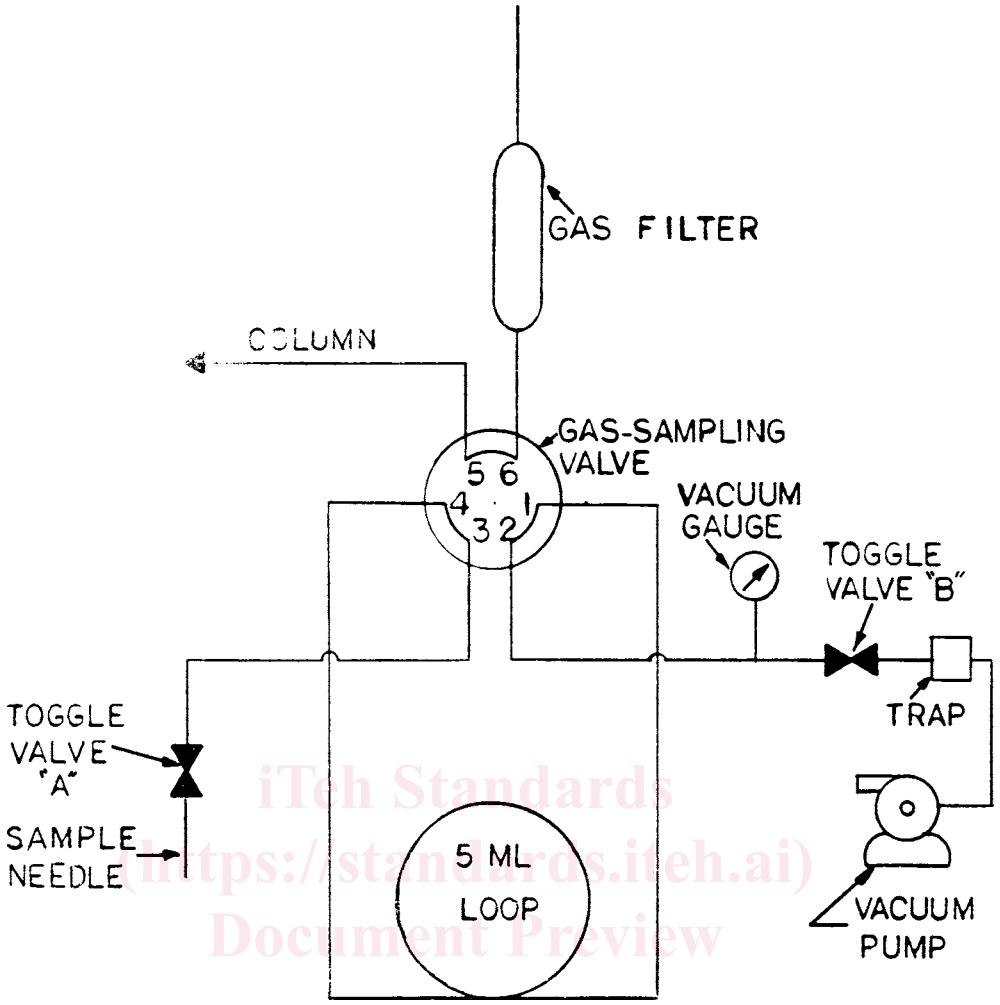

FIG. 1 Schematic Drawing of Gas-Sampling Apparatus

6.3 *Gas Sampling Apparatus* as shown in Fig. 1, including:

6.3.1 *Trap*, 25.4 mm (1 in.) outside diameter by 0.305 m (1 ft) long containing 1 part silica-gel absorbant and 1 part 5A molecular-sieve packing.

6.3.2 *Pressure-Vacuum Gage*, 0–30 psig and 30 in. Hg.

6.4 *Gastight GC Syringe*, 10 µL.

6.5 *Gastight GC Syringe*, 0 to 5.0 cc (internal standard method only).

7. Reagents and Materials

7.1 A 2.0 m by 6 mm outside diameter, 4-mm inside diameter glass column, packed with Porapak Q or QS (100 to 120 mesh) porous polymer or Tenax GC porous polymer (60 to 80 mesh), packed into a 3.2 or 3.18 mm (⅛ in.) outside diameter by 3.66 m (12 ft) long stainless-steel tube.[3]

7.2 *Acetaldehyde Standard Solution*, prepared and analyzed by the procedure described in Annex A1.

7.3 *Acetaldehyde/Propionaldehyde Standard Solution*, prepared by Annex A2 (internal standard method only).

7.4 *Phenolic Polymer Bottle Cap*, 28 mm outside diameter, containing a 6.35-mm (¼-in.) hole drilled in the top and snugly fitted with a seal cut from 1.59-mm (1⁄16-in.) butyl rubber and lined with a liner cut from 0.08-mm (0.003-in.) fluoropolymer film to prevent absorption of acetaldehyde into the butyl rubber seal.

NOTE 2—The phenolic caps and the butyl rubber seals may be reused after the test, but the fluoropolymer liner must be discarded after it is punctured.

7.5 *Nitrogen* (oxygen-free) or helium (GC).

7.6 *Hydrogen*, prepurified or zero-gas.

7.7 *Air*, breathing, water-pumped.

7.8 *Acetaldehyde*, reagent-grade (internal standard method only).

[3] Poropak is a registered trademark of Waters Associates, Inc., Framingham, MA. Tenax is a registered trademark of Enka Glanzstoff B.V. of Arnhem, Netherlands. Both polymers are available from laboratory supply houses.

7.9 *Propionaldehyde*, reagent-grade (internal standard method only).

7.9.1 *High-purity 1-propanol*, distilled in glass (internal standard method only).

7.10 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. All reagents shall conform to the specifications of the committee on Analytical Reagents of the American Chemical Society where such specifications are available.[4]

8. Conditioning

8.1 Purge the PET bottles for approximately 20 s with a stream (1 L/s) of dry nitrogen within a maximum of 1 h after the bottles are blown.

8.2 Cap the bottles after purging them.

8.3 Store the bottles at 24 ± 1 h at 21.5 ± 1.5°C (72 ± 3°F).

9. Procedure for External-Calibration Test Method

9.1 Operate the gas chromatograph according to the following conditions:

9.1.1 Optimize the air and hydrogen flow rates to the flame ionization detector according to the manufacturer's recommendations.

9.1.2 Optimize the carrier gas-flow rate.

9.1.3 Set the GC oven-temperature controller at an isothermal temperature that will result in a retention time of at least 2 min about 140°C (284°F) for columns packed with Poropak Q or QS porous polymer or 110°C (230°F) for columns packed with Tenax GC porous polymer.

9.1.4 Turn on the vacuum pump.

9.1.5 Prepare to integrate the area of acetaldehyde and to report the concentration in µg/L.

9.2 Determine the acetaldehyde in the gas space of a conditioned beverage bottle as follows (refer to Fig. 1):

9.2.1 Close toggle Valve A and open toggle Valve B to evacuate the sample loop.

9.2.2 Close toggle Valve B and observe the vacuum gage to determine if there are any leaks in the system.

9.2.3 If leaks are present, determine the cause and eliminate them. Then begin again at 9.2.1. If there are no leaks, continue with 9.2.4.

9.2.4 Take the bottle obtained in Section 8 and push the sample needle through the hole in the phenolic polymer cap, piercing the butyl rubber gasket and the fluoropolymer liner.

9.2.5 In order to purge air from the system, quickly open and close toggle Valve A once.

9.2.6 Open toggle Valve B for approximately 30 s to evacuate the sample loop.

9.2.7 Close toggle Valve B and open toggle Valve A to allow the sample loop to fill with sample.

NOTE 3—The procedures in 9.2.5, 9.2.6, and the first part of 9.2.7 ("close toggle Valve B") may be eliminated if the first sample from a bottle is discarded.

9.2.8 Allow the pressure in the sample loop to re-equilibrate to atmospheric pressure, as indicated by a mark on the gage.

9.2.9 Close toggle Valve A and remove the bottle from the sample needle.

9.2.10 Switch the six-port gas-sampling valve to flush the sample loop onto the column packing and simultaneously start the data-acquisition system.

9.2.11 After the integration of the acetaldehyde peak is complete, switch the six-port valve pack to the sampling position.

9.2.12 Open toggle Valve B to evacuate the sample loop for the next determination.

10. Calculations for External Calibration Test Method

10.1 The calculation of the gas-space acetaldehyde concentration in the test bottles is as follows:

$$\text{Acetaldehyde concentration (in µg/L gas space)} = F \times A_a \quad (1)$$

where:

A_a = area of acetaldehyde peak in the sample, and

F = µg/L (AA in calibration standard)/Area counts in calibration standard.

11. Calibration for External Standard Test Method

11.1 The calibration is similar to the procedure except that the calibration standard gas mixture is prepared in a glass bottle.

11.2 Obtain a glass-bottle known volume (approximately 1 L).

11.3 Insert eight to ten 2-mm glass beads into the glass bottle.

11.4 Follow the sample preparation described in 8.1 and 8.2.

11.5 Inject a sample from the bottle used for the calibration into the gas chromatograph to ensure a satisfactory blank response with no acetaldehyde or other interference.

11.6 With a 10-µL syringe, inject 4 µL of a standard solution of acetaldehyde in water at a concentration of approximately 1 mg/mL through the seal of the glass bottle. The concentration of the acetaldehyde solution and the volume of the glass bottle must be accurately known.

11.7 Thoroughly shake the glass bottle with glass beads in it to ensure mixing of the acetaldehyde solution with the dry nitrogen. Condition the bottle at room temperature for 30 min to 1 h to allow it to come to equilibrium.

11.8 Follow the procedure in 9.2.1-9.2.12 in triplicate.

11.9 Calibrate the instrument using the average area count from the three injections.

12. Procedure for Internal Standardization Test Method

12.1 Operate the gas chromatograph according to the conditions outlined in 9.1.1, 9.1.2, and 9.1.3.

12.2 Using 10-µL syringe, inject an 8 µL, 0.5 % propionaldehyde (internal standard) in 1-propanol solution into the inner volume of the 2-L bottle, and allow to vaporize (approximately 15 to 30 min). If bottle capacity differs from 2 L, adjust the internal standard accordingly, for example, for 1-L bottle use 4.0 µL internal standard solution, etc.

12.3 Place the bottle in a 50°C (122°F) oven for 10 to 15 min to thermally mix the gases.

[4] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, and the "United States Pharmacopeia."