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:*

D 883 Terminology Relating to Plastics[2]

D 1193 Specification for Reagent Water[3]

D 1600 Terminology for Abbreviated Terms Relating to Plastics[2]

E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods[4]

E 355 Practice for Gas Chromatography Terms and Relationships[4]

E 380 Practice for Use of the International System of Units (SI) (the Modernized Metric System)[4]

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method[4]

3. Terminology

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

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

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

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

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.

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[1] These test methods are under the jurisdiction of ASTM Committee D-20 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.

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[2] *Annual Book of ASTM Standards*, Vol 08.01.

[3] *Annual Book of ASTM Standards*, Vol 11.01.

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

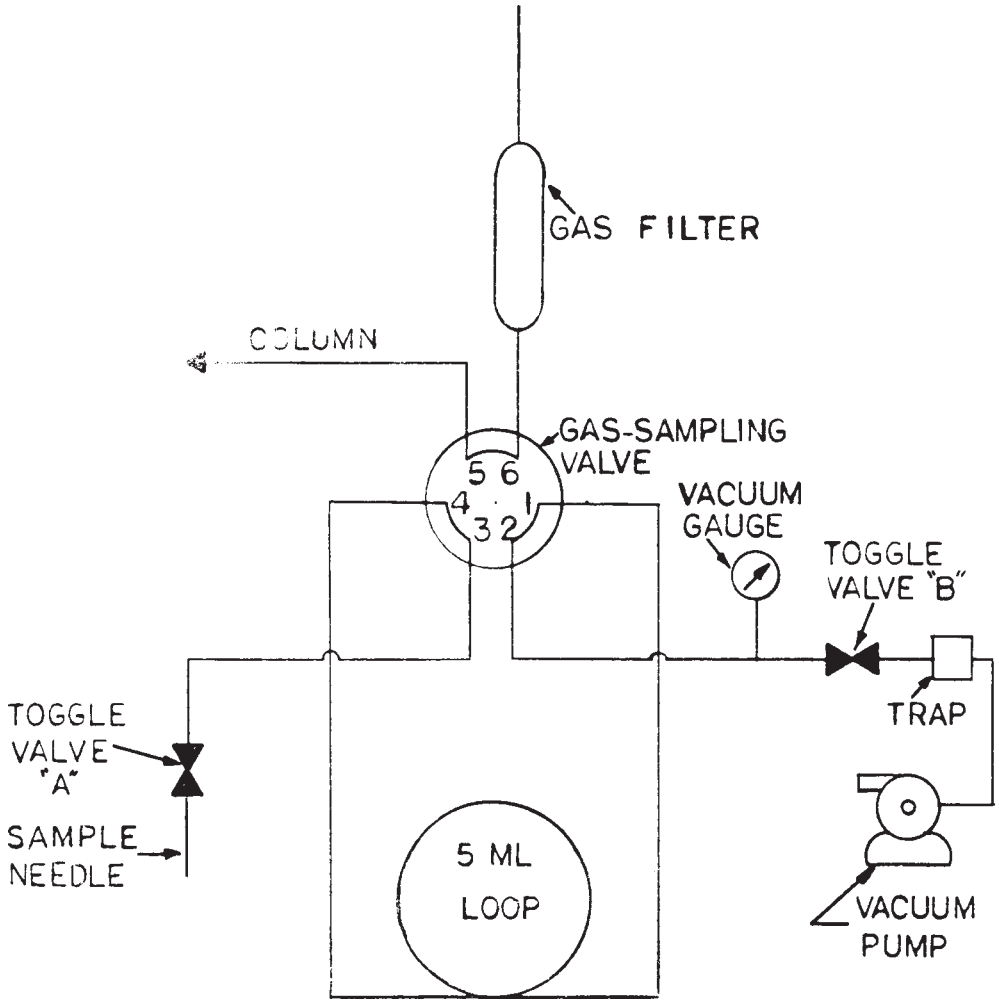


FIG. 1 Schematic Drawing of Gas-Sampling Apparatus

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.[5]

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).

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.[6]

[5] 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.

[6] "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."

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.

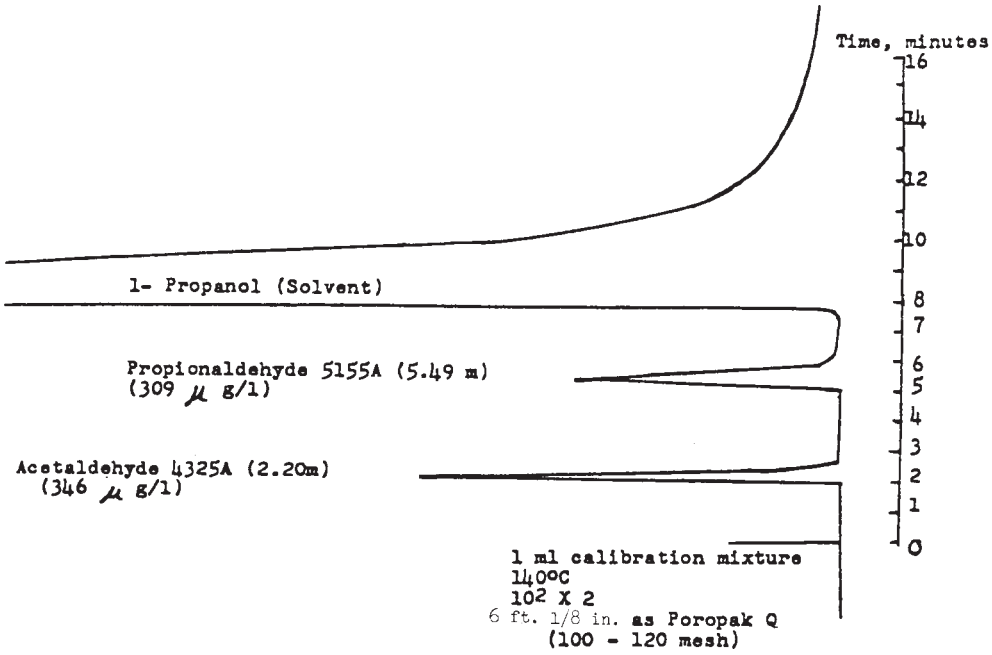
12.3 Place the bottle in a 50°C (122°F) oven for 10 to 15 min to thermally mix the gases.

12.4 Remove a 5.0-mL aliquot with the gas syringe after pushing the syringe needle through the hole in the phenolic polymer cup, piercing the butyl rubber gasket and the fluoropolymer liner. Lock the syringe and withdraw it from the bottle.

12.5 Pressurize the locked syringe to 1.25 mL (approximately 60 psi).

12.6 Insert the syringe into the gas chromatograph, unlock the syringe valve, displace the contents rapidly, and remove the syringe.

12.7 Prime the syringe 3 to 5 times in air to prepare the syringe for the next determination.



Acetaldehyde, Weight, %	Propionaldehyde, Weight, %	Acetaldehyde, Area Counts	Propionaldehyde, Area Counts	R_F[A]
0.560	0.500	4325	5155	1.33
		4144	4888	1.32

[A] R_F = weight percent/area percent response factor; propionaldehyde taken as 1.00.

FIG. 2 Chromatogram of Calibration Solution

13. Calculations for Internal Calibration Test Method

13.1 From the peak areas of acetaldehyde and propionaldehyde, calculate the weight of acetaldehyde in terms of micrograms per litres of interior bottle volume from:

$$\text{Acetaldehyde, } \mu g/L = \frac{A_a (R_f)\,(0.834)\,(10^6)\,W_p S}{A_p (V)} \quad (2)$$

where:

A_a = area of acetaldehyde peak,
A_p = area of propionaldehyde peak,
S = internal standard, µL,
R_f = relative response factor (weight percent/area percent of acetaldehyde relative to propionaldehyde taken as 1.00),
W_p = weight fraction of propionaldehyde in internal standard solution,
0.834×10^6 = density of propionaldehyde internal standard solution at − 30°C (−22°F), µg/L, and
V = volume of bottle interior, mL.

14. Calibration for Internal Standard Test Method

14.1 Prepare a calibration mixture containing acetaldehyde and propionaldehyde in 1-propanol according to A2.1.

14.2 Prepare an internal standard solution for addition to the sample according to A2.2.

14.3 Conduct calibration for the determination of acetaldehyde diffused from bottle polymer into the headspace as follows:

14.3.1 Remove the calibration mixture from the freezer, shake, and replace the cap with a fresh cap.

14.3.2 Prime the 10-µL syringe and withdraw a 4-µL aliquot.

14.4 Inject the aliquot into a glass 1-L (32-oz) bottle (a glass carbonated beverage bottle is suitable) and immediately stopper with a septum cap lined with fluoropolymer film.

14.5 Allow the calibration solution to evaporate in the capped bottle and place it in a 50°C (122°F) oven for 10 to 15 min to assure evaporation and thermal mixing of the components.

14.6 After priming the gas syringe, use it to remove a 5.0-mL aliquot from the bottle. Lock the syringe and withdraw it from the bottle.

14.7 Pressurize the syringe (about 60 psi) to 1.25 mL, insert it into the gas chromatograph, unlock the syringe valve, and inject its contents rapidly; remove the syringe.

14.8 From the peak areas of the acetaldehyde and propionaldehyde, calculate the weight percent to area percent response factor for acetaldehyde relative to propionaldehyde, which is taken as 1.9 (Fig. 2).

15. Report

15.1 The type of calibration (internal or external) used.

15.2 The average acetaldehyde content to two places to the right of the decimal of a uniform sample of bottles, representing each injection mold cavity in which they were blown.

15.3 The maximum acetaldehyde content in any single bottle of the above sample.

15.4 The number of bottles tested.

15.5 The date the test is started and finished.

15.6 Complete identification and description of the containers including the date of manufacture, size, design, and materials.

15.7 Temperature of the test room.

15.8 Age of the preform before blowing.

15.9 Time between bottle blow molding and capping.

16. Precision and Bias [7]

16.1 This precision statement is based on a round robin conducted in 1979 by five laboratories analyzing PET bottles blown by the laboratories, under slightly different conditions from parisons that were obtained from the same sample of material. Each laboratory made from six to twelve determinations.

16.2 For the material tested:

16.2.1 The within-laboratory standard deviation, S_r, is 0.21.

16.2.2 The between-laboratory standard deviation, $S_R = (S_r^2 + S_L^2)^{1/2} = 0.28$. $I_r = 0.58$ ($I_r = 2.83\,S_r$; see 16.3). $I_r = 0.79$ [$(I_r = 2.83\ (S_r^2 + S_L^2)^{1/2}$ where S_L, the square root of between-laboratory component of variance, is 0.19].

16.3 *Repeatability*—In comparing two averages for the same material, obtained by the same operator, using the same equipment on the same day, the averages should be judged not equivalent if they differ by more than the I_r for that material.

16.4 *Reproducibility*—In comparing two averages for the same material, obtained by different operators, using different equipment on different days, the averages should be judged not equivalent if they differ by more than S_R for the material.

16.5 The judgments in accordance with 14.3 and 14.4 will be correct in approximately 95 % of such comparisons.

16.6 For further information, see Practices E 177 and E 691.

17. Keywords

17.1 acetaldehyde; headspace gas chromatography; PET bottles; polyethylene; terephthalate

[7] Supporting data are available from ASTM Headquarters. Request RR: D20-1122.

ANNEXES

(Mandatory Information)

A1. PREPARATION AND ASSAY OF ACETALDEHYDE STANDARD SOLUTION

A1.1 Scope

A1.1.1 This test method describes the preparation and assay of 1.0 mg/mL aqueous acetaldehyde standard solution. Acetaldehyde has a tendency to polymerize and oxidize, and aqueous solutions must be carefully prepared as described to avoid problems.

A1.2 Summary of Test Method

A1.2.1 The acetaldehyde is weighed into distilled water saturated with nitrogen. An aliquot of this standard acetaldehyde solution is reacted with a 30 to 50 % excess of a sodium bisulfite solution for 30 min. The excess sodium bisulfite is reacted with an excess of a standard solution of iodine. The excess iodine is immediately titrated with a standard solution of sodium thiosulfate, using starch indicator.

A1.3 Apparatus

A1.3.1 *Micro Distillation Apparatus.*

A1.3.2 *Analytical Balance.*

A1.3.3 *Variable Transformer Controlled-Heating Mantle.*

A1.3.4 *250-mL Volumetric Flask.*

A1.3.5 *Pasteur Pipettes.*

A1.4 Reagents and Materials

A1.4.1 *Acetaldehyde*, Eastman Organic Chemicals, Catalog No. 468, or equivalent.

A1.4.2 *Anti-bumping Granules*.

A1.4.3 *Distilled Water*, as defined by Type II of Specification D 1193.

A1.4.4 *Nitrogen* (oxygen-free).

A1.4.5 *Ice*.

A1.4.6 *Sodium Bisulfite Solution*—Dissolve 12 g of reagent-grade sodium bisulfite in 1 L of distilled water containing 50 mL of reagent-grade ethyl alcohol.

A1.4.7 *Iodine Solution* (0.1 *N*)—Dissolve 12.7 g of reagent-grade iodine in 1 L of distilled water containing 40 g of reagent-grade potassium iodine.

A1.4.8 *Sodium Thiosulfate Solution* (0.1 *N*)—Prepare an aqueous solution from reagent-grade sodium thiosulfite and standardize with reagent-grade potassium iodate to ±0.0002 normality units.

A1.4.9 *Starch Indicator* (0.2 %)—Dissolve 2 g of reagent-grade starch in 1 L of distilled water containing 10 mg of reagent-grade mercuric iodide.

A1.4.10 *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.[6]

A1.5 Procedure

A1.5.1 Set up the distillation apparatus with chilled water [5°C (41°F) or less] through the condenser and the receiver flask immersed in ice. Place about 50 mL of acetaldehyde in the distillation flask and heat gently to distill the acetaldehyde.

A1.5.2 Discard the first 5 to 10 mL of distillate, and then collect the next 10 to 20 mL of acetaldehyde distilling over at 22°C (72°F).

A1.5.3 Remove the receiver flask, flush with nitrogen and stopper.

A1.5.4 Fill a 250-mL volumetric flask with about 245 mL of distilled water. Bubble nitrogen through the water for about 20 min to remove any dissolved oxygen.

A1.5.5 Tare the weight of flask, water, and stopper on the balance, and then quickly add about 250 mg of freshly distilled acetaldehyde to the water. This is difficult because of the volatility of acetaldehyde and is best done using a Pasteur pipette. Stopper the flask and mix well.

A1.5.6 Dilute the flask to the mark with deaerated water, mix well, and flush the headspace with nitrogen.

A1.5.7 Analyze three 2.0-mL aliquots of this solution by the standard titration procedure below and determine the exact concentration of acetaldehyde in the solution. This should be done as soon as possible after the solution is prepared.

A1.5.8 Pipet 5.0 mL of the sodium bisulfite solution into an iodine flask.

A1.5.9 Pipet 5.0 mL of the acetaldehyde solution into the iodine flask and seal the stopper of the iodine flask with distilled water.

A1.5.10 Allow the acetaldehyde and sodium bisulfite solution to react 30 min at room temperature with stirring.

A1.5.11 Open the iodine flask and pipet 25.0 mL of the iodine solution into the flask while stirring the solution.

A1.5.12 Immediately titrate the excess iodine with the sodium thiosulfate solution, using the starch indicator.

A1.5.13 Perform a reagent-blank determination by repeating A1.5.8-A1.5.12 and substituting distilled water for the acetaldehyde in A1.5.9.

A1.5.14 Take an average of triplicate titrations. As soon as possible, transfer the acetaldehyde solution by Pasteur pipette into small vials with fluoropolymer film-lined septa. Fill the vials to overflowing to eliminate a headspace and then seal. Mark each vial with the concentration and store in the refrigerator until required for use.

NOTE A1.1—This entire operation should be completed in the same day. Each small vial of standard should be used no more than a week (or until an air space appears) before being discarded for a fresh vial. If this procedure is followed exactly, unopened aqueous acetaldehyde solutions can be safely stored without deterioration for several months.

A1.6 Calculations

A1.6.1 Calculations shall be made as follows:

$$\text{Acetaldehyde, mg/mL} = \frac{(S - B) \times N \times E}{A} \qquad \text{(A1.1)}$$

where:

S = sample titration, mL,
B = reagent blank titration, mL
N = normality of the sodium thiosulfate solution,
E = equivalent weight of acetaldehyde (22.03), and
A = millilitre (5.0) of the acetaldehyde standard solution used in A1.5.9.

A1.7 Report[8]

A1.7.1 Report the following information:

A1.7.1.1 Acetaldehyde standard solution identification.

A1.7.1.2 The milligram/millilitre of the acetaldehyde assayed.

A1.7.1.3 Reference to the preparation and assay method.

A1.7.1.4 Date of the assay.

[8] For further information, consult Kolthoff and Belcher, *Volumetric Analysis*, III, pp 383, 384 (1957).

A2. PREPARATION OF ACETALDEHYDE/PROPIONALDEHYDE INTERNAL STANDARD SOLUTION

A2.1 A 0.5 % calibration mixture is prepared by adding and accurately mixing (nearest 0.1 mg) 0.5 mL consecutively of propionaldehyde and acetaldehyde (cold) into 95 mL chilled 1-propanol. This solution is prepared in a 118-mL (4-oz) glass bottle fitted with a punched metal cap, butyl rubber septum, and Teflon outer liner. Store this capped solution in the freezer at − 30°C (−22°F). It has a density of 0.834.

A2.2 Similarly, prepare a solution of 0.5 % propionaldehyde in 1-propanol for internal standard addition to the sample and store in the freezer. It, too, has a density of 0.834 g/cc.