Designation: F2013 – 10 (Reapproved 2023)

Standard Test Method for Determination of Residual Acetaldehyde in Polyethylene Terephthalate Bottle Polymer Using an Automated Static Head-Space Sampling Device and a Capillary GC with a Flame Ionization Detector[1]

This standard is issued under the fixed designation F2013; 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 a gas chromatographic procedure for the determination of the ppm residual acetaldehyde (AA) present in poly(ethylene terephthalate) (PET) homopolymers and co-polymers which are used in the manufacture of beverage bottles. This includes sample types of both amorphous and solid-stated pellet and preform samples, as opposed to the bottle test, Test Method D4509, an acetaldehyde test requiring 24 h of desorption time at 23 °C into the bottle headspace and then the concentration of the headspace quantified by a similar GC method.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.4 *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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D4509 Test Methods for Determining the 24-Hour Gas (AIR) Space Acetaldehyde Content of Freshly Blown PET Bottles (Withdrawn 2004)[3]

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

3.1 The terms employed in this test method are commonly used in normal laboratory practice and require no special comment.

4. Summary of Test Method

4.1 A specified size (< 1000 µm) of granulated sample is weighed into a 20 mL head-space vial, sealed, and then heated at 150 °C for 60 min. After heating, the gas above the sealed sample of PET polymer is injected onto a capillary GC column. The acetaldehyde is separated, and the ppm of acetaldehyde is calculated.

5. Significance and Use

5.1 This test method is of particular use as a quality control tool for a molding or synthesis operation. Acetaldehyde is a volatile degradation product generated during melt processing of PET. Thus, it becomes trapped in the sidewalls of a molded article and desorbs slowly into the contents packaged therein. In some foods and beverages AA can impart an off-taste that is undesirable, thus, it is important to know its concentration in PET articles that are to be used in food contact applications.

5.2 The desorption conditions of 150 °C for 60 min are such that no measurable AA is generated by the sample during the desorption process.

6. Sources of Error

6.1 A bias is known to exist if the ratio of sample mass (mg) to head-space vial volume (mL) exceeds a value of ten.

6.2 Acetaldehyde is very volatile and must be handled carefully to avoid sample loss during the calibration procedure.

[1] This test method is under the jurisdiction of ASTM Committee F02 on Primary Barrier Packaging and is the direct responsibility of Subcommittee F02.15 on Chemical/Safety Properties.

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[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.

[3] The last approved version of this historical standard is referenced on www.astm.org.

Storing the standard vials in a refrigerator (4 °C ± 2 °C) is a must to minimize the error due to volatility.

6.3 Failure to achieve a tight seal on the head-space vial will result in the loss of acetaldehyde during storage and desorption, producing a false low value.

6.4 Failure to grind the sample to the appropriate particle size may lead to a false low value for residual AA due to the increased path length for desorption.

6.5 Samples submitted for "residual AA measurement" should be stored in a freezer (< –10 °C) until they are tested. Failure to do so can result in lower than expected results.

6.6 Excessive grinding of samples can cause residual AA contained therein to be desorbed. Extensive excessive grinding can lead to actual melting of the polymer and AA generation. Samples which have been chilled in liquid nitrogen properly should only be in the grinder for ~30 s or less.

7. Apparatus

7.1 *Gas Chromatograph,* equipped with a flame ionization detector.

7.2 *Integrator* or a PC with data acquisition software.

7.3 *Head-Space Sampler*—(a static head-space sampler).

7.4 *Column,* 30 m by 0.53 mm inside diameter (DVB porous megabore capillary column or equivalent).

7.5 *Vials,* 20 mL, head-space, with 20 mm septa, 20 mm aluminum caps, and crimper for 20 mm caps.

7.6 *Crimper,* 20 mm.

7.7 *Decrimper,* 20 mm.

7.8 *Wiley Mill,* equipped with an 800 µm to 1000 µm screen, or equivalent.

7.9 *Syringe,* (gas tight) calibrated, with certificate of calibration.

7.10 *Small Vacuum Cleaner,* with hose attachment for cleaning.

7.11 *Analytical Balance,* capable of accurately weighing to at least ±0.0001 g.

7.12 *Hammer.*

7.13 *Air for EID.*

7.14 *Helium 99.9995 % purity as carrier gas.*

7.15 *Hydrogen 99.9995 % purity* for flame ionization detector (FID) or can be used as carrier gas.

7.16 *Spatular.*

7.17 *Dewer flask.*

7.18 *Glass jar or manila envelope.*

7.19 *Wipe paper or tissue.*

7.20 *Digital syringe,* equipped with a 10 L glass syringe.

8. Reagents and Materials

8.1 *Acetaldehyde (AA),* 500 ppm AA in water (or 1000 ppm), purchased certified standard.

8.2 *Liquid Nitrogen,* plant grade (R-3, S-3).

9. Calibration and Standardization

NOTE 1—The following procedure should be performed and recorded once every three months.

9.1 Break open a certified AA standard ampule (ampules must be stored in a refrigerator) or prepare AA standard by the attached supplemental procedure. (See Appendix X5.)

9.2 Using the syringe, fill it by placing the tip in the liquid standard and quickly moving the plunger up and down several time to evacuate any bubbles, then pull the plunger back past the 2.000 µL mark to 2.200 µL to 2.250 µL.

9.3 Wipe the syringe needle with a tissue.

9.4 Depress the plunger until the digital readout is 2.000 µL.

9.5 Smear the excess liquid that is on the syringe tip on the OUTSIDE of the headspace vial.

9.6 Place the syringe inside of the vial so that the tip just touches the bottom of the vial.

9.7 Quickly inject the liquid standard into the vial and swirl the syringe tip around the inside of the vial to smear all liquid on the vial walls.

9.8 Remove the syringe and IMMEDIATELY cap the vial.

9.9 Calculate the weight of AA based on the standard's certified value and a 2.000 µL injection volume.

NOTE 2—Acetaldehyde is very volatile. The AA ampules must be stored in a refrigerator, and the standards prepared immediately after breaking open an ampule.

9.10 Analyze the working standard by the procedure described in Section 11, starting with 11.2.11.

9.11 Calculate an AA response factor for the standard using the following equation:

$$\text{response factor of AA} = \text{Wt of AA in µg/area of AA} \quad (1)$$

NOTE 3—Due to the error associated with the certified standard, 9.1 – 9.11 should be performed five times using five different standard ampules.

9.12 Average the five response factors obtained, and use this value for the sample analyses.

9.13 Manually enter the calculated response factor in the calibration list of the integrator or data system.

NOTE 4—During a series of sample analyses, a periodic check of instrument performance is recommended by placing a few liquid standard samples throughout the sample set. If these values fall out of the acceptable range as specified by the certificate of analysis, recalibration (9.1 – 9.12) should be performed.

10. Sample Preparation

10.1 *Parisons or Preforms or Plaques*—May be cryogenically ground whole, or can be broken into small pieces with a hammer (using liquid nitrogen) and then ground with the aid of grinding mill equipped with a 20-mesh or <1000-µm screen. The grind should be thoroughly homogenized before sampling for AA. If the appropriate size screen is not available on the large grinding mill, then it is suggested that the sample be ground to 3 mm to 6 mm on the large mill and the sample thoroughly homogenized. A portion can then be taken to a smaller mill equipped with the 20 mesh or <1000 µm screen