Designation: F2013 – 10

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

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D4509 Test Methods for Determining the 24-Hour Gas (AIR) Space Acetaldehyde Content of Freshly Blown PET Bottles (Withdrawn 2004)[3]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. Storing the standard vials in a refrigerator (4 ± 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.

[1] This test method is under the jurisdiction of ASTM Committee F02 on Flexible 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.

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 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 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 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 and cryogenically ground again before analysis. Again the final sample should be thoroughly homogenized.

10.2 *Pellets*—May be cryogenically ground in a small grinding mill using liquid nitrogen. The final sample should be thoroughly homogenized before sampling for analysis.

NOTE 5—Samples, either preforms, plaques, or pellets, should be chilled in the liquid nitrogen for several minutes until the liquid nitrogen stops boiling and then dropped immediately into the grinder. Sample

should be sufficiently ground in a few seconds. The grinder should not be allowed to operate more than 20 to 30 s as in such cases undesirable sample heating can occur.

11. Procedure

NOTE 6—Refer to the general operating manual for gas chromatograph, the head-space sampler, and the series integrator for instructions in performing steps in this procedure.

11.1 Adjust the gas chromatograph to the conditions specified in Appendix X1. Adjust the head-space sampler to the conditions in Appendix X2. Set the series integrator to the conditions in Appendix X3.

11.2 *Sample Analysis:*

11.2.1 Place 2 to 3 of polymer pellets (or crushed preform) into a small Dewar flask.

11.2.2 Cover the polymer with 20 to 40 mL of liquid nitrogen.

11.2.3 Allow the polymer to chill under the liquid nitrogen for approximately 3 min (or until most of the liquid N2 has evaporated).

11.2.4 Turn on the Wiley mill equipped with a 800 to 1000-µm screen.

11.2.5 Slowly pour the remaining liquid nitrogen from the Dewar flask through the Wiley mill, followed by the chilled polymer sample (tapping the sample may be required).

11.2.6 Collect the ground polymer in a small glass jar or small manila envelope.

11.2.7 Turn off the Wiley mill and clean it with a vacuum cleaner.

11.2.8 Allow the ground polymer sample to come to room temperature (approximately 10 min).

11.2.9 Weigh approximately 0.2000 (± 0.0200) g, recorded to the nearest 0.0001 g, into a 20-mL head-space vial.

11.2.10 Place a septum (with TFE-fluorocarbon side down towards the inside of the vial) on the vial. Place an aluminum cap on top of the septum, and crimp the cap with a crimper UNTIL THE CAP CANNOT BE TURNED. Remove the center piece of the aluminum cap (if it exists).

11.2.11 Place the vial in the appropriate position in the head-space sampler.

11.2.12 Set up head space sampler and a GC acquisition program condition as listed in Table X1.1 and Table X2.1, following instrument operating instructions from manufacturer.

11.2.13 The head-space sampler will heat the sample for 60 min at 150°C and then automatically inject the head-space gas and start the gas chromatograph and integrator or data acquisition software.

11.2.14 The final report will appear on the integrator or the data system when the GC is finished.

11.2.15 Determine the peak area for the AA from integrator or data acquisition software.

11.2.16 To determine the mass of AA from the sample, area of AA multiplied by response factor.

11.2.17 To determine the concentration in ppm of AA in the polymer sample, divide the mass of AA (reported in 11.2.16) by the sample weight in the vial (recorded in 11.2.9 as grams of polymer).

12. Calculation

12.1 The AA response factor is calculated as described in 9.11 and 9.12. The ppm of AA can be calculated manually by multiplying the response factor and the area of the AA peak, and then dividing this number by the sample weight in the vial (in grams).

13. Report

13.1 Report the ppm or µg/g of AA to two decimal places.

14. Precision and Bias

14.1 The following was taken from work completed by the International Society of Beverage Technologists (ISBT) subcommittee concerning standardization of method to determine residual AA in PET.

14.2 The number of laboratories, materials, and determinations in this study meets the minimum requirements for determining precision in accordance with Practice E691. A complete report is on file at ASTM Headquarters.[4]

14.3 This round robin was conducted by having one laboratory mold PET preforms on a 48-cavity injection molding machine and selecting 6 of those cavities as the sample set. Even though these preforms all came from one PET sample (material), each cavity has its own unique AA value, and thus, were treated as six different materials. Also, two different types of precision and bias were calculated, one based on each laboratory using their own calibration standard solution and another when each laboratory calibrated with a "common" calibration standard.

	Practice E691 Study	Minimum
Laboratories:	6	6
Materials:	6	4
Determinations:	3	2

14.4 *Precision and Bias With Each Laboratory Using Their Own Calibration Standard*—Precision, characterized by repeatability, *Sr* and *r*, and reproducibility, *SR* and *R*, has been determined for the materials to be as follows:

Materials	Average	*Sr*	*SR*	*r*	*R*
Material A	5.21	0.1812	0.6403	0.5074	1.7928
Material B	6.25	0.4060	0.7464	1.1368	2.0899
Material C	6.37	0.2880	0.6713	0.8066	1.8796
Material D	7.21	0.3285	0.7743	0.9198	2.1680
Material E	7.01	0.4217	0.8350	1.1808	2.3380
Material F	5.88	0.3930	0.7168	1.1003	2.0071

14.4.1 Since the materials used in this study are all from one specific type of material (PET), but have different AA levels because they are from different cavities, it makes more sense to have one set of precision values rather than one for each cavity. This will be derived by squaring each *Sr* and *SR*, averaging each of Sr^2 and SR^2 across materials and taking the square root.

Sr	*SR*	*r*	*R*
0.3466	0.7335	0.9705	2.0538

14.4.1.1 *Standard Deviation (Sr)*—Sr is the square root of the average within laboratory variance.

[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:F02-1015.

14.4.1.2 *Standard Deviation (SR)*—SR is the square root of the sum of the within laboratory variance and between laboratory variance of the laboratory means.

14.4.1.3 *Repeatability*—r is the interval representing the largest expected difference between two test results for the same material, obtained by the same operator using the same equipment on the same day in the same laboratory. A difference larger than *r* indicates more variation is present than expected.

14.4.1.4 *Reproducibility*—R is the interval representing the largest expected difference between two test results for the same material, obtained by different operators using different equipment in different laboratories, not necessarily on the same day. A difference larger than *R* indicates more variation is present than expected.

14.5 *Precision and Bias When Each Laboratory Uses a Common Calibration Standard*—Precision, characterized by repeatability, *Sr* and *r*, and reproducibility, *SR* and *R*, has been determined for the materials to be as follows:

Materials	Average	*Sr*	*SR*	*r*	*R*
Material A	5.42	0.1849	0.4128	0.5178	1.1596
Material B	6.47	0.4123	0.6438	1.1545	1.8026
Material C	6.59	0.2703	0.5020	0.7567	1.4057
Material D	7.45	0.3113	0.6333	0.8716	1.7732
Material E	7.26	0.4014	0.5747	1.1240	1.6090
Material F	6.10	0.3854	0.5085	1.0792	1.4237

14.5.1 Since the materials used in this study are all from one specific type of material (PET), but have different AA levels because they are from different cavities, it makes more sense to have one set of precision values rather than one for each cavity. This will be derived by squaring each *Sr* and *SR*, averaging each of Sr^2 and SR^2 across materials and taking the square root.

Sr	*SR*	*r*	*R*
0.3376	0.5518	0.9453	1.5450

14.6 *Bias*—There are no recognized polymer standards by which to estimate bias of this test method. Testing a known liquid standard with all laboratories using common calibration did not show any laboratory bias between laboratories or between the average of all laboratories and the known value.

15. Keywords

15.1 AA test; acetaldehyde; carbonated soft drink; ground parison AA; PET bottles; 24 hours headspace; water

APPENDIXES

(Nonmandatory Information)

X1. HEWLETT-PACKARD 6890 SERIES GC CONDITIONS

TABLE X1.1 Hewlett-Packard 6890 Series GC Conditions

Temp 1 Isothermal	90°C
Time 1	8.00 min
Injector Temperature	250°C
Detector Temperature	250°C
Head Pressure	10 psi
Column-Flow	12.2 mL/min Helium
Velocity	85 cm/s
Split Ratio	2.0
Detector Air Flow	300 mL/min
Detector Hydrogen Flow	30 mL/min
Detector Makeup Flow	20 mL/min helium

X2. HEWLETT-PACKARD 7694 HEAD-SPACE SAMPLER CONDITIONS

TABLE X2.1 Hewlett-Packard 7694 Head-Space Sampler Conditions

Oven Temp	150°C
Loop Temp	160°C
Transfer Line Temp	170°C
Carrier Pressure	11.5 psi
Vial Pressure	10.5 psi
Vial Eq. Time	60 min
Pressurize Time	0.2 min
Loop Fill Time	0.2 min
Loop Eq. Time	0.1 min
Inject Time	0.2 min
GC Cycle Time	9 min

X3. HEWLETT-PACKARD 6890 SERIES INTEGRATOR METHOD FILE

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* LIST: METH  @

RUN PARAMETERS
ZERO   = 0
ATT 2^ = 0
CHT SP = 0.5
AR REJ = 200
THRSH  = –2
PK WD  = 0.04

TIMETABLE EVENTS
EMPTY

CALIBRATION
ESTD
REF % RTW:   5.000  NON-REF % RTW:   5.000

LEVEL: 1          RECALIBRATIONS: 3

CAL#    RT     LV     AMT     AMT/AREA
  1R  2.545   1 1.5030E+00  1.4933E-04

CAL#    NAME
  1 ACETALDEHYDE

INTEGRATION PLOT TYPE ..... FILTERED
Presentation plot ..... NO

RUN DATA STORAGE
Store signal data ..... YES
Device ..... M
Bunched or raw data ..... RAW
Store processed peaks .....  NO

CALIBRATION OPTIONS
RF of uncalibrated peaks .... 0.0000E+00
Calibration fit ..... P
Disable post-run RT update .. NO
SAMPLE AMT ..... 1.0000E+00
MUL FACTOR ..... 1.0000E–02

REPORT OPTIONS
Suppress local report ..... NO
HEIGHT% report ..... NO
Report uncalibrated peaks ... YES
Extended report ..... YES

PRINT & POST-RUN LIST OPTIONS
Large font ..... YES
Store post-run report ..... NO
External post-run report .... NO
List run parameters .....NO
List timetable ..... NO
List calibration table ..... NO
List remote method ..... NO
Form-feed before report ..... NO
Form-feed after report ..... NO
Skip perforations in report . NO
Skip perforations in plot ... NO
RANGE: C1,BUFFER ..... 5!, 5!
INJECTOR 1 (not installed)
     INJECTOR 2 (not installed)
TRAY (not installed)
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FIG. X3.1 Hewlett Packard 6890 Series Integrator Method File