Designation: D 4275 – 09

Standard Test Method for Determination of Butylated Hydroxy Toluene (BHT) in Polymers of Ethylene and Ethylene–Vinyl Acetate (EVA) Copolymers By Gas Chromatography[1]

This standard is issued under the fixed designation D 4275; 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 describes a procedure for the determination of **butylated hydroxy toluene (BHT) (2,6-di-t-butyl-4-methyl-hydroxybenzene)** in polymers of ethylene and ethylene-vinyl acetate (EVA) copolymers by solvent extraction followed by gas chromatographic analysis. Detection of the compound is achieved by flame ionization, and quantitative analysis is obtained by use of internal or external standards, as described in Practices E 260, E 355, and E 594.

1.2 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

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.* Specific precautionary statements are given in Section 9.

NOTE 1—There is no known ISO equivalent for this test method.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D 4968 Guide for Annual Review of Test Methods and Specifications for Plastics

D 7210 Practice for Extraction of Additives in Polyolefin Plastics

E 260 Practice for Packed Column Gas Chromatography

E 355 Practice for Gas Chromatography Terms and Relationships

E 594 Practice for Testing Flame Ionization Detectors Used in Gas or Supercritical Fluid Chromatography

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

IEEE/ASTM SI-10 Practice for Use of the International System of Units (SI) (the Modernized Metric System)

3. Terminology

3.1 Definitions—Units and symbols used in this test method are those recommended in Practice IEEE/ASTM SI-10. Chromatographic terms and relationships are as described in Practice E 355.

3.2 *Abbreviations:*Abbreviations:

3.2.1 *BHT*—Butylated hydroxy toluene (2,6-di-tert-butyl-4-methyl-hydroxybenzene).

3.2.2 *MM*—Methyl myristate.

3.2.3 *EVA*—Ethylene-vinyl acetate copolymers.

3.2.4 *LDPE*—Low-density polyethylene.

3.2.5 *HDPE*—High-density polyethylene.

4. Summary of Test Method

4.1 The BHT from a finely ground polymer sample is extracted by shaking or refluxing with cyclohexane or isopropanol. A known volume of this extract is injected into a gas chromatographic column packed with a liquid-coated solid support. Passing through this column in a stream of carrier gas, BHT is separated from the extraction solvent and other components. Responses of BHT and any internal standard are measured by a flame ionization detector. This signal is recorded to indicate the relative concentration and retention time of BHT.

5. Significance and Use

5.1 Separation and identification of stabilizers used in the manufacture of polyethylene are necessary in order to correlate performance properties with polymer composition.

[1] This test method is under the jurisdiction of ASTM Committee D20 on Plastics and is the direct responsibility of Subcommittee D20.70 on Analytical Methods.

Current edition approved Aug. 1, 2009. Published August 2009. Originally approved in 1983. Last previous edition approved in 2002 as D 4275 - 02.

[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.

5.2 The BHT extraction procedure is made effective by the insolubility of the polymer sample in solvents generally used for gas chromatographic analysis.

6. Interferences

6.1 Any material eluting at or near the BHT or MM retention times will cause erroneous results. Prior to extraction, solvent blanks shall be analyzed to confirm the absence of interfering peaks.

7. Apparatus

7.1 *Reflux Extraction*, consisting of 250-mL round-bottom flask with condenser and heating mantle to fit.

7.2 *Wiley Mill*, with 10 and 20-mesh screens.

7.3 *Wrist-Action Shaker*.

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

7.5 *Chromatographic Column*, 3.2-mm outside diameter times 1.8 m packed with 20 % UCW-98 on 80/100 mesh Chromosorb P, a similar packed column, or an equivalent capillary column, such as a HP-1 or DB-1.

7.6 *Integrator*, capable of measuring the net peak area on the back side of a solvent peak.

7.7 *Gas Chromatographic Syringe*, 10 µL.

7.8 *Analytical Balance*, capable of weighing to ±0.0001 g.

7.9 *Pressure Regulators*, for all required gas cylinders.

7.10 *Filter-Dried Assemblies*, for each required gas cylinder.

7.11 *Soap Film Flowmeter and Stopwatch*, or other means of measuring gas flow rates.

8. Reagents and Materials

8.1 *Cyclohexane*, reagent grade.

8.2 *Isopropyl Alcohol*, reagent grade.

8.3 *Methyl Myristate,*[3] 99^{+} %, boiling point 323°C (internal standard).

8.4 *Butylated Hydroxy Toluene*, food grade (2,6-di-tert-butyl-4-methyl-hydroxybenzene).

8.5 *Hydrogen Cylinder*, prepurified.

8.6 *Nitrogen Cylinder*, prepurified, oxygen-free for carrier gas.

NOTE 2—Helium or hydrogen may also be used as the carrier gas.

8.7 *Air*, breathing or water-pumped.

9. Safety Precautions

9.1 Cyclohexane and isopropyl alcohol are flammable. This extraction procedure should be carried out in a fume hood.

10. Preparation of Gas Chromatograph

10.1 Install the chromatographic column and condition overnight at 200°C with carrier gas flow rate of 35 mL/min. Do not connect the exit end of the column to the detector during this conditioning period. Turn off hydrogen and air flows to the detector while the column is disconnected.

10.2 Connect the exit end of the column to the detector. Set optimum hydrogen and air flow rates for the detector as specified for the chromatograph model in use, or as determined experimentally.

10.3 Set chromatograph temperatures as follows:

10.3.1 Oven (chromatographic column), 160°C.

10.3.2 Injection block, 220°C.

10.3.3 Detector block, 240°C.

11. Calibration by Internal Standard

11.1 Weigh a syringe containing approximately 80 mg of methyl myristate.

11.2 Transfer syringe contents to a 2-L volumetric flask and immediately reweigh the syringe (±0.1 mg).

11.3 Dilute to volume with extraction solvent (cyclohexane or isopropyl alcohol) and store in a tightly stoppered flask.

11.4 Weigh and transfer 20 ± 0.1 mg of BHT into a 500-mL volumetric flask.

11.5 Dissolve BHT in the internal standard solution in accordance with 11.3 and dilute to volume using this same solution.

11.6 Inject 2 µL of this calibration mixture into the gas chromatograph equilibrated to the conditions of 10.3.

11.7 Chromatograph BHT and MM and record their respective peak areas using an integrator.

NOTE 3—The BHT and methyl myristate peak elute at approximately 3.5 and 8 min, respectively.

11.8 Using BHT and MM areas from 11.7, determine the relative response factor (R_f) as follows:

$$R_f = \frac{concentration\ (mg/L)\ BHT \times area\ MM}{concentration\ (mg/L)\ MM \times area\ BHT} \quad (1)$$

11.9 Average response factors for five replicate injections of the calibration mixture.

12. Calibration by External Standard

12.1 Weigh 100 ± 1 mg of BHT into a 200-mL volumetric flask.

12.2 Dissolve in the selected extraction solvent (cyclohexane or isopropyl alcohol) and dilute to volume.

12.3 Pipet 2.0, 4.0, 6.0, and 8.0 mL of the above stock solution into a series of 100-mL volumetric flasks and dilute to volume with the appropriate solvent.

12.4 Inject 2 µL of each dilute standard into the gas chromatograph equilibrated to the conditions of 10.3.

12.5 Measure the BHT peak height (mm) and multiply by the attenuation and range to obtain the total peak height for each standard. Integrated peak areas can also be used.

12.6 Repeat injection of each standard and average the total peak height (or area) results for duplicate injections.

12.7 Plot the total peak height (or area) on the *y*-axis versus concentration (µg/mL) for each standard on the *x*-axis. The slope of this curve is proportional to the flame response for BHT.

NOTE 4—Chromatographic response for BHT should be determined by each analyst every day. Observe that the curve intercept should be zero.

[3] The sole source of supply of the methyl myristate known to the committee at this time is Aldrich Chemical Co., P.O. Box 355, Milwaukee, WI 53201. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.