Designation: D 4275 – 02

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 similar or equivalent ISO standard.

2. Referenced Documents

2.1 *ASTM Standards:*

D 4968 Guide for Annual Review of Test Methods and Specifications for Plastics[2]

E 260 Practice for Packed Column Gas Chromatography[2]

E 355 Practice for Gas Chromatography Terms and Relationships[3]

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

E 594 Practice for Testing Flame Ionization Detectors Used in Gas Chromatography[3]

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method[3]

3. Terminology

3.1 Definitions—Units and symbols used in this test method are those recommended in Practice E 380. 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 that may contain an internal standard. 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.

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 should be analyzed to confirm the absence of interfering peaks.

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[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/(D20.70.02) Chromatography.

Current edition approved August 10, 2002. Published October 2002. Originally published as D 4275 – 83. Last previous edition D 4275 – 96.

[2] *Annual Book of ASTM Standards*, Vol 08.03.

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

[4] Discontinued; see *1997 Annual Book of ASTM Standards*, Vol 14.02.

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*,[5] 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 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.

13. Sample Preparation

13.1 Grind HDPE, LDPE, and EVA samples containing less than 10 % vinyl acetate to 20-mesh size.

13.2 Grind samples containing greater than 20 % vinyl acetate to 10-mesh size.

14. Procedure

14.1 *Isopropyl Alcohol Extraction*:

14.1.1 For analysis of LDPE or EVA, weigh 3 ± 0.001 g of ground sample into a 250-mL round-bottom flask.

14.1.2 Pipet 25.0 mL of isopropyl alcohol internal standard solution prepared in 11.3 into the flask and connect it to the condenser.

[5] Available from Aldrich Chemical Co., P.O. Box 355, Milwaukee, WI 53201.

NOTE 5—With external standard calibration, substitute the appropriate solvent for internal standard solution in 11.3 in the above procedure.

14.1.3 Reflux 2 h and cool to room temperature before removing the flask from the condenser.

14.2 *Cyclohexane Extraction*:

14.2.1 For HDPE, repeat 14.1.1-14.1.3 , substituting cyclohexane for isopropyl alcohol.

NOTE 6—IPA can be used for HDPE extractions, but the recovery was found to be 10 % lower than with cyclohexane.

14.2.2 For LDPE or EVA, weigh 3 ± 0.001 g of ground sample into a 250-mL round-bottom flask. Pipet 25.0 mL of cyclohexane internal standard solution prepared in 11.3 into the flask and insert the stopper. Shake at room temperature for 2 h on a wrist-action shaker.

14.3 *Extract Analysis*—Inject 2 µL of sample extract into the gas chromatograph equilibrated to conditions of 10.3. Measure areas of BHT and methyl myristate peaks (if using internal standard calibration) and record as *A*BHT and *A*MM, respectively.

15. Calculation

15.1 *Internal Standard*—Using the response factor (R_f) determined in 11.8 and area responses from chromatography of sample extracts, calculate the BHT content of each sample from the following equation:

$$ppm\ BHT = \frac{(A_{BHT})(R_f)(C)(V)}{(A_{MM})\ (W)} \quad (2)$$

where:

A_{BHT} = area of BHT peak in sample chromatogram,
A_{MM} = area of methyl myristate peak in sample chromatogram,
R_f = response factor from 11.8,
C = concentration of MM in the internal solution, mg/L,
V = volume of internal standard solution used for extraction, mL, and
W = weight of sample extracted, g.

15.2 *External Standard*—Using the calibration slope from 12.7, calculate the BHT content of each sample from the following equation:

$$BHT\ (in\ ppm\ by\ weight) = \frac{BV}{SW} \quad (3)$$

where:

B = BHT area or peak height from sample chromatogram,
V = volume of extraction solution, mL,
W = weight of sample extracted, g, and
S = slope of calibration curve (from 12.7).

16. Report

16.1 Report the following information:

16.1.1 Sample identification,

16.1.2 Sample preparation method used,

16.1.3 Gas chromatography analysis method used, including type of calibration, and

16.1.4 Concentration of BHT in the polymer, ppm.

17. Precision and Bias

17.1 *Precision*—Table 1 is based on a round robin conducted in accordance with Practice E 691 involving two materials tested by five laboratories. For each material, all samples were prepared at one source, but specimens were prepared at the laboratories that tested them. Each test result was an average of two individual determinations. Each laboratory obtained two test results for each sample.

17.2 Samples included HDPE and EVA (0 to 19 % VA) with BHT levels of 70 to 930 µg/g.

17.3 For HDPE containing 150 to 350-µg/g ppm BHT, values determined using cyclohexane extraction averaged 10 % higher than those derived from isopropanol extraction.

17.4 *Bias*—There are no recognized standards by which to estimate the bias of this test method.

NOTE 7—Caution should be exercised with the between-laboratory results since fewer than six laboratories participated in the round-robin study.

18. Keywords

18.1 butylated hydroxy toluene; BHT; ethylene-vinyl acetate; gas chromatography; polyethylene

TABLE 1 Summary of Method Precision

Extraction Solvent	Expressed as Percent of the Average		
	$CV\%_r$[A]	$CV\%_r$[B]	$CV\%_R$[C]
Isopropanol	2.7	5.0	7.4
Cyclohexane	2.9	4.9	7.4

[A] $CV\%_r$ = within laboratory coefficient of variation between a pair of replicates (expressed in percent).

[B] $CV\%_r$ = within laboratory coefficient of variation of the average of two analyses on different days (expressed in percent).

[C] $CV\%_R$ = between laboratory coefficient of variation of the average (expressed in percent).