Designation: D 5815 – 95 (Reapproved 2001)ε1

Standard Test Method for Determination of Phenolic Antioxidants and Erucamide Slip Additives in Linear Low-Density Polyethylene Using Liquid Chromatography (LC)[1]

This standard is issued under the fixed designation D 5815; 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.

ε[1] NOTE—Several sections were changed editorially in March 2001.

1. Scope

1.1 This test method covers a liquid-chromatographic procedure for the separation of some additives currently used in linear low-density polyethylene. These additives are extracted with either isobutanol or isopropanol prior to liquid-chromatographic separation. The ultraviolet absorbance (200 nm) of the compound(s) is measured; quantitation is performed using the internal standard method.

1.2 *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 equivalent ISO standard.

2. Referenced Documents

2.1 *ASTM Standards:*

D 883 Terminology Relating to Plastics[2]

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

E 131 Terminology Relating to Molecular Spectroscopy[3]

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

IEEE/ASTM SI-10 Standard for Use of the International System of Units (SI): The Modern Metric System[5]

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of plastic terms used in this test method, see Terminologies D 883 and D 1600.

3.2 For units, symbols, and abbreviations used in this test method refer to Terminology E 131 or IEEE/ASTM SI-10.

3.3 *Abbreviations:*Abbreviations:

3.3.1 *BHEB*—2,6-di-t-butyl-4-ethyl-phenol or butylated hydroxyethyl benzene.

3.3.2 *BHT*—2,6-di-t-butyl-cresol or butylated hydroxy toluene.

3.3.3 *LC*—Liquid chromatography.

3.3.4 *LLDPE*—Linear low-density polyethylene.

3.4 *Trade Names*:

3.5 *Irganox 1010*—Tetrakis[methylene(3,5-di-t-butyl-4-hydroxy hydrocinnamate)]methane.

3.6 *Irganox 1076*—Octadecyl-3,5-di-t-butyl-4-hydroxy hydrocinnamate.

3.7 *Isonox 129*[6]—2,2′-ethylidene *bis* (4,6-di-t-butyl phenol).

3.8 *Kemamide-E—Cis*-13-docosenamide, erucamide.

3.9 *Tinuvin P*—2(2′-hydroxy-5′-methyl phenyl)benzotriazole.

4. Summary of Test Method

4.1 The LLDPE sample is ground to a 20-mesh particle size and extracted by refluxing with either isobutanol or isopropanol.

4.2 The solvent extract is analyzed by liquid chromatography.

4.3 Additive concentrations are determined relative to an internal standard (contained in the solvent) using reverse phase chromatography (C-18 column) with ultraviolet (UV) detection at 200 nm.

NOTE 2—Isopropanol is recommended as the extraction solvent for lower crystallinity LLDPE (0.925 density and below) and isobutanol is recommended as the extraction solvent for higher crystallinity LLDPE containing Irganox 1010.

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

Current edition approved Oct. 10, 1995. Published December 1995.

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

[3] *Annual Book of ASTM Standards*, Vol 03.06.

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

[5] *Annual Book of ASTM Standards*, Vol 14.04.

[6] CAS No. 112–84–5.

5. Significance and Use

5.1 Separation and identification of stabilizers used in the manufacture of linear low-density polyethylene are necessary in order to correlate performance properties with polymer composition. This test method provides a means to determine BHT, BHEB, Isonox 129, erucamide slip, Irganox 1010, and Irganox 1076 levels in linear low-density polyethylene samples. This test method should be applicable for the determination of other antioxidants such as Ultranox 626, Ethanox 330, Santanox R, and Topanol CA, but the applicability of this test method has not been investigated for these antioxidants.

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

5.3 Under optimum conditions, the lowest level of detection for a phenolic antioxidant is approximately 2 ppm.

5.4 Other methods that have been successfully used to remove additives from the plastics matrix include thin film, microwave, ultrasonic, and supercritical fluid extractions. Other methods have been successfully used to separate additive including SFC and GC.

6. Interferences

6.1 Any material eluting at or near the same retention time as the additive can cause erroneous results. A polymer-solvent-extract solution containing no internal standard should be examined to minimize the possibility of interferences.

6.2 A major source of interferences can be from solvent impurities. For this reason, the solvents should be examined prior to use by injecting a sample of solvent on the HPLC system and analyzing as in Section 10.

7. Apparatus

7.1 *Liquid Chromatograph*, equipped with a variable wavelength ultraviolet detector, heated column, and gradient elution capabilities. The liquid chromatograph should be equipped with a means for a 10-µL sample-solution injection such as a sample loop.

7.2 *Chromatographic Column*, RP-18, 5-µm particle size, 15 cm by 4.6 mm.

7.3 *Computer System or Integrator*, coupled with the chromatograph to measure peak area.

7.4 *Wiley Mill*, equipped with a 20-mesh screen and water-cooled jacket to prevent thermodegradation of antioxidants such as BHT and BHEB.

7.5 *Recorder*, millivolt scale dependent upon the output of the detector.

7.6 *Reflux Extraction Apparatus*, consisting of a condenser, (24/40 ground-glass joint), a flat bottom 125-mL flask having a 24/40 ground-glass joint, and a hot plate with magnetic stirrer. See Fig. X1.1 in Appendix X1.

7.7 *Filter System*, (Teflon[7]), for nonaqueous solutions (pore size of 0.22 µm).

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

8. Reagents and Materials

8.1 *Tinuvin-P*, 2(2′hydroxy-5′-methyl phenyl)benzotriazole.

8.2 *Isobutanol*:

8.2.1 *Isobutanol T-P*, HPLC grade, spectroquality or chromatography quality reagent isobutanol with approximately 50 mg/L (to the nearest 0.1 mg) of Tinuvin-P added as an internal standard.

8.2.2 *Isobutanol*, HPLC grade, spectroquality or chromatography quality reagent.

8.3 *Isopropanol*:

8.3.1 *Isopropanol T-P*, HPLC grade, spectroquality or chromatography quality reagent isopropanol with approximately 50 mg/L (to the nearest 0.1 mg) mg/L of Tinuvin-P added as an internal standard.

8.3.2 *Isopropanol*, HPLC grade, spectroquality or chromatography quality reagent.

8.4 *Water*, HPLC, or UV quality reagent, degassed by sparging with high-purity helium or by filtration under vacuum.

8.5 *Acetonitrile*, HPLC, spectroquality or chromatography quality reagent (a reagent whose UV cutoff is about 190 nm).

9. Safety Precautions

9.1 Isopropanol and isobutanol are flammable. This extraction procedure should be carried out in a fume hood.

10. Preparation of Liquid Chromatograph

10.1 Set the chromatograph to operate at the following conditions:

NOTE 3—A Vydac 201HS5415, separations group, was used in this test method. The gradient described in 10.1 provides complete separation of antioxidants and slip using this C-18 column. If another column is used then a different gradient may be needed to provide a complete separation of the additives.

10.1.1 *Initial Mobile Phase Condition*—50 % acetonitrile: 50 % water.

10.1.2 *Final Mobile Phase Condition*—100 % acetonitrile: 0 % water.

10.1.3 *Gradient Length*—11 min.

10.1.4 *Gradient Curve*—Linear.

10.1.5 *Flow Rate*—1.0 mL/min.

10.1.6 *Hold at 100 % Acetonitrile*—0 % water for 8 min.

10.1.7 *At 19.1-Min Return to 50 % Acetonitrile*—50 % water at a flow of 1.5 mL/min for 5 min.

10.1.8 *At 25-Min Return to 1.0 mL/min*—Flow rate.

10.1.9 *Detector*—Ultraviolet detector set at 200 nm, range set at about 0.1 AUFS.

10.1.10 *Chart Speed*—0.5 in./min.

10.1.11 *Column*—Reverse phase C-18, 5 µm, 15 cm by 4.6 mm.

10.1.12 *Temperature*—Column set at 60°C.

10.1.13 *Sample Size*—10 µL.

11. Sample Preparation

11.1 Grind the sample to a particle size of 20-mesh using a water-cooled Wiley mill.

NOTE 4—Grind 7 to 8 g of the sample to run the analysis. It is important

[7] Registered trademark of DuPont.