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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.

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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.

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to minimize the time of grinding to prevent any thermodegradation of the additives in the polymer.

11.2 Weigh 5 ± 0.01 g of the sample into a 125-mL flat-bottom flask, add a stirring bar, add by pipet 50.0 mL of isobutanol T-P or isopropanol T-P solvent containing the internal standard, and boil for 90 min (with stirring) using the reflux apparatus.

NOTE 5—The internal standard is present in the isobutanol or isopropanol extraction solvent (approximately 50 µg/mL). Isopropanol is recommended as the extraction solvent for lower crystallinity LLDPE and isobutanol is recommended as the extraction solvent for higher crystallinity LLDPE containing Irganox 1010.

11.3 Cool the solution to room temperature by raising the flask off the hot plate while still attached to the condenser.

11.4 Pipet 9 mL of cool sample extract directly from the extraction flask into a 10-mL volumetric flask.

11.5 Add 1.0 mL of 2-propanol (contains no internal standard) to the 9.0 mL of extract. Cap the flask and mix thoroughly.

11.6 Attach a filter disk assembly to a 5-µL Luer-Lok tip hypodermic syringe. See Fig. X1.2 in Appendix X1.

11.7 Decant 4 mL of the solvent extract into the above syringe.

11.8 Insert the plunger and carefully apply pressure to force the solvent extract through the filter into a sample vial.

12. Calibration by Internal Standard

12.1 Into a 125-mL flat-bottom flask, weigh to the nearest 0.1 mg approximately 50 mg each of the desired additive and Tinuvin-P. Dissolve the components in 5 to 10 mL of warm (that is, about 50°C) isobutanol or isopropanol. Transfer the solution mixture to a 1000-mL volumetric flask and dilute to volume with isobutanol or isopropanol. Cap the flask and mix thoroughly.

12.2 Standardize the liquid chromatograph detector response by injection of 10 µL of the solution at the conditions listed in 10.1.

12.3 Measure the peak areas using a computer or an integrator and calculate the relative response factor (R):

$$R = \frac{\text{concentration(mg/}L\text{) additive} \times \text{area Tinuvin}-P}{\text{concentration (mg/}L\text{) Tinuvin}-P \times \text{area additive}} \quad (1)$$

12.4 Average the response factors for three replicate injections of the calibration mixture.

NOTE 6—Tinuvin-P cannot be used as an internal standard when this compound is expected to be found as an additive in samples being analyzed.

13. Procedure

13.1 Ensure that the liquid chromatograph is set at the conditions prescribed in Section 10.

13.2 Inject 10 µL of the sample solution into the liquid chromatograph system.

14. Calculation

14.1 *Internal Standard*—Using the response factor determined in 12.3 and area responses from chromatography of sample extracts, calculate the additive content of each sample from the following equation:

$$\text{additive, ppm} = \frac{A \times R \times C\text{is} \times V}{W \times A\text{is}} \quad (2)$$

where:

A = area of additive,
R = relative response factor,
Cis = concentration of internal standard,
V = volume of extraction solvent (Tinuvin-P added), mL,
W = weight of sample extracted, g, and
Ais = area in internal standard.

15. Report

15.1 Report the additive, ppm, calculated in 14.1.

16. Precision and Bias

16.1 Table 1 is based on an interlaboratory study conducted in 1993 and 1994 in accordance with Practice E 691 involving four materials tested by seven laboratories. The additives in these materials were prepared at two different concentrations by one laboratory. The materials were sent out to participants for grinding, solvent extraction, and further analysis. Each test result is an individual determination. Each laboratory obtained three test results for each material. Each test was performed on a different day. Some test results were obtained using isopropanol and some were obtained using isobutanol as the extracting solvent with all results being combined for statistical analyses.

16.2 There are no recognized standards by which to estimate bias of this test method. Targeted additive levels are given in Table 1 to be used as an estimate for recovery.

17. Keywords

17.1 additive; antioxidants; BHEB; BTH; erucamide slip; extraction; Irganox 1010; Irganox 1076; linear low-density polyethylene (LLDPE); liquid chromatography (LC)

TABLE 1 Precision and Repeatability Statement for Additive Content (ppm) in Linear Low-Density Polyethylene

Material	Target	Average	Sr [A]	SR [B]	r [C]	R [D]
BHT	200	162	11.9	15.5	33.4	43.5
BHT	800	623	41.7	77.7	117	218
BHEB	200	170	10.3	15.0	28.7	42.0
BHEB	700	612	19.8	84.8	55.4	237
Isonox 129	200	209	14.5	32.3	40.6	90.4
Isonox 129	800	763	18.8	75.3	52.7	211
Irganox 1010	400	363	18.7	52.1	52.3	146
Irganox 1010	1000	926	55.2	127	155	357
Irganox 1076	700	603	27.2	71.9	76.1	201
Irganox 1076	1250	1099	35.5	85.9	99.4	240
Erucamide	500	516	22.1	116	61.8	326
Erucamide	1000	1022	18.8	40.5	52.6	114

[A] Sr is the within-laboratory standard deviation of the average ((median/other function)).
[B] SR is the between-laboratories standard deviation of the average ((median/other function)).
[C] r is the within-laboratory repeatability limit = 2.8 Sr.
[D] R is the between-laboratories reproducibility limit = 2.8 SR.

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