Designation: D 1996 – 97

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

This standard is issued under the fixed designation D 1996; 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 liquid chromatograph procedure for the separation of some additives currently used in low density polyethylene. These additives are extracted with 2-propanol 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.* For a specific hazards statement, see Section 9.

NOTE 1—There is no similar or equivalent ISO standard.

2. Referenced Documents

2.1 *ASTM Standards:*

E 131 Terminology Relating to Molecular Spectroscopy[2]

E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods[2, 3]

E 380 Practice for Use of the International System of Units (SI)[2]

E 682 Practice for Liquid Chromatography Terms and Relationships[4]

3. Terminology

3.1 *Abbreviations:*Abbreviations:

3.1.1 *BHEB*—2,6-di-t-butyl-4-ethyl-hydroxybenzene or butylated hydroxyethylbenzene.

3.1.2 *BHT*—2,6-di-t-butyl-4-methyl hydroxybenzene or butylated hydroxytoluene.

3.1.3 *Irganox 1010*—tetrakis[methylene(3,5-di-t-butyl-4-hydroxyhydrocinnamate)].

3.1.4 *Irganox 1076*—octadecyl 3-(3′,5′-t-butyl-4-hydroxyphenyl) propionate.

3.1.5 *Isonox 129*—2,2′-ethylidene bis(4,6-di-t-butyl hydroxybenzene).

3.1.6 *Kemamide-E*—cis-13-docosenamide, erucamide.

3.1.7 *LC*—liquid chromatography.

3.1.8 *LDPE*—low density polyethylene.

3.1.9 *Tinuvin P*—2(2′-hydroxy-5′-methyl phenyl) benzotriazole, Ciba-Geigy Industrial Chemicals.

4. Summary of Test Method

4.1 The LDPE sample is ground to a 20-mesh particle size and extracted by refluxing with 2-propanol.

4.2 The solvent extract is examined 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.

5. Significance and Use

5.1 Separation and identification of stabilizers used in the manufacture of low density polyethylene are necessary in order to correlate performance properties with polymer composition. This test method provides a means to determine the BHT, BHEB, Isonox-129, erucamide slip, Irganox-1010 and Irganox-1076 levels in low density polyethylene samples.

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.

6. Interferences

6.1 Any material eluting at or near the same retention times as the additive or as the internal standard 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; therefore, the solvents should be examined prior to use.

[1] This test method is under the jurisdiction of ASTM Committee D-20 on Plastics and is the direct responsibility of Subcommittee D20.15 on Thermoplastic Materials.

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

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

[4] *Annual Book of ASTM Standards*, Vol 14.01.

***A Summary of Changes section appears at the end of this standard.**

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-microliter sample solution injection such as a sample loop.

7.2 *Chromatographic Column*, RP-18, 5 micron spherical particle, 15 by 4.6 mm; Vydac 201TP5415, Separations Group or equivalent.

7.3 *Computer System or Integrator* coupled with the chromatograph is recommended 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*, mv 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. (See Appendix X1, Fig. X1.1.)

7.7 *Filter Systems (PTFE)*, for non-aqueous solutions (pore size of 0.22 microns).

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 *2-Propanol*:

8.2.1 2-Propanol T-P, HPLC grade, spectroquality or chromatography quality reagent 2-Propanol with 51.8 mg/L Tinuvin-P added as an internal standard.

8.2.2 2-Propanol, HPLC grade, spectroquality or chromatography quality reagent.

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

8.4 *Acetonitrile*, HPLC, spectroquality or chromatography quality reagent, a reagent whose UV cut-off is about 190 nm.

9. Hazards

9.1 2-Propanol is 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:

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 micron, 15 by 4.6 mm.

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

10.1.13 *Sample Size*—10 µL.

11. Calibration by Internal Standard

11.1 Weigh accurately into a 125-mL flat bottom flask 50 ± 1 mg of the desired additive. Weigh 51.8 mg of Tinuvin-P into the flask. Dissolve the components in 5 to 10 mL of warm 2-propanol. Transfer the solution mixture to a 1000-mL volumetric flask and dilute to volume with 2-propanol.

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

11.3 Measure the peak areas using a computer or an integrator and calculate the relative response factor *R* as follows:

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

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

NOTE 2—Tinuvin-P cannot be used as an internal standard when this compound is expected as an additive in samples being analyzed.

12. Sample Preparation

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

NOTE 3—Grind 7 to 8 g of the sample to run the analysis. It is important to minimize the time of grinding to prevent any thermodegradation of the additives in the polymer.

12.2 Weigh 5 ± 0.01 g of the sample into the flask, add a stirring bar, add by pipet 50.0 mL of 2-propanol solvent containing the internal standard, and boil for 1 h (with stirring) using the reflux apparatus.

NOTE 4—The internal standard is present in the extraction 2-propanol extraction solvent (51.8 µg/mL).

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

12.4 Attach a filter disk assembly to a 5-mL Luer-Lok tip hypodermic syringe. (See Appendix X1, Fig. X1.2.)

12.5 Decant 4 mL of the solvent extract into the syringe described in 12.4.

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

13. Procedure

13.1 Ensure that the liquid chromatograph is set at the conditions prescribed in 10.1.

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

13.3 Typical LC chromatograms are shown in Appendix X2, Fig. X2.1.

14. Calculation

14.1 *Internal Standard*—Using the response factor determined in 11.3 and area responses from chromatography of sample extracts, calculate the additive content of each sample from the following equation:

$$\text{Additive (ppm)} = \frac{A \times R \times Cis \times V}{W \times Ais} \quad (2)$$

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

15. Report

15.1 Report the additive (ppm) calculated in 14.1.

16. Precision and Bias

16.1 Table 1 and Table 2 are based on a round robin conducted in 1990 in accordance with Practice E 691. Table 1 is for antioxidants which involved two materials tested by 14 labs. These materials were prepared by one laboratory and sent out for grinding, solvent extraction, and further analysis. Table 2 is for erucamide slip which involved two materials tested by 11 labs. These samples were prepared at two different concentrations by one laboratory. Samples were sent out also 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 and each test was performed on a different day.

TABLE 2 Precision and Repeatability Statement Slip Content (ppm) in Low Density Polyethylene by LC

NOTE 1—Values expressed in units of ppm.

Material	Level	Average	S_r[A]	S_R[B]	r[C]	R[D]
Slip	low	456	36.8	58.1	103.2	162.6
Slip	high	1392	91.6	140.0	56.4	393.5

NOTE 5—**Caution:** The following explanations of *r* and *R* (16.2-16.2.3) are only intended to present a meaningful way of considering the approximate precision of this test method. The data in Table 1 should not be rigorously applied to acceptance or rejection of material, as those data are specific to the round robin and may not be representative of other lots, conditions, materials, or laboratories. Users of this test method should apply the principles outlined in Practice E 691 to generate data specific to their laboratory and materials, or between specific laboratories. The principles of 16.2-16.2.3 would then be valid for such data.

16.2 *Concept of r and R*—If S_r and S_R have been calculated from a large enough body of data, and for test results that were individual test values, then the following applies:

16.2.1 Repeatability limit, *r* (comparing two test results for the same material, obtained by the same operator using the same equipment on the same day). The two test results should be judged not equivalent if they differ by more than the *r* value for that material.

16.2.2 Reproducibility limit, *R* (comparing two test results for the same material, obtained by different operators using different equipment in different laboratories). The two test results should be judged not equivalent if they differ by more than the *R* value for that material.

16.2.3 Any judgment in accordance with 16.2.1 or 16.2.2 would have an approximate 95 % (0.95) probability of being correct.

16.3 There are no recognized standards by which to estimate bias of this test method.

17. Keywords

17.1 additive; antioxidants; BHEB; BHT; Erucamide (slip); extraction; Irganox-1010; Irganox 1076; Isonox-129; liquid chromatography (LC); low density polyethylene (LDPE)

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

NOTE 1—Values expressed in units of ppm.

Material	Level	Average	S_r[A]	S_R[B]	r[C]	R[D]
BHT	low	167	12.9	22.1	36.1	61.8
BHT	high	628	47.6	90.1	133.3	252.4
BHEB	low	190	11.95	20.6	33.5	57.7
BHEB	high	730	47.9	86.9	134.04	243.3
Isonox-129	low	238	13.0	20.2	36.5	56.5
Isonox-129	high	943	41.8	70.7	116.8	197.8
Irganox 1010	low	244	14.7	24.6	41.3	68.8
Irganox 1010	high	919	43.9	57.2	122.8	160.1
Irganox 1076	low	252	10.3	16.3	28.8	45.5
Irganox 1076	high	1009	48.9	69.2	137.1	193.8

[A] S_r = within-laboratory standard deviation for the indicated material. It is obtained by pooling the within-laboratory standard deviations of the test results from all of the participating laboratories $S_r = [(S_1)^2 + (S_2)^2 + (S_n)^2]$.
[B] S_R = between-laboratories reproducibility expressed as standard deviation $S_R = (S_{fr}^2 + S_L^2)^{1/2}$.
[C] r = within-laboratory critical interval between two test results = $2.8 \times S_r$.
[D] R = between-laboratories critical interval between two test results = $2.8 \times S_R$.