Designation: D 5524 – 94

An American National Standard

AMERICAN SOCIETY FOR TESTING AND MATERIALS
100 Barr Harbor Dr., West Conshohocken, PA 19428
Reprinted from the Annual Book of ASTM Standards. Copyright ASTM

Standard Test Method for Determination of Phenolic Antioxidants in High Density Polyethylene Using Liquid Chromatography[1]

This standard is issued under the fixed designation D 5524; 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 covers a liquid-chromatographic procedure for the separation of some additives currently used in high-density polyethylene. These additives are extracted with cyclohexane prior to liquid-chromatographic separation. The ultraviolet absorbance (200 nm) of the compound(s) is measured; quantitation is performed using the internal standard method.

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

1.2 The values stated in SI units are to be regarded as the standard.

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.

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

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

3. Terminology

3.1 *Definitions*—For definitions of plastics terms used in this test method, see Terminologies D 883 and D 1600.

3.2 *Symbols:Symbols*—For the units, symbols, and abbreviations used in this test method, refer to Terminology E 131 or Practice E 380.

3.3 *Abbreviations:*

3.3.1 *LC*—liquid chromatography.

3.3.2 *HDPE*—high-density polyethylene.

3.4 *Trade Names*:

3.5 *BHT*—2,6-di-t-butyl-cresol or butylated hydroxy toluene.[5]

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

3.7 *Irganox 1010*—tetrakis[methylene(3,5-di-t-butyl-4- hydroxyhydrocinnamate)]methane.[7]

3.8 *Irganox 1076*—octadecyl-3,5-di-t-butyl-4-hydroxy- hydrocinnamate.[8]

3.9 *Isonox 129*—2,2′-ethylidene bis(4,6-di-t-butyl phenol).[7]

3.10 *Tinuvin P*—2(2′-hydroxy-5′-methyl phenyl) benzotriazole.[7]

4. Summary of Test Method

4.1 The HDPE sample is ground to a 20-mesh particle size and extracted by refluxing with cyclohexane.

4.2 The solvent extract is examined by LC.

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 HDPE are necessary in order to correlate performance properties with polymer composition. This test method provides a means of determining BHT, BHEB, Isonox 129, Irganox 1010, and Irganox 1076 levels in HDPE samples. This test method should be applicable for the determination of other antioxidants such as Cyanox 425, Cyanox 1790, Cyanox 2246, Ultranox 236, and Ultranox 246, 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 The lowest level of detection for a phenolic antioxidant is approximately 2 ppm under optimum conditions.

[1] This test method is under the jurisdiction of ASTM Committee D-20 on Plastics and is the direct responsibility of Subcommittee D20.70 on Analytical Methods.
Current edition approved March 15, 1994. Published May 1994.

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

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

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

[5] Available from PMC Specialties; Uniroyal, Inc.; Borg Warner; and Rhone Poulank.

[6] Available from R-M Industries and Gallard Schlesinger Corp.

[7] Available Ciba-Geigy.

[8] Available from Ciba-Geigy; Uniroyal, Inc.; Ethyl Corp.; and Borg Warner.

5.4 Other procedures that have been used successfully to remove additives from the plastics matrix include thin-film, microwave,[9] ultrasonic,[10] and supercritical fluid extractions.[10, 11, 12] Other procedures have been used successfully to separate additives, including SFC[12] and capillary GC.[13]

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 UV 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.

NOTE 2—Vydac 201HS5415 column, Separations Group, was used in this test method. The gradient described in 10.1 provides complete separation of antioxidants using this RP-18 column. An equivalent column may also be used.

7.3 *Computer System or Integrator*, coupled with the chromatograph, recommended for measuring peak area.

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

7.5 *Recorder*, MV-scale, dependent on 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* (PTFE),[14] for nonaqueous solutions (pore size of 0.22 µm), equipped with a glass S CC syringe.

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 *Cyclohexane*:

8.2.1 *Cyclohexane T-P*—HPLC grade, spectro-quality or chromatography-quality reagent cyclohexane with 51.8 mg/L Tinuvin-P added as an internal standard.

8.2.2 *Cyclohexane*—HPLC grade, spectro-quality 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, spectro-quality or chromatography-quality reagent (a reagent whose UV cutoff is approximately 190 nm).

8.5 *2-Propanol*—HPLC grade, spectro-quality or chromatography-quality reagent.

9. Precautions

9.1 Cyclohexane and 2-Propanol are flammable. This extraction procedure should be conducted 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 and 50 % water.

10.1.2 *Final Mobile Phase Condition*—100 % acetonitrile and 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 and 0 % water for 8 min.

10.1.7 Return to 50 % acetonitrile and 50 % water at 19.1 min at a flow of 1.5 mL/min for 5 min.

10.1.8 Return to 1.0 mL/min flow rate at 25 min.

10.1.9 *Detector*—UV detector set at 200 nm and range set at 0.1 Aufs.

10.1.10 *Chart Speed*—12.7 mm (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 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.

11.2 Weigh 5 ± 0.01 g of the sample into a 125-mL flat-bottom flask; add a stirring bar; by pipet, add 50.0 mL of cyclohexane T-P 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 cyclohexane extraction solvent (51.8 µg/mL).

11.3 Cool the solution to room temperature by raising the flask off the hot plate while it is still attached to the condenser.Table 1

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

[9] Freitag, W., and John, O., "Fast Separation of Stabilizers from Polyolefins by Microwave Heating," *Die Angewandte Makromolekulare Chemie*, Vol 175, 1990, pp. 181–185.

[10] Nielson, Richard, "Overview of Polyolefin Additive Analysis," *Waters Report*, Waters Chromatography Division, Milford, MA.

[11] Arpino, P. J., et al., "Investigation of Antioxidants and UV Stabilizers from Plastics, Part 1: Comparison of HPLC and SFC; Preliminary SFC/MS Study," *Journal of High Resolution Chromatography*, Vol 13, 1990, pp. 5–12.

[12] Raynor, Mark W., et al., "Polymer Additive Characterization by Capillary Supercritical Fluid Chromatography/Fourier Transform Infrared Microscopy," *Analytical Chemistry*, Vol 60, 1988, pp. 427–433.

[13] Nagata, M., and Kishioka, Y., "Determination of Additives in Polyolefins and Petroleum Resin by Capillary GC," *Journal of High Resolution Chromatography*, Vol 14, 1991, pp. 639–642.

[14] Registered Trademark of DuPont.

TABLE 1 Precision and Repeatability Statement Additive Content (ppm) in HDPE (Values Expressed in ppm Units)

Material	Level	Average	Sr^A	SR^B	r^C	R^D
BHT	low	201	19.2	49.7	53.6	139.2
BHT	high	626	52.7	77.0	147.5	215.6
BHEB	low	198	19.4	45.5	54.2	127.5
BHEB	high	590	35.8	68.8	100.4	192.8
Isonox 129	low	181	12.2	33.9	34.0	94.8
Isonox 129	high	693	42.0	127.2	117.7	356.3
Irganox 1010	low	172	19.3	25.7	54.2	71.9
Irganox 1010	high	715	70.6	92.3	197.8	258.5
Irganox 1076	low	208	27.8	31.4	77.8	88.0
Irganox 1076	high	780	46.1	72.3	129.2	202.4

[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*.

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 disc assembly to a 5-µL Luer-Lok tip hypodermic syringe (see Fig. X1.2 in Appendix X1).

11.7 Decant 2 mL of the solvent extract into the above syringe.

11.8 Insert the plunger and apply pressure carefully to force the solvent extract through the filter into a waste vial. This will precondition the filter.

11.9 Decant 4 mL of the solvent extract into the syringe again.

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

12. Calibration by Internal Standard

12.1 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 5–10 mL of warm cyclohexane. Transfer the solution mixture to a 1000-mL volumetric flask, add 100 mL 2-propanol, and dilute to volume with cyclohexane. 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 integrator, and calculate the relative response factor (*R*).

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

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

NOTE 5—Tinuvin-P cannot be used as an internal standard when this compound is expected to be found as an additive in the 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 the 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 in internal standard.

15. Report

15.1 Report the additive (ppm) calculated in 14.1.

16. Precision and Bias

16.1 *Precision*—Table 1 is based on an interlaboratory study[15] conducted in 1991 in accordance with Practice E 691 involving four materials tested by ten 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.

NOTE 6—**Caution:** The following explanations of *r* and *R* (16.2-16.2.3) are intended only to present a meaningful way of considering the approximate precision of this test method. The data in Table 1 should not be applied rigorously to the 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 *Sr* and *SR* have been calculated from a sufficiently large body of data, and for test results that were individual test values:

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

[15] Supporting data have been filed at ASTM Headquarters. Request RR:D20-1182.