Designation: D 6042 – 96

Standard Test Method for Determination of Phenolic Antioxidants and Erucamide Slip Additives in Polypropylene Homopolymer Formulations Using Liquid Chromatography (LC)[1]

This standard is issued under the fixed designation D 6042; 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 polypropylene. These additives are extracted with a cyclohexane:methylene chloride mixture using either reflux or ultrasonic bath prior to liquid-chromatographic separation. The ultraviolet absorbence (200 nm) of the compound(s) is measured, and 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 similar or 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 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 For definitions of plastic terms used in this test method, see Terminologies D 883 and D 1600.

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

3.3 *Abbreviations:Abbreviations:*

3.3.1 *LC*—liquid chromatography.

3.3.2 *PP*—polypropylene.

3.4 *Trade Names*:

3.5 *Vitamin E*—α-Tocopherol, or 3,4-dihydro-2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)-2H-1-benzopyran-6-ol.

3.6 *Irgafos 168*—Tris(2,4 di-tert-butylphenyl) phosphite.

3.7 *Irganox 3114*—Tris(3,5-di-t-butyl-4-hydroxybenzyl) isocyanurate.

3.8 *Kemamide-E*—cis-13-docosenamide or erucamide.

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

3.10 *Irganox 1076*—octadecyl-3,5-di-t-butyl-4-hydroxy hydrocinnamate.

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

4. Summary of Test Method

4.1 The PP sample is ground to a 20-mesh particle size (850 microns) and extracted by refluxing with a mixture of 75:25 methylene chloride:cyclohexane or placing in an ultrasonic bath with the same mixture.

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 polypropylene is necessary in order to correlate performance properties with polymer composition. This test method provides a means to determine erucamide slip, Vitamin E, Irgafos 168, Irganox 3114, Irganox 1010, and Irganox 1076 levels in polypropylene samples. This test method should be applicable for the determination of other antioxidants, such as Ultranox 626, Ethanox 330, Santanox R, and BHT, but the applicability of this test method has not been investigated for these antioxidants.

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[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 Nov. 10, 1996. Published April 1997.

[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.

5.2 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.

NOTE 2—Other methods that have been used successfully to remove additives from the plastics matrix include thin film, microwave, ultrasonic, and supercritical fluid extractions. Other methods have been used successfully to separate additives including SFC and capillary GC.

5.4 Irgafos 168 is a phosphite antioxidant. Phosphites are known to undergo both oxidation and hydrolysis reactions. Less Irgafos 168 may be seen in the polymer than originally added to the polymer due to oxidation during processing. The HPLC separation is capable of separating the phosphite, phosphate (oxidation product), and hydrolysis product. If standards are obtained, then the reaction products also can be quantified. No significant breakdown of the phosphite antioxidant has been seen due to either extraction technique or the separation presented in this standard.

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.

6.3 The oxidation product of Irgafos 168 can overlap with other additives with retention times of components that elute between Irganox 1010 and Irgafos 168. Standards should be run to ensure that components of interest do not coelute with the oxidation product of Irgafos 168.

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.

NOTE 3—A Zorbax RX C-18 Column, MAC MOD Analytical, Inc., was used for this test method. The gradient described in 10.1 provides complete separation of antioxidants using this C-18 column.

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.

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 with magnetic stirrer (see Fig. 1).

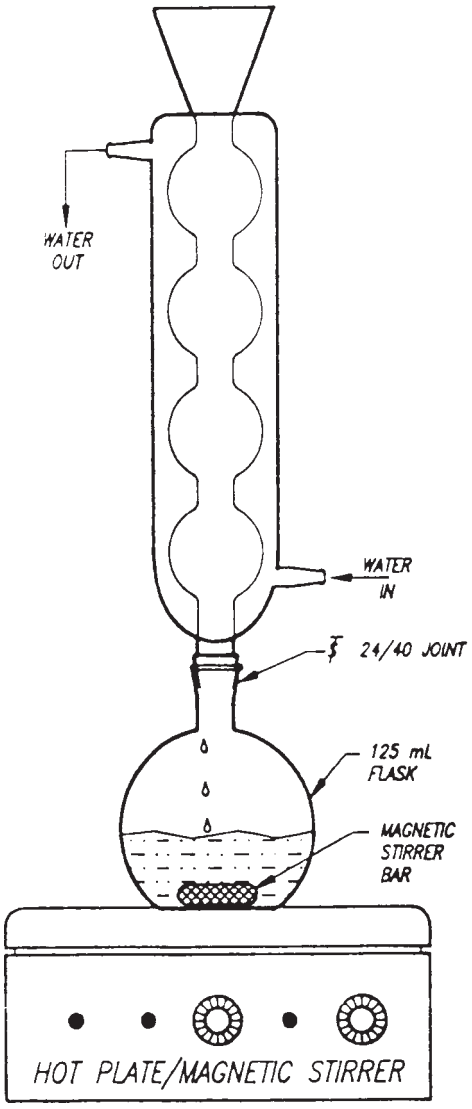

FIG. 1 Sample Extraction

7.7 *Ultrasonic Bath Apparatus*, consisting of the ultrasonic bath, a flat bottom 125-mL flask having a 24/40 ground-glass joint, and a 24/40 ground-glass stopper.

7.8 *Filter System* (Teflon)[5] for nonaqueous solutions (pore size of 0.22 µm) equipped with a glass 5-cm^3 syringe.

7.9 *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 *Methylene Chloride*, HPLC grade, spectral quality or chromatography quality reagent.

8.3 *Cyclohexane*, HPLC grade, spectral quality or chromatography quality reagent.

8.4 *75:25 Methylene Chloride:Cyclohexane T-P*, mixture with 51.8 mg/L Tinuvin-P added as an internal standard.

[5] Registered trademark of DuPont.

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

8.6 *Acetonitrile*, HPLC, spectral quality or chromatography quality reagent (a reagent whose UV cut-off is about 190 nm).

8.7 *Isopropanol*, HPLC, spectral quality or chromatography quality reagent.

9. Safety and Precautions

9.1 Methylene chloride and cyclohexane are flammable. Perform this extraction procedure in a fume hood.

10. Preparation of Liquid Chromatograph

10.1 Set the chromatograph to operate at the following conditions (see Fig. 2 for an example chromatogram):

10.1.1 *Initial Mobile Phase Condition*—75 % acetonitrile: 25 % water or whatever is appropriate for column used in order to retain Tinuvin P longer than solvent breakthrough.

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

10.1.3 *Gradient Length*—5 min or whatever is appropriate to cause a complete separation of additives and have a total chromatogram analysis time of 20 min or less.

10.1.4 *Gradient Curve*—Linear.

10.1.5 *Flow Rate*—1.5 mL/min.

10.1.6 Hold at 100 % acetonitrile: 0 % water for 10 min or whatever is required to allow all additives to elute.

10.1.7 At 15.1 min return to 75 % acetonitrile:25 % water at a flow of 1.5 mL/min for 5 min.

10.1.8 *Detector*—Ultraviolet detector set at 200 nm, range set at about 0.1 Aufs.

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

10.1.10 *Temperature*—Column set at 50°C.

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

11.2 For reflux extraction, 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 methylene chloride:cyclohexane 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 extraction solvent (51.8 µg/mL).

11.3 For ultrasonic bath extraction, weigh 5 ± 0.01 g of the sample into a 125-mL flat bottom flask, add by pipet 50.0 mL of methylene chloride:cyclohexane T-P solvent containing the internal standard, stopper flask, and place in an ultrasonic bath. Turn on the ultrasonic bath and extract for 1 h.

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

11.5 Attach a filter disc assembly to a 5-µL Luer-Lok tip hypodermic syringe (see Fig. 3).

11.6 Decant or pipet 4 mL of the solvent extract into the above syringe.

11.7 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 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 isopropanol. Transfer the solution mixture to a 1000 mL

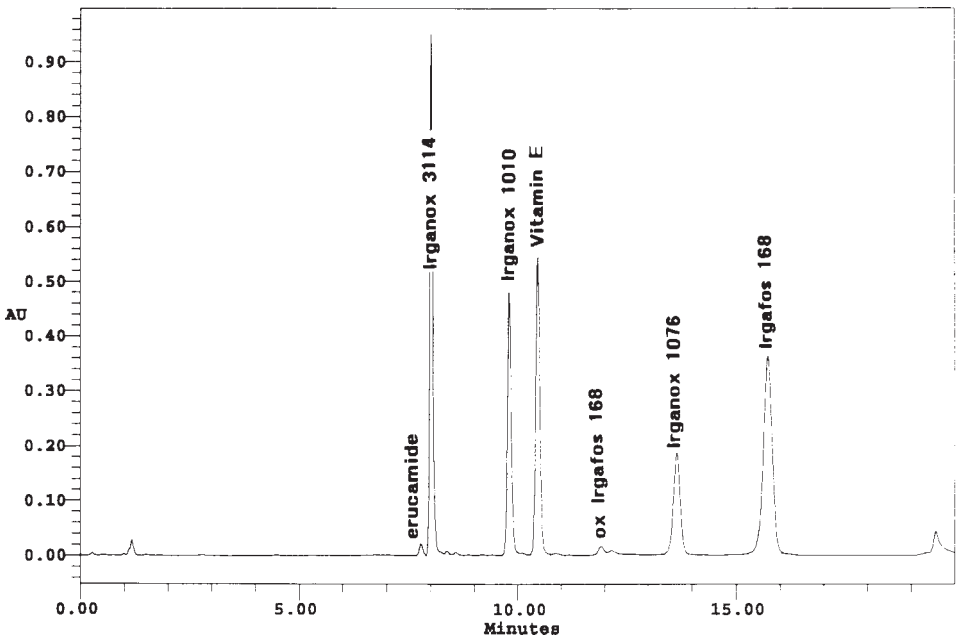

FIG. 2 HPLC Separation of Six Additives

volumetric flask and dilute to volume with isopropanol. Cap flask and mix thoroughly.

NOTE 6—Vitamin E must be prepared and used in the same day or stored in an amber bottle due to photodecomposition.

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*).

$$R = \frac{\text{Concentration (mg/L) Additive} \times \text{Area Tinuvin}-\text{P}}{\text{Concentration (mg/L) Tinuvin}-\text{P} \times \text{Area Additive}} \quad (1)$$

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

NOTE 7—Tinuvin-P cannot be used as 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:

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

where:

A = area of additive,
R = 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[6] conducted in 1995 in accordance with Practice E 691 involving two materials tested using two different techniques at eleven different laboratories. The additives in these materials were prepared at two different companies. 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 using either the ultrasonic or reflux extraction method (or both). Each test was performed on a different day.

NOTE 8—**Caution:** The following explanations of *r* and *R* (16.2 through 16.23) only are intended 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 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 through 16.23 then would be valid for such data.

TABLE 1 Precision and Repeatability for Additive Content (ppm) in Polypropylene Reflux and Ultrasonic Extraction

NOTE 1—Number of labs completing the reflux study = eight.

Material	Target	Average	Sr^A	SR^B	r^C	R^D
Vitamin E	1000	1110	64.2	64.2	180	180
Erucamide	1000	1040	50.7	40.5	142	113
Irgafos 168	1000	1060	94.9	94.9	266	266
Irganox 1010	1000	891	24.8	173	69.5	483
Irganox 1076	1000	1110	42.5	127	119	355
Irganox 3114	1000	1150	39	103	109	288

[A] Sr = 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] SR = 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 × Sr.
[D] R = between-laboratories critical interval between two test results = 2.8 × SR.

16.1.1 *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.

16.1.2 *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.

16.1.3 Any judgment in accordance with 16.1.2 or 16.1.3 would have an approximate 95 % (0.95) probability of being correct.

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.

[6] Supporting data are available from ASTM Headquarters. Request RR:D 20-1193.

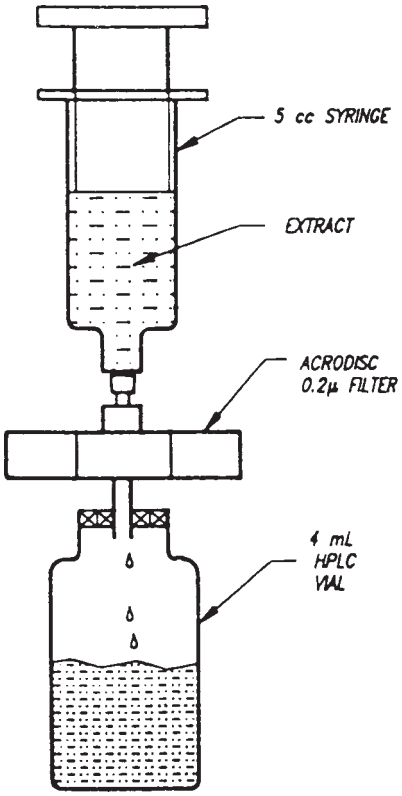

FIG. 3 Final Preparation of Sample Extract

17. Keywords

17.1 additive; antioxidants; erucamide slip; extraction; Irgafos 168; Irganox 1010; Irganox 1076; Irganox 3114; liquid chromatography (LC); polypropylene (PP); vitamin E