Designation: D 6953 – 03

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

This standard is issued under the fixed designation D 6953; 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 polyethylene. These additives are extracted with either isopropanol (resin densities < 0.94 g/cm^3) or cyclohexane (resin densities > 0.94 g/cm^3) prior to liquid-chromatographic separation. The ultraviolet absorbance of the eluting compound(s) is measured and quantitation is performed using external calibration.

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]

D 4697 Guide for Maintaining Test Methods in the User's Laboratory[3]

E 131 Terminology Relating to Molecular Spectroscopy[4]

E 169 Practices for General Techniques of Ultraviolet-Visible, and Near-Infrared Spectrophotometers[4]

E 275 Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near-Infrared Spectrophotometers[4]

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method[5]

E 1657 Practice for Testing Variable-Wavelength Photometric Detectors Used in Liquid Chromatography[4]

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

3. Terminology

3.1 *Definitions*:

3.1.1 For definitions of plastic terms and detector terminology used in this test method, see Terminologies D 883, D 1600, and E 1657.

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

3.2 *Additives:*

3.2.1 *BHEB, Prodox 500*—2,6-di-t-butyl-4-ethylphenol or butylated hydroxyethyl benzene, CAS No. 4130-42-1.

3.2.2 *BHT, CAO-3, Noclizer M-17*—2,6-di-t-butylcresol or butylated hydroxy toluene, CAS No. 128-37-0.

3.2.3 *Irgafos 168*—Tris(2,4-di-t-butylphenyl)-phosphite, CAS No. 31570-04-4.

3.2.3.1 *Oxidized Irgafos 168*—Tris(2,4-di-t-butylphenyl)-phosphate.

3.2.4 *Irganox 1010*—Tetrakis[methylene(3,5-di-t-butyl-4-hydroxyhydrocinnamate)] methane CAS No. 6683-19-8.

3.2.5 *Irganox 1076*—Octadecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)-propionate, CAS No. 2082-79-3.

3.2.6 *Isonox 129*—2,2'-ethylidene bis(4,6-di-t-butylphenol), CAS No. 112-84-5.

3.2.7 *Kemamide-E, Erucamide*—Cis-13-docosenamide, CAS No. 112-84-5.

3.2.8 *TNPP, Weston 399*—Tris(nonylphenyl)phosphite, CAS No. 26523-78-4.

3.2.8.1 *Hydrolyzed TNPP*—Nonylphenol, CAS No. 104-40-5.

3.2.8.2 *Oxidized TNPP*—Tris(nonylphenyl)phosphate, CAS No. 26569-53-9 (available in small quantities from GE Specialty Chemicals as XR2616).

4. Summary of Test Method

4.1 The polyethylene sample is ground to a 1-mm (~20 mesh) or 0.5-mm (~40 mesh) particle size and extracted by refluxing with either isopropanol or cyclohexane.

4.2 The solvent extract is analyzed by liquid chromatography.

[1] This test method is under the jurisdiction of ASTM Committee D20 on Plastics and is the direct responsibility of Subcommittee D20.70 on Analytical Methods.
Current edition approved July 10, 2003. Published August 2003.

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

[3] *Annual Book of ASTM Standards*, Vol 07.02.

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

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

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4.3 Additive concentrations are determined from external calibration curves using reverse phase chromatography (C-8 or C-18 column) with ultraviolet (UV) detection at wavelengths corresponding to the wavelengths of an absorption apex of each additive (except erucamide which does not have an absorption maximum in the accessible UV region).

5. Significance and Use

5.1 Separation and identification of stabilizers used in the manufacture of polyethylene resins 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, Irgafos 168, Irganox 1010, Irganox 1076 and TNPP levels in 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 stability of these during extraction has not been investigated.

5.2 The additive extraction procedure is made effective by the relatively low solubility of the polymer sample in solvents generally used for liquid chromatographic analysis. In this method, isopropanol and cyclohexane were chosen because of their excellent extraction efficiencies as well as for safety reasons. Other solvents including ethylacetate, isobutanol, chloroform and methylene chloride can also be used.

5.3 Methods other than refluxing that have been used to remove additives from the polymer matrix include microwave, ultrasonic, and supercritical fluid extractions. For the separation of the extracted additives, SFC and GC have been used successfully for several of the additives.

5.4 Under optimum conditions, the lowest level of detection for an antioxidant is approximately 2 ppm.

6. Interferences

6.1 Any material eluting at or near the same retention time as the additive can cause erroneous results. This includes degradation products of the additives.

6.2 A major source of interferences can be from solvent impurities. For this reason, the solvents should be examined by HPLC using the same analysis conditions as for the samples (see Section 12).

6.3 The grinding process may cause a low bias. For example, some erucamide slip is known to be lost to the grinder surface and excessive grinding may cause degradation of the antioxidants.

7. Apparatus

7.1 *Liquid Chromatograph*, equipped with a multiple wavelength (see Practices E 169 and E 275) or photodiode array ultraviolet detector, heated column compartment, and gradient elution capabilities. The liquid chromatograph should be equipped with a means for a 10-µL injection such as a sample loop.

7.2 *Chromatographic Column*, C-8 or C-18 reverse phase, 5-µm particle size, 15 cm by 4.6 mm or equivalent, capable of separating the additives and their degradation products.

7.3 *Data Acquisition/Handling System*, providing the means for determining chromatographic peak areas and for handling and reporting data. This is best accomplished using a computer with appropriate software.

7.4 *Mill—Cutting Mill (Wiley) or Centrifugal Grinding Mill (Brinkmann)*, equipped with 1-mm (~20 mesh) and 0.5-mm (~40 mesh) screens.

7.5 *Reflux Extraction Apparatus*, consisting of a condenser, (24/40 ground-glass joint), a round-bottom 125-mL flask having a 24/40 ground-glass joint, and a heating mantle.

7.6 *Boiling Chips*.

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

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

7.9 *Top Loading Balance*, capable of weighing to ±0.01 g.

8. Reagents and Materials

8.1 *Solvents*:

8.1.1 *Isopropanol*—HPLC grade, spectro-quality or chromatography quality reagent.

8.1.2 *Cyclohexane*—HPLC grade, spectro-quality or chromatography quality reagent.

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

8.1.4 *Acetonitrile*—HPLC, spectro-quality or chromatography quality reagent (a reagent whose UV cutoff is about 190 nm).

8.2 *Additives*:

8.2.1 High purity additives and degradation products (see 3.2).

9. Precautions

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

10. Preparation of Solutions

10.1 *Polymer Samples*:

10.1.1 Grind the sample to a particle size of 1 mm, that is, ~20 mesh (density < 0.94 g/cm^3) or 0.5 mm, that is, ~40 mesh (density > 0.94 g/cm^3).

NOTE 2—Unless sample amount is limited, grind a minimum of 10 g. It is important to minimize the time of grinding to prevent any thermal degradation of the additives in the polymer. Some erucamide is known to be lost during grinding.

NOTE 3—A cutting-type mill is needed for film samples. Because of its higher efficiency, a centrifugal-type mill is recommended for pellet samples.

10.1.2 Weigh, to the nearest 0.01 g, approximately 5 g of the sample, that is, W_{sample}, into a pre-weighed (to the nearest 0.01 g) 125-mL flat-bottom flask containing boiling chips, that is, W_{flask}. Add approximately 50.0 mL of isopropanol or cyclohexane and boil for a minimum of 2 h.

NOTE 4—Isopropanol is used as the extraction solvent for densities of less than 0.94 g/cm^3 and cyclohexane for densities higher than 0.94 g/cm^3.

10.1.3 Cool the solution to room temperature by raising the flask from the heating mantle while still attached to the condenser.

10.1.4 Weigh the cooled flask to the nearest 0.01 g, that is, $W_{(flask + sol)}$.

10.1.5 Attach a filter disk assembly to a 5-mL Luer-Lok tip hypodermic syringe.

10.1.6 Decant approximately 4 mL of the solvent extract into the above syringe.

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

10.1.8 Calculate the amount (mg) of sample per kg of solution, $[Sample]_{sol}$:

$$[Sample]_{sol} = \frac{10^6 W_{sample}}{(W_{(flask+sol)} - W_{flask})} \quad (1)$$

10.2 *Concentrated Additive Standards*:

10.2.1 Prepare two to three mixtures in 125-mL septum bottles by weighing the bottles, including septum and cap, to the nearest 0.1 mg.

10.2.2 Weigh into a bottle, to the nearest 0.1 mg, approximately 0.2 g of each additive.

10.2.3 Fill the bottle with either isopropanol or cyclohexane, cap and weigh the bottle on a top loading balance to the nearest 10 mg.

10.2.4 Agitate the bottle to speed up dissolution.

10.2.5 Calculate the concentration, $[Additive]_{conc}$, of each additive in the concentrated standard in mg/kg (that is, ppm) as follows:

$$[Additive]_{conc} = \frac{10^6 W_{add}}{(W_{Tadd} + W_{sol})} \quad (2)$$

where:

W_{add} = weight (g) of individual additive,
W_{Tadd} = total weight (g) of all additives, and
W_{sol} = weight (g) of solvent.

10.3 *Dilute Additive Standards*:

10.3.1 Prepare four dilute standards of each concentrated standard by weighing 30-mL septum bottles, including septum and cap, to the nearest 0.1 mg.

10.3.2 Add with a 5-mL syringe, 0.5 mL, 1.0 mL, 2.0 mL, and 5.0 mL of a concentrated solution to each of four of the 30-mL bottles and weigh to the nearest 0.1 mg.

10.3.3 Fill the bottles with isopropanol or cyclohexane, cap, mix and weigh to the nearest 1 mg.

10.3.4 Calculate the concentration, $[Additive]_{dil}$, of each additive in the dilute standards in mg/kg (that is, ppm) as follows:

$$[Additive]_{dil} = \frac{W_{conc}[Additive]_{conc}}{(W_{conc} + W_{sol})} \quad (3)$$

where:

W_{conc} = weight (g) of concentrated standard solution,
$[Additive]_{conc}$ = concentration (mg/kg) of additive in concentrated standard (see 10.2.5), and
W_{sol} = weight (g) of solvent used for dilution.

11. Performance Requirements

11.1 *Resolution*—The resolution (R) provides an indication of the component separation and band broadening of a column. For Gaussian-shaped peaks, the resolution is defined as:

$$R = \frac{2(t_{R,2} - t_{R,1})}{(W_1 + W_2)} \quad (4)$$

where:

$t_{R,1}$, $t_{R,2}$ = peak elution time in minutes of Additives 1 and 2, and
W_1, W_2 = peak width in minutes of Additives 1 and 2 determined by measuring the distance between the baseline intercepts of lines drawn tangent to the peak inflection points.

11.1.1 For an extracted additives mixtures containing any combination (including degradation products) of those listed in 3.2, the resolution of any two peaks measured at a single wavelength must be greater than one, that is, $R > 1$. For peaks with $R \leq 1$, two wavelengths are needed to measure the two components (see 15.2).

NOTE 5—A resolution of $R = 1$ represents a peak overlap of approximately 3 %.

11.2 *Plate Count Number*—A 10-cm column packed with 5-µm particles is expected to have a plate count in excess of 60 000 plates calculated in accordance with the following expression:

$$N = 16\left(\frac{t_R}{W}\right)^2 \quad (5)$$

where:

t_R = peak elution time in minutes, and
W = peak width in minutes as determined as outlined in Section 11.

11.2.1 No minimum number is required as long as the resolution requirement of 11.1 is met.

12. Preparation of Liquid Chromatograph

12.1 *Flow Rate*—2.0 mL/min.

12.2 *Mobile Phase Gradient*:

12.2.1 *Initial Mobile Phase*—60 % acetonitrile and 40 % water.

12.2.2 *Final Mobile Phase Condition*—100 % acetonitrile and 0 % water.

12.2.3 *Gradient Length*—6 min.

12.2.4 *Gradient Curve*—Linear.

12.2.5 Hold at 100 % acetonitrile and 0 % water for 3 min.

12.2.6 Return to 60 % acetonitrile and 40 % water at 9 min at a flow rate of 2 mL/min for 4 min.

NOTE 6—The flow rate and gradient conditions listed in 12.1 and 12.2 have been used successfully with a 15-cm by 4.6-mm column packed with 5-µm C-8 reverse phase particles (see Fig. 1). The optimum flow rate (that is, 1.0 to 2.0 mL/min) and the exact gradient will depend on the column used and the additive formulations typically analyzed (see Section 11 for performance requirements).

12.3 *Detector*—Ultraviolet detector with a range setting of about 0.1 AUFS at the following wavelengths:

200 nm for erucamide slip
210 nm for oxidized Irgafos 168
217 nm for TNPP and its degradation products
270 nm for Irgafos 168
280 nm for BHEB, BHT, Irganox 1010, Irganox 1076 and Isonox 129

NOTE 7—Erucamide does not have an absorption peak in the accessible UV region. The absorption at 200 nm represents the tailing end of an absorption peak at a wavelength of less than 190 nm. Because of the steep slope of the shoulder, a wavelength precision of better than 1 nm is needed to avoid unacceptable fluctuations in detector response (that is, extinction

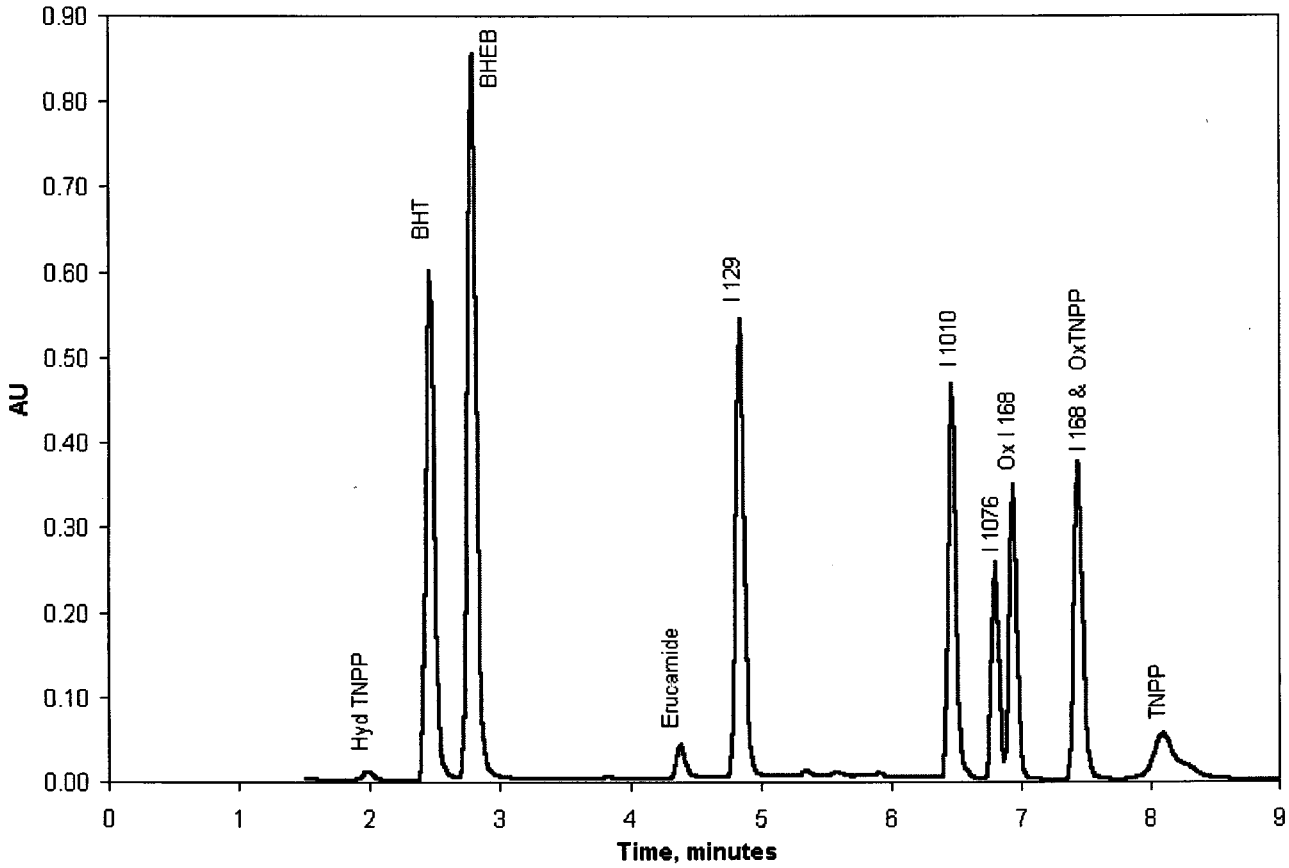

FIG. 1 Chromatogram of Multicomponent Antioxidant Standard Recorded at 200 nm

coefficient). Frequent injections of an erucamide standard are recommended.

12.4 *Column*—C-8 or C-18 reverse phase, 5-µm particle size, 15 cm by 4.6 mm or equivalent.

12.5 *Temperature*—A column temperature of between 50°C and 60°C is suggested.

12.6 *Sample Size*—10 µL.

13. Calibration

13.1 Identify the retention time of each additive/degradation product by referring to Fig. 1 or by injecting single component solutions.

13.2 Inject 10 µL of each of the four dilute standard mixtures prepared in 10.3 into the liquid chromatograph system.

13.3 Measure the peak areas using a computer or an integrator.

13.4 Plot peak areas versus concentration for each additive and fit the points to a linear regression line. This line should have a zero intercept, that is, the general equation for the regression line should be $A = kC$, where A is the peak area of the additive in the standard, k is the slope of the regression line, and C is the solution concentration of the additive.

14. Procedure

14.1 Use liquid chromatographic conditions as prescribed in Section 12.

14.2 Inject 10 µL of each sample solution and, with each sample batch, 10 µL of one dilute standard solution into the liquid chromatograph.

14.3 Check detector responses and retention times for the additives in the standard. To decide if corrective action or sample re-run is required, the use of quality control charts with warning and control limits is recommended (see Guide D 4697 and Taylor[6]).

14.4 Identify the additives in the sample from their retention times.

14.5 Perform area integration of each additive peak at the appropriate wavelength. If a peak area exceeds the area count of the most concentrated calibration standard, dilute the sample solution and re-analyze.

15. Calculation

15.1 For additive peaks with a resolution $R > 1$, calculate the concentration in mg/kg (that is, ppm) of each additive in the polyethylene sample as follows:

$$[Additive]_{sample} = \frac{10^6\left(\frac{A}{k}\right)}{[Sample]_{sol}} \quad (6)$$

[6] Taylor, J. K., *Quality Control of Chemical Measurements*, Lewis Publishers, Inc., 1987.

where:

A = area of additive peak,
k = slope of calibration curve, that is, linear regression line, and
$[Sample]_{sol}$ = concentration of sample in solution (see 10.1.8).

15.2 For samples which contain additive products that are not chromatographically resolved (that is, $R < 1$) such as for example Irgafos 168 and oxidized TNPP on a C-8 reverse phase column, calculate the concentrations in mg/kg (that is, ppm) of Irgafos 168 (C_I) and oxidized TNPP (C_T) by combining Eq 7 and 8 as follows:

$$A_{217} = k_{I217}C_I + k_{T217}C_T \quad (7)$$

$$A_{270} = k_{I270}C_I + k_{T270}C_T \quad (8)$$

$$C_I = \frac{10^6(k_{T270}A_{217} - k_{T217}A_{270})}{(k_{I217}k_{T270} - k_{I270}k_{T217})} \quad (9)$$

$$C_T = \frac{10^6(k_{I270}A_{217} - k_{I217}A_{270})}{\{(k_{I270}k_{T217} - k_{I217}k_{T270})[Sample]_{sol}\}} \quad (10)$$

where:

A_{217}, A_{270} = area of peak (Irgafos 168 plus TNPP) measured at 217 nm and 270 nm, respectively,
k_{I217}, k_{I270} = slope of Irgafos 168 calibration curve at 217 nm and 270 nm, respectively, and
k_{T217}, k_{T270} = slope of oxidized TNPP calibration curve at 217 nm and 270 nm, respectively.

16. Report

16.1 Report the additives (ppm) calculated in Section 15.

17. Precision and Bias

17.1 Tables 1-4 show the results of round robin studies conducted between 1990 and 1994 in accordance with Practice E 691. The materials used were prepared by one laboratory and sent out to participants for grinding, solvent extraction and further analysis. Each test is an individual determination. Each laboratory obtained three test results for each material, and each test was performed on a different day.

NOTE 8—The round robins were performed in support of Methods D 1996, D 5524, and D 5815. Although these methods use an internal standard approach rather than the external calibration described in this consolidated method, the results are considered valid. Firstly, the calibration approach is not a major contributor to the overall precision, and secondly, if there is a difference to be associated with the calibration, the external calibration should produce the better precision.

17.2 There are no recognized standards by which to estimate bias of this test method. The additive levels are given as high/low or as a target level.

NOTE 9—Supporting data for the HDPE round robin are available at ASTM headquarters: Research Report D20-1182.

17.3 For TNPP, results from a single laboratory show a repeatability standard deviation of 3.2 % based on 50 analyses of a LLDPE resin over a period of one year.

TABLE 1 Precision for Additive Content (ppm) in Low Density Polyethylene[A]

Material	Level	Average	S_r[B]	S_R[C]	r[D]	R[E]
BHT	low	167	13	22	36	62
BHT	high	628	48	90	133	252
BHEB	low	190	12	21	34	58
BHEB	high	730	48	87	134	243
Isonox 129	low	238	13	20	36	56
Isonox 129	high	943	42	71	117	198
Irganox 1010	low	244	15	25	41	69
Irganox 1010	high	919	44	57	123	160
Irganox 1076	low	252	10	16	29	46
Irganox 1076	high	1009	49	69	137	194

[A] Based on 14 participating laboratories.
[B] S_r is the within-laboratory standard deviation of the average (median/other function).
[C] S_R is the between-laboratories standard deviation of the average (median/other function).
[D] r is the within-laboratory repeatability limit = 2.8 S_r.
[E] R is the between-laboratory reproducibility limit = 2.8 S_R.

TABLE 2 Precision for Slip Content (ppm) in Low Density Polyethylene[A]

Material	Level	Average	S_r[B]	S_R[C]	r[D]	R[E]
Slip	low	456	37	58	103	163
Slip	low	1392	92	140	56	394

[A] Based on 11 participating laboratories.
[B] S_r is the within-laboratory standard deviation of the average (median/other function).
[C] S_R is the between-laboratories standard deviation of the average (median/other function).
[D] r is the within-laboratory repeatability limit = 2.8 S_r.
[E] R is the between-laboratory reproducibility limit = 2.8 S_R.

TABLE 3 Precision for Additive Content (ppm) in Linear Low Density Polyethylene[A]

Material	Level	Average	S_r[B]	S_R[C]	r[D]	R[E]
BHT	200	162	12	16	33	44
BHT	800	623	42	78	117	218
BHEB	200	170	10	15	29	42
BHEB	700	612	20	85	55	237
Isonox 129	200	209	14	32	41	90
Isonox 129	800	763	19	75	53	211
Irganox 1010	400	363	19	52	52	146
Irganox 1010	1000	926	55	127	155	357
Irganox 1076	700	603	27	72	76	201
Irganox 1076	1250	1099	36	86	99	240
Erucamide	500	516	22	116	62	326
Erucamide	1000	1022	19	40	53	114

[A] Based on 7 participating laboratories.
[B] S_r is the within-laboratory standard deviation of the average (median/other function).
[C] S_R is the between-laboratories standard deviation of the average (median/other function).
[D] r is the within-laboratory repeatability limit = 2.8 S_r.
[E] R is the between-laboratory reproducibility limit = 2.8 S_R.

TABLE 4 Precision for Additive Content (ppm) in HDPE[A]

Material	Level	Average	S_r[B]	S_R[C]	r[D]	R[E]
BHT	low	167	13	22	36	62
BHT	high	628	48	90	133	252
BHEB	low	190	12	21	34	58
BHEB	high	730	48	87	134	243
Isonox 129	low	238	13	20	36	56
Isonox 129	high	943	42	71	117	198
Irganox 1010	low	244	15	25	41	69
Irganox 1010	high	919	44	57	123	160
Irganox 1076	low	252	10	16	29	46
Irganox 1076	high	1009	49	69	137	194

[A] Based on 10 participating laboratories.
[B] S_r is the within-laboratory standard deviation of the average (median/other function).
[C] S_R is the between-laboratories standard deviation of the average (median/other function).
[D] r is the within-laboratory repeatability limit = 2.8 S_r.
[E] R is the between-laboratory reproducibility limit = 2.8 S_R.

18. Keywords

18.1 additive; antioxidants; erucamide slip; extraction; polyethylene

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