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Plastics – Determination of phenolic antioxidants and erucamide slip additives in polypropylene homopolymer formulations – Liquid chromatography (LC)

塑料 – 均聚聚丙烯（PP-H）中酚类抗氧剂和芥酸酰胺爽滑剂的测定

液相色谱法

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Issued by: General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China;

Standardization Administration of the People's Republic of China.

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Foreword

This standard modifies and adopts American Society for Testing and Materials ASTM D6042-2004 “Standard test method for determination of phenolic antioxidants and erucamide slip additives in polypropylene homopolymer formulations using liquid chromatography” (English version).

This standard is redrafted in accordance with ASTM D6042-2004. In Appendix A, it lists the detailed comparison between the clause numbers of this standard and ASTM D6042-2004. In Appendix B, it provides the technical differences and their causes for reference.

For ease of use, this standard is subjected to the following editorial changes:

- ADD the foreword to the national standard;

- MODIFY the “Normative references”.

Appendix A, Appendix B and Appendix C of this standard are informative.

This standard was proposed by China Petroleum & Chemical Corporation.

This standard shall be under the jurisdiction of the National Plastics Standardization Technical Committee Petrochemical Plastic Resin Products Branch (SAC/TC 15/SC 1).

The responsible drafting organization of this standard: China Petroleum & Chemical Corporation Beijing Yanshan Branch Resin Application Research Institute.

The participating drafting organization of this standard: Beijing Institute of Additives.

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Plastics – Determination of phenolic antioxidants and erucamide slip additives in polypropylene homopolymer formulations – Liquid chromatography (LC)

1 Scope

This standard specifies the use of liquid chromatography for the determination of some commonly used additives in polypropylene homopolymer (PP-H). These additives are subjected to reflux extraction by the mixed solvent of dichloromethane/cyclohexane AND separation by liquid chromatography. The UV absorption is measured at 200 nm AND it is quantified by internal standard method.

This standard applies to the determination of the contents of phenolic antioxidants and erucamide slip additives in polypropylene homopolymer formulations: α-tocopherol or 3,4-dihydro-2,5,7,8-tetramethyl-2-(4,8,12-trimethyl tridecyl)-2H-1-benzofuran-6-phenolic hydroxyl group (hereinafter referred to as vitamin E), 3 (2,4-di-tert-butylphenyl) phosphite ester (hereinafter referred to as antioxidant 168), tris-(3,5-di-tert-butyl-4-hydroxyphenyl) isocyanurate (hereinafter referred to as antioxidant 3114), tetra-[(3,5-di-tert-butyl-4-hydroxyphenyl) propionic acid] pentaerythrilol ester (hereinafter referred to as antioxidant 1010), AND the (3,5-di-tert-butyl-4-hydroxyphenyl) propionate octadecyl alcohol (hereinafter referred to as antioxidant 1076). This standard can also be used for the detection of other antioxidants, such as antioxidant Ultranox 626, antioxidant Ethanox 330, antioxidant Santanox R and antioxidant BHT; however, its applicability to these antioxidants has not been studied.

Under the best detection conditions, the detection limit of phenolic antioxidant can reach 2 mg/kg.

Note: Other methods that can effectively extract additives from plastics include thin film extraction method, microwave extraction method, ultrasonic extraction method, and supercritical fluid extraction method. Other effective methods for separating the additives include supercritical fluid chromatography (SFC) and capillary gas chromatography (GC).

2 Normative references

The provisions in following documents become the provisions of this Standard through reference in this Standard. For the dated references, the subsequent amendments (excluding corrections) or revisions do not apply to this Standard; however, parties who reach an agreement based on this Standard are encouraged to study if the latest versions of these documents are applicable. For undated references, the latest edition of the referenced document applies.

5 Reagents and materials

5.1 Vitamin E: Industrial reagents.

5.2 Antioxidant 168: Industrial reagents.

5.3 Antioxidants 3114: Industrial reagents.

5.4 Erucamide: Industrial reagents.

5.5 Antioxidant 1010: Industrial reagents.

5.6 Antioxidants 1076: Industrial reagents.

5.7 Tinuvin P: 2 (2'-hydroxy-5'-methylphenyl) benzotriazole, industrial reagents.

5.8 Dichloromethane: liquid chromatography grade.

5.9 Cyclohexane: liquid chromatography grade.

WARNING - Dichloromethane and cyclohexane are toxic and flammable, so the extraction operation shall be carried out in a fume hood.

5.10 Mixed solvent of dichloromethane/cyclohexane containing internal standard: The volume ratio of dichloromethane to cyclohexane is 75/25 AND the concentration of internal standard Tinuvin P is 51.8 mg/L.

5.11 Water: GB/T 6682-2008, level I.

5.12 Acetonitrile: liquid chromatography grade.

5.13 Isopropanol: liquid chromatography grade.

6 Instruments

6.1 Liquid chromatograph: equipped with the UV detector of variable wavelength OR diode array detector, column oven, and gradient elution device.

6.2 Column: C_{18} column, 5 μm, 150 mm × 4.6 mm.

6.3 Chromatographic workstation or integrator.

6.4 Shear grinder: with 20 mesh sieve.

6.5 Analytical balance: accurate to ± 0.0001 g.

6.6 Single line pipette: capacity 50 mL, category A in GB/T 12808-1991.

6.7 Reflux extraction device: it is composed of such devices as the condenser (glass grinding mouth), 125 mL flat bottom flask (glass grinding mouth), the

7.2 Sample preparation

7.2.1 IMMERSE 7 g ~ 8 g of PP-H samples in liquid nitrogen; COOL it for 10 min; PLACE it into the grinding machine (6.4) to grind it to 850 μm (20 mesh) ~ 425 μm (40 mesh) particles. During grinding, the grinding time is minimized to avoid thermal degradation of the additives in the polymer.

7.2.2 Reflux extraction: WEIGH 5 g ± 0.01 g of the sample obtained from 7.2.1; PLACE it into a 125 mL flat bottom flask; PLACE in the stirring bar; USE the pipette (6.6) to add 50.0 mL of the mixed solvent of dichloromethane/cyclohexane containing the internal standard (5.10); under the stirring reflux of the reflux extraction device (6.7), MAKE it boil for 90 min.

7.2.3 REMOVE the flat bottom flask together with the condenser tube from the heating plate; COOL the solution to room temperature.

7.2.4 CONNECT the filter tray to a 5 mL glass syringe; slowly POUR out or USE syringe to transfer appropriate amount of extract into the upper syringe; INSERT the syringe piston; PUSH it carefully; FILTER the extract into the sample vial (the final preparation of the sample extraction is as shown in Figure 3).

7.3 Determination of relative response factors

7.3.1 Standard solution preparation: respectively and accurately WEIGH 50 mg ± 1 mg of each additive to be determined into 125 mL flat bottom flask; ADD 51.8 mg of Tinuvin P. USE appropriate amount of isopropyl alcohol (5.13) to dissolve it; after the dissolving is complete, COOL it to room temperature; TRANSFER the solution into a 1000 mL volumetric flask (6.9); USE isopropanol to dilute it to the mark; COVER the volumetric flask; SHAKE it uniformly. The Vitamin E (5.1) must be prepared before use, OR otherwise stored in a brown bottle to prevent photodegradation.

7.3.2 FOLLOW 7.1 to set the liquid chromatographic conditions; INJECT 10 μL of standard solution (7.3.1) for determination.

7.3.3 FOLLOW the formula (1) to calculate the relative response factor f_i:

$$f_i = \frac{C_i \times A_{is}}{C_{is} \times A_i} \quad \text{.....(1)}$$

Where:

f_i - The relative response factor of additive i;

C_i - The concentration of additive i, in milligrams per liter (mg/L);

C_{is} - The concentration of internal standard, in milligrams per liter (mg/L);

A_i - The peak area of additive i;

X_i - The content of the additive i to be measured, expressed in mass fraction, in milligrams per kilogram (mg/kg);

A_i - The peak area of additive i;

f_i - The relative response factor of additive i;

C_{is} - The concentration of internal standard, in milligrams per liter (mg/L);

V - Volume of extraction solution (containing Tinuvin P) in milliliters (mL);

W - The mass of the extracted sample, in grams (g);

A_{is} - Internal standard peak area.

9 Precision and deviation

Since the inter-laboratory test data have not yet been obtained, the precision and deviation of the test method is unknown. When the inter-laboratory data is obtained, a description of the precision and the deviation will be added to the next revision.

The precision of ASTM D6042-2004 is listed as an informative appendix for reference (SEE Appendix C).

10 Test report

The test report shall contain the following:

a) Indicate the reference to this standard;

b) Sample identification, including all relevant sample information;

c) Report the mass of the test sample;

d) Report the test results (the amount of additives in PP-H);

e) Test personnel;

f) Test date.

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