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Replacing GB/T 17338-1998

Determination of residual acrylonitrile monomer in styrene-acrylonitrile copolymers and rubber-modified acrylonitrile-butadiene-styrene resins and their products used for food packaging

食品包装用苯乙烯-丙烯腈共聚物和

橡胶改性的丙烯睛-丁二烯-苯乙烯

树脂及其成型品中残留丙烯腈单体的测定

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Standardization Administration Committee.

Table of Contents

Foreword

This Standard replaces GB/T 17338-1998 “Determination of residual acrylonitrile monomer in styrene-acrylonitrile copolymers and rubber-modified acrylonitrile-butadiene-styrene resins and their products used for food packaging”.

This Standard modifies the previous standard structure based on GB/T 20001.4-2001 “Rules for drafting STANDARDs - Part 4: Methods of chemical analysis”.

This Standard was proposed by and shall be under the jurisdiction of Ministry of Health of the People's Republic of China.

Drafting organizations of the first method of this Standard: Shanghai Gaoqiao Petrochemical Co. Chemical Factory, and Shanghai Health and Epidemic Prevention Station.

Drafting organizations of the second method of this Standard: Shanghai Health and Epidemic Prevention Station, Guangxi Zhuang Autonomous Region Food Hygiene Supervision and Inspection, and Shanghai Luwan District Health and Epidemic Prevention Station.

Main drafters of the first method of this Standard: Wu Keqin, Wang Junfu, Dong Jianfang and Pan Xihe.

Main drafters of the second method of this Standard: Zhu Yingmin, Shen Wen, Ye Bisha and Lao Baofa.

The previous standard was issued in 1998 for the first time. This Standard is the first revision.

Determination of residual acrylonitrile monomer in styrene-acrylonitrile copolymers and rubber-modified acrylonitrile-butadiene-styrene resins and their products used for food packaging

1 Scope

This Standard specifies the method for determination of residual acrylonitrile monomer in acrylonitrile - styrene copolymers (AS) and acrylonitrile-butadiene-styrene copolymers (ABS) by headspace gas chromatography (HP-GC).

This Standard is applicable to the determination of residual acrylonitrile monomer in acrylonitrile-styrene, acrylonitrile-butadiene-styrene resins and their products, and the determination of residual acrylonitrile monomer in rubber-modified acrylonitrile-butadiene-styrene resins and their products.

The detection limits of this method: Nitrogen-Phosphorus Detector method (NPD) is 0.5 mg/kg; Flame Ionization Detector method (FID) is 2.0 mg/kg.

The First Method: Gas Chromatography Nitrogen-Phosphorus Detector method (NPD)

2 Principle

Place the sample in a headspace bottle. Add acetonitrile solvent that contains the known amount of internal standard substance. Immediately seal it. After it is completely dissolved, heat the headspace bottle to make vapor-liquid equilibrium, and draw headspace in quantification to conduct NPD determination. Quantify it based on the response value of internal standard substance.

3 Reagents

3.1 Reagent purity: it shall use analytical reagent. If other grades of reagents are used, they must have a sufficiently high purity so as not to reduce the accuracy of determination.

3.2 Solvents: N,N-dimethylformamide or N,N-Dimethylacetamide (DMA). When conducting chromatography of solvent headspace, there must be no interfering peaks at retention time of acrylonitrile (AN) and propionitrile (PN).

3.3 Propionitrile: chromatographic grade.

3.4 Acrylonitrile: chromatographic grade.

4 Apparatus

4.1 Gas chromatograph

It shall be equipped with nitrogen-phosphorus detector.

It is better to use the device that can automatically collect and analyze the headspace, for example, manual collection and analysis of headspace shall be attached with the following equipment:

4.1.1 Thermostatic bath that can be maintained at 90°C±1°C.

4.1.2 Gas tight syringe used for headspace collection and injection.

4.2 Headspace bottle sealer.

4.3 5.0 mL headspace sampling bottle.

4.4 Aluminum sealing bottle cap.

4.5 Silicone rubber or butyl rubber with good gas tightness of which inner surface is covered with polytetrafluoroethylene membrane.

5 Analysis steps

5.1 Internal standard calibration

5.1.1 Prepare polymer solvent that contains the known amount of internal standard substance (PN).

5.1.2 Fill certain amount of the solvent (3.2) in advance into a 100 mL flask.

gasket and aluminum cap, fully shake it to make the polymer in the bottle completely dissolved or dispersed.

5.3 Gas chromatographic conditions

5.3.1 Chromatographic column: Φ 3mm×4m stainless steel column.

Fill in 101 white test acidic carrier body (60~80 mesh) painted with 15% of polyethylene glycol-20M.

5.3.2 Temperature

Column temperature: 130°C;

Vaporization temperature: 180°C;

Detector temperature: 200°C.

5.3.3 Gas speed

Carrier gas nitrogen (N_2) flow rate: 25 mL/min ~ 30 mL/min.

5.3.4 Other conditions

Nitrogen of 99.95% or greater purity.

Hydrogen shall be dried and purified.

Air shall be dried and purified.

5.4 Determination

Place headspace bottle in a 90°C bath for thermal equilibrium for 50 min. Use a heated gas syringe to extract 2.0 mL of headspace that has reached to vapor-liquid equilibrium from the bottle. Immediately inject gas chromatograph to determine. Operation conditions of gas chromatograph shall be set according to 5.3. If it uses commodity instrument of automated headspace analysis, it shall adjust according to the instructions for use of this instrument.

5.5 Result calculation

Calculate the content of residual acrylonitrile in sample (c, mg/kg) according to equation (5):

$$c = \frac{m_s' \times A_i' \times R_f \times 1\,000}{A_s' \times m} \qquad \cdots\cdots(5)$$

7 Regents

7.1 N,N-dimethylformamide (DMF): analytical reagent. There must be no interfering peaks at retention time of acrylonitrile.

7.2 Acrylonitrile (AN): analytical reagent.

7.3 GDX-102 (60~80 mesh).

7.4 Acrylonitrile standard stock solution: weigh 0.0500 g of acrylonitrile; add N,N-dimethylformamide to dilute constant volume to 50 mL. Per milliliter of this storage solution equals to 1.0 mg of acrylonitrile. Store it in the refrigerator.

7.5 Acrylonitrile standard solution: draw 0.2 mL, 0.4 mL, 0.6 mL, 0.8 mL and 1.6 mL of stock solution. Respectively move them to 10 mL flasks. Separately add N,N-dimethylformamide to dilute constant volume to scale. Well mix it (each milliliter equals 20 μg, 40 μg, 60 μg, 80 μg and 160 μg of acrylonitrile respectively).

8 Apparatus

8.1 Gas chromatograph (with flame ionization detector).

8.2 1 mL centered type glass syringe.

8.3 12 mL headspace determination bottle with rubber cover that is coated with polyvinyl fluoride silicon and aluminum cap.

8.4 Electric heated water bath.

9 Analysis steps

All samples shall be stored in sealing bottle. The prepared sample solution shall be analyzed within 24h. If it exceeds 24h, it shall report the storage time of solution.

9.1 Sample processing

Weigh 0.5g~1g (accurate to 0.001 g) of homogeneous sample in headspace determination bottle. Add 3 mL of N,N-dimethylformamide. Immediately seal it with cover. Sample shall be determined after it is dissolved.

9.2 Gas chromatographic conditions

9.2.1 Chromatographic column: Φ 4mm×2m glass column. Fill GDX-102

(60~80 mesh).

9.2.2 Temperature

Column temperature: 170°C;

Vaporization temperature: 180°C;

Detector temperature: 220°C.

9.2.3 Gas speed

Carrier gas nitrogen (N_2) flow rate: 40 mL/min;

Hydrogen flow rate: 44 mL/min;

Air flow rate: 500 mL/min.

9.2.4 Other conditions

Instrument sensitivity: 10^1;

Attenuation: 1;

Paper speed: 0.7 cm/min.

9.3 Determination

9.3.1 Adjust gas chromatography to the best working condition (referring to 9.2). Put the test sample in the 90°C±1°C water bath for accurate heating for 40 min. Take 1.0 mL of liquid gas into chromatogram. When necessary, adjust the amount of headspace to suit sample determinations of different amounts.

9.3.2 Standard curve making: separately add 3.0 mL of N,N-dimethylformamide into 5 empty headspace bottles. Then respectively take 0.2 mL of standard solution (7.5) and put into determination bottles. The content of acrylonitrile of each determination bottle shall equal to 4 μg, 8 μg, 12 μg, 16 μg, and 32 μg respectively. Immediately seal the bottle cover. Well mix it. Place in 90°C water bath. Use same sample for the following determination, i.e., respectively take 1.0 mL of headspace. Fill in the chromatograph. Measure the peak height. Take acrylonitrile content as abscissa while peak height as ordinates to draw the standard curve. Quantify based on sample's peak height.

9.4 Result calculation

It is shown in equation (6).

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