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NATIONAL STANDARD OF THE
PEOPLE'S REPUBLIC OF CHINA

GB 31604.29-2023

**National food safety standard - Food contact materials and
products - Determination of migration of acrylic acid and
methacrylic acid and their esters**

食品安全国家标准

食品接触材料及制品 丙烯酸和甲基丙烯酸及其酯类迁移量的测定

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National food safety standard -
Food contact materials and products - Determination of
migration of acrylic acid and methacrylic acid and their
esters

1 Scope

This Standard specifies the determination method for the migration of acrylic acid and methacrylic acid and their esters in food contact materials and products.

Part 1 – Gas chromatography-mass spectrometry applies to the determination of migration of 18 kinds of acrylate and methacrylate in food contact materials and products, including 2-acrylic acid-2-methylpropyl ester, ethylacrylate, n-butyl acrylate, isopropyl acrylate, acrylic acid n-propyl ester, 2-propenoic acid, 1,1-dimethylethyl ester, acrylic acid benzyl ester, 2-octyl acrylate, sec-butyl acrylate, ethyl methacrylate, isobutyl methacrylate, butyl methacrylate, 2-methyl-2-acrylic acid-1,1-dimethylethyl ester, phenyl methacrylate, 2-methyl-2-propyl acrylate, benzyl methacrylate, sec-butyl methacrylate and isopropyl methacrylate.

Part 2 – Liquid chromatography applies to the determination of migration of 6 kinds of acrylic acid, methacrylic acid and their esters in food contact materials and products, including acrylic acid, methacrylic acid, 2-hydroxyethyl acrylate, 2-hydroxyethyl-2-methyl-2-acrylate, methyl acrylate and methyl methacrylate.

Part 1 – Gas chromatography-mass spectrometry

2 Principle

The water-based food simulants as well as oil and fat food simulants obtained from the migration test are headspace sampled; the 95% (volume fraction) ethanol and isooctane simulants are directly sample after diluted with ethyl acetate; the target substance is separated in the gas chromatography capillary column, detected by mass spectrometry, and quantified by the external standard method.

3 Reagents and materials

Unless otherwise specified, all the reagents in this method are analytical reagents, and the water is grade-1 water specified by GB/T 6682.

3.1 Reagents

3.1.1 Methanol (CH_4O): chromatographic pure.

3.1.2 Ethyl acetate ($\text{C}_4\text{H}_8\text{O}_2$): chromatographic pure.

3.1.3 Sodium chloride (NaCl).

3.1.4 Anhydrous acetic acid ($\text{C}_2\text{H}_4\text{O}_2$).

3.1.5 Absolute ethanol ($\text{C}_2\text{H}_6\text{O}$).

3.1.6 95% ethanol ($\text{C}_2\text{H}_6\text{O}$).

3.1.7 Isooctane (C_8H_{18}).

3.2 Preparation of reagents

3.2.1 Food simulant: Prepare in accordance with the provisions of GB 5009.156.

3.2.2 Isooctane-ethyl acetate solution (1+4): Mix 25 mL of isooctane and 100 mL of ethyl acetate evenly.

3.2.3 95% ethanol-ethyl acetate solution (1+4): Mix 25 mL of 95% ethanol and 100 mL of ethyl acetate evenly.

3.3 Standards

18 kinds of acrylate and methacrylate standards (see Appendix A): purity $\geq 98\%$, or standard products certified by the country and awarded a standard substance certificate.

3.4 Preparation of standard solutions

3.4.1 Standard stock solutions (1 000 mg/L): Accurately weigh 18 standards (accurate to 0.1 mg). The weighing mass calculation method is 25 mg divided by the conversion coefficient, which is shown in Appendix A. Dissolve them in ethyl acetate respectively and then transfer them to the 25 mL volumetric flasks; use ethyl acetate to dilute to the mark and mix well. Transfer the solutions to brown glass containers and store them in the dark at 4 °C for 6 months.

3.4.2 Mixture of standard intermediate solution A (50 mg/L): Respectively and accurately pipette 0.5 mL of the standard stock solutions (1 000 mg/L) into the 10 mL volumetric flasks; add methanol to adjust the volume to the mark; mix well. Transfer the solutions to brown glass containers and store them in the dark at 4 °C for 6 months.

3.4.3 Mixture of standard intermediate solution B (50 mg/L): Respectively and accurately pipette 0.5 mL of the standard stock solutions (1 000 mg/L) into the 10 mL volumetric flasks; add ethyl acetate to adjust the volume to the mark; mix well. Transfer the solutions to brown glass containers and store them in the dark at 4 °C for 6 months.

3.4.4 Water-based food simulant series standard working solutions: Respectively and accurately pipette 100 μL , 150 μL , 200 μL , 400 μL and 1 000 μL of the mixtures of standard intermediate solution A (50 mg/L) into the 100 mL volumetric flasks; use 50% (volume fraction) ethanol solution to adjust the volume. The concentrations of each target substance in the obtained standard working solutions are 0.050 mg/L, 0.075 mg/L, 0.10 mg/L, 0.20 mg/L, and 0.50 mg/L, respectively. Respectively pipette 10.0 mL of solutions of each concentration into the 20 mL glass headspace bottles to which 3.0 g of sodium chloride has been added; immediately use a spacer and an aluminum cap to seal them, for later testing. Use the same method to prepare a series of standard working solutions of the same concentration with water, 4% (volume fraction) acetic acid, 10% (volume fraction) ethanol, and 20% (volume fraction) ethanol. Prepare when necessary.

3.4.5 Oil and fat food simulant series standard working solutions: Respectively and accurately weigh 5.00 g (accurate to 0.01 g) of olive oil simulant into five 20 mL glass headspace bottles; use a pipette to respectively pipette 30 μL , 80 μL , 100 μL , 150 μL , and 300 μL of the mixture of standard intermediate solution B (50 mg/L) into the 20 mL glass headspace bottles; immediately use a spacer and an aluminum cap to seal them; vortex evenly, for later testing. The concentrations of each target substance in the obtained standard working solutions are 0.30 mg/kg, 0.80 mg/kg, 1.0 mg/kg, 1.5 mg/kg, and 3.0 mg/kg, respectively. Prepare when necessary.

3.4.6 Isooctane series standard working solutions: Respectively pipette 50 μL , 150 μL , 200 μL , 300 μL and 600 μL of the mixture of standard intermediate solution B (50 mg/L) into the 10 mL volumetric flasks; use isooctane-ethyl acetate solution (1+4) to adjust the volume to the mark; mix well. The concentrations of each target substance in the obtained standard working solution are 0.25 mg/L, 0.75 mg/L, 1.0 mg/L, 1.5 mg/L and 3.0 mg/L, respectively. Prepare when necessary.

3.4.7 95% (volume fraction) ethanol series standard working solutions: Respectively pipette 50 μL , 150 μL , 200 μL , 300 μL , and 600 μL of the mixture of standard intermediate solution B (50 mg/L) into the 10 mL volumetric flasks; use 95% ethanol-ethyl acetate solution (1+4) to adjust the volume to the mark. The concentrations of each target substance in the obtained standard working solution are 0.25 mg/L, 0.75 mg/L, 1.0 mg/L, 1.5 mg/L and 3.0 mg/L, respectively. Prepare when necessary.

4 Instruments and apparatuses

4.1 Gas chromatograph-mass spectrometer, equipped with electron impact source (EI) and headspace sampler.

4.2 Vortex oscillator.

4.3 Electronic balance: The sensitivity is 0.1 mg and 0.01 g, respectively.

- d) Oscillation speed: 500 r/min.
- e) Injection volume: 250 μ L.

5.4.2 The reference conditions for gas chromatography mass spectrometry measurement are as follows:

- a) Chromatographic column: polyethylene glycol capillary column: column length 30.0 m, inner diameter 0.25 mm, film thickness 0.25 μ m, or an analytical column with equivalent performance.
- b) Programmed temperature rise: initial temperature 35 °C, kept for 8 min; increased to 60 °C at 5 °C/min, kept for 3 min; increased to 160 °C at 20 °C/min, kept for 2 min; increased to 220 °C at 40 °C/min, kept for 3 min.
- c) Inlet temperature: 290 °C.
- d) Mass spectrometry joint temperature: 280 °C.
- e) Ion source temperature: 230 °C;
- f) Carrier gas: He (purity>99.999%), constant flow 1.0 mL/min.
- g) Injection volume: 1 μ L.
- h) Injection method: split injection, the split ratio of water-based food simulant test solution is 20:1; the split ratio of oil and fat food simulant test solution is 50:1; the split ratio of isooctane test solution and 95% (volume fraction) ethanol test solution is 2:1.
- i) Ionization method: EI.
- j) Solvent delay: 5.0 min.
- k) Mass spectrometry scanning mode: selected ion mode (SIM).
- l) SIM acquisition parameters: see Appendix B.

5.5 Preparation of the standard curve

According to the apparatus reference conditions listed in 5.4.1 and 5.4.2, inject the series standard working solutions into the gas chromatograph-tandem mass spectrometer respectively, and measure the corresponding peak areas. Draw the standard working curve with the concentration of the target substance in the standard series working solution as the abscissa and the corresponding quantitative ion peak area as the ordinate. See Appendix C for the typical total ion chromatogram of standard working solutions.

5.6 Qualitative determination

S – contact area between the sample and the soak solution in the migration test, in square decimeters (dm²);

F – ratio (S/V) of the contact area (S) of food contact materials and products to the volume (V) of food or food simulants under actual use conditions, in square decimeters per kilogram (dm²/kg). In actual use situations, when S/V is known, F is the actual S/V; when S/V cannot be estimated, F is 6 dm²/kg, that is, 6 dm² of food contact materials and products contact 1 kg of food or food simulants; the density of various liquid foods is usually measured in 1 kg/L.

Express it as the arithmetic mean of two independent measurement results obtained under repeatability conditions; retain 2 significant figures as the calculation result.

6.2 Calculation of specific migration of acrylic acid and methacrylic acid and their esters in food contact materials and products such as sealed products (expressed in mg/kg)

When the intended use is known, for food contact materials and products such as sealed products, when the specific migration of acrylic acid, methacrylic acid and their esters is expressed in mg/kg, it is calculated according to Formula (2).

$$X_2 = \frac{(c - c_0) \times V}{S} \times \frac{S_0}{m_2} \dots\dots\dots (2)$$

Where:

X₂ – specific migration of the target substance (based on acrylic acid/methacrylic acid), in milligrams per kilogram (mg/kg);

c – content of the target substance (based on acrylic acid/methacrylic acid) in the sample soak solution, in milligrams per liter (mg/L) or milligrams per kilogram (mg/kg);

c₀ – content of the target substance (based on acrylic acid/methacrylic acid) in the blank soak solution, in milligrams per liter (mg/L) or milligrams per kilogram (mg/kg);

V – volume or mass of the sample soak solution, in liters (L) or kilograms (kg);

S – contact area between the sample and the soak solution in the migration test, in square decimeters (dm²);

S₀ – area of the sealed product that comes into contact with food during actual use, in square decimeters (dm²);

m₂ – mass of solid food in the actual container used for sealed products, or mass of food corresponding to the volume of actual contact with liquid food, in kilograms (kg); the volume of various liquid foods is converted into the corresponding mass according to the density of 1 kg/L.

of acrylic acid, methacrylic acid and their esters (based on acrylic acid and methacrylic acid respectively) in oil and fat food simulants, isooctane and 95% (volume fraction) ethanol are all 0.1 mg/kg, and the quantitation limits are 0.3 mg/kg. When the S/V in the migration test is different from the S/V in actual use, this method converts the detection limit and quantitation limit of the target substance in each food simulant and chemical substitute solvent according to Chapter 6.

Part 2 – Liquid chromatography

9 Principle

The water-based food simulants and 95% (volume fraction) ethanol simulants obtained from the migration test are filtered and directly injected. The oil and fat food simulants and isooctane simulants are extracted with methanol and then injected. The target substance is separated in a liquid chromatography column, detected with a UV detector or diode array detector, and quantified using the external standard method.

10 Reagents and materials

Unless otherwise specified, all the reagents in this method are analytical reagents, and the water is grade-1 water specified by GB/T 6682.

10.1 Reagents

10.1.1 Methanol (CH_4O): chromatographic pure.

10.1.2 Acetonitrile (CH_3CH): chromatographic pure.

10.1.3 Phosphoric acid (H_3PO_4): guaranteed reagent.

10.1.4 Anhydrous acetic acid ($\text{C}_2\text{H}_4\text{O}_2$).

10.1.5 Absolute ethanol ($\text{C}_2\text{H}_6\text{O}$).

10.1.6 95% ethanol ($\text{C}_2\text{H}_6\text{O}$).

10.1.7 Isooctane (C_8H_{18}).

10.2 Preparation of reagents

10.2.1 Food simulant: Prepare in accordance with the provisions of GB 5009.156.

10.2.2 80% methanol solution: Measure 80 mL of methanol and 20 mL of water and mix evenly.

10.2.3 0.1% phosphoric acid solution: Weigh 1.00 g of phosphoric acid into a 1 L volumetric flask; use water to dilute to the mark; mix well.

10.3 Standards

6 kinds of standards of acrylic acid, methacrylic acid and their esters (see Appendix D): purity $\geq 98\%$, or standard products certified by the country and awarded a reference material certificate.

10.4 Preparation of standard solution

10.4.1 Standard stock solution (1 000 mg/L): Accurately weigh 6 standards (accurate to 0.1 mg). The weighing mass calculation method is 25 mg divided by the conversion coefficient. The conversion coefficient is shown in Appendix D. Dissolve them in methanol respectively and transfer them into the 25 mL volumetric flasks; use methanol to dilute to the mark; mix well. Transfer the solutions to brown glass containers and store them in the dark at 4 °C for 6 months.

10.4.2 Mixture of standard intermediate solution (50 mg/L): Respectively and accurately pipette 0.5 mL of the standard stock solution (1 000 mg/L) into the 10 mL volumetric flasks; add methanol to adjust the volume to the mark; mix well. Transfer the solutions to brown glass containers and store them in the dark at 4 °C for 6 months.

10.4.3 Water-based food simulant series standard working solution: Respectively and accurately pipette 25 μL , 50 μL , 100 μL , 200 μL , 500 μL of the mixture of standard intermediate solution (50 mg/L) into the 5 mL volumetric flasks; use 50% (volume fraction) ethanol solution to adjust the volume. The concentrations of each target substance in the obtained standard working solution are 0.25 mg/L, 0.50 mg/L, 1.0 mg/L, 2.0 mg/L, and 5.0 mg/L, respectively. Use the same method to prepare standard working solutions of the same concentration series with water, 4% (volume fraction) acetic acid, 10% (volume fraction) ethanol, and 20% (volume fraction) ethanol. Prepare when necessary.

10.4.4 Oil and fat food simulant series standard working solutions: Respectively weigh 5.00 g (accurate to 0.01 g) of olive oil simulant into 6 centrifuge tubes; use a pipette to respectively pipette 30 μL , 60 μL , 100 μL , 150 μL and 300 μL of the mixture of standard intermediate solutions (50 mg/L); vortex and mix; add 5 mL of methanol; vortex for 1 min; centrifuge at 4 000 r/min for 5 min; pass the upper solution through a microporous filter membrane before testing. The concentrations of each target substance in the obtained standard working solutions are 0.30 mg/kg, 0.60 mg/kg, 1.0 mg/kg, 1.5 mg/kg, and 3.0 mg/kg, respectively. Prepare when necessary.

10.4.5 Isooctane series standard working solution: Respectively pipette 5.00 mL of isooctane into 6 centrifuge tubes; use a pipette to respectively pipette 30 μL , 60 μL , 100 μL , 120 μL , 300 μL of the mixture of standard intermediate solution (50 mg/L); vortex and mix; then, add 5.00 mL of 80% methanol solution; vortex and mix for 1 minute; centrifuge at 4 000 r/min for 5 minutes; remove the lower solution and filter it before testing. The concentrations of each target substance in the obtained standard working

12.3 Preparation of blank test solution

Follow the steps described in 12.1 and 12.2 to process food simulants, isooctane and 95% (volume fraction) ethanol simulants that are not in contact with food contact materials.

12.4 Apparatus reference conditions

The reference conditions for liquid chromatography determination are as follows:

- a) Chromatographic column: C₁₈ column, column length 100 mm, inner diameter 4.6 mm, particle size 3 μ m or analytical column of equivalent performance.
- b) Mobile phase: 0.1% phosphoric acid solution (A) and acetonitrile (B). See Appendix E for the gradient elution procedure.
- c) Flow velocity: 1.0 mL/min.
- d) Detection wavelength: 210 nm.
- e) Injection volume: 20 μ L;
- f) Column temperature: 30 °C.

12.5 Drawing of the standard curve

According to the instrument reference conditions listed in 12.4.1, respectively inject the series standard working solutions into the liquid chromatograph and measure the corresponding peak areas. Draw the standard working curve with the concentration of the target substance in the standard working solution as the abscissa and the corresponding peak area of the target substance as the ordinate. See Appendix F for typical liquid chromatograms of standard working solutions.

12.6 Determination of test solution

According to the instrument reference conditions listed in 12.4.1, inject the sample solution (12.2) and blank test solution (12.3) sequentially to obtain the peak area of the target substance. Calculate the concentrations c and c_0 of the target substance in the sample solution and blank test solution based on the standard curve.

13 Expression of analysis results

Same as Chapter 6.

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