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National Food Safety Standard - Food Contact Materials and Products - Determination of Migration of Benzophenone Substances

食品安全国家标准　食品接触材料及制品　二苯甲酮类物质迁移量的测定

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National Food Safety Standard - Food Contact Materials and Products - Determination of Migration of Benzophenone Substances

1 Scope

This Standard specifies the methods for the determination of migration of eight benzophenone substances in food contact materials and products.

Method 1 - liquid chromatography is applicable to the determination of migration of (2-hydroxy-4-methoxyphenyl) (2-hydroxyphenyl) ketone, 2,4-dihydroxybenzophenone, (2-hydroxy-4-methoxyphenyl) phenyl ketone, 4-4′-dihydroxybenzophenone, 2-hydroxy-4-n-octoxy-benzophenone, 2-hydroxy-4-n-hexyloxy-benzophenone, benzophenone and 4-4′-difluoro-benzophenone in plastics, paints and coatings, rubber, and food contact materials and products using inks in water, 4% (volume fraction) acetic acid, 10% (volume fraction) ethanol, 20% (volume fraction) ethanol, 50% (volume fraction) ethanol food simulants, as well as chemical alternative solvents - 95% (volume fraction) ethanol and isooctane.

Method 2 - liquid chromatography - tandem mass spectrometry is applicable to the determination of migration of (2-hydroxy-4-methoxyphenyl) (2-hydroxyphenyl) ketone, 2,4-dihydroxybenzophenone, (2-hydroxy-4-methoxyphenyl) phenyl ketone, 4-4′-dihydroxybenzophenone, 2-hydroxy-4-n-octoxy-benzophenone, 2-hydroxy-4-n-hexyloxy-benzophenone, benzophenone and 4-4′-difluoro-benzophenone in plastics, paints and coatings, rubber, and food contact materials and products using inks in water, 4% (volume fraction) acetic acid, 10% (volume fraction) ethanol, 20% (volume fraction) ethanol, 50% (volume fraction) ethanol and olive oil food simulants, as well as chemical alternative solvents - 95% (volume fraction) ethanol and isooctane.

Method 1 - Liquid Chromatography

2 Principle

After food contact materials and products are subject to migration test in accordance with GB 31604.1 and GB 5009.156, adopt liquid chromatography for detection. Water, 4% (volume fraction) acetic acid, 10% (volume fraction) ethanol, 20% (volume fraction) ethanol and 50% (volume fraction) ethanol food simulants are directly injected; chemical alternative solvent - 95% (volume fraction) ethanol is diluted by water, filtered, then, injected. Use nitrogen to blow the chemical alternative solvent - isooctane, then, use methanol-water to re-dissolve it, filter, then, inject the sample. Adopt the external standard method of peak area for quantitative

determination.

3 Reagents and Materials

Unless it is otherwise specified, the reagents used in this Method are all analytically pure, and the water is Grade-1 water specified in GB/T 6682.

3.1 Reagents

3.1.1 Glacial acetic acid (CH_3COOH).

3.1.2 Absolute ethanol (C_2H_5OH).

3.1.3 Isooctane (C_8H_{18}).

3.1.4 Methanol (CH_3OH): chromatographically pure.

3.1.5 Dimethyl sulfoxide (C_2H_6OS).

3.2 Preparation of Reagents

3.2.1 4% (volume fraction) acetic acid solution, 10% (volume fraction) ethanol solution, 20% (volume fraction) ethanol solution and 50% (volume fraction) ethanol solution are prepared in accordance with GB 5009.156.

3.2.2 95% (volume fraction) ethanol solution: evenly mix absolute ethanol and water in a volume ratio of 95 : 5.

3.2.3 Methanol-water solution (7 + 3): evenly mix methanol and water in a volume ratio of 7 : 3.

3.3 Reference Materials

3.3.1 (2-hydroxy-4-methoxyphenyl) (2-hydroxyphenyl) ketone ($C_{14}H_{12}O_4$, CAS: 131-53-3): purity ≥ 98%, or a standard substance certified by the state and awarded a reference material certificate.

3.3.2 2,4-dihydroxybenzophenone ($C_{13}H_{10}O_3$, CAS: 131-56-6): purity ≥ 98%, or a standard substance certified by the state and awarded a reference material certificate.

3.3.3 (2-hydroxy-4-methoxyphenyl) phenyl ketone ($C_{14}H_{12}O_3$, CAS: 131-57-7): purity ≥ 98%, or a standard substance certified by the state and awarded a reference material certificate.

3.3.4 4-4′-dihydroxybenzophenone ($C_{13}H_{10}O_3$, CAS: 611-99-4): purity ≥ 98%, or a standard substance certified by the state and awarded a reference material certificate.

3.3.5 2-hydroxy-4-n-octoxy-benzophenone ($C_{21}H_{26}O_3$, CAS: 1843-05-6): purity ≥ 98%, or a standard substance certified by the state and awarded a reference material certificate.

3.3.6 2-hydroxy-4-n-hexyloxy-benzophenone ($C_{19}H_{22}O_3$, CAS: 3293-97-8): purity ≥ 98%, or a standard substance certified by the state and awarded a reference material certificate.

3.3.7 Benzophenone ($C_{13}H_{10}O$, CAS: 119-61-9): purity ≥ 98%, or a standard substance certified by the state and awarded a reference material certificate.

3.3.8 4-4′-difluoro-benzophenone ($C_{13}H_8F_2O$, CAS: 345-92-6): purity ≥ 98%, or a standard substance certified by the state and awarded a reference material certificate.

3.4 Preparation of Standard Solutions

3.4.1 Standard stock solutions (1,000 mg/L)

Accurately weigh-take 50 mg (accurate to 0.1 mg) of each of the eight benzophenone reference materials, respectively use methanol to dissolve them, then, transfer them to eight 50 mL volumetric flasks. Use methanol to reach a constant volume to the scale and evenly mix them. Transfer the solutions to brown glass containers and store them airtight at 4 °C away from light. They shall remain valid for 6 months.

3.4.2 Standard mixed intermediate solution

Respectively draw-take 0.5 mL of 4-4′-dihydroxybenzophenone, benzophenone and 4-4′-difluoro-benzophenone standard stock solutions (1,000 mg/L) and 2.0 mL of the standard stock solutions (1,000 mg/L) of the other five benzophenone substances into a 100 mL volumetric flask. Use methanol to reach a constant volume to the scale, evenly mix it to obtain a Standard mixed intermediate solution, in which, the concentration of 4-4′-dihydroxybenzophenone, benzophenone and 4-4′-difluoro-benzophenone is 5.0 mg/L, and the concentration of the other five benzophenone substances is 20.0 mg/L. Transfer the solution to a brown glass container and store it airtight at 4 °C away from light. It shall remain valid for 3 months.

3.4.3 Standard mixed series of working solutions

3.4.3.1 Standard mixed series of working solutions of water, 4% (volume fraction) acetic acid, 10% (volume fraction) ethanol, 20% (volume fraction) ethanol and 50% (volume fraction) ethanol

Respectively draw-take 40 μL, 100 μL, 200 μL, 400 μL and 600 μL of the standard mixed intermediate solution into five 10 mL volumetric flasks. Use the corresponding food simulants to reach a constant volume to the scale, evenly mix them to obtain standard mixed series of working solutions, in which, the concentration of 4-4′-dihydroxybenzophenone, benzophenone and 4-4′-difluoro-benzophenone is 0.020 mg/L, 0.050 mg/L, 0.10 mg/L, 0.20 mg/L and 0.30 mg/L, and the concentration of the other five benzophenone substances is 0.080 mg/L, 0.20 mg/L, 0.40 mg/L, 0.80 mg/L and 1.2 mg/L. Prepare them right before use.

3.4.3.2 Standard mixed series of working solutions of chemical alternative solvent - 95% (volume fraction) ethanol

5 Analytical Procedures

5.1 Preparation of test solutions

5.1.1 Migration test

In accordance with the requirements of GB 31604.1 and GB 5009.156, conduct a migration test. After the soaking solution returns to room temperature, handle it in accordance with 5.1.2. If the soaking solution obtained from the migration test cannot be immediately tested, it shall be stored in a refrigerator at 4 °C away from light for no more than 72 hours. After returning to room temperature, it shall be handled in accordance with 5.1.2.

5.1.2 Treatment of soaking solutions

5.1.2.1 Food simulant test solutions of water, 4% (volume fraction) acetic acid, 10% (volume fraction) ethanol, 20% (volume fraction) ethanol and 50% (volume fraction) ethanol

Transfer-take an appropriate amount of water, 4% (volume fraction) acetic acid, 10% (volume fraction) ethanol, 20% (volume fraction) ethanol and 50% (volume fraction) ethanol soaking solutions obtained after the migration test; centrifuge at 5,000 r/min for 5 minutes. Reserve the supernatant for determination.

5.1.2.2 Chemical alternative solvent - 95% (volume fraction) ethanol test solution

Draw-take 7 mL of 95% (volume fraction) ethanol soaking solution obtained after the migration test into a 10 mL volumetric flask, use water to reach a constant volume to the scale and evenly mix it. Take about 1 mL of it and filter it through the microporous filter membrane. Reserve it for determination.

5.1.2.3 Chemical alternative solvent - isooctane test solution

Draw-take 2 mL of isooctane soaking solution obtained after the migration test into a 10 mL stoppered centrifuge tube, accurately add 100 μL of dimethyl sulfoxide and evenly mix it. In a 40 °C water bath, use nitrogen to blow it to near dryness. Accurately add 2 mL of the methanol-water solution (7 + 3), conduct vortex oscillation for 30 s to dissolve the residue. Take about 1 mL of it and filter it through a microporous filter membrane. Reserve it for determination.

5.1.3 Preparation of blank test solution

In accordance with 5.1.1 and 5.1.2, handle the food simulants and chemical alternative solvents not in contact with food contact materials and products to obtain blank test solution.

5.2 Reference Conditions of Instrument

5.2.1 Chromatographic column: C_{18} column, column length 250 mm, inner diameter 4.6 mm, particle size 5 μm; or one with equivalent performance.

6 Expression of Analysis Results

6.1 Calculation of Specific Migration Amount of Benzophenones in Food Contact Materials and Products of Non-sealed Products (expressed in mg/kg)

For food contact materials and products other than lids, sealing rings, connectors and other sealing products (hereinafter referred to as sealing products), when expressed in mg/kg, the specific migration amount of benzophenones is calculated in accordance with Formula (1).

$$X_1 = \frac{(c - c_0) \times V}{S} \times \frac{S_0}{V_1} \qquad \cdots\cdots (1)$$

Where,

X_1---the specific migration amount of benzophenones, expressed in (mg/kg);

c---the content of benzophenones in the soaking solution, expressed in (mg/L) or (mg/kg);

c_0---the content of benzophenones in the blank soaking solution, expressed in (mg/L) or (mg/kg);

V---the volume or mass of the specimen soaking solution in the migration test, expressed in (L) or (kg);

S---the area of contact between the specimen and the soaking solution in the migration test, expressed in (dm^2);

S_0---the area of non-sealed product that comes into contact with food in actual use, expressed in (dm^2);

V_1---the mass of non-sealed product that actually comes into contact with solid food, or the mass of food corresponding to the volume that actually comes into contact with liquid food, expressed in (kg); the volume of various liquid foods is converted into the corresponding mass based on a density of 1 kg/L.

If the actual contact area / volume (i.e., S_0/V_1) of the specimen is unknown, then, the calculation shall be based on that every 6 dm^2 of the specimen area is in contact with 1 kg of food.

The calculation result, which is expressed as the arithmetic mean of the results of two independent determinations obtained under repeatability conditions, shall at least retain 2 significant figures.

6.2 Calculation of Specific Migration Amount of Benzophenones in Food Contact Materials and Products of Sealed Products (expressed in mg/kg)

When the intended purpose is known, and the specific migration amount of benzophenones in food contact materials and products of sealed products is expressed in mg/kg, it is calculated in accordance with Formula (2).

$$X_2 = \frac{(c - c_0) \times V}{S} \times \frac{S_0}{V_2} \quad \cdots\cdots (2)$$

Where,

X_2---the specific migration amount of benzophenones, expressed in (mg/kg);

c---the content of benzophenones in the soaking solution, expressed in (mg/L) or (mg/kg);

c_0---the content of benzophenones in the blank soaking solution, expressed in (mg/L) or (mg/kg);

V---the volume or mass of the specimen soaking solution in the migration test, expressed in (L) or (kg);

S---the area of contact between the specimen and the soaking solution in the migration test, expressed in (dm^2);

S_0---the area of sealed product that comes into contact with food in actual use, expressed in (dm^2);

V_2---the mass of sealed product that actually uses a container to hold solid food, or the mass of food corresponding to the volume that actually comes into contact with liquid food, expressed in (kg); the volume of various liquid foods is converted into the corresponding mass based on a density of 1 kg/L.

The calculation result, which is expressed as the arithmetic mean of the results of two independent determinations obtained under repeatability conditions, shall at least retain 2 significant figures.

6.3 Calculation of Specific Migration Amount of Benzophenones in Food Contact Materials and Products of Sealed Products (expressed in mg/PCS)

When the intended purpose is unknown, and the specific migration amount of benzophenones in food contact materials and products of sealed products is expressed in mg/PCS, it is calculated in accordance with Formula (3). It is necessary to indicate the migration test method used and the contact area between a single sealed product and the food simulant in the migration test.

$$X_3 = \frac{(c - c_0) \times V}{n} \quad \cdots\cdots (3)$$

Where,

X_3---the specific migration amount of benzophenones, expressed in (mg/PCS);

c---the content of benzophenones in the soaking solution, expressed in (mg/L) or (mg/kg);

c_0---the content of benzophenones in the blank soaking solution, expressed in (mg/L) or (mg/kg);

Method 2 - Liquid Chromatography - Tandem Mass Spectrometry

9 Principle

After food contact materials and products are subject to migration test in accordance with GB 31604.1 and GB 5009.156, adopt liquid chromatography - tandem mass spectrometry for detection. Water, 4% (volume fraction) acetic acid, 10% (volume fraction) ethanol, 20% (volume fraction) ethanol and 50% (volume fraction) ethanol food simulants are directly injected; food simulant - olive oil is extracted by methanol and blown to near dryness by nitrogen, use methanol-water solution to re-dissolve it, filter it, then, inject the sample; chemical alternative solvent - 95% (volume fraction) ethanol is diluted by water, filtered, then, injected. Use nitrogen to blow the chemical alternative solvent - isooctane, then, use methanol-water to re-dissolve it, filter it, then, inject the sample. Adopt the external standard method of peak area for quantitative determination.

10 Reagents and Materials

Unless it is otherwise specified, the reagents used in this Method are all analytically pure, and the water is Grade-1 water specified in GB/T 6682.

10.1 Reagents

10.1.1 Glacial acetic acid (CH_3COOH).

10.1.2 Absolute ethanol (C_2H_5OH).

10.1.3 Isooctane (C_8H_{18}).

10.1.4 Dimethyl sulfoxide (C_2H_6OS).

10.1.5 Olive oil: complies with the requirements of GB 5009.156.

10.1.6 Acetone (CH_3COCH_3).

10.1.7 Methanol (CH_3OH): chromatographically pure.

10.1.8 Formic acid (HCOOH): chromatographically pure.

10.2 Preparation of Reagents

10.2.1 4% (volume fraction) acetic acid solution, 10% (volume fraction) ethanol solution, 20% (volume fraction) ethanol solution and 50% (volume fraction) ethanol solution are prepared in accordance with GB 5009.156.

fraction) ethanol

Respectively draw-take 20 μL, 50 μL, 100 μL, 200 μL and 400 μL of the standard mixed intermediate solution (methanol) into five 10 mL volumetric flasks. Use the corresponding food simulant to reach a constant volume to the scale, evenly mix it to obtain the standard mixed series of working solutions, in which, the concentration of 2-hydroxy-4-n-hexyloxy-benzophenone is 0.010 mg/L, 0.025 mg/L, 0.050 mg/L, 0.10 mg/L and 0.20 mg/L, and the concentration of the other seven benzophenones is 0.020 mg/L, 0.050 mg/L, 0.10 mg/L, 0.20 mg/L and 0.40 mg/L. Prepare them right before use.

10.4.3.2 Standard mixed series of working solutions of oily food simulant

Respectively and accurately weigh-take 5 g (accurate to 0.001 g) of olive oil food simulant into five 25 mL stoppered centrifuge tubes, respectively and accurately add 50 μL of the standard mixed series of intermediate solutions (acetone); thoroughly shake them and let stand to obtain standard mixed series of working solutions, in which, the concentration of 2-hydroxy-4-n-hexyloxy-benzophenone and 2-hydroxy-4-n-octoxy-benzophenone is 0.30 mg/kg, 0.50 mg/kg, 0.80 mg/kg, 1.0 mg/kg and 2.0 mg/kg, and the concentration of the other six benzophenones is 0.025 mg/kg, 0.050 mg/kg, 0.10 mg/kg, 0.20 mg/kg and 0.30 mg/kg. Respectively and accurately add 5 mL of methanol, conduct vortex oscillation for 30 s; at 5,000 r/min, centrifuge for 5 min, then, immediately transfer all the supernatant to five 10 mL stoppered centrifuge tubes. In a 40 °C water bath, use nitrogen to blow them to near dryness. Respectively and accurately add 1 mL of methanol-water solution (7 + 3), conduct vortex oscillation for 30 s to dissolve the residue. At 5,000 r/min, centrifuge for 5 min. Take the supernatant and filter it through a microporous filter membrane. Reserve them for determination. Prepare them right before use.

10.4.3.3 Standard mixed series of working solutions of chemical alternative solvent - 95% (volume fraction) ethanol

Respectively draw-take 20 μL, 50 μL, 100 μL, 200 μL and 400 μL of the standard mixed intermediate solution (methanol) into five 10 mL volumetric flasks, use 95% (volume fraction) ethanol to reach a constant volume to the scale, evenly mix them to obtain the standard mixed series of working solutions, in which, the concentration of 2-hydroxy-4-n-hexyloxy-benzophenone is 0.010 mg/L, 0.025 mg/L, 0.050 mg/L, 0.10 mg/L and 0.20 mg/L, and the concentration of the other seven benzophenones is 0.020 mg/L, 0.050 mg/L, 0.10 mg/L, 0.20 mg/L and 0.40 mg/L. Respectively draw-take 7 mL of the standard mixed series of working solutions of 95% (volume fraction) ethanol into five 10 mL volumetric flasks, use water to reach a constant volume to the scale and evenly mix them. Prepare them right before use.

10.4.3.4 Standard mixed series of working solutions of chemical alternative solvent - isooctane

Respectively draw-take 20 μL, 50 μL, 100 μL, 200 μL and 400 μL of the standard mixed intermediate solution (methanol) into five 10 mL volumetric flasks, use isooctane to reach a constant volume to the scale, evenly mix them to obtain the standard mixed series of working

solutions, in which, the concentration of 2-hydroxy-4-n-hexyloxy-benzophenone is 0.010 mg/L, 0.025 mg/L, 0.050 mg/L, 0.10 mg/L and 0.20 mg/L, and the concentration of the other seven benzophenones is 0.020 mg/L, 0.050 mg/L, 0.10 mg/L, 0.20 mg/L and 0.40 mg/L. Respectively draw-take 2 mL of the standard mixed series of working solutions of isooctane into five 10 mL stoppered centrifuge tubes; respectively and accurately add 100 μL of dimethyl sulfoxide, and evenly mix them. In a 40 °C water bath, use nitrogen to blow them to near dryness. Respectively and accurately add 2 mL of the methanol-water solution (7 + 3), conduct vortex oscillation for 30 s to dissolve the residue, then, filter them through a microporous filter membrane. Reserve them for determination. Prepare them right before use.

10.5 Material

Same as 3.5.

11 Instruments and Equipment

11.1 Liquid chromatograph - tandem mass spectrometer: equipped with electrospray ion source (ESI).

11.2 Balance: with a division value of 0.1 mg and 1 mg respectively.

11.3 Vortex mixer.

11.4 Centrifuge: with a speed ≥ 5,000 r/min.

11.5 Nitrogen concentration device.

12 Analytical Procedures

12.1 Preparation of test solutions

12.1.1 Migration test

In accordance with the requirements of GB 31604.1 and GB 5009.156, conduct a migration test. After the soaking solution returns to room temperature, handle it in accordance with 12.1.2. If the soaking solution obtained from the migration test cannot be immediately tested, it shall be stored in a refrigerator at 4 °C away from light for no more than 72 hours. After returning to room temperature, it shall be handled in accordance with 12.1.2.

12.1.2 Treatment of soaking solutions

12.1.2.1 Food simulant test solutions of water, 4% (volume fraction) acetic acid, 10% (volume fraction) ethanol, 20% (volume fraction) ethanol and 50% (volume fraction) ethanol

Same as 5.1.2.1.

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