GB

NATIONAL STANDARD OF THE

PEOPLE'S REPUBLIC OF CHINA

GB 31604.46-2023

National Food Safety Standard - Food Contact Materials and Products - Determination of Free Phenol and Migration

食品安全国家标准　食品接触材料及制品　游离酚的测定和迁移量的测定

Issued on: September 6, 2023 **Implemented on: March 6, 2024**

Issued by: National Health Commission of the People's Republic of China;
State Administration for Market Regulation.

Table of Contents

National Food Safety Standard - Food Contact Materials and Products - Determination of Free Phenol and Migration

1 Scope

This Standard specifies the method for the determination of food contact materials and products - free phenol and the determination of migration.

In this Standard, Part 1 is applicable to the determination of free phenol in epoxy phenolic resin coatings for food contact; Part 2 is applicable to the determination of free phenol migration in food contact materials and products; Part 3 is applicable to the determination of phenol migration in food contact materials and products.

Part 1 - Determination of Free Phenol

2 Principle

The free phenol in the specimen reacts with bromine to generate bromophenol. The remaining bromine reacts with potassium iodide. The precipitated iodine is titrated with sodium thiosulfate. In accordance with the consumption of sodium thiosulfate solution, calculate the content of free phenol.

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 Hydrochloric acid (HCl): mass fraction 36% ~ 38%.

3.1.2 Trichloromethane ($CHCl_3$).

3.1.3 Ethanol (C_2H_6O).

3.1.4 Potassium iodide (KI).

3.1.5 Soluble starch [$(C_6H_{10}O_5)_n$].

3.1.6 Bromine water (Br_2): content ≥ 3%.

3.1.7 Anhydrous sodium carbonate (Na_2CO_3).

3.1.8 Potassium bromide (KBr).

3.2 Preparation of Reagents

3.2.1 Potassium iodide solution (100 g/L): weigh-take 1.00 g of potassium iodide, use water to dissolve it and dilute to 10 mL.

3.2.2 Starch indicator solution (10 g/L): weigh-take 1.0 g of soluble starch, add 5 mL of water to adjust it to a paste, while stirring, add the paste to 90 mL of boiling water, and boil for 1 min ~ 2 min; cool and dilute to 100 mL. The usage period is 2 weeks.

3.3 Reference Materials

3.3.1 Sodium thiosulfate pentahydrate ($Na_2S_2O_3 \bullet 5H_2O$, CAS No.: 10102-17-7): working reference reagent, or a standard substance certified by the state and awarded a reference material certificate.

3.3.2 Potassium bromate ($KBrO_3$, CAS No.: 7758-01-2): working reference reagent, or a standard substance certified by the state and awarded a reference material certificate.

3.3.3 Standard solution for volumetric analysis of bromine: a standard substance certified by the state and awarded a reference material certificate.

3.4 Preparation of Standard Solutions

3.4.1 Sodium thiosulfate standard titration solution [$c(Na_2S_2O_3) = 0.1$ mol/L]

Weigh-take 26 g of sodium thiosulfate ($Na_2S_2O_3 \bullet 5H_2O$), add 0.2 g of anhydrous sodium carbonate, dissolve it in 1,000 mL of water, and slowly boil it for 10 min; cool and place it in a brown reagent bottle. Store it in the dark for 2 weeks, then, filter it. Before use, calibrate it in accordance with GB/T 5009.1. Sodium thiosulfate standard titration solution of the same concentration for volumetric analysis can also be used.

3.4.2 Brome standard solution [$c\left(\frac{1}{2}Br_2\right) = 0.1$ mol/L]

Weigh-take 3.0 g of potassium bromate and 25.0 g of potassium bromide, dissolve it in 1,000 mL of water, and evenly shake it. Before use, calibrate it in accordance with GB/T 5009.1. Standard solution of the same concentration for volumetric analysis of bromine can also be used.

4 Instruments and Equipment

4.1 Balance: with a division value of 0.01 g and 0.1 mg, respectively.

4.2 Steam distillation apparatus: see Appendix A for the schematic diagram; or automatic steam distillation apparatus.

V_2---the volume of sodium thiosulfate standard titration solution consumed by specimen titration, expressed in (mL);

c---the actual concentration of sodium thiosulfate standard titration solution, expressed in (mol/L);

V_3---the constant volume of the distilled liquid, expressed in (mL);

m---the mass of the sample, expressed in (g);

V_4---the volume of the distilled liquid transferred-taken during the titration, expressed in (mL).

The result shall retain 2 significant figures.

7 Precision

The absolute difference between the results of two independent determinations obtained under repeatability conditions shall not exceed 5% of the arithmetic mean.

8 Others

In this method, the detection limit is 0.4 g/kg and the quantitation limit is 2.0 g/kg.

Part 2 - Determination of Free Phenol Migration

9 Principle

Under alkaline conditions (pH 9.0 ~ 10.5), free phenol reacts with 4-aminoantipyrine under the catalysis of potassium ferricyanide to generate antipyrine dye. The antipyrine dye in water is extracted with chloroform. Then, use a spectrophotometer to determine the absorbance value of the test solution at 460 nm, compare it with the standard series to obtain the free phenol content in the soaking solution, and further calculate the amount of free phenol migration. For antipyrine dyes in other food simulants and alterative solvents, use a spectrophotometer to determine the absorbance value of the test solution at 500 nm, compare it with the standard series to obtain the free phenol content in the soaking solution, and further calculate the amount of free phenol migration.

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

Take phenol into a distillation bottle with an air condenser, heat and distill it, and collect the distillate at 182 °C ~ 184 °C. After cooling, the distillate shall be white. Store it in a brown bottle and tightly store it in a cool and dark place. Accurately weigh-take 1.0 g (accurate to 0.1 mg) of refined white phenol into a 1 L volumetric flask, use water to dilute to the scale and evenly mix it. In accordance with GB 8538-2016, calibrate it.

10.4.2 Standard intermediate solution (100 mg/L)

Use an appropriate amount of ethanol to dilute the calibrated standard stock solution (1,000 mg/L) to 100 mg/L. Store it in a refrigerator at 4 °C and away from light. It shall remain valid for 1 month.

10.4.3 Standard intermediate solution (10 mg/L)

Use an appropriate amount of water to dilute the calibrated standard stock solution (1,000 mg/L) to 10 mg/L. Prepare it right before use.

10.4.4 Standard series of working solutions in aqueous solution

Respectively and accurately transfer-take 0 mL, 1.0 mL, 2.0 mL, 4.0 mL, 6.0 mL and 10.0 mL of the standard intermediate solution (10 mg/L) into six 200 mL volumetric flasks; use water to reach a constant volume to the scale and evenly mix them. The concentration of phenol in the standard series of working solutions is respectively 0.00 mg/L, 0.05 mg/L, 0.10 mg/L, 0.20 mg/L, 0.30 mg/L and 0.50 mg/L.

10.4.5 Standard series of working solutions in 4% (volume fraction) acetic acid solution

Respectively and accurately transfer-take 0 mL, 0.125 mL, 0.50 mL, 1.00 mL, 1.50 mL and 3.00 mL of the standard intermediate solution (100 mg/L) into six 50 mL volumetric flasks; use 4% (volume fraction) acetic acid solution to reach a constant volume to the scale and evenly mix them. The concentration of phenol in the standard series of working solutions is respectively 0.00 mg/L, 0.25 mg/L, 1.00 mg/L, 2.00 mg/L, 3.00 mg/L and 6.00 mg/L.

10.4.6 Standard series of working solutions in 10% (volume fraction) ethanol solution

Respectively and accurately transfer-take 0 mL, 0.125 mL, 0.50 mL, 1.00 mL, 1.50 mL and 3.00 mL of the standard intermediate solution (100 mg/L) into six 50 mL volumetric flasks; use 10% (volume fraction) ethanol solution to reach a constant volume to the scale and evenly mix them. The concentration of phenol in the standard series of working solutions is respectively 0.00 mg/L, 0.25 mg/L, 1.00 mg/L, 2.00 mg/L, 3.00 mg/L and 6.00 mg/L.

10.4.7 Standard series of working solutions in isooctane

Respectively and accurately transfer-take 0 mL, 0.25 mL, 0.50 mL, 1.00 mL, 1.50 mL and 3.00 mL of the standard intermediate solution (100 mg/L) into six 50 mL volumetric flasks; use isooctane to reach a constant volume to the scale and evenly mix them. The concentration of phenol in the standard series of working solutions is respectively 0.00 mg/L, 0.50 mg/L, 1.00

aminoantipyrine solution and 1.0 mL of potassium ferricyanide solution. Each time a reagent is added, thoroughly shake it; let it stand for 10 min, and reserve it for testing.

If the soaking solution is colored or turbid, take 50.0 mL of the soaking solution into a distillation bottle, add a few glass beads, heat and distill it. When about 90% of the total volume has been distilled, stop distillation. After slightly cooling, add 10 mL of water to the distillation bottle and continue distillation, until 50 mL of distilled liquid is collected. Transfer-take all the distilled liquid into a conical flask, follow the operation after "add 7.20 g of sodium carbonate" in the previous paragraph to obtain the test solution.

12.2.3 Treatment of 10% (volume fraction) ethanol soaking solution and 20% (volume fraction) ethanol soaking solution

Transfer-take 50.0 mL of the soaking solution into a conical flask, and successively add 1.0 mL of ammonium chloride buffer solution, 1.0 mL of 4-aminoantipyrine solution and 1.0 mL of potassium ferricyanide solution. Each time a reagent is added, thoroughly shake it; let it stand for 10 min, and reserve it for later testing.

If the soaking solution is colored or turbid, take 50.0 mL of the soaking solution into a distillation bottle, add a few glass beads, heat and distill it. When about 90% of the total volume has been distilled, stop distillation. After slightly cooling, add 10 mL of water to the distillation bottle and continue distillation, until 50 mL of distilled liquid is collected. Transfer-take all the distilled liquid into a conical flask, follow the operation after "successively add 1.0 mL of ammonium chloride buffer solution" in the previous paragraph to obtain the test solution.

12.2.4 Treatment of 50% (volume fraction) ethanol soaking solution and 95% (volume fraction) ethanol (chemical alternative solvent) soaking solution

Transfer-take 10.0 mL of the soaking solution into a conical flask, add 40.0 mL of water, and evenly mix it. In accordance with 12.2.3, conduct the treatment to obtain the test solution.

If the soaking solution is colored or turbid, take 10.0 mL of the soaking solution into a distillation bottle, add 40.0 mL of water and a few glass beads, heat and distill it. When about 90% of the total volume has been distilled, stop distillation. After slightly cooling, add 10 mL of water to the distillation bottle and continue distillation, until 50 mL of distilled liquid is collected. Transfer-take all the distilled liquid into a conical flask, follow the operation after "successively add 1.0 mL of ammonium chloride buffer solution" in 12.2.3 to obtain the test solution.

12.2.5 Treatment of isooctane (chemical alternative solvent) soaking solution

Transfer-take 50.0 mL of the soaking solution into a separatory funnel, add 50.0 mL of water and evenly mix it. Shake it for 2 min, let it stand to obtain stratification. In accordance with 12.2.3, conduct the treatment. Take the aqueous layer (lower layer) solution and filter it through a nylon filter membrane; reserve it for later testing.

12.3 Blank Test

17.1.2 Absolute ethanol (C_2H_6O).

17.1.3 95% ethanol.

17.1.4 Isooctane (C_8H_{18}).

17.1.5 Olive oil: chemically pure, in line with the requirements of GB 5009.156.

17.1.6 Methanol (CH_4O): chromatographically pure.

17.1.7 Acetonitrile (C_2H_3N): chromatographically pure.

17.2 Preparation of Reagents

17.2.1 Water-based food simulants: prepared in accordance with the stipulations of GB 5009.156.

17.2.2 80% methanol solution: measure-take 80 mL of methanol and 20 mL of water, and evenly mix it.

17.3 Reference Material

Same as 10.3.

17.4 Preparation of Standard Solutions

17.4.1 Standard stock solution (1,000 mg/L)

Same as 10.4.1.

17.4.2 Standard intermediate solution (100 mg/L)

Accurately transfer-take 1.00 mL of the standard solution (1,000 mg/L) into a 10 mL volumetric flask, use methanol to dilute it and reach a constant volume, and evenly mix it. Store it in a refrigerator at 4 °C away from light. It shall remain valid for 1 month.

17.4.3 Standard intermediate solution (10 mg/L)

Accurately transfer-take 0.50 mL of the standard solution (1,000 mg/L) into a 50 mL volumetric flask, use methanol to dilute it and reach a constant volume. Prepare it right before use.

17.4.4 Standard series of working solutions of water-based food simulants

Respectively and accurately transfer-take 0.01 mL, 0.05 mL, 0.10 mL, 0.30 mL and 0.60 mL of the standard intermediate solution (100 mg/L) into five 10 mL volumetric flasks. Use 4% (volume fraction) acetic acid solution to reach a constant volume. Thus, standard working solutions with a mass concentration of 0.10 mg/L, 0.50 mg/L, 1.00 mg/L, 3.00 mg/L and 6.00 mg/L are obtained.

The preparation of standard working solutions of water, 10% (volume fraction) ethanol solution, 20% (volume fraction) ethanol solution, and 50% (volume fraction) ethanol solution is carried out in accordance with the preparation method of 4% (volume fraction) acetic acid solution standard working solution.

17.4.5 Standard series of working solutions of oil and fat food simulants

Respectively and accurately weigh-take 5.0 g (accurate to 0.01 g) of olive oil into 5 stoppered glass centrifuge tubes, and respectively add 0.015 mL, 0.05 mL, 0.10 mL, 0.15 mL and 0.30 mL of the standard intermediate solution (100 mg/L). Conduct vortex mixing to respectively obtain standard working solutions of 0.30 mg/kg, 1.00 mg/kg, 2.00 mg/kg, 3.00 mg/kg and 6.00 mg/kg.

17.4.6 Standard series of working solutions of isooctane

Respectively and accurately transfer-take 0.10 mL, 0.50 mL, 1.00 mL, 3.00 mL and 6.00 mL of the standard intermediate solution (10 mg/L) into five 10 mL volumetric flasks and use 80% methanol solution to reach a constant volume. Thus, standard working solutions with a mass concentration of 0.10 mg/L, 0.50 mg/L, 1.00 mg/L, 3.00 mg/L and 6.00 mg/L are respectively obtained.

17.4.7 Standard series of working solutions of 95% (volume fraction) ethanol

Respectively and accurately transfer-take 0.02 mL, 0.10 mL, 0.20 mL, 0.40 mL and 0.60 mL of the standard intermediate solution (100 mg/L) into five 10 mL volumetric flasks and use 95% (volume fraction) ethanol solution to reach a constant volume. Thus, standard working solutions with a mass concentration of 0.20 mg/L, 1.00 mg/L, 2.00 mg/L, 4.00 mg/L and 6.00 mg/L are respectively obtained.

17.5 Materials

17.5.1 Hydrophilic PTFE filter membrane: polytetrafluoroethylene (PTFE), with a pore size of 0.45 μm.

17.5.2 Nylon filter membrane: with a pore size of 0.45 μm.

18 Instruments and Equipment

18.1 Liquid chromatograph: equipped with a fluorescence detector.

18.2 Vortex oscillator.

18.3 Analytical balance: with a division value of 0.01 g and 0.1 mg, respectively..

18.4 Centrifuge: with a rotating speed ≥ 4,000 r/min.

18.5 Pipette: with a measuring range of 100 μL, 1 mL and 5 mL, respectively.

19 Analytical Procedures

19.1 Preparation of Test Solutions

19.1.1 Migration test

Food contact materials and products shall be subject to migration test in accordance with the requirements of GB 31604.1 and GB 5009.156. If the soaking solution obtained from the migration test cannot be immediately tested, it can be stored at room temperature or a refrigerator at 4 °C, with a storage period of no more than 3 days. If the next step of test is carried out, the soaking solution shall recover to room temperature before use.

19.1.2 Treatment of soaking solutions

19.1.2.1 Preparation of water-based food simulant test solutions

Transfer-take 1 mL ~ 2 mL of the soaking solution obtained in the migration test, filter it through the hydrophilic PTFE filter membrane and reserve it for testing.

19.1.2.2 Preparation of oil and fat food simulant test solutions

Accurately weigh-take 5.0 g (accurate to 0.01 g) of the olive oil soaking solution obtained from the migration test into a stoppered glass centrifuge tube, accurately transfer-take 10.0 mL of 80% methanol solution into the centrifuge tube; at 2,500 r/min, conduct vortex oscillation for 5 min; at 4,000 r/min, conduct centrifugation for 5 min; take the upper layer of solution, filter it through the nylon filter membrane, and reserve it for later testing.

19.1.2.3 Treatment of isooctane (chemical alternative solvent) soaking solution

Accurately transfer-take 5.00 mL of the isooctane soaking solution obtained from the migration test into a stoppered glass centrifuge tube, and accurately transfer-take 5.00 mL of 80% methanol solution into the centrifuge tube. At 1,500 r/min, conduct vortex oscillation for 1 min; at 4,000 r/min, conduct centrifugation for 5 min; take the lower layer of solution, filter it through the nylon filter membrane, and reserve it for later testing.

19.1.2.4 Preparation of 95% (volume fraction) ethanol (chemical alternative solvent) soaking solution

Accurately transfer-take 5.00 mL of the 95% (volume fraction) ethanol soaking solution obtained from the migration test into a stoppered glass centrifuge tube, accurately transfer-take 5.00 mL of water into the centrifuge tube, and evenly mix it; filter it through the hydrophilic PTFE filter membrane, and reserve it for later testing.

19.1.2.5 Preparation of blank test solution

In accordance with 19.1.1 and 19.1.2, handle the food simulants and chemical alternative solvents that are not in contact with the food contact materials and products.

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

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

V---the volume or mass of the specimen soaking solution, 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 the sealed product that comes into contact with food during actual use, expressed in (dm^2);

V_3---the mass of the food actually contained in the container of the sealed product, expressed in (kg); the volume of various liquid foods is converted into the corresponding mass based on a density of 1 kg/L.

The result shall retain 2 significant figures.

20.3 Calculation of Specific Phenol Migration in Food Contact Materials and Products of Sealed Products (expressed in mg/PCS)

When the specific phenol migration in food contact materials and products of sealed products is expressed in mg/PCS, calculate in accordance with Formula (7). 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.

$$X_6 = \frac{(c - c_0) \times V}{n} \qquad \cdots\cdots(7)$$

Where,

X_6---the specific migration of phenol, expressed in (mg/PCS);

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

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

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

n---the number of sealed products for soaking, expressed in (PCS).

The result shall retain 2 significant figures.

21 Precision

The absolute difference between the results of two independent determinations obtained under repeatability conditions shall not exceed 10% of the arithmetic mean.

This is an excerpt of the PDF (Some pages are marked off intentionally)

------ The End ------