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Method of Test for Food Utensils, Containers and Packages - Test of Metal Alloy (the Direct Contact Surface Material with Food is Synthetic Resins)

1. Scope

This method is applicable to the inspection of metal alloy food utensils, containers and packages in which the direct contact surface material with food is synthetic resins.

2. Migration test

2.1. Evaporation residue test

2.1.1. Method

After migration of the sample, the migration solution is analyzed by weighing.

2.1.1.1. Equipment

2.1.1.1.1. Water bath: capable of controlling temperature at ±1°C.

2.1.1.1.2. Oven: with an automatic temperature controller, capable of controlling temperature at ±1°C.

2.1.1.2. Chemicals

Ethanol (95%), reagent grade;
Chloroform, reagent grade;
Glacial acetic acid, reagent grade.

2.1.1.3. Apparatus

2.1.1.3.1. Evaporating dish: quartz or platinum.

2.1.1.4. Reagents

2.1.1.4.1. 4% Acetic acid

Dilute 40 mL of glacial acetic acid with water to 1000 mL.

2.1.1.4.2. 20% Ethanol

Dilute 210 mL of ethanol with water to 1000 mL.

2.1.1.5. Sample solution preparation

Wash the sample with water and then air-dry. According to the migration conditions listed in Table 1, add the food simulant preheated to the specified temperature whose volume is about 80% of the capacity of the sample, or add 2 mL of the food simulant preheated to the specified temperature per cm^2 surface area of the sample. Cover with aluminum foil or a watch glass when 4% acetic

acid is used as the food simulant, and place in an oven preadjusted to the specified temperature. After 30 min, take the migration solution out as the sample solution.

Table 1. Migration conditions for the evaporation residue test

Application	Food simulant	Migration condition
Simulate the contact with foods containing pH > 5	Water	60°C, 30 min[a]
		95°C, 30 min[b]
Simulate the contact with foods containing pH 5 or lower	4% Acetic acid	60°C, 30 min[a]
		95°C, 30 min[b]
Simulate the contact foods containing alcohol	20% Ethanol	60°C, 30 min

[a]The condition used for those products which are heated to below 100°C during food processing or cooking.

[b]The condition used for those products which are heated to equal or higher than 100°C during food processing or cooking.

2.1.1.6. Determination

2.1.1.6.1. Evaporation residue

Accurately transfer 200-300 mL of the sample solution into an evaporating dish predried to constant weight at 105°C, and then evaporate to dryness in a boiling water bath. Place the evaporating dish in an oven, and dry at 105°C for 2 hr. Remove the evaporating dish from the oven, place in a desiccator to cool to room temperature, and weigh the evaporating dish. Take the same amount of the food simulant, and perform the same procedure as the blank solution. Calculate the amount of evaporation residue in the migration solution by the following formula:

The amount of the evaporation residue in the migration solution

$$(\text{ppm}) = \frac{(a - b) \times 1000 \times V}{M \times 2 \times A}$$

Where,

a: the weight of the sample solution after drying (mg)

b: the weight of the blank solution after drying (mg)

M: the volume of the sample solution (mL)

V: the volume of the migration solution (mL)

A: the area of the sample in contact with the food simulant (cm^2)

2.1.1.6.2. Chloroform-soluble extract(note)

Add 50 mL of chloroform to the evaporation residue using water as the food simulant in section 2.1.1.6.1. Dissolve the residue by gentle heating and filter. Transfer the filtrate into an evaporating dish predried to constant weight at 105°C. Wash the residue with 25 mL of chloroform twice, heat and filter. Combine the filtrates, and evaporate to dryness in a boiling water bath. Place the evaporating dish in the oven, and dry at 105°C for 2 hr. Remove the evaporating dish from the oven, place in a desiccator to cool to room temperature, and weigh immediately. Take 50 mL of chloroform, and perform the same procedure described above as the blank solution. Calculate the amount of the chloroform-soluble extract by the following formula:

The amount of the chloroform-soluble extract (ppm)

$$= \frac{(a - b) \times 1000 \times V}{M \times 2 \times A}$$

Where,

a: the weight of the chloroform-soluble extract in the sample solution (mg)

b: the weight of the chloroform-soluble extract in the blank solution (mg)

M: the volume of the sample solution (mL)

V: the volume of the migration solution (mL)

A: the area of the sample in contact with water (cm^2)

Note: When the evaporation residue in section 2.1.1.6.1 is over 30 ppm, conduct the chloroform-soluble extract test.

2.2. Phenol test

2.2.1. Method

After migration of the sample, the migration solution is analyzed by colorimetry.

2.2.1.1. Equipment

2.2.1.1.1. Spectrophotometer: with the visible light wavelength range.

2.2.1.1.2. Oven: with an automatic temperature controller, capable of controlling temperature at ±1°C.

2.2.1.2. Chemicals

Phenol, reagent grade;
Boric acid, reagent grade;
4-Aminoantipyrine, reagent grade;
Potassium ferricyanide, reagent grade;
Sodium hydroxide, reagent grade;
Ammonia hydroxide (25%), reagent grade.

2.2.1.3. Reagents

2.2.1.3.1. 1 N Sodium hydroxide

Dissolve and dilute 4 g of sodium hydroxide with water to 100 mL.

2.2.1.3.2. 1 M Boric acid

Dissolve and dilute 6.2 g of boric acid with water to 100 mL.

2.2.1.3.3. Boric acid buffer solution

Mix 1 N sodium hydroxide and 1 M boric acid at a ratio of 9:10 (v/v).

2.2.1.3.4. 4-Aminoantipyrine solution

Dissolve and dilute 1.36 g of 4-aminoantipyrine with water to 1000 mL.

2.2.1.3.5. Potassium ferricyanide solution

Dissolve 8.6 g of potassium ferricyanide with appropriate amount of water, add 1.8 mL of ammonia hydroxide, and dilute with water to 1000 mL.

2.2.1.4. Standard solution preparation

Transfer about 1 g of phenol accurately weighed to a 100-mL volumetric flask. Dissolve and dilute to volume with water as the standard stock solution. When to use, transfer appropriate amount of the standard stock solution, and dilute with water to 2-25 μg/mL as the standard solutions.

2.2.1.5. Sample solution preparation

Wash the sample with water and then air-dry. According to the migration conditions listed in Table 2, add water preheated to the

specified temperature whose volume is about 80% of the capacity of the sample, or add 2 mL of water preheated to the specified temperature per cm^2 surface area of the sample. Cover with aluminum foil, and place in an oven preadjusted to the specified temperature. After 30 min, take the migration solution out as the sample solution.

Table 2. Migration conditions for the phenol test

Migration condition	Remark
60°C, 30 min.	The condition used for those products which are heated to below 100°C during food processing or cooking
95°C, 30 min.	The condition used for those products which are heated to equal or higher than 100°C during food processing or cooking

2.2.1.6. Standard curve preparation

Accurately transfer 10 mL of the standard solutions to each 50-mL volumetric flask, add 3 mL of boric acid buffer solution, and mix well. Add 5 mL of 4-aminoantipyrine solution and 2.5 mL of potassium ferricyanide solution, dilute with water to volume, and place at room temperature for 10 min. Take 10 mL of water, and perform the same procedure described above as the blank solution. Establish the standard curve based on the absorbance at 510 nm.

2.2.1.7. Determination

Accurately transfer 10 mL of the sample solution to a 50-mL volumetric flask, add 3 mL of boric acid buffer solution, and follow the same procedure described in section 2.2.1.6. Calculate the amount of phenol in the migration solution by the following formula based on the absorbance of the sample solution:

$$\text{The amount of phenol in the migration solution (ppm)} = \frac{C \times V}{2 \times A}$$

Where,

C: the concentration of phenol in the sample solution calculated by the standard curve (μg/mL)

V: the volume of the migration solution (mL)

A: the area of the sample in contact with water (cm^2)

2.3. Formaldehyde test

2.3.1. Method

After migration of the sample, the migration solution is analyzed by colorimetry.

2.3.1.1. Equipment

2.3.1.1.1. Spectrophotometer: with the visible light wavelength range.

2.3.1.1.2. Steam distiller.

2.3.1.1.3. Water bath: capable of controlling temperature at ±1°C.

2.3.1.1.4. Oven: with an automatic temperature controller, capable of controlling temperature at ±1°C.

2.3.1.2. Chemicals

Potassium iodide, reagent grade;
Iodine, reagent grade;
Sodium thiosulfate, reagent grade;
Sodium carbonate anhydrous, reagent grade;
Acetic acid, reagent grade;
Formaldehyde (37%), reagent grade;
Hydrochloric acid, reagent grade;
Ammonium acetate, reagent grade;
Acetylacetone, reagent grade;
Potassium hydroxide, reagent grade;
Sulfuric acid, reagent grade;
Starch, reagent grade;
Phosphoric acid (85%), reagent grade.

2.3.1.3. Apparatus

2.3.1.3.1. Volumetric flask: 100 mL, 200 mL and 1000 mL.

2.3.1.3.2. Burette: 25 mL, amber.

2.3.1.3.3. Test tube: with glass-stopper, i.d. 1.5 cm, glass.

2.3.1.4. Reagents

2.3.1.4.1. 0.1 N Iodine

Dissolve 36 g of potassium iodide in 100 mL of water, and add 14 g of iodine immediately. After dissolution, add 3 drops of hydrochloric acid, and dilute with water to 1000 mL.

2.3.1.4.2. 1 N Potassium hydroxide

Dissolve and dilute 5.6 g of potassium hydroxide with water to 100 mL.

2.3.1.4.3. 10% Sulfuric acid

Add 5.7 mL of sulfuric acid into 10 mL of water slowly, and then dilute with water to 100 mL.

2.3.1.4.4. 0.1 N Sodium thiosulfate

Accurately transfer 26 g of sodium thiosulfate and 0.2 g of sodium carbonate anhydrous to a 1000-mL volumetric flask, dissolve and dilute to volume with recently boiled and thoroughly cooled water.

2.3.1.4.5. Starch solution

Triturate 1 g of starch with 10 mL of cool water, and pour slowly, with constant stirring, into 200 mL of boiling water. Boil the mixture until a thin, translucent fluid is obtained. Allow to settle, and use only the clear, supernatant liquid. Prepare before use.

2.3.1.4.6. Acetylacetone solution

Dissolve 150 g of ammonium acetate in water, add 3 mL of acetic acid and 2 mL of acetylacetone, and dilute with water to 1000 mL. Prepare before use.

2.3.1.4.7. 20% Phosphoric acid

Dilute 23.5 mL of phosphoric acid with water to 100 mL.

2.3.1.5. Standard solution preparation

Transfer 1 g of formaldehyde accurately weighed to a 100-mL volumetric flask containing 5 mL of water, dissolve and dilute to volume with water. Take 10 mL of the above solution, add 50 mL of 0.1 N iodine and 20 mL of 1 N potassium hydroxide, and mix well. After standing at room temperature for 15 min, add 15 mL of 10% sulfuric acid, and titrate with 0.1 N sodium thiosulfate using the starch solution as an indicator. Take 10 mL of water, and perform the same procedure described above as the blank solution. Calculate the amount of formaldehyde (C) in the formaldehyde solution by the following formula:

$$\text{The amount of formaldehyde C (\%)} = \frac{1.501 \times (V_0 - V) \times f}{W}$$

Where,

V: the titration volume of 0.1 N sodium thiosulfate (mL)

V_0: the titration volume of 0.1 N sodium thiosulfate for the blank solution (mL)

f: the titer of 0.1 N sodium thiosulfate

W: the weight of the formaldehyde solution (g)

Accurately transfer 200/C g of the formaldehyde solution to a 100-mL volumetric flask, and dilute to volume with water (equivalent to 20000 μg/mL formaldehyde). Then dilute with water to 0.5-8 μg/mL as the standard solutions.

2.3.1.6. Sample solution preparation

Wash the sample with water and then air-dry. According to the migration conditions listed in Table 3, add water preheated to the specified temperature whose volume is about 80% of the capacity of the sample, or add 2 mL of water preheated to the specified temperature per cm^2 surface area of the sample. Cover with aluminum foil, and place in an oven preadjusted to the specified temperature. After 30 min, take the migration solution out, transfer 25 mL of the migration solution into a distillation flask, and add 1 mL of 20% phosphoric acid. The end of the condenser must be immersed in 5-10 mL of water in a 200-mL volumetric flask. Distill and collect about 190 mL of the distillate. Then dilute to volume with water as the sample solution.

Table 3. Migration conditions for the formaldehyde test

Migration condition	Remark
60°C, 30 min	The condition used for those products which are heated to below 100°C during food processing or cooking
95°C, 30 min	The condition used for those products which are heated to equal or higher than 100°C during food processing or cooking

2.3.1.7. Standard curve preparation

Accurately transfer 5 mL of the standard solutions to each test tube,

and add 5 mL of the acetylacetone. Mix well, and heat in a boiling water bath for 10 min. Take 10 mL of water, and perform the same procedure described above as the blank solution. Establish the standard curve based on the absorbance at 415 nm.

2.3.1.8. Determination

Accurately transfer 5 mL of the sample solution to a test tube, add 5 mL of the acetylacetone solution, and perform the same procedure described in section 2.3.1.7. Calculate the amount of formaldehyde in the migration solution by the following formula based on the absorbance of the sample solution:

The amount of formaldehyde in the migration solution (ppm)

$$= \frac{C \times 8 \times V}{2 \times A}$$

Where,

C: the concentration of formaldehyde in the sample solution calculated by the standard curve (μg/mL)

V: the volume of the migration solution (mL)

A: the area of the sample in contact with water (cm^2)

2.4. Epichlorohydrin monomer test

2.4.1. Method

After migration of the sample, the migration solution is analyzed by gas chromatography/mass spectrometry (GC-MS).

2.4.1.1. Equipment

2.4.1.1.1. Gas chromatograph/mass spectrometer (GC-MS).

2.4.1.1.1.1. Ion source: electron ionization (EI)

2.4.1.1.1.2. Column: DB-624 capillary column, film thickness 1.4 μm, 0.25 mm i.d. × 30 m, or an equivalent product.

2.4.1.1.2. Oven: with an automatic temperature controller, capable of controlling temperature at ±1°C.

2.4.1.2. Chemicals

n-Pentane, reagent grade;

Epichlorohydrin, reference standard.

2.4.1.3. Standard solution preparation

Transfer about 1 g of epichlorohydrin reference standard accurately

weighed to a 100mL volumetric flask, dissolve and dilute to volume with *n*-pentane as the standard stock solution. When to use, take appropriate amount of the standard stock solution, and dilute with *n*-pentane to 0.1-5 μg/mL as the standard solutions.

2.4.1.4. Sample solution preparation

Wash the sample with water and then air-dry. Add *n*-pentane whose volume is about 80% of the capacity of the sample, or add 2 mL of *n*-pentane per cm^2 surface area of the sample. Cover with aluminum foil, and place in an oven preadjusted to 25°C. After 1 hr, take the migration solution out as the sample solution.

2.4.1.5. Identification and determination

Accurately inject 1 μL of the sample solution and the standard solutions separately into GC-MS, and operate according to the following conditions. Identify epichlorohydrin base on the retention time and relative ion intensities(Note 1). Calculate the amount of epichlorohydrin monomer in the migration solution by the following formula:

The amount of epichlorohydrin monomer in the migration solution

$$(\text{ppm}) = \frac{C \times V}{2 \times A}$$

Where,

C: the concentration of epichlorohydrin monomer in the sample solution calculated by the standard curve (μg/mL)

V: the volume of the migration solution (mL)

A: the area of the sample in contact with *n*-pentane (cm^2)

GC-MS operating conditions(Note 2):

Column: DB-624 capillary column, film thickness 1.4 μm, 0.25 mm i.d.× 30 m.

Oven temperature:

Initial temperature: 40°C, hold for 1 min;

Temperature gradient rate: 8°C/min;

Middle temperature: 70°C, hold for 1 min;

Temperature gradient rate: 30°C/min;

Final temperature: 250°C, hold for 2 min.

Carrier gas flow rate: helium, 1 mL/min.
Injector temperature: 230°C.
Interface temperature: 220°C.
Ion source temperature: 230°C.
Ionization mode: EI, 70 eV.
Injection mode: split, 1:1.
Detection mode: selected ion monitoring (SIM). Detection ions are as follows:

Analyte	Quantitative ion *(m/z)*	Qualitative ion *(m/z)*
Epichlorohydrin monomer	57	62, 49

Note:

1. Relative ion intensities are calculated by peak areas of qualitative ions divided by peak areas of quantitative ions (≤ 100%). Maximum permitted tolerances for relative ion intensities are as follows:

Relative ion intensity (%)	Tolerance (%)
> 50	± 10
> 20-50	± 15
> 10-20	± 20
≤ 10	± 50

2. All the parameters can be adjusted depending on the instruments used if the above conditions are not applicable.

2.5. Vinyl chloride monomer test

2.5.1. Method

After migration of the sample, the migration solution is analyzed by gas chromatography/mass spectrometry (GC-MS).

2.5.1.1. Equipment

2.5.1.1.1. Gas chromatograph/mass spectrometer (GC-MS)

2.5.1.1.1.1. Ion source: electron ionization (EI)

2.5.1.1.1.2. Column: DB-624 capillary column, film thickness 1.4 μm, 0.25 mm i.d. × 30 m, or an equivalent product.

2.5.1.2. Chemicals

Ethanol, GC grade;

Vinyl chloride (50 μg/mL in ethanol), reference standard.

2.5.1.3. Standard solution preparation

Accurately take appropriate amount of vinyl chloride reference standard, and dilute with precooled ethanol (< 5°C) to 0.01-0.2 μg/mL as the standard solutions. Store in a freezer.

2.5.1.4. Sample solution preparation

Wash the sample with water and then air-dry. Add the precooled ethanol (< 5°C) whose volume is about 80% of the capacity of the sample, or add 2 mL of precooled ethanol (< 5°C) per cm^2 surface area of the sample. Cover with aluminum foil, and place under 5°C. After 24 hr, take the migration solution out as the sample solution.

2.5.1.5. Identification and determination

Accurately inject 1 μL of the sample solution and the standard solutions separately into GC MS and operate according to the following conditions. Identify vinyl chloride base on the retention time and relative ion intensities(Note1). Calculate the amount of vinyl chloride in the migration solution by the following formula:

$$\text{The amount of vinyl chloride in the migration solution (ppm)} = \frac{C \times V}{2 \times A}$$

Where,

C: the concentration of vinyl chloride in the sample solution calculated by the standard curve (μg/mL)

V: the volume of the migration solution (mL)

A: the area of the sample contact with ethanol (cm^2)

GC-MS operating conditions(note2):

Column: DB-624 capillary column, film thickness 1.4 μm, 0.25 mm i.d. × 30 m.

Oven temperature:

Initial temperature: 35°C, hold for 1 min;

Temperature gradient rate: 7°C/min;

Middle temperature: 70°C, hold for 0 min;

Temperature gradient rate: 60°C/min;

Final temperature: 250°C, hold for 1 min.

Carrier gas flow rate: helium, 1 mL/min.

Injector temperature: 220°C.
Interface temperature: 230°C.
Ion source temperature: 250°C.
Ionization mode: EI, 70 eV.
Injection mode: split, 1:1.
Detection mode: selected ion monitoring (SIM). Detection ions are as follows:

Analyte	Quantitative ion *(m/z)*	Qualitative ion *(m/z)*
Vinyl chloride monomer	62	64, 63

Note:

1. Relative ion intensities are calculated by peak areas of qualitative ions divided by peak areas of quantitative ions (≤ 100%). Maximum permitted tolerances for relative ion intensities are as follows:

Relative ion intensity (%)	Tolerance (%)
> 50	± 10
> 20-50	± 15
> 10-20	± 20
≤ 10	± 50

2. All the parameters can be adjusted depending on the instruments used if the above conditions are not applicable.

Remark

Limits of quantification (LOQs) in the migration test are 2 ppm for phenol, 4 ppm for formaldehyde, 0.1 ppm for epichlorohydrin monomer and 0.01 ppm for vinyl chloride monomer.

Reference

The Pharmaceutical Society of Japan. 2015. Method of Analysis in Health Science. KANEHARA & Co., LTD. Tokyo, Japan.