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National Food Safety Standard - Determination of Formaldehyde in Foods

食品安全国家标准 食品中甲醛的测定

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National Food Safety Standard - Determination of Formaldehyde in Foods

1 Scope

This Standard specifies the determination method of formaldehyde in foods.

The first method of this Standard is applicable to the determination of formaldehyde in beer; the second method is applicable to the determination of formaldehyde in foods.

Method I Spectrophotometry

2 Principle

The sample is subjected to steam distillation; and the formaldehyde in the distillate reacts with acetylacetone to form a yellow substance with maximum absorption at 415 nm. Within a certain range, its absorbance value is proportional to the formaldehyde content.

3 Reagents and Materials

Unless otherwise specified, all the reagents used in this method are analytically pure; and the water is Grade 3 water specified in GB/T 6682.

3.1 Reagents

3.1.1 Glacial acetic acid ($C_2H_4O_2$).

3.1.2 Acetylacetone ($C_5H_8O_2$).

3.1.3 Ammonium acetate ($C_2H_7O_2N$).

3.1.4 Phosphoric acid (H_3PO_4).

3.1.5 Dimethyl silicone oil.

3.2 Preparation of reagents

3.2.1 Acetylacetone solution: Weigh 25.0 g of ammonium acetate and dissolve it in 90 mL of water; then add 0.4 mL of acetylacetone and 3.0 mL of glacial acetic acid; dilute to 100 mL

with water; mix well; and transfer to a brown reagent bottle. Prepare immediately before use.

3.2.2 Phosphoric acid solution (200 g/L): Weigh 20 g of phosphoric acid; dilute to 100 mL with water; mix well; and store at room temperature.

3.3 Standard sample

Formaldehyde (CH_2O, CAS No.: 50-00-0) standard solution: 1,000 mg/L, or other standard samples certified by the state and awarded with standard substance certificates.

NOTE: Formaldehyde standard solution can also be prepared and calibrated with 36% ~38% formaldehyde solution. For specific operations, see Appendix A.

3.4 Preparation of standard solution

3.4.1 Formaldehyde standard intermediate solution (100 mg/L): Accurately pipette 1.00 mL of 1,000 mg/L formaldehyde standard solution; dilute with water and make constant volume to 10 mL; prepare a formaldehyde standard intermediate solution with a mass concentration of 100 mg/L; store at 2 ℃ ~8 ℃ away from light; and the validity period is 3 months.

3.4.2 Formaldehyde standard working solution (1.0 mg/L): Accurately pipette 1.0 mL of 100 mg/L formaldehyde standard intermediate solution; dilute with water and make constant volume to 100 mL; prepare a formaldehyde standard working solution with a mass concentration of 1.0 mg/L. Prepare immediately before use.

3.4.3 Formaldehyde series standard working solution: Accurately pipette 0 mL, 0.50 mL, 1.0 mL, 2.0 mL, 4.0 mL, 8.0 mL and 10.0 mL of 1.0 mg/L formaldehyde standard working solution into 25 mL stoppered colorimetric tubes; add water to make constant volume to 10 mL; and prepare formaldehyde series standard working solutions with mass concentrations of 0 mg/L, 0.050 mg/L, 0.10 mg/L, 0.20 mg/L, 0.40 mg/L, 0.80 mg/L and 1.0 mg/L, respectively. Prepare immediately before use.

4 Instruments and Equipment

4.1 Spectrophotometer.

4.2 Steam distillation apparatus.

4.3 Water bath: controllable temperature 100 ℃ ± 1 ℃, accuracy 0.1 ℃.

5 Analysis Procedures

5.1 Preparation of specimen

Beer specimens shall be sealed and stored; before testing, mix the specimens evenly and remove

the carbon dioxide in the specimens by filtering with medium-speed filter paper.

5.2 Analysis of specimen

5.2.1 Distillation

Accurately pipette 25.00 mL of the specimen; place it in a 500 mL distillation flask; add 20 mL of phosphoric acid solution (200 g/L), 1 mL of dimethyl silicone oil, and 50 mL of water; and perform steam distillation. Pre-add 10 mL of water to a 250 mL receiving flask; insert the receiving tube below the liquid surface; and place it in an ice bath. When about 195 mL of distillate is collected; take it out. Place it at room temperature for 30 min; transfer it to a 200 mL volumetric flask; add water to the scale; shake it well and set aside.

5.2.2 Color development

Accurately pipette 10.0 mL of the distillate prepared in 5.2.1 and place it in a 25 mL stoppered colorimetric tube.

Add 1 mL of acetylacetone solution (3.2.1) to the stoppered colorimetric tube; cover the stopper; and mix well. Place the stoppered colorimetric tube in a boiling water bath for 5 min; take it out; and cool it to room temperature.

5.3 Blank test

Except for not adding the specimen, all other procedures are carried out according to Procedure 5.2.

5.4 Drawing of standard curve

According to the method of 5.2.2, treat the formaldehyde series standard working solution (3.4.3) and the specimen at the same time and in the same way. After cooling to room temperature, place it in a 1 cm colorimetric dish; adjust the zero point as per the zero point of the formaldehyde series standard working solution as a reference; and measure the absorbance value at 415 nm. Use the concentration of the series standard working solution as the horizontal axis and its absorbance value as the vertical axis to draw a standard curve.

5.5 Determination of specimen solution

Place the solution obtained in 5.2 and 5.3 in a 1 cm colorimetric dish and measure the absorbance at 415 nm. If the sample result exceeds the standard linear range, dilute it with a blank specimen solution and then measure it again.

NOTE: The obtained sample solution shall be measured within 1 h.

ultraviolet detector.

11.2 Electronic balance: Sensitivity is 1 mg.

11.3 Constant temperature water bath oscillator: Controllable temperature at 25 ℃ ±1 ℃, accuracy of 0.1 ℃.

11.4 Vortex mixer.

11.5 Centrifuge: Speed ≥4,000 r/min.

11.6 0.45 μm organic filter membrane.

12 Analysis Procedures

12.1 Preparation of specimen

For solid specimens, take the edible part; mash it and prepare it into a uniform specimen; put it into a clean container; seal it and mark it; and store it in a refrigerator. Liquid specimens shall be sealed and stored; and the specimen shall be mixed evenly before testing. For specimens containing carbon dioxide, remove carbon dioxide by filtering with medium-speed filter paper.

12.2 Analysis of specimen

12.2.1 Derivatization

For wine samples, accurately pipette 5.00 mL of the specimen. For other samples, weigh 2 g of the prepared specimen (accurate to 0.01 g); place it in a 50 mL plastic centrifuge tube; accurately add 20 mL of the derivatization solution (10.2.3); cover the tube tightly; vortex to mix. Place in a constant temperature water bath oscillator; shake at 25 ℃ ± 1 ℃ for 1 h to allow it to react fully.

12.2.2 Extraction

Immediately add 8 g of sodium chloride to the above test solution; vortex and mix for 30 s; centrifuge at no less than 4,000 r/min for 5 min; take the upper solution into a 20 mL volumetric flask. Add 10 mL of acetonitrile to the centrifuge tube; vortex and mix for 30 s; centrifuge at no less than 4,000 r/min for 5 min. Combine the upper solution; and make constant volume to the scale with acetonitrile; and mix well. Filter through a 0.45 μm organic filter membrane and provide for liquid chromatography determination.

12.3 Blank test

Except for not adding the specimen, all other procedures are carried out according to Procedure 12.2.

12.4 Reference conditions of instrument

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

12.4.2 Mobile phase: acetonitrile-water (50:50, volume ratio).

12.4.3 Column temperature: 30 ℃.

12.4.4 Detection wavelength: 350 nm.

12.4.5 Flow rate: 1 mL/min.

12.4.6 Injection volume: 20 μL.

12.5 Drawing of standard curve

Accurately pipette 0 mL, 0.050 mL, 0.10 mL, 0.20 mL, 0.40 mL, 0.60 mL and 0.80 mL of 100 mg/L formaldehyde standard intermediate solution into 50 mL plastic centrifuge tubes respectively. According to the derivatization and extraction procedures in 12.2, obtain formaldehyde series standard working solutions with mass concentrations of 0 mg/L, 0.25 mg/L, 0.50 mg/L, 1.0 mg/L, 2.0 mg/L, 3.0 mg/L and 4.0 mg/L respectively.

Inject the standard series working solutions into the high-performance liquid chromatograph in order from low to high concentration; determine the corresponding peak area; and draw a standard curve with the concentration of the standard working solution as the horizontal axis and the peak area as the vertical axis. For the liquid chromatogram of the standard solution, see Figure B.1 in Appendix B.

12.6 Determination of specimen solution

Inject the specimen solution into the liquid chromatograph to obtain the corresponding peak area and obtain the formaldehyde concentration in the specimen solution according to the standard curve.

NOTE: The sample solution obtained after derivatization shall be determined within 24 h.

13 Expression of Analysis Results

The formaldehyde content in the specimen is calculated according to Formula (2).

$$X = \frac{(\rho - \rho_0) \times V}{m \times 1\,000} \times 1\,000 \qquad \cdots\cdots\cdots\cdots\cdots\cdots (2)$$

Where:

X - formaldehyde content in the specimen, in mg/kg or mg/L;

Appendix A

Preparation and Calibration of Formaldehyde Standard Solution

A.1 Reagents

Unless otherwise specified, all the reagents used in this method are analytically pure; and water is Grade 1 water as specified in GB/T 6682.

A.1.1 Formaldehyde solution (CH_2O).

A.1.2 Sulfuric acid (H_2SO_4).

A.1.3 Sodium hydroxide (NaOH).

A.1.4 Soluble starch.

A**.1.5** Iodine (I_2).

A.1.6 Sodium thiosulfate ($Na_2S_2O_3$).

A.2 Preparation of reagents

A.2.1 Sulfuric acid solution (1 mol/L): Pipette 54 mL of sulfuric acid; slowly inject it into an appropriate amount of water; cool it to room temperature; and then make constant volume to 1,000 mL with water.

A.2.2 Iodine solution (0.1 mol/L): Prepare according to the method in 4.9 of GB/T 601.

A.2.3 Sodium hydroxide solution (1 mol/L): Prepare according to the method in 4.1 of GB/T 601.

A.2.4 Starch indicator (5 g/L): Weigh 0.5 g of soluble starch; add 5 mL of water to make it into a paste; slowly pour the paste into 90 mL of boiling water while stirring; stir well. Boil for 2 min; cool and dilute to 100 mL. Prepare immediately before use.

A.2.5 Sodium thiosulfate standard titration solution (0.100 mol/L): Prepare and calibrate according to the method in 4.6 of GB/T 601.

A.3 Preparation of formaldehyde standard solution

Pipette 7.0 mL of 36%~38% formaldehyde solution; add 0.5 mL of 1 mol/L sulfuric acid solution; make constant volume to 250 mL with water; and mix well. Pipette 10.0 mL of the above solution into a 100 mL volumetric flask; and add water to make constant volume to the

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