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National Food Safety Standard - Determination of Fluorine in Foods

食品安全国家标准 食品中氟的测定

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State Administration for Market Regulation.

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National Food Safety Standard - Determination of Fluorine in Foods

1 Scope

This Standard specifies the determination method for fluorine in foods.

The first method of this Standard is applicable to the determination of fluoride content in foods other than table salt and brick tea, and the second method is applicable to the determination of fluoride content in brick tea.

Method I - Ion Chromatography

2 Principle

The fluorine in the specimen is fixed with alkali, ashed at high temperature, and converted into the form of salt. Under neutral or weakly alkaline conditions, it is separated by ion exchange chromatography column, determined by electrical conductivity detector, and quantified by the external standard method.

3 Reagents and Materials

Unless otherwise specified, all reagents used in this Method are guaranteed reagents, the water is Grade-1 water specified in GB/T 6682, and all utensils used are made of plastic (polyethylene or polypropylene).

3.1 Reagents

3.1.1 Potassium hydroxide (KOH).

3.1.2 Sodium hydroxide (NaOH).

3.1.3 Sodium carbonate (Na_2CO_3).

3.1.4 Sodium bicarbonate ($NaHCO_3$).

3.2 Preparation of Reagents

3.2.1 Eluent (sodium carbonate 8.0 mmol/L and sodium bicarbonate 0.25 mmol/L): weigh-take 0.848 g of sodium carbonate and 0.021 g of sodium bicarbonate, dissolve them in an appropriate amount of water, and reach a constant volume of 1,000 mL.

3.2.2 Sodium hydroxide solution (100 g/L): weigh-take 10.0 g of sodium hydroxide, dissolve it in an appropriate amount of water, and reach a constant volume of 100 mL.

3.2.3 Saturated potassium hydroxide solution: weigh-take 110 g of potassium hydroxide, add 100 mL of water to dissolve it, and mix it well.

3.3 Standard Substance

Sodium fluoride (NaF, CAS No.: 7681-49-4): purity ≥ 99%, or fluorine standard solution certified by the state and awarded with a standard substance certificate.

3.4 Preparation of Standard Solutions

3.4.1 Fluorine standard stock solution (1,000 mg/L): accurately weigh-take 0.2210 g (accurate to 0.0001 g) of sodium fluoride dried to constant weight at 95 °C ~ 105 °C into a beaker, use water to dissolve it, transfer it to a 100 mL volumetric flask, add water to a constant volume, and mix it well. At 0 °C ~ 4 °C, store it sealed and away from light, and it shall remain valid for 6 months.

3.4.2 Fluorine standard intermediate solution (10.0 mg/L): accurately transfer-take 1.00 mL of fluorine standard stock solution (1,000 mg/L) into a 100 mL volumetric flask, add water to a constant volume and mix it well. At 0 °C ~ 4 °C, store it sealed and away from light, and it shall remain valid for 1 month.

3.4.3 Fluorine standard series working solutions: respectively and accurately transfer-take 0.000 mL, 0.0100 mL, 0.0250 mL, 0.0500 mL, 0.250 mL, 1.00 mL, 5.00 mL and 10.00 mL of fluorine standard intermediate solution (10.0 mg/L) into 50 mL volumetric flasks, add water to a constant volume and mix them well. The concentration of the fluorine standard series working solutions is respectively 0.000 mg/L, 0.00200 mg/L, 0.00500 mg/L, 0.0100 mg/L, 0.0500 mg/L, 0.200 mg/L, 1.00 mg/L and 2.00 mg/L. Prepare them right before use.

NOTE: the mass concentration range of fluorine in the standard series working solutions can be determined based on the sensitivity of the instrument and the actual fluorine content in the specimen.

3.5 Materials

3.5.1 Strong acid cation exchange resin: H type (2.5 mL).

3.5.2 Syringe: 2.5 mL or 5.0 mL.

3.5.3 0.45 μm aqueous membrane syringe filter.

3.5.4 Ion purification columns: Ag type (1 mL) and Na type (1 mL) or equivalent columns.

4 Instruments and Equipment

4.1 Ion chromatograph: equipped with electrical conductivity detector and suppressor.

4.2 Balance: the division value is respectively 0.0001 g and 0.001 g.

4.3 Nickel crucible (50 mL).

4.4 Adjustable electric heating plate or adjustable electric stove.

4.5 Muffle furnace.

4.6 High-speed pulverizer.

4.7 Homogenizer.

5 Analytical Steps

NOTE: all plastic utensils and nickel crucibles need to be soaked in sodium hydroxide solution (100 g/L) overnight, repeatedly rinsed with tap water, and finally rinsed with water.

5.1 Preparation of Specimens

5.1.1 Solid specimens

5.1.1.1 Dry specimens

Specimens with low moisture content, such as: grains and beans, shall be evenly pulverized by a high-speed pulverizer; uniform powdery specimens, such as: special medical formula foods and corn flour, shall be evenly mixed.

5.1.1.2 Fresh specimens

Specimens with high moisture content, such as: vegetables and fruits, shall be washed and dried when necessary, and the edible part shall be taken and homogenized; for specimens, such as: meat, aquatic products and eggs, the edible part shall be taken and homogenized.

5.1.2 Semi-solid or solid-liquid mixed specimens

If the specimen is a homogeneous system, it shall be thoroughly mixed and uniform; if the specimen is a non-homogeneous system, it shall be homogenized.

5.1.3 Liquid specimens

Thoroughly mix the specimen.

5.2 Specimen Pre-treatment

5.3.1.3 Flow rate: 1.2 mL/min.

5.3.1.4 Suppressor: electrochemical suppression.

5.3.1.5 Detection cell temperature: 35 °C.

5.3.1.6 Column oven temperature: 30 °C.

5.3.1.7 Injection volume: 25 μL.

5.3.2 Carbonate elution system

5.3.2.1 Chromatographic columns: analytical column (250 mm × 4 mm, particle size 5 μm) and guard column (50 mm × 4 mm, particle size 5 μm), with quaternary ammonium polystyrene / divinylbenzene copolymer resin as the filler or others with equivalent performance.

5.3.2.2 Reference mobile phase: 8.0 mmol/L Na_2CO_3 + 0.25 mmol/L $NaHCO_3$, isocratic elution.

5.3.2.3 Flow rate: 0.7 mL/min.

5.3.2.4 Detection cell temperature: 35 °C.

5.3.2.5 Column oven temperature: 45 °C.

5.3.2.6 Injection volume: 20 μL.

5.4 Preparation of Standard Curve

Respectively inject the standard series working solutions into the ion chromatograph, determine the corresponding fluoride ion peak height or peak area, and with the fluoride ion concentration of the standard working solution as the horizontal axis and the fluoride ion peak height or peak area as the vertical axis, draw a standard curve. The chromatograms of the fluorine standard solution are shown in Figure A.1 and Figure A.2 in Appendix A.

5.5 Determination of Specimen Solution

Inject the specimen solution into the ion chromatograph to obtain the corresponding fluoride ion peak height or peak area. In accordance with the standard curve, obtain the fluoride ion concentration in the specimen solution.

6 Expression of Analytical Results

The fluorine content in the specimen is calculated in accordance with Formula (1).

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

Where,

10.1.1 Sodium acetate ($CH_3COONa \bullet 3H_2O$).

10.1.2 Glacial acetic acid (CH_3COOH).

10.1.3 Sodium citrate ($Na_3C_6H_5O_7 \bullet 2H_2O$).

10.1.4 Perchloric acid ($HClO_4$).

10.1.5 Hydrochloric acid (HCl).

10.2 Preparation of Reagents

10.2.1 Sodium acetate solution (3 mol/L): weigh-take 204 g of sodium acetate and dissolve it in 300 mL of water. Add acetic acid (1 mol/L) to adjust the pH to 7.0 and add water to a constant volume of 500 mL.

10.2.2 Sodium citrate solution (0.75 mol/L): weigh-take 110 g of sodium citrate, dissolve it in 300 mL of water, add 14 mL of perchloric acid, and add water to a constant volume of 500 mL.

10.2.3 Total ionic strength adjustment buffer: mix equal amounts of sodium acetate solution (3 mol/L) and sodium citrate solution (0.75 mol/L). Prepare it right before use.

10.2.4 Hydrochloric acid solution (1 + 11): measure-take 10 mL of hydrochloric acid, add 110 mL of water and mix it well.

10.2.5 Acetic acid solution (1 mol/L): measure-take 3 mL of glacial acetic acid, dissolve it in an appropriate amount of water, and reach a constant volume of 50 mL.

10.3 Standard Substance

Same as 3.3.

10.4 Preparation of Standard Solutions

10.4.1 Fluoride standard stock solution (1,000 mg/L): see 3.4.1.

10.4.2 Fluorine standard intermediate solution (50.0 mg/L): accurately transfer-take 5.00 mL of fluorine standard stock solution (1,000 mg/L) into a 100 mL volumetric flask, add water to reach a constant volume and mix it well. At 0 °C ~4 °C, store it sealed and away from light, and it shall remain valid for 2 months.

10.4.3 Fluorine standard series working solutions: respectively and accurately transfer-take 0.200 mL, 0.500 mL, 1.00 mL, 2.00 mL, 5.00 mL, 8.00 mL and 10.0 mL of fluorine standard intermediate solution (50.0 mg/L) into 50 mL volumetric flasks, then, respectively add 25 mL of total ionic strength adjustment buffer and 10 mL of hydrochloric acid solution (1 + 11), add water to reach a constant volume and mix them well. The concentration of the fluorine standard series working solutions is respectively 0.200 mg/L, 0.500 mg/L, 1.00 mg/L, 2.00 mg/L, 5.00 mg/L, 8.00 mg/L and 10.0 mg/L. Prepare them right before use.

11 Instruments and Equipment

11.1 Electrode: fluoride ion selective electrode and saturated calomel electrode, or equivalent composite fluoride ion selective electrode.

11.2 Acidometer: with an accuracy of 0.01, or an ion meter or potentiometer with equivalent accuracy.

11.3 Magnetic stirrer.

11.4 Balance: the division value is respectively 0.0001 g and 0.001 g.

11.5 High-speed pulverizer.

11.6 Water bath.

11.7 Sieve mesh: particle size ≤ 425 μm (sieve opening ≥ 40 mesh).

12 Analytical Steps

12.1 Preparation of Specimens

Divide the brick tea into 4 ~ 8 portions, take specimens from different spots in each portion and evenly mix them. Take a sampling size of not lower than 20 g, use a high-speed pulverizer to evenly pulverize it to a particle size of less than 425 μm (equivalent to above 40 mesh).

12.2 Specimen Pre-treatment

Weigh-take 0.2 g ~ 0.5 g (accurate to 0.001 g) of the prepared specimen into a 50 mL stoppered conical flask, add 10 mL of water, thoroughly mix it, place it in a boiling water bath for 15 min, take out and cool to room temperature. In several times, transfer 25 mL of total ionic strength adjustment buffer to a 50 mL volumetric flask, add 10 mL of hydrochloric acid solution (1 + 11), add water to a constant volume and mix it well, and let it stand for later use. Meanwhile, perform a blank test.

12.3 Preparation of Standard Curve

Respectively connect the fluoride ion selective electrode and the saturated calomel electrode to the negative terminal and the positive terminal of the acidometer. Insert the electrode into a 50 mL beaker filled with water and place it on a magnetic stirrer for constant stirring. After the equilibrium potential is reached, the potential value can be determined. Successively determine the potential value of the standard working solutions in the sequence from low concentration to high concentration. With the logarithmic value of the fluoride ion concentration as the horizontal axis and the potential value as the vertical axis, draw a standard curve.

12.4 Determination of Specimen Solution

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