National Standards of People's Republic of China

GB 5009.16-2014

National Food Safety Standard

Determination of Tin in Foods

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Issued by National Health and Family Planning Commission
Ministry of Agriculture

Foreword

This standard will replace GB / T 5009.16-2003 "Determination of Tin in Foods".

Compared to GB/T 5009.16-2003, this standard maintains the following major changes:

- Name of the standard is modified into “National Standard for Food Safety - Determination of Tin in Foods”.
- Standard solution preparation is modified;
- Canned food specimen preparation method is increased;
- Description of the instrument measurement section is modified;
- Limit of quantification is added;
- Detection limit is modified; and
- Calculation equation is modified.

National Food Safety Standard

Determination of Tin in Foods

1. Scope

This standard specifies the determination of hydride of tin in foods by atomic fluorescence spectroscopy and phenylfuoron colorimetry.

This standard applies to determination of tin in canned solid foods, canned drinks, canned jams, and canned infant formula and supplementary foods.

Method I Hydride Generation Atomic Fluorescence Spectroscopy

2. Principle

Tin hydride (SnH_4) will be generated under the effects of sodium borohydride after the specimen digests and will be carried into the atomizer by the carrier gas for atomization. Illuminated by tin hollow cathode lamp, the tin atom in ground state will be activated to high-energy state and fluorescence of characteristic wavelengths will be emitted when such tin atoms are deactivated and return to the ground state. The fluorescence intensity of tin atoms is proportional to its tin content. Compare the limit of quantification to that of the standard series solution.

3. Reagents and materials

Note: except otherwise stated, reagents applied herein shall be the analytical pure reagents, and the water be Class II water specified in GB/T6682.

3.1 Reagents

3.1.1 Sulfuric acid (H_2SO_4): guaranteed pure reagent.

3.1.2 Nitric acid (HNO_3): guaranteed pure reagent.

3.1.3 Perchloric acid ($HClO_4$): guaranteed pure reagent.

3.1.4 Thiourea (CH_4N_2S).

3.1.5 Ascorbic acid ($C_6H_8O_6$).

3.1.6 Sodium borohydride ($NaBH_4$).

3.1.7 Sodium hydroxide (NaOH).

3.2 Reagent compounding

3.2.1 Nitric acid - perchloric acid mixture solution (4 + 1): measure and take 400 ml and 100 ml nitric acid perchlorate and mix them well.

3.2.2 Sulfuric acid solution (1+9): measure and take 100 ml sulfuric acid and pour it into 900 ml of water, and mix them well.

3.2.3 Thiourea (150 g/l) + a scorbic acid (150 g/l) mixture solution: measure and take respectively 15.0 g thiourea and 15.0 g ascorbic acid and dissolve them in water, dilute them to 100 ml, and place them into a brown bottle for dark preservation or extemporaneous preparation.

3.2.4 Sodium hydroxide solution (5.0 g/l): weigh and take 5.0 g of sodium hydroxide and dissolve it in 1,000 ml of water.

3.2.5 Sodium borohydride solution (7.0 g/l): weigh and take 7.0 g of sodium borohydride, and dissolve it in sodium hydroxide solution for extemporaneous preparation.

3.3 Standard products

Reference material Tin metal (Sn), reference material with a purity of 99.99% or reference material certified and granted by the State with reference material certificate.

3.4 Formulation of standard solution

3.4.1 Tin standard solution (1.0 mg/ml): weigh and take 0.1 g (accurate to 0.000 1 g) Tin metal reference material; place it into a small beaker; add 10.0 ml of sulfuric acid and cover it by pan; heat it up till tin is fully dissoved; remove the pan; continue the heating till thick white smoke occurs; cool it down and slowly add 50 ml of water; transfer it into a 100 ml flask; wash the beaker by sulfuric acid solution (1 +9) repeatedly; pour solution into volumetric flask and dilute it to the mark; mix it well.

3.4.2 Standard tin use solution (1.0 μg/ml): imbibe and take 1.0 ml tin standard solution and transfer it into a 100 ml volumetric flask; dilute it with sulfuric acid solution (l +9) to the mark. The concentration of this solution is 10.0 μg/ml. Imbibe and take 10.0 ml of this solution and transfer it in 100 ml flask, and dilute it with sulfuric acid solution (1 + 9) to the mark.

4. Equipment and facilities

4.1 Atomic fluorescence spectrometer.

4.2 Electric hot plate.

4.3 Electronic balance: sensor volume of 0.1 mg and 1mg.

5. Analytical procedures

5.1 Specimen preparation

For canned foods, weigh and take edible contents of foods and make them into homogenized or even powder.

5.2 Specimen digestion

5.2.1 Weigh and take 1.0 g ~ 5.0 g specimen and transfer it into the conical flask; add 20.0 ml nitric acid - perchloric acid mixed solution (4 + 1); add 1.0 ml of sulfuric acid and 3 glass beads, and let it stand overnight. On the following day, place it onto electric hot plate to heat up and dissolve it; if the acid is too small, it is ok to supplement an appropriate amount of nitric acid; disgest continuously till white smoke rises; take it down and cool it down when the liquid volume is close to 1 ml; transfer by water the digested specimen into the 50 ml volumetric flask, dilute it by water to mark; shake it up for use. At the same time, conduct blank test (if tin content in the specimen solution goes beyond the range indicated by the standard curve, then dilute it with

water and supplement sulfuric acid, so that the concentration of the sulfuric acid solution with constant volume will be identical with that of the standard series solution).

5.2.2 Take 10.0 ml of the specimen diluted to mark in 5.2.1 and transfer it into 25 ml colorimetric tube; add 3.0 ml of sulfuric acid solution (l + 9); add 2.0 ml of thiourea (150 g/l) + ascorbic acid (l50 g/l); mix them well and then dilute it with water to 25 ml; and shake it up for use.

5.3 Reference conditions for equipment

Reference conditions for atomic fluorescence spectrometer analysis:

- Negative high voltage: 380 V;
- Lamp current: 70 mA;
- Atomization temperature: 850℃
- Furnace height: 10 mm;
- Shrouding gas flowrate:1, 200 ml/min;
- Carrier gas flow rate: 500 ml/ min;
- Measurement mode: standard curve method;
- Reading mode: peak area;
- Delay time:1s;
- Reading time:15s;
- Dosing time: 8s;
- Injection volume: 2.0 ml.

5.4 Formulation of standard series solution

Standard curve: respectively imbibe standard tin use solution 0.00 ml, 0.50 ml, 2.00 ml, 3.00 ml, 4.00 ml, 5.00 ml and transfer them to 25 ml colorimetric tubes; add sulfuric acid solution (1 + 9) 5.00 ml, 4.50 ml, 3.00 ml, 2.00 ml, 1.00 ml, and 0.00 ml into it; add 2.0 ml thiourea (150 g/l) + ascorbic acid (150 g/l) mixture solution; dilute it with water to 25 ml. The concentration of the standard series solution: 0ng / ml, 20 ng / ml, 80 ng / ml, l20 ng / ml, 160 ng / ml and 200 ng / ml respectively.

5.5 Instrument determination

Set up the optimal measurement conditions of instrument as per 5.3 and set the appropriate parameter points as per model of instrument and the workstations applied; ignite and preheat up the instrument; determine the standard curve and specimen solution after it is preheated for 30 minutes.

6. Statement of analysis result

Tin content in the specimens is to be calculated as per Formula (1):

$$X = \frac{(c_1 - c_0) \times V_1 \times V_3}{m \times V_2 \times 1\,000} \qquad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1)$$

In the formula:

X- tin content in specimen, in milligram per kilogram (mg/kg);

C_1- determined concentration of digested specimen solution, in nanogram per milliliter (ng / ml);

C_0- concentration of blank digestion solution of the specimen, in nanogram per milliliter (ng / ml);

V_1- constant volume of specimen digestion solution, in milliliter (ml);

V_3- constant volume of solution for purpose of measurement, in milliliter (ml);

m- specimen mass, in gram (g);

V_2- volume of specimen digestion solution taken for purpose of determination, in milliliter (ml);

1000- conversion factor.

When the calculated result is smaler than 10 mg/kg, the hundredth behind the decimal shall be kept; when the calculated result is bigger than less than 10 mg/kg, a two-digit valid number shall be retained.

7. Precision

Absolute difference between two independent determination results obtained under the repeatability conditions shall not exceed 10% of their arithmetic mean.

8. Others

When the specimen volume is 1.0g, the limit of quantification under this method shall be 2.5 mg/kg.

Method II Phenylfluorone Colorimetry

9. Principle

After the specimen is digested, tetravalent tin ions and phenylfluorone form sparingly soluble orange-red complex in weak acid solution, and compares limit of quantification to that of the standard series solution in the presence of protective colloid.

10. Reagents and materials

Note: except otherwise stated, the reagents applied under this method are analytical pure reagents and water is Class III water specified under GB / T6682.

10.1 Reagents

10.1.1 Tartaric acid ($C_4H_4O_6H_2$).

10.1.2 Ascorbic acid ($C_6H_8O_6$)

10.1.3 Phenolphthalein ($C_{20}H_{14}O_4$).

10.1.4 Ammonia (NH_4OH).

10.1.5 Sulfuric acid (H_2SO_4).

10.1.6 Ethanol (C_2H_5OH).

10.1.7 Methanol (CH_3OH).

10.1.8 Phenylfluorone ($C_{19}H_{12}O_5$).

10.1.9 Animal glue (Gelatin).

10.2 Reagent compounding

10.2.1 Tartaric acid solution (100 g/l): weigh and take 100 g of tartaric acid and dissolve it into 1l of water.

10.2.2 Ascorbic acid solution (10.0 g/l): weigh and take 10.0 g of ascorbic acid and dissolve it into 1l of water for purpose of extemporaneous preparation.

10.2.3 Animal glue solution (5.0 g/l): weigh and take 5.0 g of animal glue and dissolve it into 1l of water for purpose of extemporaneous preparation.

10.2.4 Ammonia solution (1+1): weigh and take 100 ml of ammonia water and pour it into 100 ml of water, and mix them well.

10.2.5 Sulfuric acid solution (1+9): weigh and take 10 ml of sulfuric acid, mix and pour it slowly into 90 ml of water and shake them up.

10.2.6 Phenylfluorone solution (0.1 g/l): weigh and take 0.01g (accurate to 0.001 g) of phenylfluorone, add an iota of methanol and a few drops of sulfuric acid to dissolve it, with the methanol being diluted to 100 ml.

10.2.7 Phenolphthalein indicator solution (10.0 g/l): weigh and take 1.0 g of phenolphthalein and dissolve it by ethanol to 100 ml.

10.3 Standard products

Refernence material of Tin metal (Sn), refernence material with a purity of 99.99% or refernence material certified and granted by the State with refernence material certificate.

10.4 Formulation of standard solution

10.4.1 Tin standard solution (1.0 mg/ml): weigh and take 0.1 g (accurate to 0.0001 g) of Tin metal; transfer it into a small beaker; add 10 ml of sulfuric acid; cover it with a pan; heat it up till the tin is completely dissolved; remove the pan; continue to heat until thick white smoke occurs; cool it down slowly; add 50 ml of water and transfer it into 100 ml of volumetric flask; wash the beaker by sulfuric acid solution (1 + 9) repeatedly; pour the wash lotion into flask; dilute it to mark and mix it well.

10.4.2 Standard use solution of tin: imbibe and take 10.0 ml of tin standard solution; transfer it into a 100 ml volumetric flask; dilute it by sulfuric acid solution (1 + 9) to the mark and mix it well; dilute it again till each milliliter is equivalent to 10.0 μg tin.

11. Equipment and facilities

11.1 Spectrophotometer.

11.2 Electronic balance: a sensor volume of 0.1 mg and 1 mg.

12. Analytical procedures

12.1 Specimen preparation

12.1.1 Specimen is digested, the same as that described in 5.2.1.

12.1.2 Imbibe and take 1.00 ml ~ 5.00 ml specimen digestion solution and the same amount of reagent blank solution; transfer them into 25 ml colorimetric tube, respectively; add 0.5ml of tartaric acid solution (100 g/l) and 1 drop of phenolphthalein indicator solution (100 g/l) into specimen digestion solution and reagent blank solution and mix it well; add ammonia solution (1 + 1) to each of them till it becomes pink; add 3.0 ml of sulfuric acid solution (1 + 1), 1.0 ml of animal glue solution (5.0 g/l) and 2.5 ml of ascorbic acid solution (l 0.0 g/l); add water till the volume is 25 ml and mix it well; then add 2.0 ml of phenylfuoron solution (0.1 g/l) and mix it well; stand for 1h and measure.

12.2 Standard curve mapping

Imbibe and take 0.00 ml, 0.20 ml, 0.40 ml, 0.60 ml, 0.80 ml and 1.00 ml of tin standard solution (equivalent to 0.00 μg, 2.00 μg, 4.00 μg, 6.00 μg, 8.00 μg, and 10.00 μg of tin); transfer it into 25 ml colorimetric tube; add 0.5 ml of tartaric acid solution (100 g/l) and 1 drop of phenolphthalein indicator solution (10.0 g/l) into each and mix it well; add ammonia solution (1 + 1) into each till it becomes pink; add 3.0 ml of sulfuric acid solution (1 + 9), 1.0 ml of animal gelatin solution (5.0 g/l) and 2.5 ml of ascorbic acid solution (10.0 g/l); add water then till the volume reaches 25 ml and mix it well; then add 2.0 ml of phenylfuoron solution, mix it well and allow it to stand for 1h; and measure then.

Use 2 cm cuvette to measure absorbance at 490 nm of wavelength; after zero tube absorbance is subtracted from all standard points, take concentration of the standard series solution as the horizontal axis and absorbance as vertical axis to map the standard curve or calculate the linear regression equation.

12.3 Determination of specimen solution

Use 2 cm cuvette to adjust zero point per standard series solution zero tube; measure absorbance of reagent blank solution and specimen solution respectively at 490 nm of wavelength; compare the resulting absorbance to standard curve or substitute it into regression equation to calculate the content.

13. Statement of analysis result

Tin content in the specimen shall be calculated as per Formula (2):

$$X = \frac{(m_1 - m_2) \times V_1}{m_3 \times V_2} \qquad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (2)$$

In the formula:

X- tin content in the specimen, in milligram per kilogram or milligram per liter (mg/kg or mg/l);

m_1- tin mass in specimen digestion solution for purpose of determination, in microgram (μg);

m_2- tin mass in reagent blank solution, in microgram;

V_1- constant volume of specimen digestion solution, in milliliter (ml);

m_3- specimen mass, in gram (g);

V_2- volume of specimen digestion solution for purpose of determination, in milliliter (ml).

Calculation result shall retain two-digit valid number.

14. Precision

Absolute difference between two independent determination results obtained under the repeatability conditions shall not exceed 10% of their arithmetic mean.

15. Others

When 1.0g of such specimen and 5.0 ml of digestion solution are taken for determination, the quantitative limit of this method shall be 20 mg/kg.