GB

NATIONAL STANDARD OF THE

PEOPLE'S REPUBLIC OF CHINA

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National food safety standard - Determination of iodine in foods

食品安全国家标准 食品中碘的测定

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National food safety standard - Determination of iodine in foods

1 Scope

This standard specifies the determination method of iodine content in food.

The method 1 Inductively coupled plasma mass spectrometry is suitable for the determination of iodine in food.

The method 2 Redox titration is suitable for the determination of iodine in algae and its products.

The method 3 Arsenic-cerium catalytic spectrophotometry is suitable for the determination of iodine in food, vegetables, fruits, beans and their products, milk and their products, meat, fish and eggs.

The method 4 Gas chromatography is applicable to the determination of nutritional fortifier iodine in infant formula foods and dairy products (except infant formula foods for special medical purposes and formula foods for special medical purposes).

Method 1 -- Inductively coupled plasma mass spectrometry (ICP-MS)

2 Principle

The iodine in the specimen is extracted by tetramethylammonium hydroxide solution and measured by inductively coupled plasma mass spectrometer. It is qualitatively determined by the specific mass of iodine element 127 (mass-to-charge ratio, m/z), the mass spectrometry signal intensity ratio between iodine element and internal standard element which is proportional to the concentration of the iodine element is used for quantification, to determine the iodine content in the specimen.

standard intermediate solution. Use diluent to make its volume reach to 100 mL.

3.4.4 Iodine series standard solution: Respectively, pipette appropriate volume of iodine standard solution. Use the diluent to make a series standard solution which has the concentration of 0 μg/L, 0.100 μg/L, 1.00 μg/L, 5.00 μg/L,10.0 μg/L, 15.0 μg/L, 20.0 μg/L. It may also adjust the concentration range of the series standard solution according to the iodine concentration in the sample solution.

3.4.5 Internal standard element standard solution (1000 mg/L): Tellurium (Te), indium (In), rhodium (Rh), rhenium (Re) and any other single-element or multi-element internal standard stock solution.

3.4.6 Internal standard solution: First use water to dilute the internal standard element standard solution 10 times or 100 times. Then take an appropriate amount of the solution and use the diluent to prepare an internal standard solution of appropriate concentration. The internal standard solution can be added manually and quantitatively to the standard series and sample solutions; it can also be added online by the instrument. After the internal standard is mixed with the sample solution, the reference concentration of the internal standard is about 10 μg/L ~ 100 μg/L.

Note: For samples with complex matrices, an appropriate amount of isopropanol can be added to the internal standard, to make the volume fraction 1% ~ 2%.

4 Instruments and equipment

4.1 Inductively coupled plasma mass spectrometer (ICP-MS).

4.2 Analytical balance: Sensitivity is 0.1 mg and 1 mg.

4.3 Constant temperature drying oven or constant temperature water bath shaker.

4.4 Sample crushing equipment: Homogenizer, high-speed crusher.

4.5 Centrifuge: The speed is greater than 3000 r/min.

4.6 Vortex mixer.

5 Analytical procedures

5.1 Preparation of specimen

5.1.1 Solid samples

cell gas He gas flow rate 4 mL/min ~ 5 mL/min; when each sample is measured, the flushing time of the sample injection system is greater than 60 s.

5.3.2 Measurement reference conditions

After the tuning instrument meets the measurement requirements, edit the measurement method and select the iodine isotope (^{127}I) and the internal standard tellurium isotope (^{125}Te, ^{130}Te) or ^{103}Rh or ^{115}In or ^{185}Re.

Note: If the ICP-MS instrument changes from an acidic injection system to an alkaline system, it is recommended to replace all injection pump tubes and clean the injection system with 0.5% TMAH solution for 1 h ~ 2 h, until the ^{127}I signal is stable.

5.4 Preparation of standard curve

Inject iodine standard solution into ICP-MS. Measure the signal response value of iodine element and internal standard element. Take the mass concentration of iodine element as the abscissa, the ratio of the response signal value of iodine element and the selected internal standard element as the ordinate, to draw standard curve.

5.5 Measurement of sample solution

Inject the blank and sample solution into the inductively coupled plasma mass spectrometer, respectively. Measure the signal response values of the iodine element and the selected internal standard element. Calculate the ratio of the response signal value of the iodine element and the selected internal standard element. Obtain the mass concentration of iodine in the liquid to be measured according to the standard curve.

6 Expression of analysis results

The iodine content in the specimen is calculated according to formula (1):

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

Where:

X - The content of iodine in the specimen, in milligrams per kilogram (mg/kg);

ρ - The mass concentration of iodine element in the sample solution, in micrograms per liter (μg/L);

ρ_0 - The mass concentration of iodine element in the sample blank solution, in micrograms per liter (μg/L);

10 Reagents and materials

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

10.1 Reagents

10.1.1 Anhydrous sodium carbonate (Na_2CO_3).

10.1.2 Liquid bromine (Br_2).

10.1.3 Sulfuric acid (H_2SO_4).

10.1.4 Sodium formate ($CHNaO_2$).

10.1.5 Sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$).

10.1.6 Potassium iodide (KI): Reference substance.

10.1.7 Methyl orange.

10.1.8 Soluble starch.

10.2 Reagent preparation

10.2.1 Sodium carbonate solution (50 g/L): Weigh 5 g of anhydrous sodium carbonate. Use water to dissolve it and make its volume reach to 100 mL.

10.2.2 Saturated bromine water: Measure 5 mL of liquid bromine and place it in a brown glass bottle with a stopper which is coated with Vaseline. Add 100 mL of water. Shake it sufficiently to make it a saturated solution (a small amount of liquid bromine is left at the bottom of the solution; the operation shall be done in ventilation hood).

10.2.3 Sulfuric acid solution (3 mol/L): Measure 180 mL of sulfuric acid and slowly pour it into a beaker containing 700 mL of water. Keep stirring. Cool to room temperature. Use water to dilute it to 1000 mL. Mix well.

10.2.4 Sulfuric acid solution (1 mol/L): Measure 57 mL of sulfuric acid and slowly pour it into a beaker containing 700 mL of water. Keep stirring. Cool to room temperature. Use water to dilute it to 1000 mL. Mix well.

10.2.5 Potassium iodide solution (150 g/L): Weigh 15.0 g of potassium iodide. Use water to dissolve and dilute it to 100 mL. Store it in a brown bottle. Prepare it before use.

10.2.6 Sodium formate solution (200 g/L): Weigh 20.0 g of sodium formate. Use

11.9 Brown acid burette: 25 mL; the minimum scale is 0.1 mL.

11.10 Micro acid burette: 1 mL or 5 mL; the minimum scale is 0.01 mL.

12 Analytical procedures

12.1 Specimen preparation

Same as 5.1.

12.2 Specimen analysis

12.2.1 Weigh 2 g ~ 5 g of the specimen (accurate to 0.01 g). Place it in a 50 mL porcelain crucible. Add 5 mL ~ 10 mL of sodium carbonate solution to fully infiltrate the specimen. Let it stand for 5 min. Place it in a 101 °C ~ 105 °C constant temperature drying oven to dry it. Take it out.

12.2.2 Heat and carbonize the dried specimen until it is smoke-free. Place it in a muffle furnace at 550 °C ± 25 °C for 40 minutes. Cool to room temperature. Take it out. Add a small amount of water to grind it. Transfer the solution and residue into a 250 mL beaker. Use water to rinse the crucible several times and merge it into the beaker. The total volume of solution in the beaker is about 150 mL ~ 200 mL. After boiling for 5 min, use filter paper to filter it into a 250 mL iodine flask while it is hot, to prepare for use.

12.2.3 Add 2 ~ 3 drops of methyl orange solution to the iodine measuring flask. Use 1 mol/L sulfuric acid solution to adjust it o red. Add 5 mL of saturated bromine water. Heat and boil until the yellow color disappears. After cooling slightly, add 5 mL of sodium formate solution. Heat to boil for 2 minutes. Use water bath to cool to below 30 °C. Then add 5 mL of 3 mol/L sulfuric acid solution and 5 mL of potassium iodide solution. Cover the bottle cap and place it in the dark for 10 minutes. Use sodium thiosulfate standard solution to titrate the solution until it becomes light yellow. Add 1 mL of starch solution. Continue titration until the blue color just disappears. At the same time, do a blank test and record the consumed sodium thiosulfate standard solution volume.

13 Expression of analysis results

The iodine content in the specimen is calculated according to formula (2):

$$X = \frac{(V - V_0) \times c \times 21.15 \times f}{m} \times 1\,000 \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (2)$$

Where:

$$H_3AsO_3 + 2Ce^{4+} + H_2O \rightarrow H_3AsO_4 + 2Ce^{3+} + 2H^+$$

In the reaction system, Ce^{4+} is yellow and Ce^{3+} is colorless. The absorbance value of the remaining Ce^{4+} is measured by a spectrophotometer. The iodine content is linearly related to the logarithm of the absorbance value, to calculate the total iodine content in the food.

17 Reagents and materials

Unless otherwise specified, the reagents used in this method are analytically pure; the water is grade-2 water as specified in GB/T 6682.

17.1 Reagent

17.1.1 Anhydrous potassium carbonate (K_2CO_3).

17.1.2 Zinc sulfate ($ZnSO_4 \cdot 7H_2O$).

17.1.3 Potassium chlorate ($KClO_3$).

17.1.4 Sulfuric acid (H_2SO_4): Premium grade pure.

17.1.5 Sodium hydroxide (NaOH).

17.1.6 Arsenic trioxide (As_2O_3).

17.1.7 Sodium Chloride (NaCl): Premium grade pure.

17.1.8 Ammonium cerium sulfate [($Ce(NH_4)_4(SO_4)_4 \cdot 2H_2O$) or ($Ce(NH_4)_4 (SO_4)_4 \cdot 4H_2O$)].

17.1.9 Potassium iodide (KI): Reference substance.

17.2 Reagent preparation

17.2.1 Potassium carbonate-sodium chloride mixed solution: Weigh 30 g of anhydrous potassium carbonate and 5 g of sodium chloride. Dissolve them in 100 mL of water. It can be stored for 6 months at room temperature.

17.2.2 Zinc sulfate-potassium chlorate mixed solution: Weigh 5 g of potassium chlorate in a beaker. Add 100 mL of water. Heat to dissolve. Add 10 g of zinc sulfate. Stir to dissolve. It can be stored for 6 months at room temperature.

17.2.3 Sulfuric acid solution (2.5 mol/L): Measure 140 mL of sulfuric acid and slowly pour it into a beaker containing 700 mL of water. Stir continuously. Cool to room temperature. Use water to dilute to 1000 mL. Mix well.

17.2.4 Arsenious acid solution (0.054 mol/L): Weigh 5.3 g of arsenic trioxide,

18.5 Constant temperature drying oven.

18.6 Adjustable electric furnace: 1000 W.

18.7 Vortex mixer.

18.8 Analytical balance: Sensitivity is 1 mg and 0.1 mg.

18.9 Stopwatch timer

19 Analytical procedures

19.1 Specimen preparation

Same as 5.1.

19.2 Ashing of specimen

Accurately pipette 0.5 mL of iodine standard application series solutions (with iodine content of 0 ng, 25 ng, 50 ng, 100 ng, 150 ng, 200 ng, 250 ng); weigh 0.3 g ~ 1.0 g (accurate to 0.001 g) of specimen in a porcelain crucible. Add 1 mL ~ 2 mL of water to the solid specimen (liquid sample, homogenized sample and standard solution do not need to add water). Respectively add 1 mL of potassium carbonate-sodium chloride mixed solution and 1 mL of zinc sulfate-potassium chlorate mixed solution and stir well. Iodine standard series and specimens are placed in a constant temperature drying oven at 103 °C ± 2 °C and dried for 3 hours. Then the dried specimens are carbonized on an adjustable electric furnace for about 30 min in a fume hood (the iodine standard series do not need to be carbonized). During carbonizing, cover the porcelain crucible but leave a gap, until the specimen no longer smokes. Then put the iodine standard series and the carbonized specimen in the muffle furnace, to ash it at 600 °C for 4 hours. After the furnace temperature drops to room temperature, take it out. The ashed specimen shall have uniform white or light gray-white.

19.3 Preparation of standard curve and determination of sample solution

Add 8 mL of water to the crucible after ashing. Let it stand for 1 hour to fully infiltrate the ash sintered on the crucible. Stir to dissolve salt substances. Then stand for at least 1 hour to completely precipitate the ash (the standing time shall not exceed 4 hours). Pipette 2.0 mL of the supernatant into a test tube (**Caution**: Do not pipette the sediment). Iodine standard series solutions are arranged in order from high concentration to low concentration. Add 1.5 mL of arsenous acid solution to each tube. Use a vortex mixer to mix it thoroughly, to release the gas. Then place it in a 30 °C ± 0.2 °C constant temperature water bath for 15 min.

is less than or equal to 1 mg/kg and greater than 0.1 mg/kg, the absolute difference between two independent determination results obtained under repeatability conditions shall not exceed 15% of the arithmetic mean. When it is less than or equal to 0.1 mg/kg, the absolute difference between two independent determination results obtained under repeatability conditions must not exceed 20% of the arithmetic mean.

22 Others

When calculated with a sampling volume of 0.3 g, the method quantification limit is 0.1 mg/kg.

Method 4 -- Gas chromatography

23 Principles

The iodine in the specimen reacts with methyl ethyl ketone under sulfuric acid conditions to generate methyl ethyl ketone and iodine derivatives, which are separated by gas chromatography, detected by an electron capture detector, quantified by an external standard method.

24 Reagents and materials

Unless otherwise stated, all reagents in this method are of analytical grade. The water is the grade-1 water as specified in GB/T 6682 or the high-purity water used in instrument analysis as specified in GB/T 33087-2016.

24.1 Reagent

24.1.1 Amylase: Enzyme activity ≥ 1.5 U/mg.

24.1.2 Potassium iodide (KI) or potassium iodate (KIO_3): Reference substance.

24.1.3 Hydrogen peroxide (H_2O_2).

24.1.4 Potassium ferrocyanide [$K_4Fe(CN)_6 \cdot 3H_2O$].

24.1.5 Zinc acetate [$Zn(CH_3COO)_2$].

24.1.6 Butanone (C_4H_8O): Chromatographically pure.

24.1.7 Sulfuric acid (H_2SO_4): Supreme grade pure.

26.1.1 According to the identification of the ingredient list in the product label, the specimen containing no starch

Weigh 5 g of uniformly mixed solid specimen or 20 g of liquid specimen (accurate to 0.01 g) in a 150 mL conical flask. Use about 25 mL of hot water at about 40 °C to dissolve the solid specimen.

26.1.2 According to the identification of the ingredient list in the product label, the specimen containing starch

Weigh 5 g of uniformly mixed solid specimen or 20 g of liquid specimen (accurate to 0.01 g) into a 150 ml conical flask. Add 0.2 g of amylase. Use 25 ml of hot water at about 40 °C to dissolve the solid specimen. Enzymatically hydrolyze in a constant temperature drying oven at 60 °C for 30 minutes. Take it out to cool.

26.2 Preparation of specimen test solution

26.2.1 Precipitation

Transfer the above-treated sample solution into a 100 mL volumetric flask. Add 5 mL of potassium ferrocyanide solution and 5 mL of zinc acetate solution. Use water to make its volume reach to the mark. Shake well and let stand for 10 minutes. Filter it. Pipette 10 mL of the filtrate into a 100 mL separatory funnel. Add 10 mL of water.

26.2.2 Derivation and extraction

Add 0.7 mL of sulfuric acid, 0.5 mL of methyl ethyl ketone, 2.0 mL of hydrogen peroxide solution to the separatory funnel. Mix well and keep it at room temperature for 20 minutes. Add 20 mL of n-hexane. Shake and extract for 2 minutes. After standing for stratification, transfer the aqueous phase into another separatory funnel. Perform the second extraction. Combine the organic phases and use water to wash it for 2 ~ 3 times. After filtering and dehydrating through anhydrous sodium sulfate, transfer it into a 50 mL volumetric flask. Use n-hexane to make the volume reach to the mark. This is the sample measurement solution. Perform the reagent blank at the same time.

26.3 Preparation of working solution for determination of iodine standard

Pipette 1.0 mL, 2.0 mL, 4.0 mL, 8.0 mL, 12.0 mL of iodine standard working solution, which is equivalent to 1.0 μg, 2.0 μg, 4.0 μg, 8.0 μg, 12.0 μg of iodine. Other analysis steps are processed simultaneously with the specimen.

26.4 Instrument reference conditions

The instrument reference conditions are as follows:

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