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National Food Safety Standard - Determination of Total Mercury and Organic-mercury in Food

食品安全国家标准

食品中总汞及有机汞的测定

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National Food Safety Standard - Determination of Total Mercury and Organic-mercury in Food

1 Scope

Part 1 of this Standard specifies the methods for the determination of total mercury in food.

Part 1 of this Standard is applicable to the determination of total mercury in food.

Part 2 of this Standard specifies the methods for the determination of methyl mercury in food.

Part 2 of this Standard is applicable to the determination of methyl mercury in aquatic animals and their products, as well as rice and edible fungi.

Part 1 - Determination of Total Mercury in Food

Method 1 - Atomic Fluorescence Spectrometry

2 Principle

After the specimen is heated and digested by acid, in the acidic medium, the mercury in the specimen is reduced to atomic-state mercury by potassium borohydride or sodium borohydride, which is brought into the atomizer by the carrier gas (argon). Under the irradiation of mercury hollow cathode lamp, the ground-state mercury atoms are excited to a high-energy state. When they return from the high-energy state to the ground-state, they emit fluorescence with a characteristic wavelength. The fluorescence intensity is directly proportional to the mercury content, which is quantified by the external standard method.

3 Reagents and Materials

Unless it is otherwise specified, the reagents used in this Method are of top-grade purity, and the water is Grade-1 water specified in GB/T 6682.

3.1 Reagents

3.1.1 Nitric acid (HNO_3).

3.1.2 Hydrogen peroxide (H_2O_2).

3.1.3 Sulfuric acid (H_2SO_4).

3.1.4 Potassium hydroxide (KOH).

3.1.5 Potassium borohydride (KBH_4): analytically pure.

3.1.6 Potassium dichromate ($K_2Cr_2O_7$).

3.2 Preparation of Reagents

3.2.1 Nitric acid solution (1 + 9): measure-take 50 mL of nitric acid; slowly add it to 450 mL of water; mix it up.

3.2.2 Nitric acid solution (5 + 95): measure-take 50 mL of nitric acid; slowly add it to 950 mL of water; mix it up.

3.2.3 Potassium hydroxide solution (5 g/L): weigh-take 5.0 g of potassium hydroxide; use water to dissolve it and dilute to 1,000 mL; mix it up.

3.2.4 Potassium borohydride solution (5 g/L): weigh-take 5.0 g of potassium borohydride; use potassium hydroxide solution (5 g/L) to dissolve it and dilute to 1,000 mL; mix it up. Prepare it right before use.

3.2.5 Nitric acid solution of potassium dichromate (0.5 g/L): weigh-take 0.5 g of potassium dichromate; use nitric acid solution (5 + 95) to dissolve it and dilute to 1,000 mL; mix it up.

NOTE: this method may also use sodium borohydride as a reducing agent: weigh-take 3.5 g of sodium borohydride; use sodium hydroxide solution (3.5 g/L) to dissolve it and reach a constant volume of 1,000 mL; mix it up. Prepare it right before use.

3.3 Standard Substance

Mercury chloride ($HgCl_2$, CAS No.: 7487-94-7): purity ≥ 99%.

3.4 Preparation of Standard Solutions

3.4.1 Standard stock solution of mercury (1,000 mg/L): accurately weigh-take 0.1354 g of mercury chloride; use nitric acid solution of potassium dichromate (0.5 g/L) to dissolve it and transfer to a 100 mL volumetric flask; dilute it to a constant volume to the scale; mix it up. Store it at 2 °C ~ 8 °C in the refrigerator; keep away from light; it shall remain valid for 2 years. Or a mercury standard solution certified by the country and awarded with a standard substance certificate.

3.4.2 Standard intermediate solution of mercury (10.0 mg/L): accurately draw 1.00 mL

a clean polyethylene bottle; seal and store it for later use.

5.1.2 In terms of fresh samples, such as: vegetables, fruits, fish, meat and eggs, wash and dry them; take the edible part and homogenize it; put it into a clean polyethylene bottle; seal it; store it at 2 °C ~ 8 °C in the refrigerator for later use.

5.1.3 In terms of milk and dairy products, after homogenizing it, put it into a clean polyethylene bottle; seal it; store it at 2 °C ~ 8 °C in the refrigerator for later use.

5.2 Digestion of Specimens

5.2.1 Method of microwave digestion

Weigh-take 0.2 g ~ 0.5 g of solid specimen (accurate to 0.001 g; for samples with relatively more water content, the sampling amount may be properly increased to 0.8 g), or accurately weigh-take 1.0 g ~ 3.0 g of liquid specimen (accurate to 0.001 g). For samples that are difficult to digest, for example, vegetable oils, weigh-take 0.2 g ~ 0.5 g (accurate to 0.001 g). Place it in a digestion tank; add 5 mL ~ 8 mL of nitric acid; put on the lid and let it stand for 1 h. For samples that are difficult to digest, add 0.5 mL ~ 1 mL of hydrogen peroxide; tightly screw the lid; in accordance with the standard operating procedures of the microwave digestion apparatus (please refer to Table A.1 in Appendix A for the reference conditions of microwave digestion), conduct the digestion. After cooling it down, take it out; slowly open the lid of the tank to exhaust air; use a small amount of water to rinse the inner lid. Place the digestion tank on a temperature-controllable electric heating plate or in the ultrasonic water bath; at 80 °C, heat it up or ultrasonically degas for 3 min ~ 6 min to drive off the brown gas. Take out the digestion inner tank; transfer the digestion solution to a 25 mL volumetric flask. Use a small amount of water to rinse the inner tank in 3 times; combine the washing liquid in a volumetric flask and reach a constant volume to the scale; mix it up for later use. Meanwhile, conduct a blank test.

5.2.2 Method of pressure tank digestion

Weigh-take 0.2 g ~ 1.0 g of solid specimen (accurate to 0.001 g; for samples with relatively more water content, the sampling amount may be properly increased to 2 g), or accurately weigh-take 1.0 g ~ 5.0 g of liquid specimen (accurate to 0.001 g). For samples that are difficult to digest, for example, vegetable oils, weigh-take 0.2 g ~ 0.5 g (accurate to 0.001 g). Place it in a digestion tank; add 5 mL of nitric acid; let it stand for 1 h or overnight. Put on the inner lid; tightly screw the stainless steel enclosure; put it in a constant-temperature drying oven; at 140 °C ~ 160 °C, maintain for 4 h ~ 5 h. Let it naturally cool down to room temperature; slowly loosen the stainless steel enclosure. Take out the digestion inner tank; use a small amount of water to rinse the inner lid. Put the digestion tank on a temperature-controllable electric heating plate or in the ultrasonic water bath; at 80 °C, heat it up or conduct ultrasonic degassing for 3 min ~ 6 min to drive off the brown gas. Take out the digestion inner tank; transfer the digestion solution to a 25 mL volumetric flask; use a small amount of water to rinse the

inner tank in 3 times; combine the washing liquid in a volumetric flask and reach a constant volume to the scale; mix it up for later use. Meanwhile, conduct a blank test.

5.2.3 Method of reflux digestion

5.2.3.1 Grains

Weigh-take 1.0 g ~ 4.0 g (accurate to 0.001 g) of specimen; place it in a conical flask of the digestion device. Add several glass beads; add 45 mL of nitric acid and 10 mL and sulfuric acid; rotate the conical flask to prevent local carbonization. After installing the condenser pipe, heat it up at a low temperature. When it starts foaming, stop heating. After foaming stops, heat to reflux for 2 h. If the solution turns brown during the heating process, add 5 mL of nitric acid and continue to reflux for 2 h. Conduct digestion, until the sample is completely dissolved, which is generally pale yellow or colorless. After cooling, carefully add 20 mL of water from the upper end of the condenser pipe; continue to heat and reflux for 10 min. After leaving it to cool down, use an appropriate amount of water to rinse the condenser pipe; incorporate the rinsing liquid into the digestive fluid. Filter the digestive fluid through glass wool into a 100 mL volumetric flask; use a small amount of water to wash the conical flask and filter. Incorporate the washing liquid into the volumetric flask; add water to the scale; mix it up for later use. Meanwhile, conduct a blank test.

5.2.3.2 Vegetable oils and animal fats

Weigh-take 1.0 g ~ 3.0 g (accurate to 0.001 g) of specimen; place it in a conical flask of the digestion device. Add several glass beads; add 7 mL of sulfuric acid; carefully mix it up, until the solution turns brown, then, add 40 mL of nitric acid. The subsequent steps are the same as 5.2.3.1 “After installing the condenser pipe, heat it up with a small fire…. Meanwhile, conduct a blank test”.

5.2.3.3 Potatoes and soy products

Weigh-take 1.0 g ~ 4.0 g (accurate to 0.001 g) of specimen; place it in a conical flask of the digestion device. Add several glass beads, 30 mL of nitric acid and 5 mL of sulfuric acid; rotate the conical flask to prevent local carbonization. The subsequent steps are the same as 5.2.3.1 “After installing the condenser pipe, heat it up with a small fire…. Meanwhile, conduct a blank test”.

5.2.3.4 Meat and eggs

Weigh-take 0.5 g ~ 2.0 g (accurate to 0.001 g) of specimen; place it in a conical flask of the digestion device. Add several glass beads, 30 mL of nitric acid and 5 mL of sulfuric acid. Rotate the conical flask to prevent local carbonization. The subsequent steps are the same as 5.2.3.1 “After installing the condenser pipe, heat it up with a small fire…. Meanwhile, conduct a blank test”.

5.2.3.5 Milk and dairy products

mg/L, 2.0 mg/L, 3.0 mg/L, 4.0 mg/L and 6.0 mg/L.

NOTE: in accordance with the type and measuring range of the detector configured in the instrument, or the actual content of mercury in the sample, the range of mass concentration of mercury in the standard series solutions may be determined.

11 Instruments and Equipment

11.1 Direct mercury meter.

11.2 Electronic balance: with a division value of 0.01 mg, 0.1 mg and 1 mg.

11.3 Homogenizer.

11.4 High-speed pulverizer.

11.5 Sample boat: nickel boat or quartz boat.

11.6 Carrier gas: oxygen (99.9%) or air; argon-hydrogen mixture (9 : 1, volume ratio) (99.9%).

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

NOTE: the glassware needs to be soaked in nitric acid solution (1 + 4) for 24 h; use tap water to repeatedly rinse it, and finally, use water to thoroughly rinse it.

12 Analytical Procedures

12.1 Pre-treatment of Specimens

12.1.1 In terms of grains and beans, take the edible part and evenly crush it, with a particle size of 425 μm or less (equivalent to 40 mesh or more). Put it into a clean polyethylene bottle; seal and store it for later use.

12.1.2 In terms of samples with relatively more water content, for example, vegetables, if necessary, wash and drain them; take the edible part and homogenize it. For samples like aquatic products, meat and eggs, take the edible part and homogenize it. Put it in a clean polyethylene bottle; seal it; store it at 2 °C ~ 8 °C in the refrigerator for later use.

12.1.3 In terms of quick-frozen and canned food, thawed quick-frozen food and canned food samples, take the edible part and homogenize it. Put it in a clean polyethylene bottle; seal it; store it at 2 °C ~ 8 °C in the refrigerator for later use.

12.1.4 For milk and dairy products, shake them well.

12.2 Determination

12.2.1 Reference conditions of instrument

In accordance with the performance of the used direct mercury meter, adjust to the optimum state. The reference conditions of catalytic pyrolysis gold amalgam cold atomic absorption mercury meter are shown in Table B.1 in Appendix B; the reference conditions of catalytic pyrolysis gold amalgam atomic fluorescence mercury meter are shown in Table B.2; the reference conditions of pyrolysis cold atomic absorption mercury meter are shown in Table B.3.

12.2.2 Sample boat purification

After the sample ash remaining in the sample boat is cleaned up, adopt the built-in heating program of the instrument or muffle furnace to conduct high-temperature burning (600 °C ~ 800 °C) for more than 20 min to remove the mercury residue.

12.2.3 Drawing of standard curve

Respectively draw 0.1 mL of the low-concentration and high-concentration standard series solutions of mercury and place them in the sample boat. The mercury mass of the low-concentration standard series is respectively 0.0 ng, 1.0 ng, 5.0 ng, 10.0 ng, 20.0 ng, 30.0 ng and 40.0 ng; the mercury mass of the high-concentration standard series is respectively 40.0 ng, 80.0 ng, 100 ng, 200 ng, 300 ng, 400 ng and 600 ng. In accordance with the reference conditions of the instrument (Appendix B), adjust the instrument to the optimum state. In accordance with the mercury mass from low to high, successively determine the standard series solutions; record the signal response value. Take the mercury mass (ng) in each series standard solution as the x-coordinate; take the corresponding signal response value as the y-coordinate; respectively draw the standard curve of low-concentration or high-concentration mercury.

12.2.4 Determination of specimen

In accordance with the sample type, accurately weigh-take 0.05 g ~ 0.5 g (accurate to 0.0001 g or 0.001 g) of sample in the sample boat. In accordance with the reference conditions set by the instrument (Appendix B), conduct the determination; obtain the corresponding atomic absorption or atomic fluorescence spectral signal value. Read the corresponding mercury mass from the standard curve; calculate the mercury content in the sample. Conduct parallel sample determination on each sample; take the average value.

13 Expression of Analytical Results

The mercury content in the specimen shall be calculated in accordance with Formula (2).

$$X = \frac{m_0 \times 1\,000}{m \times 1\,000 \times 1\,000} \qquad \cdots\cdots\cdots\cdots\cdots\cdots (2)$$

17 Reagents and Materials

Unless it is otherwise specified, the reagents used in this Method are of top-grade purity, and the water is Grade-1 water specified in GB/T 6682.

17.1 Reagents

17.1.1 Nitric acid (HNO_3).

17.1.2 Hydrochloric acid (HCl).

17.1.3 Hydrogen peroxide (H_2O_2) (30%).

17.1.4 Anhydrous calcium chloride ($CaCl_2$): analytically pure.

17.1.5 Potassium permanganate ($KMnO_4$): analytically pure.

17.1.6 Potassium dichromate ($K_2Cr_2O_7$): analytically pure.

17.1.7 Stannous chloride ($SnCl_2 \bullet 2H_2O$): analytically pure.

17.2 Preparation of Reagents

17.2.1 Potassium permanganate solution (50 g/L): weigh-take 5.0 g of potassium permanganate; place it in a 100 mL brown bottle; use water to dissolve it and dilute to 100 mL; mix it up.

17.2.2 Nitric acid solution (5 + 95): measure-take 50 mL of nitric acid; slowly pour it into 950 mL of water; mix it up.

17.2.3 Nitric acid solution of potassium dichromate (0.5 g/L): weigh-take 0.5 g of potassium dichromate; use nitric acid solution (5 + 95) to dissolve it and dilute to 1,000 mL; mix it up.

17.2.4 Stannous chloride solution (100 g/L): weigh-take 10 g of stannous chloride; dissolve it in 20 mL of hydrochloric acid. Heat it up in a water bath at 90 °C; slightly shake it. After the stannous chloride is dissolved into a transparent shape, cool it down; use water to dilute to 100 mL; add several pieces of metal tin. Store it in a cool and dark place. Once turbidity is found, it shall be re-prepared.

17.2.5 Nitric acid solution (1 + 9): measure-take 50 mL of nitric acid; slowly add it to 450 mL of water; mix it up.

17.3 Standard Substance

Mercury chloride ($HgCl_2$, CAS No.: 7487-94-7): purity ≥ 99%.

17.4 Preparation of Standard Solutions

17.4.1 Standard stock solution of mercury (1,000 mg/L): same as 3.4.1.

17.4.2 Standard intermediate solution of mercury (10.0 mg/L): same as 3.4.2.

17.4.3 Standard working solution of mercury (50.0 μg/L): same as 3.4.3.

17.4.4 Standard series solutions of mercury: same as 3.4.4.

18 Instruments and Equipment

18.1 Mercury meter: equipped with gas circulation pump, gas drying device, mercury vapor generating device and mercury vapor absorption bottle, or full-automatic mercury measuring instrument.

18.2 Balance: with a division value of 0.01 mg, 0.1 mg and 1 mg.

18.3 Microwave digestion system.

18.4 Pressure digester.

18.5 Constant-temperature drying oven (200 °C ~ 300 °C).

18.6 Temperature-controllable electric heating plate (50 °C ~ 200 °C).

18.7 Ultrasonic water bath.

18.8 Homogenizer.

18.9 High-speed pulverizer.

NOTE: the glassware and PTFE digestion inner tank need to be soaked in nitric acid solution (1 + 4) for 24 h; use tap water to repeatedly rinse it, and finally, use water to thoroughly rinse it.

19 Analytical Procedures

19.1 Pre-treatment of Specimens

Same as 5.1.

19.2 Digestion of Specimens

Same as 5.2.

19.3 Determination

19.3.1 Reference conditions of instrument

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