Method 2: Hydride Generation Atomic Fluorescence Spectrometry

9. Principle

After the food sample is processed by wet digestion or dry ashing, thiourea is added to pre-reduce pentavalent arsenic to trivalent arsenic, and sodium borohydride or potassium borohydride are added to reduce to arsine hydrogen, which is loaded by argon The quartz atomizer is decomposed into atomic arsenic. It produces atomic fluorescence under the excitation of the high-intensity arsenic hollow cathode lamp. Its fluorescence intensity is proportional to the concentration of arsenic in the test solution under fixed conditions, and is quantitative compared with the standard series .

10.Reagents and Materials

Note: Unless otherwise specified, the reagents used in this method are all superior grade, the water is the first grade water specified in GB/T 6682.

10.1 Reagents

10.1.1 Sodium hydroxide (NaOH).
10.1.2 Potassium hydroxide (KOH).
10.1.3 Potassium borohydride (KBH_4): analytically pure.
10.1.4 Thiourea (CH_4 N_2 O_2 S): analytically pure.
10.1.5 Hydrochloric acid (HCI).
10.1.6 Nitric acid (HNO_3).
10.1.7 Sulfuric acid (H_2 SO_4).
10.1.8 Perchloric acid ($HClO_4$).
10.1.9 Magnesium nitrate [$Mg(NO_3)_2 \cdot 6H_2O$]: analytically pure.
10.1.10 Magnesium oxide (MgO): analytically pure.
10.1.11 Ascorbic acid ($C_6H_8O_6$).

10.2 Reagent preparation

10.2.1 Potassium hydroxide solution (5 g/L): Weigh 5.0 g of potassium hydroxide. Dissolve in water and dilute to 1, 000 mL.
10.2.2 Potassium borohydride solution (20 g/L): Weigh 20.0 g of potassium borohydride. Dissolve it in 1,000 mL of 5 g/L potassium hydroxide solution and mix well.
10.2.3 Thiourea + ascorbic acid solution: Weigh 10.0 g of thiourea. Add about 80 mL of water, heat to dissolve, after cooling, add 10.0 g of ascorbic acid and dilute to 100 mL. Compound it when it is in need.
10.2.4 Sodium hydroxide solution (100 g/L): Weigh 10.0 g of sodium hydroxide, dissolve it in water and dilute to 100 mL.
10.2.5 Magnesium nitrate solution (150 g/L): Weigh 15.0 g of magnesium nitrate. Dissolve it in water and dilute to 100 mL.
10.2.6 Hydrochloric acid solution (1+1): Measure 100 mL of hydrochloric acid, slowly pour it into 100 mL of water, and mix.
10.2.7 Sulfuric acid solution (1+9): Measure 100 mL of sulfuric acid. Slowly pour into 900 mL of water and mix.
10.2.8 Nitric acid solution (2+98): Measure 20 mL of nitric acid. Slowly pour into 980 mL of water and mix well.

10.3 Standard substance
Arsenic trioxide (As_2O_2) standard substance: purity≥99%

10.4 Standard Solution Preparation

10.4.1 Arsenic standard stock solution (100 mg/L. Calculated as As): accurately weigh 0.013 2 g of arsenic trioxide dried at 100 °C for 2 h. Add 1 mL of 100 g/L sodium hydroxide solution and a small amount of water to dissolve. Transfer to In a 100mL volumetric flask, add an appropriate amount of hydrochloric acid to adjust its acidity to near neutral. Dilute to the mark with water. Store at 4°C protected from light, and the shelf life is one year. Or purchase standard solution substances that have been certified by the country and have been granted a standard substance certificate.
10.4.2 Arsenic standard solution (1.00 mg/L. calculated as As): accurately draw 1.00 mL of arsenic standard stock solution (100 mg/L) into a 100 mL volumetric flask and dilute to the mark with nitric acid solution (2+98). Compound it when it is in need.

11 Instruments and Equipment
Note: The glassware and PTFE digestion inner tank need to be soaked in nitric acid solution (1 + 4) for 24 hours, rinsed repeatedly with water, and finally rinsed with deionized water.

11.1 Atomic fluorescence spectrometer.
11.2 Balance: Sensitivity is 0.1 mg and 1 mg.
11.3 Tissue homogenizer.
11.4 High-speed crusher.
11.5 Temperature control electric heating plate: 50 °C~200 C.
11.6 Muffle furnace

12 Analysis steps

12.1 Sample preparation
See 5.1.
12.2 Sample digestion

12.2.1 Wet digestion
Weigh 1.0 g~2.5 g for solid samples and 5.0 g~10.0 g (or mL) for liquid samples (accurate to 0.001 g). Place them in a 50 mL~100 ml conical flask and make two reagent blanks at the same time . Add 20 mL of nitric acid, 4 mL of perchloric acid, 1.25 mL of sulfuric acid, and place overnight. The next day, it is heated and digested on an electric hot plate. If the digestion solution is processed to about 1 mL, there are still undecomposed substances or the color becomes darker. Remove and let cool, add 5 mL to 10 mL of nitric acid, and then digest to about 2 mL. Repeat this two or three times to avoid carbonization. Continue heating until the digestion is complete, and then continue to evaporate until the white smoke of perchloric acid is dispersed, and the white smoke of sulfuric acid begins to emerge. Cool. Add 25 mL of water, and then evaporate to emit sulfuric acid white smoke. Cool, transfer the contents to a 25 mL volumetric flask or colorimetric tube with water, add 2 mL of thiourea + ascorbic acid solution. Add water to the mark. Mix well, place for 30 minutes, and wait for testing. Perform a blank test according to the same--operation method.

12.2.2 Dry ashing method
Weigh 1.0 g ~ 2.5 g for the solid sample. Take 4.00 mL (g) (accurate to 0.001 g) for the liquid sample, place it in a 50 mL ~ 100 ml crucible, and make two reagent blanks at the same time. Add 10mL of 150 g/L magnesium nitrate, mix well, evaporate to dryness on low heat, cover 1 g of magnesium oxide on the dry slag, and char on the electric furnace until there is no black smoke. Move to 550 ° C muffle furnace for ashing for 4 hours. Take out and let cool, carefully add 10 mL of

hydrochloric acid solution (1+1) to neutralize oxygen.Magnesium and dissolve the ash, transfer to a 25 mL volumetric flask or colorimetric tube, add 2 mL of thiourea + ascorbic acid solution to the volumetric flask or colorimetric tube, and wash the crucible with sulfuric acid solution (1+9) several times and then combine the wash Liquid to 25 mL. mark, mix well, place for 30 min, to be tested. Perform a blank test according to the same operation method.

12.3 Instrument reference conditions
Negative high voltage: 260 V; arsenic hollow cathode lamp current: 50 mA~80 mA; carrier gas: argon; carrier gas speed: 500 mL/min; shielding gas flow rate: 800 mL/min; measurement method: fluorescence intensity; reading method :Peak area.

12.4 Standard curve production

Take 6 25 mL volumetric flasks or colorimetric tubes, and add 1.00 ug/mL arsenic standard solution 0.00 mL, 0.10 mL,0.25 mL, 0.50 mL, 1.5 mL. and 3.0 mL (equivalent to arsenic concentration 0.0 ng/mL, 4.0 ng/ml, 10 ng/mL, 20 ng/mL. 60 ng/mL. 120 ng/mL, respectively). Add sulfuric acid solution (1+9>12.5 mL, 2 mL of thiourea + ascorbic acid solution, add water to the mark, mix well and place for 30 min before measuring.

After the instrument is warmed up and stabilized, the reagent blank and standard series solutions are introduced into the instrument in turn to measure the atomic fluorescence intensity. Draw a standard curve with atomic fluorescence intensity as the ordinate and arsenic concentration as the abscissa to obtain the regression equation.

12.5 Determination of sample solution
Under the same conditions, the sample solutions were introduced into the instrument for determination. Calculate the concentration of arsenic in the sample according to the regression equation.

13. Expression of analysis results

The total arsenic content in the sample is calculated according to formula (2):

$$X = \frac{(\mathrm{c} - c\circ) \times V \times 1000}{m \times 1000 \times 1000} \qquad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\ 2$$

In the formula:
X: The content of arsenic in the sample. The unit is milligram per kilogram (mg/kg) or milligram per liter (mg/L);
c: The measured concentration of arsenic in the test solution of sample C, in nanograms per milliliter (ng/mL);
c_0 : The measured concentration of arsenic in Co sample blank digestion solution. The unit is nanogram per milliliter (ng/mL);
V: The total volume of V sample digestion solution, in milligrams (mL);
m: The mass of the sample, in grams (g) or milliliters (mL);
1000: Conversion factor of 1 000.
The calculation result retains two significant digits.

14. Precision
The absolute difference between two independent determination results obtained under repeatability conditions shall not exceed 20% of the arithmetic mean.

15. detection limit
When the sample weight is 1g and the constant volume is 25mL, the method detection limit is

0.010mg/kg. The method quantification limit is 0.040mg/kg.