GB

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PEOPLE'S REPUBLIC OF CHINA

GB 5009.93-2017

National food safety standard - Determination of selenium in foods

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Foreword

This Standard replaces GB 5009.93-2010 “National food safety standard - Determination of selenium in foods”, GB/T 21729-2008 “Tea - Determination of selenium content”, SN/T 0860-2000 “Method for the determination of selenium in canned mushroom for export - Fluorometry” and SN/T 0926-2000 “Method for the determination of selenium in tea for import and export - Fluorimetry”.

Compare this Standard with GB 5009.93-2010, the main changes are as follows:

- RETAIN the hydride atomic fluorescence spectrometry as Method I, fluorescence spectrophotometry as Method II;

- ADD the inductively coupled plasma mass spectrometry as Method III.

National food safety standard - Determination of selenium in foods

1 Scope

This Standard specifies the determination of selenium content in foods by hydride atomic fluorescence spectrometry, fluorescence spectrometry and inductively coupled plasma mass spectrometry.

This Standard applies to the determination of selenium in all types of foods.

Method I -- Hydride atomic fluorescence spectrometry

2 Principle

After the sample is acid-heated and digested, in the 6 mol/L hydrochloric acid medium, the hexavalent selenium in the sample is reduced to tetravalent selenium. Sodium borohydride or potassium borohydride is used as the reducing agent to reduce the tetravalent selenium in the hydrochloric acid medium to hydrogen selenide, which is introduced by carrier gas (argon) into the atomizer for atomization. In the irradiation of selenium hollow cathode lamp, the ground-state selenium atoms are excited to a high energy state. When deactivating back to the ground state, the fluorescence of the characteristic wavelength is emitted, of which the fluorescence intensity is proportional to the selenium content. Compare with the standard series.

3 Reagents and materials

Unless otherwise indicated, the reagents used in this method are analytical regents, and the water is the Grade 2 water as specified in GB/T 6682.

3.1 Reagents

3.1.1 Nitric acid (HNO_3): excellent regent.

3.1.2 Perchloric acid ($HClO_4$): excellent regent.

3.1.3 Hydrochloric acid (HCl): excellent regent.

3.1.4 Sodium hydroxide (NaOH): excellent regent.

3.1.5 Hydrogen peroxide (H_2O_2).

3.1.6 Sodium borohydride ($NaBH_4$): excellent regent.

3.1.7 Potassium ferricyanide [$K_3Fe(CN)_6$].

3.2 Preparation of reagents

3.2.1 Nitric acid - perchloric acid mixed acid (9 + 1): MIX 900 mL of nitric acid with 100 mL of perchloric acid.

3.2.2 Sodium hydroxide solution (5 g/L): WEIGH 5 g of sodium hydroxide; DISSOLVE in 1000 mL of water; MIX well.

3.2.3 Sodium borohydride solution (8 g/L): WEIGH 8 g of sodium borohydride; DISSOLVE in sodium hydroxide solution (5 g/L); MIX well. PREPARE before use.

3.2.4 Hydrochloric acid solution (6 mol/L): WEIGH 50 mL of hydrochloric acid; slowly ADD to 40 mL of water; COOL; DILUTE with water to 100 mL; MIX well.

3.2.5 Potassium ferricyanide solution (100 g/L): WEIGH 10 g of potassium ferricyanide; DISSOLVE in 100 mL of water; MIX well.

3.2.6 Hydrochloric acid solution (5 + 95): MEASURE 25 mL of hydrochloric acid; slowly ADD to 475 mL of water; MIX well.

3.3 Standard

Selenium standard solution: 1000 mg/L, or selenium standard solution at a certain concentration certified by the state and awarded the standard substance certificate.

3.4 Preparation of standard solutions

3.4.1 Selenium standard intermediate solution (100 mg/L): accurately PIPETTE 1.00 mL of selenium standard solution (1000 mg/L) in a 10 mL volumetric flask; ADD hydrochloric acid solution (5 + 95) to the mark; MIX well.

3.4.2 Selenium standard use solution (1.00 mg/L): accurately PIPETTE 1.00 mL of selenium standard intermediate solution (100 mg/L) in a 100 mL volumetric flask; ADD hydrochloric acid solution (5 + 95) to the mark; MIX well.

3.4.3 Selenium standard series solutions: respectively PIPETTE 0 mL, 0.500 mL, 1.00 mL, 2.00 mL and 3.00 mL of selenium standard use solution (1.00 mg/L) in 100 mL volumetric flasks; ADD 10 mL of potassium ferricyanide solution (100 g/L); ADD hydrochloric acid solution (5 + 95) to the mark; MIX well for test. The mass concentrations of the selenium standard series solutions are 0 μg/L, 5.00 μg/L, 10.0 μg/L, 20.0 μg/L and 30.0 μg/L, respectively.

NOTE: The mass concentration of selenium in the standard series solutions may be determined according to the sensitivity of the instrument and the actual content of selenium in the sample.

potassium ferricyanide solution (100 g/L); ADD water to constant volume; MIX well for test. At the same time carry out the reagent blank test.

5.2.2 Microwave digestion

WEIGH 0.2 g ~ 0.8 g (to the nearest 0.001 g) of solid sample or accurately PIPETTE 1.00 mL ~ 3.00 mL of liquid sample; PLACE in the digestive tube; ADD 10 mL of nitric acid and 2 mL of hydrogen peroxide; SHAKE to mix well. DIGEST in the microwave digestion instrument, and the recommended microwave digestion conditions are shown in Annex A (set digestion conditions according to different instruments). After the digestion is completed and cool, TRANSFER the digestion solution into the conical flask; ADD a few grains of glass beads; continue to HEAT on the electric hot plate to near dry, it must not be evaporated to dry. ADD 5 mL of hydrochloric acid solution (6 mol/L); continue to HEAT until the solution becomes clear and colorless accompanied by white smoke; COOL; TRANSFER to a 10 mL volumetric flask. ADD 2.5 mL of potassium ferricyanide solution (100 g/L); ADD water to constant volume; MIX well for test. At the same time carry out the reagent blank test.

5.3 Determination

5.3.1 Instrument reference conditions

Adjust the instruments to the best condition according to their performance. Reference conditions: negative high voltage 340 V; lamp current 100 mA; atomization temperature 800 °C; furnace height 8 mm; carrier gas flow rate 500 mL/min; shielding gas flow rate 1000 mL/min; standard curve method of measurement method; peak area of reading method; delay time 1 s; reading time 15 s; solution adding time 8 s; sample injection volume 2 mL.

5.3.2 Plotting of standard curve

TAKE hydrochloric acid solution (5 + 95) as the carrier, sodium borohydride solution (8 g/L) as the reducing agent. INJECT sample continuously with the zero tube of the standard series. After the reading is stable, introduce the selenium standard series solutions into the instrument according to the order of the mass concentration from low to high, to measure their fluorescence intensity. The standard curve is plotted by taking the mass concentration as the abscissa and the fluorescence intensity as the ordinate.

5.3.3 Sample determination

Under the same test conditions as the determination of standard series solutions, the blank solution and the sample solution are respectively introduced into the instrument, and the corresponding fluorescence intensity is measured, to compare with the standard series.

NOTE: This reagent has a certain toxicity, personnel who use this reagent shall pay attention to protection.

10.2.3 Nitric acid - perchloric acid mixed acid (9 + 1): MIX 900 mL of nitric acid with 100 mL of perchloric acid.

10.2.4 Hydrochloric acid solution (6 mol/L): MEASURE 50 mL of hydrochloric acid; slowly ADD to 40 mL of water; COOL; ADD water to 100 mL; MIX well.

10.2.5 Ammonia solution (1 + 1): MIX 5 mL of water with 5 mL of ammonia.

10.2.6 EDTA mixture:

a) EDTA solution (0.2 mol/L): WEIGH 37 g of EDTA-2Na; ADD water and HEAT until completely dissolved; COOL and DILUTE to 500 mL with water;

b) Hydroxylamine hydrochloride solution (100 g/L): WEIGH 10 g of hydroxylamine hydrochloride to dissolve in water; DILUTE to 100 mL; MIX well;

c) Cresol red indicator (0.2 g/L): WEIGH 50 mg of cresol red to dissolve in a small amount of water; ADD 1 drop of ammonia solution (1 + 1); after completely dissolved, DILUTE with water to 250 mL; MIX well;

d) Respectively TAKE 50 mL of EDTA solution (0.2 mol/L) and hydroxylamine hydrochloride solution (100 g/L); ADD 5 mL of cresol red indicator (0.2 g/L); DILUTE to 1 L with water; MIX well.

10.2.7 Hydrochloric acid solution (1 + 9): MEASURE 100 mL of hydrochloric acid; slowly ADD to 900 mL of water; MIX well.

10.3 Standard

Selenium standard solution: 1000 mg/L, or selenium standard solution at a certain concentration certified by the state and awarded the standard substance certificate.

10.4 Preparation of standard solutions

10.4.1 Selenium standard intermediate solution (100 mg/L): accurately PIPETTE 1.00 mL of selenium standard solution (1000 mg/L) in a 10 mL volumetric flask; DILUTE with hydrochloric acid solution (1 %) to the mark; MIX well.

10.4.2 Selenium standard use solution (50.0 μg/L): accurately PIPETTE 0.50 mL of selenium standard intermediate solution (100 mg/L); DILUTE with hydrochloric acid solution (1 %) to 1000 mL; MIX well.

10.4.3 Selenium standard series solutions: accurately PIPETTE 0 mL, 0.200 mL, 1.00 mL, 2.00 mL and 4.00 mL of standard selenium use solution (50.0 μg/L), which are equivalent to containing 0 μg, 0.010 0 μg, 0.050 0 μg, 0.100 μg and 0.200 μg of

12.3.1 Instrument reference conditions

Adjust the instruments to the best condition according to their performance. The reference conditions: excitation light wavelength 376 nm, emission light wavelength 520 nm.

12.3.2 Plotting of standard curve

Measure the fluorescence intensity of 4,5-Benzo piaselenol in selenium standard series solution on the instrument, respectively, according to the order of mass from low to high. The standard curve is plotted by taking the mass as the abscissa and the fluorescence intensity as the ordinate.

12.3.3 Determination of sample solution

After the digested sample solution of 12.2 and the blank solution are added with hydrochloric acid solution (1 + 9) to 5 mL, ADD 20 mL of EDTA mixture, USE ammonia solution (1 + 1) and hydrochloric acid solution (1 + 9) to adjust it to pale red-orange (pH 1.5 ~ 2.0). The following steps are operated in the darkroom: ADD 3 mL of DAN reagent (1 g/L); MIX well; HEAT in the boiling water bath for 5 min; REMOVE and COOL; ADD 3 mL of cyclohexane; SHAKE for 4 min; TRANSFER all the solution into the separatory funnel; after it is layered, DISCARD the water layer, and carefully POUR the cyclohexane layer from the top of the separatory funnel into the test tube with a lid. Do not make cyclohexane mixed with water droplets, for test.

13 Expression of analysis results

The content of selenium in the sample is calculated according to equation (2):

$$X = \frac{m_1}{F_1 - F_0} \times \frac{F_2 - F_0}{m} \qquad \cdots\cdots (2)$$

where:

X - the content of selenium in the sample, in milligrams per kilogram or milligrams per liter (mg/kg or mg/L);

m_1 - the mass of selenium in the sample tube, in micrograms (μg);

F_1 - the selenium fluorescence reading of the standard tube;

F_0 - the fluorescence reading of the blank tube;

F_2 - the fluorescence reading of the sample tube;

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