National Standards of People's Republic of China

GB 5009.15-2014

National Food Safety Standard

Determination of Cadmium in Foods

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Foreword

This standard replaces GB/T 5009.15-2003 “Determination of cadmium in foods”. The main changes in this standard compared to GB/T 5009.15-2003 are as follows:

- The title of the standard is revised to “National food safety standard determination of cadmium in foods”

- Method 2 Atomic absorption spectrometry, Method 3 Colorimetry, and Method 4 Atomic fluorescence spectrometry, are deleted.

National Food Safety Standard

Determination of Cadmium in Foods

1 Scope

This standard specifies a graphite furnace atomic absorption spectrometric method for determination of cadmium in all kinds of food.

The standard is applicable to the determination of cadmium in all kinds of foods.

2 Principle

The test sample is ashed or digested with acid whereupon a specific amount of the digest is injected into the atomic absorption spectrophotometer graphite furnace and electrothermally atomised, absorbing the 228.8 nm resonance line; within a specific concentration range the absorbance is directly proportional to cadmium content, which is determined by the standard curve method.

3 Reagents and materials

Note 1: Unless otherwise indicated, all reagents used in this method are analytically pure; the water is Class 2 water specified in GB/T 6682.

Note 2: All glassware must be soaked in nitric acid solution (1+4) for not less than 24 h, rinsed repeatedly with water, and finally rinsed with deionised water and dried.

3.1 Reagents

3.1.1 Nitric acid (HNO_3): guaranteed reagent.

3.1.2 Hydrochloric acid (HCl): guaranteed reagent.

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

3.1.4 Hydrogen peroxide (H_2O_2, 30%).

3.1.5 Ammonium dihydrogen phosphate ($NH_4H_2PO_4$).

3.2 Preparation of reagents

3.2.1 Nitric acid solution (1%): Add 10.0 mL of nitric acid to 100 mL of water and dilute to 1,000 mL.

3.2.2 Hydrochloric acid solution (1+1): Slowly add 50 mL of hydrochloric acid to 50 mL of water.

3.2.3 Mixed nitric acid-perchloric acid solution (9+1): Mix 9 parts of nitric acid with 1 part of perchloric acid.

3.2.4 Ammonium dihydrogen phosphate solution (10 g/L): Weigh out 10.0 g of ammonium dihydrogen phosphate, dissolve with 100 mL of nitric acid solution (1%) and transfer quantitatively to a 1,000 mL volumetric flask; make up to the graduation mark with nitric acid solution (1%).

3.3 Reference standard material

A standard sample of cadmium metal (Cd) of 99.99% purity or a nationally authenticated reference material holding a reference material certificate.

3.4 Preparation of standard solutions

3.4.1 Cadmium standard stock solution (1,000 mg/L): Accurately weigh 1 g (accurate to 0.0001 g) of the standard sample of cadmium metal into a small beaker, dissolve with 20 mL of hydrochloric acid solution (1+1) added in portions, then add 2 drops of nitric acid; transfer to a 1,000 mL volumetric flask, make up to the graduation mark with water and mix. Alternatively, purchase nationally authenticated reference material holding a reference material certificate.

3.4.2 Cadmium standard intermediate working solution (100 ng/mL): Pipette 10.0 mL of the cadmium standard stock solution into a 100 mL volumetric flask and make up to the graduation mark with nitric acid solution (1%); dilute repeatedly this way to obtain a standard intermediate working solution containing 100.0 ng of cadmium per millilitre.

3.4.3 Standard curve working solutions: Accurately pipette 0 mL, 0.50 mL, 1.0 mL,

1.5 mL, 2.0 mL and 3.0 mL of the cadmium standard intermediate working solution into 100 mL volumetric flasks and make up to the graduation mark with nitric acid solution (1%) to obtain a standard series of solutions containing cadmium 0 ng/mL, 0.50 ng/mL, 1.0 ng/mL, 1.5 ng/mL, 2.0 ng/mL and 3.0 ng/mL, respectively.

4 Instrumentation and apparatus

4.1 Atomic absorption spectrophotometer, with graphite furnace.

4.2 Cadmium hollow cathode lamp.

4.3 Electronic balance: Sensibility reciprocal 0.1 mg and 1 mg.

4.4 Adjustable temperature hotplate, adjustable temperature electric oven.

4.5 Muffle furnace.

4.6 Thermostatic drying cabinet.

4.7 Pressure digester, pressure digestion vessel.

4.8 Microwave digestion system: Fitted with polytetrafluoroethylene or other suitable pressure vessel.

5 Analytical procedure

5.1 Test sample preparation

5.1.1 Dry test samples: For grain and pulses, exclude foreign matter; for nuts remove foreign matter and shells. Grind to a homogeneous sample of particle size not greater than 0.425 mm. Store in a clean plastic bottle and label clearly; hold ready for use at room temperature, or under storage conditions consistent with the sample.

5.1.2 Fresh (wet) test samples: Vegetables, melons, meats, fish, eggs, etc, are homogenised with a food processor or milled to a homogenate; store in a clean plastic bottle, label clearly, and hold in a refrigerator at -16°C to -18°C pending use.

5.1.3 Liquid test samples: Hold under storage conditions consistent with the sample pending use. Degas gas-containing samples before use.

5.2Digestion of test sample

The sample may be digested using any one of the following methods according to laboratory circumstances. Sample homogeneity should be assured in weighing.

a) Digestion with a pressure digestion vessel: Weigh 0.3 g - 0.5 g (accurate to 0.0001

g) of the dry test sample or 1 g - 2 g (accurate to 0.001 g) of the fresh (wet) test sample into the polytetrafluoroethylene liner vessel, add 5 mL of nitric acid and soak overnight. Then add 2 mL - 3 mL of hydrogen peroxide solution (30%) (the total volume may not exceed one third of the vessel capacity). Cover the liner vessel and tightly screw on the stainless steel case; place in the thermostatic drying cabinet, hold at 120°C-160°C for 4 h -6 h, and allow to cool naturally to room temperature inside the cabinet. After opening the vessel, heat to near dryness to drive off acid. Wash the digest into a 10 mL or 25 mL volumetric flask, rinse the liner vessel and inner cover 3 times with a little nitric acid solution (1%), combine the washings in the volumetric flask, make up to the graduation mark with nitric acid solution (1%), and mix ready for use. Run a reagent blank test in parallel.

b) Microwave digestion: Weigh out 0.3 g - 0.5 g (accurate to 0.0001 g) of the dry test sample or 1 g - 2 g (accurate to 0.001 g) of the fresh (wet) test sample, place in the microwave digester, and add 5 mL of nitric acid and 2 mL of hydrogen peroxide. The microwave digestion programme can be adjusted to the provide the optimum conditions for the instrument model. On completion of digestion, the digestion vessel is left to cool and then opened; the digest is colourless or pale yellow. Heat to near dryness to drive off acid, wash the digestion vessel 3 times with a little nitric acid solution (1%), transfer the solution to a 10 mL or 25 mL volumetric flask, make up to the graduation mark with nitric acid solution (1%), and mix ready for use. Run a reagent blank test in parallel.

c) Wet digestion: Weigh 0.3 g - 0.5 g (accurate to 0.0001 g) of the dry test sample or 1 g - 2 g (accurate to 0.001 g) of the fresh (wet) test sample into a conical flask, introduce several glass beads, add 10 mL of nitric acid-perchloric acid mixture (9+1), cover and soak overnight; with a small funnel added, digest on the electric hotplate. If the digest turns black-brown, add further nitric acid until white fumes are given off and the digest is colourless and transparent or tinged faint yellow, and leave to cool. Then wash the digest into a 10 mL - 25 mL volumetric flask, rinse the conical flask 3 times with a little nitric acid solution (1%), combine the washings in the graduated flask make up to the graduation mark with nitric acid solution (1%), and mix ready for use. Run a reagent blank test in parallel.

d) Dry ashing: Weigh 0.3 g - 0.5 g (accurate to 0.0001 g) of the dry test sample, 1 g - 2 g (accurate to 0.001 g) of the fresh (wet) test sample or 1 g - 2 g (accurate to 0.001 g) of the liquid sample into a porcelain crucible; gently carbonise in the adjustable temperature electric oven until smoke is no longer emitted, then transfer to the muffle furnace, ash for 6 h - 8 h at 500°C and cool. If a sample has not been completely ashed, add 1 mL of mixed acid and heat gently on the adjustable temperature electric oven; once the mixed acid has evaporated to dryness, transfer the sample back into the muffle furnace and continue ashing at 500°C for 1 h - 2 h until fully digested and the ash is greyish white or grey. Leave to cool, dissolve the ash with nitric acid solution (1%), transfer the sample digest to a 10 mL or 25 mL volumetric flask, wash the porcelain crucible 3 times with a little nitric acid solution (1%) , and combine the washings in the volumetric flask; make up to the graduation mark with nitric acid solution (1%) and mix ready for use. Run a reagent blank test in parallel.

Note: The experiment must be conducted in a well ventilated fume cupboard. Wherever possible avoid digesting oil/fat-containing samples by wet digestion; digestion by the dry method is best. If digestion by the wet method is essential, the amount of sample taken should not exceed a maximum of 1 g.

5.3 Instrumentation reference conditions

Adjust instruments to the optimum conditions for the model used. The reference operating conditions for the atomic absorption spectrophotometer (with graphite furnace and cadmium hollow cathode fitted) are as follows:

☐ Wavelength 228.8 nm, slit 0.2 nm - 1.0 nm, lamp current 2 mA - 10 mA, drying temperature 105°C, drying time 20 s;

☐ Ashing temperature 400°C - 700°C, ashing time 20 s - 40 s;

☐ Atomisation temperature 1300°C - 2300°C, atomisation time 3 s - 5 s;

☐ Background correction is by deuterium lamp or Zeeman effect

5.4 Construction of standard curve

Proceeding from low to high concentration, inject into the graphite furnace 20 µL of each standard curve working solution; measure the absorbance, plot the standard curve with the concentration of the standard curve working solution as horizontal coordinate and the corresponding absorbance as vertical coordinate, and find the simple linear regression equation for the relation of absorbance versus concentration.

The standard series solutions should be cadmium standard solutions of no fewer than 5 different concentrations, and the coefficient of correlation should not be less than 0.995. If an automated sample injection unit is available, programmed dilution may be used to generate the standard series.

5.5 Examination of test sample solution

Under the same experimental conditions as in examination of the standard curve working solutions, pipette 20 µL of the sample digest (the optimum sample volume for the instrument used may be chosen), inject it into the graphite furnace, and measure the absorbance. Substitute into the simple linear regression equation of the standard series to find the content of cadmium in the sample digest, using no fewer than two replicates. If the results of measurement fall outside the range of the standard curve, make the measurements again after dilution with nitric acid solution (1%).

5.6 Use of matrix modifiers

For test samples subject to interference, inject the sample digest into the graphite furnace with 5 µL of ammonium dihydrogen phosphate matrix modifier (10 g/L). The same amount of matrix modifier as in examination of the sample must be added when the standard curve is plotted.

6 Presentation of analytical results

Calculate the cadmium content of the test sample from Equation (1).

$$X=\frac{(C1-c0)\times V}{m\times 1000}\square\square\square \quad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Where:

X - Cadmium content of test sample in units of milligrams per kilogram or milli- grams per litre (mg/kg or mg/L);

C1 - Cadmium content of the test sample digest in units of nanograms per millilitre (ng/mL);

C0 - Cadmium content of the blank solution in units of nanograms per millilitre (ng/mL);

V - Total final volume of the test sample digest in millilitre units (mL);

M - Test sample mass or volume in units of grams or millilitres (g or mL); 1000 □□ conversion

The arithmetic mean of the results of two independent determinations obtained under repeatable conditions is presented, retaining two significant digits.

7 Precision

The absolute difference between the results of two independent determinations obtained under repeatable conditions shall not exceed 20% of the arithmetic mean.

8 Other particulars

The limit of detection of the method is 0.001 mg/kg and the limit of quantitation is 0.003 mg/kg.