USDA Foreign Agricultural Service
GAIN Report
Global Agricultural Information Network

Voluntary - Public

Date: 12/3/2009
GAIN Report Number: CH9117

China - Peoples Republic of

Post: Beijing

National Food Safety Standard - Arsenic

Report Categories:

FAIRS Subject Report

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Report Highlights:

On November 20, 2009, China notified the WTO of "National Food Safety Standard of the People's Republic of China for Arsenic in Foods" as SPS/N/CHN/182. The date for submission of final comments to the WTO is January 1, 2010. The proposed date of entry into force has not been specified.

Executive Summary:

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Thanks go to the consortium of industry and 3rd country Embassies in Beijing for their assistance in translating and reviewing this standard.

This report contains an UNOFFICIAL translation of National Standard on Arsenic in Foods.

General Information:

BEGIN TRANSLATION

ICS 67.040
C

GB National Food Safety Standard
GB/T 5009.11—xxxx
To replace GB/T 5009.11—2003

Determination of Total Arsenic and Abio-arsenic in Foods

(Draft for Comments)

Issued on xx-xx-xxxx Implemented on xx-xx-xxxx

Issued by the Ministry of Health

of the People's Republic of China

Preface

This standard replaces GB/T 5009.11 -2003 Method for Determination of Total Arsenic in Food.

This standard is proposed and administrated by Ministry of Health of P. R. China.

The issuance status of all the previous editions replaced by this standard are:

GB/T 5009.11-1985, GB/T 5009.11-1996, GB/T 5009.11-2003

1. Scope

This method specifies the determination method for total arsenic in various foods.

This method is applicable to the determination of total arsenic in various foods.

Detection limit of the method: hydride atomic fluorescence spectrophotometry:0.01 mg/kg, linear range. 0 ng/mL-200 ng/ml;

Silver salt method: 0.2 mg/kg; arsenic stain method:0.25 mg/kg; borohydride reduction colorimetric method:0.05 mg/kg,

Method I Hydride Atomic Fluorescence Spectrophotometry

2 Principle

After wet digestion or dry incineration of food sample, add thiourea for pre-reduction of As^{5+} into As^{3+}, add $NaBH_4$ or KBH_4 to make As^{3+} reduce into AsH_3, which is carried into the quartz atomizer by H_2 and decomposed into atomic-states arsenic. Atomic fluorescence generates through the stimulation of special hollow arsenic cathode light. Its fluorescence intensity is proportional to arsenic concentration in the tested solution. The constant quantity should be compared with standard series.

3 Reagent

3.1 NaOH solution (2g/L),

3.2 $NaBH_4$ solution (10g/L): Weigh 10.0 g $NaBH_4$, dissolve in 1000mL 2g/L NaOH solution and blend. This solution can be stored in the refrigerator for 10 days, take it out and use in the same day (14 g KBH_4 can be replaced with 10 g $NaBH_4$).

3.3 Thiourea solution (50 g/L)

3.4 H_2SO_4 solution (1+9): Weigh 100 mL H_2SO_4, carefully pour it into 900 mL water and blend.

3.5 NaOH solution (100 g/L) (small amount is sufficient for the preparation of standard arsenic solution).

3.6 Standard arsenic solution

3.6.1 Standard arsenic stock solution: Contain 0.1 mg/mL arsenic. Accurately weigh 0.1320 g As_2O_3, which has been dried at 100 ℃ for 2h, dissolve it with 10 mL 100 g/l NaOH, transfer it into 1000 mL volumetric flask with proper amount of water, add 25 mL (1+9) H_2SO_4 and dilute to volume with water.

3.6.2 Standard arsenic solution: contain arsenic 1μg/mL. Suck 1.00 mL standard arsenic stock solution into a 100mL volumetric flask, dilute to the volume with water. This solution should be prepared and used in the same day.

3.7 Wet digestion reagent: HNO_3, H_2SO_4, perchloric acid.

3.8 Dry incineration reagent: $Mg(NO_3)2.\ 6H_2O$(150 g/L),$MgCl_2$, HCl (1+1).

4 Instrument

Atomic fluorescence spectrometer

5 Analysis Procedure

5.1 Sample digestion

5.1.1 wet digestion: weigh 1g-2.5 g solid sample and 5g-10g liquid sample (or mL) (accurate to the second decimal place), put them into 50 mL--100 mL conical flask and prepare two reagent blanks simultaneously. Add 20 mL-40 mL HNO3 and 1.25 mL H2SO4, shake it well and settle overnight, put it on the electric hot plate to heat for digestion. If there is still undecomposed substance or color turns darker when the digestion solution is treated to 10 mL, take the sample down and cool. Supplement 5 mL- 10 mL HNO3, digest it to 10 mL and observe. Repeat the process for two or three times to avoid carbonization. If digestion is still incomplete, then add 1 mL-2 mL perchloric acid, continuously heat for complete digestion, continue to evaporate until white smoke of perchloric acid releases and cool. add 25 mL water, evaporate until white smoke of H2SO4 releases, cool it, use water to transfer the content into 25 mL volumetric flask or colorimetric tube, add 2.5ml 50 g/L thiourea, add water and dilute to volume, blend for determination.

5.1.2 Dry incineration:

It is generally applied to solid sample. Weigh 1g -2.5 g sample (accurate to the second decimal place) into 50mL-100mL crucible, prepare two reagent blanks simultaneously , add 10 mL 150 g/L Mg $(NO_3)_2$ and blend, evaporate it with low heat, carefully cover 1g MgO on the dry residue, carbonize it on the electric furnace until no black smoke releases, transfer it into 550℃ high-temperature furnace and conduct incineration for 4h. Take it out, cool, carefully add 10 mL (1+1) HCl to neutralize MgO and dissolve ash, transfer into 25mL volumetric flask or colorimetric tube. Add 2.5 mL 50g/L thiourea into volumetric flask or colorimetric tube, separately wash crucibles with (1+9)H_2SO_4 to the volume of 25 mL, blend for determination.

5.2 Preparation of standard series

Take 6 25 mL volumetric flasks or colorimetric tubes, successively and accurately add 0, 0.05, 0.2 ,0.5 ,2.0 and 5.0 mL 1μg/mL standard arsenic solution (equivalent to arsenic concentration 0, 2.0 ,8.0 ,20.0 ,80.0 ,200.0 ng/mL). Respectively add 12.5 mL (1+9)H_2SO_4 and 2.5 mL 50g/L thiourea, add water to volume and blend for determination.

5.3 Determination.

5.3.1 Reference conditions of instrument: voltage of photomultiplier tube: 400 V; current of hollow arsenic cathode lamp: 35 mA; atomizer: temperature=820 –850℃; height=7 mm; flow rate of H2: carrier gas 600 mL/min; measurement mode: fluorescence intensity or direct reading of concentration. reading mode: Peak area; delay time of reading: 1s; reading duration: 15s; addition time of NaBH4 solution: 5s; addition volume of standard solution or sample solution: 2 mL,

5.3.2 Concentration measurement mode: To directly measure the fluorescence intensity, preheat and stabilize for about 20 min after starting up and setting the conditions for the instrument, press "B" key to enter into the measuring state of blank value and continuously inject sample with "0" tube of standard series. When the reading is stabilized, press gap key to record the blank value (conduct automatic deduction with instrument) to start measurement. Firstly, successively measure standard series ("0" tube isn’t measured). Then the sampler should be carefully cleaned (or replace with a sampler) and then measure with "0" tube to make the reading basically return to zero, through which reagent blank and sample can be measured. The sample should be cleaned before measuring different samples and record (or print) the measured data.

5.3.3 Automatic mode of instrument: Concentration can be measured via direct reading by using software functions provided by the instrument. Therefore, the necessary parameters, including, sample quantity (g or mL); dilution volume (mL); injection volume (mL); concentration unit of the result; frequency of repeated measurement at each point of standard series; number of points of standard series (excluding zero point) and concentration value at each point, should be entered after starting up, setting the conditions and preheating.

First, enter into the measuring state of blank value, continuously inject sample with "0" tube of standard series to obtain stable blank values and implementation of automated deduction. Then successively measure standard series ("0" tube should be measured again). Before measuring the sample solution, re-enter into the measuring state of blank value, firstly measure with "0" tube of standard series to recover the reading and keep it stable, respectively inject samples with two reagent blanks and use average value as the blank value of deduction and then measure samples in turn. After determination, return to the main menu and select "Print Report" to print out the determination results.

6 Result Calculation

If measurement mode via fluorescence intensity is used, regression calculation should be conducted for the results of standard series operations (Because "0" tube is forced to be 0 for measurement, zero point value should be entered to occupy a point position), obtain the arsenic concentrations of reagent blank solution and the measured sample liquid according to the regression equation and then calculate the arsenic content in the sample according to formula (1):

$$X = \frac{C_1 - C_0}{m} \times \frac{25}{1\,000} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1)$$

Where:

X — Arsenic content in the sample. The unit is mg/kg or mg/L

C_1— Concentration of measured liquid of sample. The unit is ng/mL ;

C_0— Concentration of reagent blank solution. The unit is ng/mL;

m — Mass or volume of sample. The unit is g or mL,

Two significant digits are reserved for calculation result.

7. Precision

For the wet digestion method, the difference between the absolute values of the two independent determination results obtained under the repeatability condition must not exceed 10% of the average arithmetic value.

For the dry incineration method, the difference between the absolute values of the two independent determination results obtained under the repeatability condition must not exceed 15% of the average arithmetic value.

8. Accuracy

The recovery rate determined by wet digestion method is 90%-105% and that by dry incineration method is 85%-100%.

Method II Silver Salt Method

9 Principle

When the sample is digested, use KI and $SnCl_2$ to reduce arsenic with high valence to As^{3+}, which generates AsH3 with zinc particles and new hydrogen, produced from the acid, and form red colloidal substance through the absorption with silver salt solution. The constant quantity should be compared with standard series.

10 Reagent

10.1 HNO_3.

10.2 H_2SO_4 .

10.3 HCl .

10.4 MgO .

10.5 Arsenic-free zinc particles.

10.6 HNO_3-perchloric acid mixed solution (4+1): Weigh 80 mLHNO_3, add 20 mL perchloric acid and blend.

10.7 Mg(NO_3)2 solution(150 g/L): Weigh 15 g [Mg $(NO_3)_2 \cdot 6H_2O$], dissolve in water and dilute to100 mL.

10.8 KI solution(150 g/L): Stored in brown bottle.

10.9 Acidic $SnCl_2$ solution: Weigh 40 g $SnCl_2 \cdot 2H_2O$, dissolve in HCl, dilute to100 mL and add a few metallic tin particles.

10.10 HCl (1+1): Weigh 50 mL HCl, add water and dilute to 100 mL,

10.11 Lead acetate solution (100 g/L),

10.12 Lead acetate cotton: Soak the cotton in lead acetate solution (100 g/L), press out the excessive solution, loosen the cotton, and dry it at 100 ℃ and store in glass bottle.

10.13 NaOH solution (200 g/I).

10.14 H_2SO_4 (6+94): Weigh 6. 0 mL H_2SO_4, add it into 80mI water and dilute to 100 mL with water after cooling.

10.15 Silver diethyldithiocarbamate－triethanolamine chloroform solution: Weigh 25 g silver diethyldithiocarbamate, put it into mortar and add small quantity of chloroform to grind it. Then transfer it into 100mL measuring cylinder, add 1.8 mL triethanolamine, wash the mortar with chloroform for several times, add the washing liquid into the measuring cylinder, dilute to 100 mL with chloroform, settle overnight, filter and store in brown bottle.

10.16 Standard arsenic stock solution: Accurately weigh 0.1320g As_2O_3, which has been dried for 2h at 100℃ in the H_2SO_4 dryer, dissolve it in 5 mL NaOH solution(200 g/L), add 25 mL H_2SO_4 (6+94) and transfer into 1000 mL volumetric flask. Then dilute to volume by adding water which has just been boiled and cooled, and store in brown bottle. Each milliliter of the solution is equivalent to 0.10 mg arsenic.

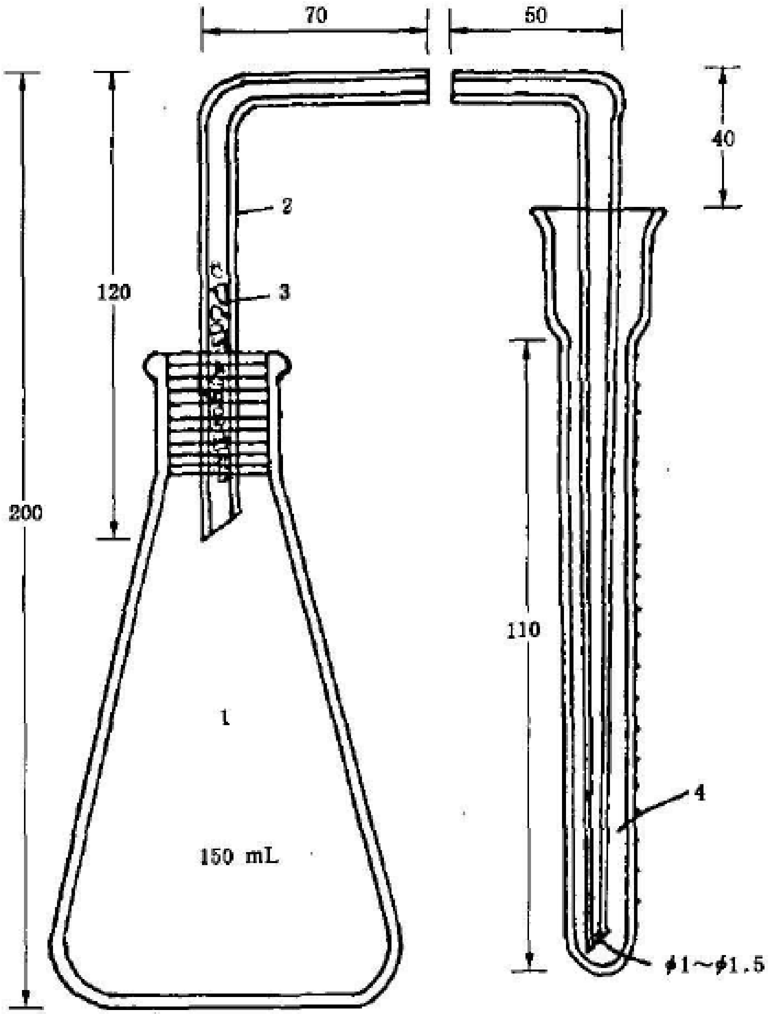
10.17 Standard arsenic solution: Suck 1.0 mL standard arsenic stock solution and put it into 100 mL volumetric flask, add 1 mL H_2SO_4 (6+94), add water and dilute to volume. Each milliliter of the solution is equivalent to 1.0 μg arsenic.

11. Instrument

11.1 spectrophotometer

11.2 arsenic determination device: See Figure 1

The unit is mm



1 -150mL conical flask;

2 - Airway tube;

3 - Cotton soaked with lead acetate;

4 - 10 mL graduated centrifuge tube

Figure 1

11.2.1 100mL-150mL conical flask: No.19 standard mouth.

11.2.2 Airway tube: When No.19 standard mouth at orifice or rubber stopper, which is washed after alkali treatment, is sealed with conical flask, there should be no leakage. diameter of the other end of the tube is 1.0 mm.

11.2.3 Absorption tube:10 mL graduated centrifuge tube is used as the absorption tube.

12 Sample treatment

12.1 HNO3-perchloric acid －H_2SO_4 method

12.1.1 Grain, noodles, vermicelli, dried tofu products, pastries, tea and other solid foods with less water content: Weigh 5.00 g or 10.00 g crushed sample, put it into 250 mL-500 mL nitrogen determination bottle, firstly add a little water to moisten the sample, then add several glass beads, 10 mL-15 mL mixed solution of HNO_3-perchloric acid, settle for a moment, slowly heat with small fire until the reaction alleviated, leave it for cooling. Then add 5 mL or 10 mL H_2SO_4 along the bottle wall, reheat it until liquid in the bottle begins to turn brown, continuously drip mixed solution of HNO_3-perchloric acid until organic matter is completely decomposed. Increase the fire until white smoke generates. When white smoke completely releases from bottle mouth and white smoke generates from liquid in the bottle again, the digestion is completely implemented. The solution should be colorless or slight yellow. Cool it (During the operation process, pay attention to prevent explosive boiling or explosion). Add 20 mL water for boiling and remove the residual HNO_3 until white smoke generates. Repeat such treatment for two times, leave the solution for cooling, transfer it into 50 mL or 100 mL volumetric flask, wash nitrogen determination bottle with water, integrate the cleaning solution into the volumetric flask, cool, add water to volume and blend. After having been diluted to volume, 10 mL solution is equivalent to 1g sample and the addition of 1 mL H_2SO_4. Take the mixed solution of HNO_3-perchloric acid and H_2SO_4 with the same quantity as that of the digestion sample, conduct reagent blank test with the same method.

12.1.2 Vegetable and fruit: Weigh 25.00 g or 50.00 g sample, which has been washed and stirred as uniform paste, put it into 250mL-500mL nitrogen determination bottle, add several glass beads, 10 mL-15 mLHNO_3-perchloric acid mixed solution and operate the following procedures in accordance with ”settle for a moment…” in 12. 1. 1. However, after having been diluted to volume, 10 mL solution is equivalent to 5g sample and the addition of 1 mL H_2SO_4.

12.1.3 Sauce, soy sauce, vinegar, cold drink, tofu, preserved bean curd, pickles: Weigh 10.0 0g or 20.00 g sample(or suck 10.0 mL or 20.0 mL liquid sample), put it into 250mL-500mL nitrogen determination bottle, add several glass beads, 5mL-15mLHNO_3-perchloric acid mixed solution and operate the following procedures in accordance with ”settle for a moment…” in 12. 1. 1. However, after having been diluted to volume, 10 mL solution is equivalent to 2g or 2 mL sample.

12.1.4 Alcoholic beverage or beverage containing CO_2: Suck 10.00 mL or 20.00 mL sample, put it into 250mL-500mL nitrogen determination bottle, add several glass beads, first heat with small fire to remove ethanol or CO_2, add 5 mL-10 mL mixed solution of HNO_3-perchloric acid, blend and operate the following procedures in accordance with ”settle for a moment…” in 12. 1. 1. However, after having been diluted to volume, 10 mL solution is equivalent to 2 mL sample.

12.1.5 Food with high sugar content: Weigh 5.00 g or 10.0 g sample, put it into 250mL - 500mL nitrogen determination bottle, firstly add a little water to moisten the sample, add several glass beads, 5 mL-l0mL HNO_3 - perchloric acid mixed solution, mix and shake well. Slowly add 5 mL or 10 mL H_2SO_4, slowly heat (sugar content is easily carbonized) when the reaction becomes alleviated and no bubble generates, continuously supplement mixed solution of HNO_3-perchloric acid along the bottle wall. When the bubbles disappear, increase the fire until organic matter is completely decomposed and white smoke generates. The solution should be colorless or slight yellow, leave it for cooling. Operate the following procedures in accordance with “Add 20 mL water for boiling….” in 12.1.1.

12.1.6 Aquatic product: Take edible part of the sample and crush it into homogenous paste, weigh 5.00 g or 10.0 g product (appropriately reduce the sample volume of marine algae, shellfish), put it into 250 mL-500 ml nitrogen determination bottle, add several glass beads, 5 mL-10 mLHNO_3-perchloric acid mixed solution, blend and operate the following procedures in accordance with “Then add 5 mL or 10 mLH_2SO_4 along the bottle wall…” in

12.2 HNO_3—H_2SO_4 method

Replace HNO_3-perchloric acid mixed solution with HNO_3 for operation.

12.3 Incineration method

12.3.1 Grain, tea and other foods with less water content: weigh 5.00g grinded sample, put it into crucible, and add 1g MgO and 10mL Mg $(NO_3)_2$ solution, blend and immerse for 4h. Then evaporate it at low temperature or in water bath pot, carbonize it with small fire until no smoke generates, transfer it into muffle furnace, heat to 550℃, calcinate it for 3 h-4 h and take it out after cooling. Add 5 mL water after moistening the sample, stir it with thin glass rod and then use a little water to wash the ash, attached on the glass rod, into the crucible, put it on the water bath to evaporate, transfer into muffle furnace, conduct incineration for 2h at 550 ℃ and take it out for cooling. add 5mL water to moisten the ash, slowly add 10 mL HCl (1+1), transfer the solution into 50 mL volumetric flask, wash the crucible with HCl (1+1) for 3 times (5 mL for each time), add the washing liquid into the volumetric flask, add water to volume and blend. After having been diluted to volume, 10 mL solution is equivalent to 1g sample and the addition amount of HCl is not less than 1.5 mL (except the amount required by neutralization). When the full amount is provided for the determination of silver salt method, the addition of HCl is not required.

Conduct the reagent blank test in accordance with the same operating method.

12.3.2 Vegetable oil: weigh 5.00 g sample, put it into 50mL ceramic crucible, add 10g $Mg(NO_3)_2$, cover 2g MgO on it, heat the crucible with small fire until smoke just generates, immediately take the crucible down to prevent the content from overflowing. When the smoke becomes smaller, heat until carbonized completely, transfer the crucible into Muffle furnace, calcinate it until incineration is completely implemented under 550 ℃ and take it out after cooling. Add 5mL water to moisten the ash, slowly add 15 mL HCl (1+1), transfer the solution into 50 mL volumetric flask, wash the crucible with HCl (1+1) for 5 times (5 mL for each time), integrate the washing liquid into the volumetric flask, dilute to volume with HCl (1+1) and blend. After having been diluted to volume, 10 mL solution is equivalent to 1g sample and the addition of 1.5ml HCl (except for the amount required by neutralization). Conduct the reagent blank test in accordance with the same operating method.

12.3.3 Aquatic product: Take edible part of the sample and crush it into homogenous paste, weigh 5.00 g, put it into crucible, add 1g MgO and 10mL $Mg(NO_3)_2$ solution, blend and immerse for 4h. Operate the following procedures in accordance with “Then evaporate it at low temperature or in water bath pot….” in 12.3.1.

13 Analysis Procedure

Suck certain amount of solution with constant volume after digestion (equivalent to 5g sample) and same amount of reagent blank solution, respectively put them into 150 mL conical flask, supplement H_2SO_4 until the total volume reaches 5 mL and add water to 50 mL~ 55 mL.

13.1 Drawing of standard curve

Suck 0, 2.0, 4.0, 6.0, 8.0,10.0mL standard arsenic solution(equivalent to 0, 2.0, 4.0, 6.0, 8.0,10.0μg), respectively put into 150 mL conical flask, add water to 40 mL and then add 10 mL H_2SO_4 (1+1),

13.2 Digest the solution with wet method

In the sample digestion solution, respectively add 3mL KI solution (150g/L) and 0.5mL acidic $SnCl_2$ solution into reagent blank solution and standard arsenic solution, blend and settle for 15 min. Respectively add 3g zinc particles, immediately stuff the airway tubes containing cotton saturated with lead acetate, insert the tube tip under the liquid in the centrifuge tube, which contains 4mL silver salt solution, react for 45 min at room temperature and remove the centrifuge tube. Then supplement chloroform to 4mL, use 1 cm cuvette to adjust zero point with zero tube, measure the absorbance at the wave length of 520 nm and draw the standard curve.

13.3 Digest the solution with incineration method

Take digestion solution for incineration method and reagent blank solution, respectively put into 150mL conical flask, suck 0, 2.0,4.0,6.0,8.0,10.0mL standard arsenic solution(equivalent to 0,2.0,4.0,6.0,8.0,10.01ag arsenic), respectively put into 150mL conical flask, add water to 43.5 mL and then add 6.5 mL HCl . Operate the following procedures in accordance with “”In sample digestion solution….” in 13.2.

14 Result Calculation

Calculate the arsenic content in the sample in accordance with formula (2).

$$X = \frac{(A_1 - A_2) \times 1\,000}{m \times V_2/V_1 \times 1\,000} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots (2)$$

Where :

X — Arsenic content in the sample. The unit is mg/kg or mg/L;

A_1— measured sample digestion solution arsenic mass in. The unit is μg;

A_2— Arsenic mass in solution of reagent blank. The unit is μg;

M —Mass or volume of sample. The unit is g or mL;

V_1— sample digestion solution total volume of. The unit is mL;

V_2— Volume of digestion solution for measured sample. The unit is mL,

Two significant digits are reserved for calculation result.

15 Precision

The difference between the absolute values of the two independent determination results obtained under the repeatability condition must not exceed 10% of the average arithmetic value.

Method III Arsenic Stain Method

16 Principle

When the sample is digested, use KI and $SnCl_2$ to reduce arsenic with high valence to As^{3+}, which generates AsH_3 with zinc particles and new hydrogen, produced from the acid. Then red colloidal substance forms through absorption by silver salt. Quantification is conducted by comparing with standard series. Color spots (from yellow to orange color) generate with $HgBr_2$ test paper. The constant quantity should be compared with standard series.

17 Reagent

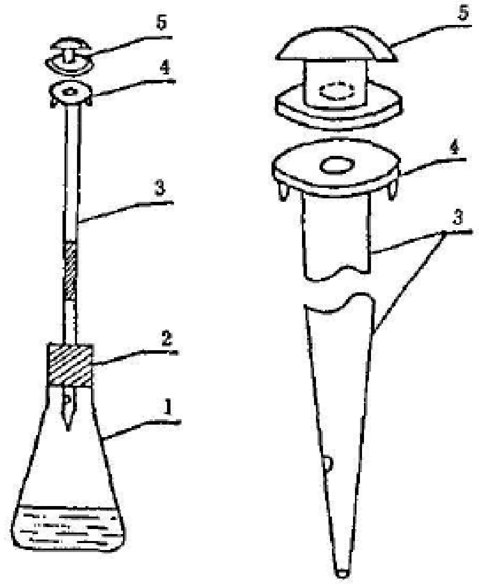
17.1 As same as 10. 1-10.14,10.16 and 10. 17 in Silver Salt Method

17.2 HgBr2-ethanol solution (50 g / L): Weigh 25 g HgBr$_2$, dissolve it with small amount of ethanol and then dilute to 500 mL.

17.3 HgBr$_2$ test paper: Immerse the circular filter paper cut to the diameter of 2cm in HgBr$_2$--ethanol solution (50 g/L) for more than 1h, store it in refrigerator and dry it in the shade before use.

18 Instrument

Arsenic determination device. See Figure 2.



1- Conical flask ;

2- Rubber stopper ;

3- Arsenic-measuring tube ;

4-Orifice ;

5-Glass cap.

Figure 2

18.1 100mL conical flask.

18.2 rubber stopper: There is a hole in the middle.

18,3 glass arsenic-measuring tube: Total length is 18 cm. Its upper section is thicker and lower section thinner. Inner diameter from the orifice to the position at 14 cm is 6.5 mm and then gradually becomes narrow downwards. Its inner diameter at the end is 1 mm -3 mm. A hole with diameter of 2 mm is located 1cm from the end. The narrow section of the tube is inserted into the rubber stopper tightly, which makes the lower section extend to the hole and justly below the rubber stopper. put the lead acetate cotton into the thicker upper section with length of 5 cm -6 cm. Its upper end is at least 3 cm from the orifice. round and flat orifice with polished upper surface is on the top of the arsenic-measuring tube, while there is a hook on each side of lower surface and used for fixing the glass cap.

18.4 glass cap: Its lower section is polished. There are crescent-shaped groove on the upper section and holes with diameter of 6.5 mm on the center. When using the glass cap, cover it on the orifice of arsenic-measuring tube to make holes match with each other. A $HgBr_2$ test paper with smooth surface facing down is located in the middle. Fix glass cap and arsenic-measuring tube with rubber band or other suitable methods.

19 Sample Digestion

As same as Chapter 12.

20 Analysis Procedure

Suck a certain amount of solution with constant volume after digestion (equivalent to 2g grain, 4g vegetable, fruit, 4mL cold drink and 5g vegetable oil. For other samples, please refer to this quantity) and same amount of reagent blank solution, respectively put them into arsenic-measuring bottles, add 5 mL KI solution(150 g/L),5 drops of acidic $SnCl_2$ solution and 5 mL HCl (if HNO_3-perchloric acid－H_2SO_4 or HNO_3－H_2SO_4 digestion solution is used as sample, the milliliter quantity of H_2SO_4 should be reduced from the sample; If digestion solution for incineration method is used, then milliliter quantity of HCl should be reduced from the sample) and add proper amount of water to 35 mL(don’t add water into vegetable oil). Suck 0, 0.5,1.0 and 2.0 mL standard arsenic solution(equivalent to 0, 0.5,1.0 and 2.0 Kg arsenic), respectively put into arsenic-measuring bottle, respectively add 5mL KI solution(150 g/L), 5 drops of acidic $SnCl_2$ solution and 5 mL HCl , respectively add water to 35 mL (add water to 60 mL when determining vegetable oil). Add 3g zinc particles into arsenic-measuring bottles containing sample digestion solution, reagent blank solution and standard arsenic solution, immediately plug the arsenic-measuring tube which contains lead acetate cotton and $HgBr_2$ test paper in advance, settle for 1h at 25℃ , take $HgBr_2$ test papers used for sample and reagent blank to compare with the standard arsenic stains.

21 Result Calculation

As same as Chapter 14.

22 Precision

The difference between the absolute values of the two independent determination results obtained under the repeatability condition must not exceed 20% of the average arithmetic value.

Method IV Borohydride Reduction Colorimetric Method

23 Principle

When the sample is digested, arsenic exists as As^{5+}. When H+ concentration in the solution is higher than 1.0 mol/L, add KI-thiourea by heating, which can reduce As^{5+} into to As^{3+}. Under acidic conditions, KBH4 can reduce As^{3+} into As3- and form AsH_3 gas, which shows yellow color after be introduced into the absorption liquid. The depth of yellow color is proportional to arsenic content in the solution. The constant quantity should be compared with standard series.

24 Reagent

24.1 KI (500 g/L) + thiourea solution(50 g/L)(1+1).

24.2 NaOH solution (400 g/L) and NaOH solution(100 g/L), 24.3 H2SO4 (1+1),

24.4 Absorption liquid

24.4.1 $AgNO_3$ solution (8g/L): Weigh 4.0 g $AgNO_3$, put it into a 500mL beaker, dissolve in proper amount of water, add 30mL HNO_3, add water to 500 mL and store in brown bottle.

24.4.2 PVA solution(4g/L): Weigh 0.4 g PVA (polymerization degree=1500-1800) in the beaker, add 100mL water, heat PVA in boiling water bath, stirring and dissolve it, maintain the temperature for 10 min, take it out and cool for use.

24.4.3 Absorption liquid: Respectively take solutions prepared in 24.4.1 and 24.4.2, add 2 volumes of ethanol (95%), blend and use it as the absorption liquid. Prepare the liquid for use.

24.5 KBH_4 tablet: Mix KBH_4 sodium chloride with mass ratio of 1:4, finely grind the mixture, fully blend and make tablets with diameter of 10 mm and thickness of 4 mm via the tablet machine. Each tablet is 0.5 g. Avoid tabletting in humid weather.

24.6 Lead acetate(100 g/L)cotton: Soak absorbent cotton in lead acetate solution(100 g/L), press out the residual solution after several minutes, spread cotton, dry at 80℃ and store in the wide-mouth glass bottle.

24.7 Citric acid(1.0 mol/L)-ammonium citrate(1.0 mol/L): Weigh 192 g citric acid, 243 gammonium citrate, dissolve in water and dilute to 1000 mL,

24.8 Standard arsenic stock solution: Weigh 0.1320g As_2O_3, which has been cooled to room temperature for 1h at 105 ℃ in the dryer, put it into 100 mL beaker, add 10 mL NaOH solution (2.5 mol / L). After it dissolved, add 5 mL perchloric acid and 5 mL H_2SO_4 , put it on the electric hot plate and heat until white smoke generates. After cooling, transfer the solution into 1000 mL volumetric flask and dilute it to volume with water. Each milliliter of solution contains 0.100 mg arsenic (As5 +)

24.9 Standard arsenic solution: Suck 1.00 mL standard arsenic stock solution into a 100mL volumetric flask and dilute to volume with water. Each milliliter of solution contains 1.00 μg arsenic (As^{5+}).

24.10 Methyl red indicator (2g/L): Weigh 0.1g methyl red and dissolve it in 50mL ethanol (95%).

25 Instrument

25.1 spectrophotometer.

25.2 AsH3 generator, See Figure 1,

26 Analysis Procedure

26.1 Sample treatment

26.1.1 Grain food: weigh 5.00g sample, put it into a 250mL conical flask, add 5.0 mL perchloric acid, 20mL HNO3 and 2.5 mL H2SO4 (1+1), settle for a few hours (or overnight) and put on the electric hot plate for heating. if the solution turns brown, HNO3 should be supplemented to completely decompose the organic matter. Take the conical flask down, leave it for cooling, add 15 mL water, reheat until white smoke generates, take the flask down, transfer the constant quantity of the digestion solution into 100 mL AsH3 generating bottle by using 20 mL water for several times. Prepare reagent blank simultaneously.

26.1.2 Vegetable and fruit: weigh 10.00 g -20.00 g sample, put it into a 250mL conical flask, add 3mL perchloric acid , 20mL HNO3 and 2.5 mL H2SO4 (1+1). Then operate in accordance with 26.1.1.

26.1.3 Animal food (except seafood): weigh 5.00 g -10.00 g sample, put it into a 250mL conical flask. Then operate in accordance with 26.1.1.

26.1.4 Seafood: weigh 0.100g -1.00 g sample, put it into a 250mL conical flask, add 2mL perchloric acid, 10mL HNO3 and 2.5 mL H2SO4 (1+1). Then operate in accordance with 26.1.1.

26.1.5 Beverage containing ethanol or CO2: suck 10.0 mL sample into a 250 mL conical flask, remove ethanol or CO2 by low-temperature heating, add 2 mL perchloric acid, 10 mLHNO3 and 2.5 mL H2SO4 (1+1). Then operate in accordance with 26.1.1.

26.1.6 Sauce food: suck 5.0 mL-10. 0 mL representative sample into a 250 mL conical flask, add 5 mL perchloric acid, 20 mL HNO3 and 2.5 mL H2SO4 (1+1). Then operate in accordance with 26.1.1.

26.2 Preparation of standard series

In the six 100mL AsH_3 generating bottles, successively add 0, 0.25, 0.5, 1.0, 2.0, 3.0mL standard arsenic solution (equivalent to 0, 0.25, 0.5, 1.0, 2.0, 3.0μg arsenic), respectively add water to 3mL and then add 2.0 mL H_2SO_4 (1+1).

26.3 Sample and standard determination

In sample and standard AsH_3 generating bottle, respectively add 0.1g ascorbic acid, 2.0 mL KI (500g/L)-thiourea solution (50 g/L), put into boiling water bath, heat for 5 min (temperature in the bottle can't exceed 800℃), take it out and cool. Add 1 drop of methyl red indicator (2g/L), add 3.5 mL NaOH solution (400 g/L) and adjust the solution just turns yellow with NaOH solution (100 g/L). Then add 1.5 ml citric acid (1.0 mol/L)-ammonium citrate solution (1.0 mol/L), add water to 40mL, add a KBH_4 tablet, immediately connect it with the absorption tube containing 4.0 mL absorption liquid through a conduit inserted with lead acetate cotton, occasionally shake AsH_3 generating bottle, react for 5 min, add another KBH_4 tablet and continue to react for 5 min. Then take down the absorption tube, using 1 cm cuvette to adjust absorbance to zero with zero tube of standard tube at the wavelength of 400nm and determine the absorbance of each tube. According to the arsenic contents and absorbance in all the tubes of standard series, draw standard curve or calculate the regression equation.

27 Result calculation

Calculate the arsenic content in the sample according to formula (3)

$$X = \frac{A \times 1\ 000}{m \times 1\ 000} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (3)$$

Where:

X —Arsenic content in the sample. The unit is mg/kg or mg/L;

A —Quality found from the standard curve of the digestion solution for determination. The unit is μg;

M —Mass or volume of sample. The unit is g or mL;

Two significant digits are reserved for calculation result.

28 Precision

The difference between the absolute values of the two independent determination results obtained under the repeatability condition must not exceed 15% of the average arithmetic value.

Determination of Abio-arsenic

29 Scope

This method specifies the determination method for total abio-arsenic in various foods.

This method is applicable to determine total abio-arsenic in various foods.

Detection limit of the method:

Atomic fluorescence spectrometry: solid sample 0.04mg/kg, liquid sample 0.004mg/L;silver salt method: 0.1 mg/kg, linear range:1.0μg-10.0μg

Method I Hydride Atomic Fluorescence Spectrophotometry

30 Principle

Arsenic in food may exist in different chemical forms, including abio-arsenic and organic arsenic. Under the condition of water bath containing 6 mol/L HCl, abio-arsenic is extracted in the form of chloride to achieve the separation of abio-arsenic and organic arsenic. Total abio-arsenic is determined under the condition of 2 mol/L HCl.

31 Reagent

31.1 HCl solution(1+1): Weigh 250 mL HCl, pour it slowly into 250 mL water and blend.

31.2 KOH solution(2 g/L): Weigh KOH 2g, dissolve it in water and dilute to 1000 mL.

31.3 KBH4 solution(7g /I): Weigh 3.5 g KBH_4, dissolve it in 500mL 2g/L KOH solution.

31.4 Mixed solution of KI (100 g/L)- thiourea (50 g/L): Weigh 10g KI and 5g thiourea, dissolve them in water, dilute to 100 mL and blend.

31.5 Standard As^{3+} (AS^{3+}) solution: Accurately weigh 0.1320g As_2O_3, add 1mL 100g/L KOH, dissolve with sub-boiling distilled water, transfer into the 100mL volumetric flask and dilute to volume. This standard solution contains 1 mg/mL As^{3+}. During the application, dilute the standard solution progressively until its concentration reaches 1μg/mL As^{3+} . It can be used for 7 days if stored in refrigerator.

32 Instrument

Glass instrument should be immersed in 15% HNO_3 for 24h before use.

32.1 Atomic fluorescence spectrometer

32.2 Constant-temperature water bath pot.

33 Analysis Procedure

33.1 Sample treatment

Solid sample: Weigh 2.50g dry sample that has been crushed over 80 mesh sieve (the weight can differ based on the sample content) into 25mL graduated test tube with stopper, add 20mL HCl (1+1) solution and blend. Or weigh 5.00 g fresh sample (sample should be firstly stirred to homogenous paste) in 25mL graduated test tube with stopper, add 5 mL HCl, dilute it to volume and blend. Put into 60 ℃ water bath pot for 18 h. During this process, shake and vibrate for several times to make the sample immersed and extracted completely, take it out for cooling, filter with absorbent cotton. Put 4 mL filtrate into 10 mL volumetric flask, add 1 mL KI-thiourea mixed solution, 8 drops of n-octanol (defoamer), dilute to volume with water, settle for 10 min and determine abio-arsenic in the sample. If the solution is turbid, determination is conducted after re-filtration and simultaneously implement reagent blank test.

Note: After the immersion and extraction of sample, dilute to 25mL with HCl (1+1) solution before filtration.

Liquid sample: Put 4mL sample into 10mL volumetric flask, add 4mL HCl (1+1) solution and 1mL KI-thiourea mixed solution, dilute to volume with 8 drops of n-octanol (defoamer) and blend. Then settle for 10min, determine the total abio-arsenic in the sample and simultaneously implement reagent blank test.

33.2 Reference conditions of the instrument:

Negative high voltage of photomultiplier tube (PMT): 340V; current of hollow arsenic cathode lamp: 40mA; height of atomizer=9 mm; flow rate of carrier gas: 600 mL/min; delay time of reading: 2s; reading duration: 12s; reading mode: peak area; addition volume of standard solution or sample solution: 0.5mL,

33.3 Standard series

Standard series of abio-arsenic determination: respectively and accurately suck 0,0.05,0.1 ,0.25,0.5, 1.0 mL 1μg/mL As^{3+} standard solution into 10mL volumetric flask, respectively add 4mL HCl (1+1) solution, 1mL KI-thiourea mixed solution, 8 drops of n-octanol and dilute to volume [equivalent to As^{3+}(As-)-containing concentration 0,5.0, 10.0, 25.0, 50.0 and 100.0 ng/mL].

34. Result calculation

Calculate arsenic content in the sample according to formula (4).

$$X = \frac{(C_1 - C_2)F}{m} \times \frac{1\,000}{1\,000 \times 1\,000} \quad \cdots\cdots\cdots\cdots\cdots\cdots (4)$$

Where:

X —Abio-arsenic in the sample. The unit is mg/kg or mg/L ;

C_1—Abio-arsenic concentration in the measured liquid of the sample. The unit is ng/mL ;

C_2—Concentration of the reagent blank. The unit is ng/mL;

M —Mass or volume of sample. The unit is g or mL;

F —Solid sample: F=10 mLX25 mL/4 mL;

Liquid sample: F= 10mL

Method II Silver Salt Method

35 Principle

When the sample in 6mol/L HCl solution has been heated by water bath of 70℃ , abio-arsenic is extracted as chloride and reduced to As^{3+} by using KI and $SnCl_2$. Then As^{3+} generates AsH_3 with zinc particles and new hydrogen produced from the acid, and form red colloidal substance through the absorption of silver salt solution. The constant quantity should be compared with standard series.

36. Reagent

36.1 HCl .

36.2 Chloroform.

36.3 Octanol.

36.4 HCl solution(1+1): Weigh 100 mL HCl , add water and dilute to 200 mL and blend.

36.5 KI solution(150 g/L): Weigh 15 g KI, dissolve in water until volume reaches 100 mL, blend and prepare before use.

36.6 Acid $SnCl_2$ solution: Weigh 40 g $SnCl_2.2H_2O$, dissolve in HCl, dilute to100 mL and add a few metallic tin particles.

36.7 Lead acetate solution(100 g/L): Weigh 10g lead acetate, dissolve in water until volume reaches 100 mL, blend.

36.8 Lead acetate cotton: Soak the absorbent cotton in lead acetate solution (100 g/L), press out the excessive solution, loosen the cotton, dry it at 100 ℃ and store in a glass bottle.

36.9 Silver salt solution: Weigh 0.25g silver diethyldithiocarbamate「$(C_2H_5)_2$ NCS_2Ag」, dissolve in small amount of chlorform, add 1.8 mL triethanolamine, dilute to 100 mL with chloroform, settle overnight, filter in brown bottle and store in refrigerator.

36.10 Standard arsenic stock solution (1.00 mg/mL): GBW (E)080385.

36.11 Standard arsenic solution (1.00 μg/mL): Accurately suck standard arsenic stock solution and progressive dilute it to 1.00 μg /mL with water.

37 Instrument

37.1 spectrophotometer.

37.2 constant temperature water bath tank.

37.3 arsenic determination device.

38 Analysis Procedure

38.1 Sample treatment

38.1.1 Solid dry sample: Weigh 1.00g -10.00g grinded or crushed sample, put it into 100mL conical flask with stopper and add 20 mL-40 mL HCl solution (1+1). It is preferred to have the sample fully immersed. Place it in 70 ℃ water bath for 1h heat insulation, take it out and cool. Then filter with absorbent cotton or single-layer gauze, wash conical flask and residues with 20 mL-30 mL water, integrate the filtrate into arsenic-measuring conical flask to make total volume reaches about 50 mL.

38.1.2 Vegetable and fruit: Weigh 1.00 g -10.00 g sample, which has been made into homogenous paste or crushed into crumbs, put into 100mL conical flask with stopper, add same amount of concentrated HCl, and then add 10 mL-20 mL HCl solution. Operate the following procedures in accordance with ”place it in 70℃ water bath….” In 38.1.1.

38.1.3 Meat and aquatic products: Weigh 1.00 g-10.00g sample, add small amount of HCl solution (1+1), grind into paste in mortar and transfer it into 100 mL conical flask with stopper for several times with 30 mL HCl solution(1+1). Operate the following procedures in accordance with ”place it in 70℃

water bath….” in 38.1.1.

38.1.4 Liquid food: Suck 10.0 mL sample into arsenic-measuring bottle, add 30mL water and 20mL HCl solution (1+1).

38.2 Preparation of standard series

Suck 0, 1.0, 3.0, 5.0, 7.0, and 9.0mL standard arsenic solution(equivalent to 0, 1.0, 3.0, 5.0, 7.0, 9.0μg arsenic), respectively put into arsenic-measuring bottle, add water to 40 mL and add 8 mL HCl solution(1+1).

38.3 Determination

In the sample digestion solution, respectively add 3mL KI solution (150g/L) and 0.5mL acidic $SnCl_2$ solution into reagent blank solution and standard arsenic solution, blend and settle for 15 min. After dripping 5~10 drops of octanol in the sample solution, respectively add 3g zinc particles into sample liquid and standard arsenic solution, immediately block with the airway tubes containing lead acetate cotton, insert the tube tip under the liquid in the centrifuge tube, which contains 5 mL silver salt solution, react for 45 min at room temperature and remove the test tube. Then supplement chloroform to 5 mL, use 1 cm cuvette to adjust zero point with zero tube, measure the absorbance at the wave length of 520 nm and draw the standard curve.

39 Result Calculation

Calculate arsenic content in the sample according to formula (5).

$$X = \frac{(m_1 - m_2)}{m_3 \times 1\,000} \times 1\,000 \qquad \cdots\cdots\cdots\cdots\cdots\cdots (5)$$

Where :

X —Abio-arsenic content in the sample. The unit is mg/kg or mg/L;

m_1—Arsenic mass in measured sample solution. The unit is μg;

m_2—Arsenic mass in reagent blank . The unit is μg;

m_3—Mass or volume of sample. The unit is g or mL

Two significant digits are reserved for the calculation result.

40 Precision

The difference between the absolute values of the two independent determination results obtained under the repeatability condition must not exceed 10% of the average arithmetic value.