GB

NATIONAL STANDARD OF THE

PEOPLE'S REPUBLIC OF CHINA

ICS 65.120

B 46

GB/T 13079-2006

Replacing GB/T 13079-1999

Determination of total arsenic in feeds

饲料中总砷的测定

Issued on: December 12, 2006 **Implemented on: March 01, 2007**

Issued by: General Administration of Quality Supervision, Inspection and Quarantine of PRC;

Standardization Administration of PRC.

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Determination of total arsenic in feeds

1 Scope

This standard specifies the method for the determination of total arsenic in feeds.

This standard is applicable to various compound feeds, concentrated feeds, premixed feeds with additives, single feeds, feed additives.

Minimum detectable concentration: The silver salt method is 0.04 mg/kg; borohydride reduction spectrophotometry is 0.04 mg/kg; atomic fluorescence spectrometry is 0.010 mg/kg.

2 Normative references

The provisions in following documents become the provisions of this Standard through reference in this Standard. For the dated references, the subsequent amendments (excluding corrections) or revisions do not apply to this Standard; however, parties who reach an agreement based on this Standard are encouraged to study if the latest versions of these documents are applicable. For undated references, the latest edition of the referenced document applies.

GB/T 6682 Water for analytical laboratory use - Specification and test methods

GB/T 14699.1 Feeding Stuffs - Sampling

GB/T 20195 Animal feeding stuffs - Preparation of test samples

3 Sampling

It is carried out, according to GB/T 14699.1.

4 Specimen preparation

It is carried out, according to GB/T 20195.

5 Silver salt method (arbitration method)

5.1 Principle

The sample is subject to acid digestion or dry ashing, to destroy the organic matter, so that the arsenic exists in ion state. The high-valent arsenic is reduced to trivalent arsenic, by potassium iodide and stannous chloride, then reduced to arsine hydrogen, by the new ecological hydrogen, which is produced by zinc particles and acid. In a closed device, it is absorbed by a chloroform solution of silver diethyldithiocarbamate (Ag-DDTC), to form a yellow or brown-red silver sol, the color depth of which is proportional to the arsenic content. It is measured by a spectrophotometer. The reaction to form colloidal silver is as follows:

$$AsH_3 + 6Ag(DDTC) = 6Ag + 3H(DDTC) + As(DDTC)_3$$

5.2 Reagents and solutions

Unless otherwise specified, the following reagents are analytically pure; the water shall meet the requirements for grade-2 water in GB/T 6682.

5.2.1 Nitric acid.

5.2.2 Sulfuric acid.

5.2.3 Perchloric acid.

5.2.4 Hydrochloric acid.

5.2.5 Acetic acid.

5.2.6 Potassium iodide.

5.2.7 L-Ascorbic acid.

5.2.8 Arsenic-free zinc particles, which has a particle size of 3.0 mm ± 0.2 mm.

5.2.9 Mixed acid solution (A): $HNO_3 + H_2SO_4 + HClO_4 = 23 + 3 + 4$.

5.2.10 Hydrochloric acid solution: c(HCl) = 1 mol/L.

Measure 84.0 mL of hydrochloric acid (5.2.4). Pour it into an appropriate amount of water. Use water to dilute it to 1 L.

5.2.11 Hydrochloric acid solution: c(HCl) = 3 mol/L.

Measure 250.0 mL of hydrochloric acid (5.2.4). Pour into an appropriate amount of water. Use water to dilute it to 1 L.

5.2.12 Lead acetate solution: 200 g/L.

5.2.13 Magnesium nitrate solution: 150 g/L.

Weigh 30 g of magnesium nitrate [$Mg(NO_3)_2 \cdot 6H_2O$]. Dissolve it in water. Dilute to

200 mL.

5.2.14 Potassium iodide solution: 150 g/L.

Weigh 75 g of potassium iodide. Dissolve it in water. Make the volume reach to 500 mL. Store it in a brown bottle.

5.2.15 Acidic stannous chloride solution: 400 g/L.

Weigh 20 g of stannous chloride ($SnCl_2 \cdot 2H_2O$). Dissolve it in 50 mL of hydrochloric acid. Add a few metal tin particles. It can be used for one week.

5.2.16 Silver diethyldithiocarbamate (Ag-DDTC)-triethylamine-chloroform absorption solution: 2.5 g/L.

Weigh 2.5 g (accurate to 0.0001 g) of Ag-DDTC in a dry beaker. Add an appropriate amount of chloroform to dissolve completely. Then transfer to a 1000 mL volumetric flask. Add 20 mL of triethylamine. Use chloroform to make the volume reach to the mark. Store it in a brown bottle in a cool dark place. If there is precipitation, it shall be filtered before use.

5.2.17 Lead acetate cotton: Soak medical absorbent cotton in lead acetate solution (100 g/L) for about 1 hour, to press off the excess solution. Dry it naturally. OR dry it at 90 °C ~ 100 °C. Store it in an airtight bottle.

5.2.18 Arsenic standard stock solution 1.0 mg/mL.

Accurately weigh 0.660 g of arsenic trichloride (110 °C, dry for 2 h). Add 5 mL of sodium hydroxide solution (5.2.21), to dissolve it. Then add 25 mL of sulfuric acid solution (5.2.20), for neutralization. Make the volume reach to 500 mL. Each millimeter of this solution contains 1.00 mg of arsenic. Store it in a plastic bottle, in a cold place.

5.2.19 Arsenic standard working solution: 1.0 μg/mL.

Accurately pipette 5.00 mL of arsenic standard stock solution (5.2.18), into a 100 mL volumetric flask. Add water to make the volume reach to the mark. This solution contains 50 μg/mL arsenic.

Accurately pipette 2.00 mL of 50 μg/mL arsenic standard solution. Add 1 mL of hydrochloric acid, into a 100 mL volumetric flask. Add water to make the volume reach to the mark. Shake well. Each millimeter of this solution is equivalent to 1.0 μg of arsenic.

5.2.20 Sulfuric acid solution: 60 mL/L.

Pipette 6.0 mL of sulfuric acid. Slowly add it to about 80 mL of water. Use water to dilute to 100 mL, after cooling.

5.4.1 Handling of samples

5.4.1.1 Mixed acid digestion method

Compound feed and single feed should be digested by nitric acid-sulfuric acid-perchloric acid. Weigh 3 g ~ 4 g of the sample (accurate to 0.0001 g). Place it in a 250 mL Kjeldahl bottle. Add a little water to wet the specimen. Add 30 mL of mixed acid solution (A) (5.2.9). Place it for more than 4 h or overnight. Put it on the electric stove, to start to digest from room temperature. After the brown gas disappears, increase the digestion temperature, until white smoke (SO_3) is emitted for a few minutes (be sure to drive off the nitric acid). At this time, the solution shall be clear and colorless or light yellow. The volume of the solution in the bottle is similar to the consumption of sulfuric acid. The residue is white. If the solution in the bottle is brown, add appropriate amount of nitric acid and perchloric acid after cooling, until the solution is completely digested. Cool it. Add 10 mL of hydrochloric acid solution (5.2.10). Boil it. Cool it slightly. Transfer to a 50 mL volumetric flask. Use water to wash the Kjeldahl flask 3 ~ 5 times. Combine the washing solution into the volumetric flask. Then use water to make the volume reach to the mark. Shake well. Prepare for determination.

When the specimen digestion solution contains less than 10 μg of arsenic, it can be directly transferred to the arsine generator. Add 7 mL of hydrochloric acid. Add water to make the volume of the solution in the bottle 40 mL. After adding 2 mL of potassium iodide, proceed according to the steps of 5.4.3.

At the same time, under the same conditions, carry out the reagent blank test.

5.4.1.2 Hydrochloric acid dissolution method

5.4.1.2.1 It should not add sulfuric acid to mineral element feed additives; the sample shall be dissolved by hydrochloric acid. Weigh 1 g ~ 3 g of specimen (accurate to 0.0001 g), into a 100 mL tall beaker. Add a little water to moisten the specimen. Slowly add 10 mL of hydrochloric acid solution (5.2.11). After the intense reaction, slowly add 8 mL of hydrochloric acid. Use water to dilute it to about 30 mL. Boil it. Transfer to a 50 mL volumetric flask. Wash the beaker 3 ~ 4 times. Combine the washing solution into the volumetric flask. Use water to make its volume reach to the mark. Shake well. Prepare for use.

When the specimen digestion solution contains less than 10 μg of arsenic, it can be directly transferred to the generator, diluted to 40 mL by water and boiled. Proceed the following steps according to the steps of 5.4.3, from "Add 2 mL of potassium iodide".

In addition, a few mineral feeds are rich in sulfur, which seriously interferes with the determination of arsenic. After dissolving the sample with hydrochloric acid, add 5 mL of lead acetate solution (5.2.12) into the tall beaker. Boil it. Let it stand for 20 minutes. The formed lead sulfide precipitate is removed by filtration. Make the volume reach to 50 mL. Proceed the following, according to the steps specified in 5.4.3.

At the same time, under the same conditions, do a reagent blank test.

5.4.1.2.2 Dissolving samples of copper sulfate and basic copper chloride: Weigh 0.1 g ~ 0.5 g (accurate to 0.0001 g) of the specimen, into the arsine generator (in case of samples with high arsenic content, first make the volume reach to the mark; divide-take specimen, so that the arsenic content in the test solution is within the working curve). Add 5 mL of water to dissolve. Add 2 mL of acetic acid (5.2.5) and 1.5 g of potassium iodide (5.2.6). Let it stand for 5 min. Add 0.2 g of L-ascorbic acid (5.2.7) to dissolve it. Add 10 mL of hydrochloric acid. Then use water to dilute to 40 mL. Shake well, Proceed the following, according to the steps specified in 9.3.

At the same time, under the same conditions, do a reagent blank test.

5.4.1.3 Dry ashing method

Additive premixed feed, concentrated feed, compound feed, single feed, feed additives may choose dry ashing method.

Weigh 2 g ~ 3 g of the specimen (accurate to 0.0001 g) into a 30 mL porcelain crucible. Add 5 mL of magnesium nitrate solution (5.2.13). Mix well. Evaporate to dryness at a low temperature or in boiling water bath. Carbonize at low temperature until smokeless. After that, transfer to a high-temperature furnace for ashing at a constant temperature of 550 °C, for 3.5 h ~ 4 h. Take it out to cool. Slowly add 10 mL of hydrochloric acid solution (5.2.11). After the intense reaction, boil and transfer to a 50 mL volumetric flask. Use water to wash the crucible, for 3 ~ 5 times. Combine the washing solution into the volumetric flask. Make the volume reach to the mark. Shake well. Prepare for test.

When the said specimen contains less than 10 μg of arsenic, it can be directly transferred to the generator. Add another 8 mL of hydrochloric acid. Add water to about 40 mL. Add 1 g of ascorbic acid (5.2.7) to dissolve. Operate according to the steps specified in 5.4.3.

At the same time, under the same conditions, do a reagent blank test.

5.4.2 Standard curve drawing

Accurately pipette 0.00 mL, 1.00 mL, 2.00 mL, 4.00 mL, 6.00 mL, 8.00 mL, 10.00 mL of arsenic standard working solution (1.0 μg/mL) to the generating bottle. Add 10 mL of hydrochloric acid. Add water to dilute to 40 mL. Follow the steps specified in 5.4.3, starting from "Add 2 mL of potassium iodide". Measure the absorbance. Obtain the parameters of the regression equation or draw standard curve. When changing the batch number of zinc particles or newly preparing Ag-DDTC absorption solution, potassium iodide solution, stannous chloride solution, the standard curve shall be drawn again.

5.4.3 Reduction reaction and colorimetric determination

6.2.1 Mixed acid solution (B): $HNO_3 + H_2SO_4 + HClO_4 = 20 + 2 + 3$.

6.2.2 Aqueous solution of methyl orange: 1 g/L; pH3.0 (red) ~ 4.0 (orange).

6.2.3 Ammonia solution: 1 + 1.

6.2.4 Tartaric acid solution: 200 g/L.

Weigh 100 g of tartaric acid. Add appropriate amount of water. Slightly heat to dissolve. Make its volume reach to 500 mL, after cooling.

6.2.5 Potassium hydride tablets: KBH_4:NaCl = 1:5

Mix potassium borohydride and sodium chloride, at a mass ratio of 1:5. Dry at 90 °C ~ 100 °C for 2 h. Press it, at a pressure of 2 kPa, to form tablet, which has a diameter of 10 mm, a thickness of 5 mm, a mass of 1.0 g ± 0.1 g. It shall be protected from moisture during pressing and storage.

6.3 Equipment

Same as 5.3.

6.4 Analytical procedures

6.4.1 Handling of samples

6.4.1 Mixed acid digestion method

For compound feed and single feed, it should adopt three-acid digestion method. Weigh 2.0 g ~ 3.0 g of the specimen (accurate to 0.0001 g). Put it in a 250 mL Kjeldahl bottle. Add a little water to wet the specimen. Add 25 mL of mixed acid solution (B) (6.2.1). Put it on the electric furnace. Start digestion from room temperature. After the sample solution is boiled, turn off the electric furnace for 10 ~ 15 minutes. Continue heating and digestion, until white smoke (SO_3) is emitted for several minutes. At this time, the solution shall be clear, colorless or light yellow; the volume is similar to the consumption of sulfuric acid; the residue is white. Slightly cool it. Transfer to a 100 mL arsine generator. Wash the Kjeldahl bottle 3 ~ 4 times. Use water to combine the washing solution into the generator, to make the volume of the solution in the bottle about 30 mL. Proceed the following steps according to 6.4.2 and 6.4.3.

At the same time, under the same conditions, do a reagent blank test.

Note: Drive off all the nitric acid during digestion; otherwise, the result will be relatively low.

6.4.1.2 Hydrochloric acid dissolution method

It should not add sulfuric acid to mineral element feed additives, but the specimen shall be dissolved with hydrochloric acid. Weigh 0.5 g ~ 2.0 g of the specimen (accurate to

0.0001 g) into the generator. Slowly add 5 mL of hydrochloric acid solution (5.2.11) dropwise. After the intense reaction, slowly add 3 mL ~ 4 mL of hydrochloric acid. Use water to dilute it to about 30 mL. Boil it. After the specimen is dissolved, proceed according to the operation steps 6.4.2 and 6.4.3.

At the same time, under the same conditions, do a reagent blank test.

6.4.1.3 Dry ashing method

For additive premixed feed, concentrated feed, compound feed, single feed, feed additives, it may choose dry ashing method.

Weigh 1.0 g ~ 2.0 g of the specimen (accurate to 0.0001 g), into a 30 mL porcelain crucible. Transfer it to a high-temperature furnace, after low-temperature carbonization. Ash it at a constant temperature of 550 °C, for 3 h. Take it out to cool. Slowly add 10 mL of hydrochloric acid solution (5.2.11). Boil it after the intense reaction. Transfer it to an arsine generator. Add water to about 30 mL. Add 1 g of ascorbic acid (5.2.7) to dissolve. Proceed according to the operation steps 6.4.2 and 6.4.3.

At the same time, under the same conditions, do a reagent blank test.

6.4.2 Ammonia water (1 + 1) to adjust the pH value of solution

Add 2 drops of methyl orange indicator (6.2.2) to the generator. Use ammonia water (1 + 1) (6.2.3), to adjust the pH value to orange. Then add hydrochloric acid solution (5.2.10) dropwise, until it just turns red. Add 6.0 mL of tartaric acid solution (6.2.4). Use water to dilute it to 50 mL.

6.4.3 Reduction reaction and colorimetric determination

Accurately pipette 5.00 mL of absorption liquid into the absorption bottle. Connect the generation absorption device (no air leak; the catheter is plugged with loose lead acetate cotton). Quickly add a piece of potassium borohydride, from the side pipe of the generator. Immediately cover the stopper tightly. When the reaction is finished, add a second slice. Gently shake the generator 2 ~ 3 times, during the reaction. After the reaction is over, use the original absorption solution (5.2.16) as a reference, to measure at 520 nm with a 1 cm colorimetric cell.

Note: During the reduction reaction, the leakage of toxic arsine gas shall be prevented.

6.4.4 Standard curve drawing

Accurately pipette 0.00 mL, 1.00 mL, 2.00 mL, 4.00 mL, 6.00 mL, 8.00 mL of arsenic standard working solution (1.0 μg/mL), into the generator bottle. Add water to 40 mL. Add 6 mL of tartaric acid solution (6.2.4). Proceed the following, according to the steps specified in 6.4.3, to measure the absorbance. Find out the parameters of the regression equation or draw the standard curve.

make its volume reach to the mark. Shake well. Prepare for use. At the same time, make a reagent blank.

At the same time, under the same conditions, do a reagent blank test.

7.4.1.2 Dry ashing method

For additive premixed feed, concentrated feed, compound feed, single feed, feed additives, it may choose dry ashing method.

Weigh 2 g ~ 5 g of the specimen (accurate to 0.0001 g) into a 30 mL porcelain crucible. Add 5 mL of magnesium nitrate solution (5.2.13). Mix well. Evaporate to dryness at low temperature or in a boiling water bath. Carbonize at low temperature to smokeless. Then transfer it into a high-temperature furnace, for ashing at a constant temperature of 550 °C for 3.5 h ~ 4 h. Take it out to cool. Slowly add 10 mL of hydrochloric acid solution (5.2.11). After the intense reaction, boil and transfer to a 50 mL volumetric flask. Add 2.5 mL of thiourea solution (7.2.3), into the volumetric flask. Use water to wash the crucible 3 ~ 5 times. Combine the washing solution into a volumetric flask. Use water to make its volume reach to the mark. Shake well. Prepare for determination. At the same time, make a reagent blank.

At the same time, under the same conditions, do a reagent blank test.

7.4.2 Standard series preparation

Accurately pipette 0.00 mL, 0.10 mL, 0.4 mL, 1.00 mL, 4.00 mL, 10.00 mL of arsenic standard working solution (1.0 μg/mL), into 50 mL volumetric flasks (each equivalent dry arsenic concentration of 0 ng/mL, 2.0 ng/mL, 8.0 ng/mL, 20.0 ng/mL, 80.0 ng/mL, 200.0 ng/mL). Add 1.5 mL of hydrochloric acid (5.2.4) and 2.5 mL of thiourea solution (7.2.3). Add water to the mark. Shake well. Prepare for determination.

7.4.3 Determination

7.4.3.1 Instrument reference conditions

Photomultiplier tube voltage: 200 V ~ 400 V;

Arsenic hollow cathode lamp current: 15 mA ~ 100 mA;

Atomizer temperature: 200 °C;

Atomizer height: 8 mm;

Carrier gas flow: 300 mL/min ~ 600 mL/mtn;

Shielding gas flow: 800 mL/min;

Reading time: 7.0 s ~ 15.0 s;

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