

ARSENIC**PRINCIPLE**

A sample is oxidized in a mixture of concentrated nitric and sulfuric acids and arsenic is determined in dilute neutralized digest solution by the silver diethyldithiocarbamate method. Arsenic in test solution is converted to arsine, which is evolved and then complexed with silver diethyldithiocarbamate. The intensity of the color of the complex is determined with a spectrophotometer or colorimeter. Arsenic concentration is ascertained by reference to a calibration curve prepared with the aid of standard arsenic solutions.

SCOPE

The method is applicable to corn starch, corn syrup and corn sugar.

SAFETY NOTES

Because of the use of hot concentrated acids and the extreme toxicity of arsine, assemble all apparatus and perform reaction in a well-ventilated fume hood. Operate behind a shield and wear protective gear in the handling and disposal of reagents and reaction products according to Good Laboratory Practice. Consult Manufacturer's Safety Data Sheets (MSDS) of all reagents.

SPECIAL APPARATUS

1. Arsenic Apparatus: Consisting of three parts: generator flask, 125-mL Erlenmeyer flask with a Ts 24/40 interchangeable joint, a scrubber tube with a Ts 24/40 joint, connected to an absorber tube by means of a ball and socket joint. Absorption tubes used with standards and samples must have the same dimensions to insure equal arsine recoveries (Fisher Scientific Company, Catalog No. 1-405 or equivalent). Alternative arsenic apparatus, without the ball and socket joint is available also (SGA Scientific Inc., Catalog No. JA-9540, without ball and socket joint).

ARSENIC — continued

2. Spectrophotometer: An instrument having a continuously variable wavelength control in the visible spectrum and equipped with matching 1.0-cm cuvetts is recommended (Note 1).
3. Water Bath: Temperature-controlled at $25 \pm 1^\circ\text{C}$

REAGENTS (Note 2)

1. Standard Arsenic Solution, 1 mg arsenic per mL:

Stock Solution: Dissolve 0.132 g of National Bureau of Standards arsenious oxide (As_2O_3) (pre-dried in a vacuum oven at 105°C for 1 hour) in 10 mL of 10% sodium hydroxide solution. Neutralize with 1N sulfuric acid solution, and add 20 mL in excess; dilute to 1-L volume with purified water and mix.

Standard Solution: Pipet 10 mL of the stock solution into a 1-L volumetric flask, add 20 mL of 1 N sulfuric acid, dilute to volume with purified water and mix. Prepare fresh daily.
2. Hydrochloric Acid, Concentrated: Reagent grade (37% HCl, sp g 1.19)
3. Lead Acetate Trihydrate Solution, 10%: Dissolve 10 g of neutral lead acetate trihydrate [$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$] in purified water, dilute to 100-mL volume and mix.
4. Potassium Iodide Solution, 15%: Dissolve 150 g of reagent grade potassium iodide (KI) in purified water, dilute to 1-L volume and mix.
5. Silver Diethyldithiocarbamate Solution, 0.5%: Dissolve 1.0 g of silver diethyldithiocarbamate [$\text{AgSCSN}(\text{C}_2\text{H}_5)_2$] (Fisher Scientific Company, No. S-666) in 200 mL of reagent grade pyridine ($\text{C}_5\text{H}_5\text{N}$) and mix. Store in a nonactinic bottle.
6. Stannous Chloride Dihydrate Solution, 40%: Dissolve 40 g of reagent grade stannous chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) in concentrated

ARSENIC — continued

hydrochloric acid, dilute to 100-mL volume with concentrated hydrochloric acid and mix.

7. Zinc Metal: Granular, 20 mesh
8. Ammonium Oxalate Monohydrate Solution, Saturated: Add 50 g of reagent grade ammonium oxalate monohydrate $[(\text{NH}_3)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}]$ to 1-L of purified water and heat to dissolve. Some solid should crystallize as the solution cools to room temperature. Allow crystals to settle and use only the clear supernatant.
9. Sodium Hydroxide Solution, 50%
10. Bromophenol Blue Indicator, 1%
11. Nitric Acid, Concentrated: Reagent grade (70% HNO_3 , sp g 1.42)
12. Sulfuric Acid, Concentrated: Reagent grade (96% H_2SO_4 , sp g 1.84)

PROCEDURE

- A. Standardization: Pipet 2.0, 5.0, and 10.0 mL of standard arsenic solution into separate generator flasks and reserve one empty flask as a blank. Add 5 mL of concentrated hydrochloric acid, 2 mL of 15% potassium iodide solution, and 0.5 mL of 40% stannous chloride solution to each flask. Dilute the contents of each flask to 40 mL with purified water, mix and allow to stand in a water bath at 25 °C for 15 minutes.

Fill each scrubber tube with glass wool moistened with 10% lead acetate solution, avoiding excess. Pipet 4.0 mL of silver diethyldithiocarbamate solution into each absorber tube. When the 15 minute standing period has elapsed, remove the generator flask from the bath, add 4 g of granular zinc (Note 3), and immediately attach the scrubber tube and absorber tube. Immerse the apparatus in the water bath at 25°C for 30 mins. Repeat the above with each assembly.

ARSENIC — continued

Using the reagent blank as a reference solution at 100% transmittance (T), determine transmittance of each solution in a 1-cm cuvet at 535 nm (Note 4).

Plot % T versus mg of arsenic on semi-logarithmic graph paper.

- B. Analysis: Weigh 5.00 g (± 0.01) of sample and transfer quantitatively into an 800-mL Kjeldahl flask. In a hood, add cautiously 50 mL of concentrated nitric acid (rinsing down any portion of the sample that might be in the neck of the flask); then, add cautiously 10 mL of concentrated sulfuric acid while swirling the flask gently.

Support the flask at an angle of about 60° on a suitable surface with a 2-inch hole, using a ringstand. Warm slightly with a gas flame and discontinue heating if foaming or reaction becomes excessive. Repeat this procedure until the reaction has quieted, then heat the flask cautiously and rotate occasionally, if necessary, to prevent caking or charring of sample upon glass exposed to flame. Maintain oxidizing conditions in the flask at all times during digestion by cautiously adding small amounts of concentrated nitric acid whenever mixture turns brown or darkens.

Continue digestion until organic matter is destroyed and copious fumes of white sulfur trioxide (SO_3) are evolved. (Final solution should be colorless or, at most, light straw color.) Cool slightly, and cautiously add 75 mL of water and 25 mL of saturated ammonium oxalate solution to assist in expelling oxides of nitrogen from solution. Evaporate again to point where SO_3 fumes appear in neck of flask.

Cool, transfer quantitatively with purified water to a 100-mL volumetric flask, dilute to volume, and mix. Titrate a 25.0-mL aliquot with the 50% sodium hydroxide solution to a bromophenol blue indicator end point. Pipet a 25.0-mL aliquot of the digest into a generator flask; add the determined amount of 50% sodium hydroxide solution to neutralize the excess sulfuric acid. Run a complete blank determination, without sample, using all reagents and steps in the procedure. To each flask add 5 mL of concentrated hydrochloric acid, 2 mL of 15% potassium iodide solution,

ARSENIC — continued

and 0.5 mL of 40% stannous chloride solution. Dilute to 40 mL with purified water, mix, and allow to stand in a 25°C water bath for 15 mins.

Fill a scrubber tube with glass wool moistened with 10% lead acetate solution, avoiding excess. Pipet 4.0 mL of silver diethyldithiocarbamate solution into the absorber tube. When the 15 min. standing period has elapsed, remove the generator flask from the bath, add 4 g of granular zinc (Note 4), and immediately attach the scrubber tube and absorber tube. Immerse the apparatus in the water bath at 25°C for 30 mins.

Using the reagent blank as a reference solution at 100% transmittance (T), determine transmittance of the solution in a 1-cm cuvet at 535 nm (Note 4).

CALCULATION

Determine arsenic content of the sample solution by reference to the standardization curve (Note 5).

$$\text{Arsenic, ppm} = \frac{\text{Micrograms of Arsenic (From Graph)} \times 4}{\text{Sample Wt. (g)}}$$

NOTES AND PRECAUTIONS

1. Alternately, a photoelectric colorimeter or color comparator may be used for color determination or color matching.
2. Reagents 2 through 12 must be arsenic free.
3. Small zinc granules adhering to the neck (24/40 joint) of the generator flask preclude a tight seal when attaching the scrubber tube and absorber. Leaks cause low and erratic results. Avoid this problem by adding the zinc granules through a small funnel, with a 0.5-inch I.D. by 2.5-inch long stem, so that particles do not contact the neck.
4. In case of excessive foaming, repeat the entire series using less zinc; however, the amount must be sufficient to provide adequate sweeping of the solutions and assembly.

ARSENIC — continued

5. Sensitivity is increased by avoiding dilution of the trapping solutions. While the 4-mL portions are too small to permit rinsing the cell between samples, carryover is insignificant if the cell is thoroughly clean and is permitted to drain into a cloth or paper towel before introducing the next solution.
6. The observed arsenic result is multiplied by 4 to correct for dilution.

REFERENCE

Food Chemicals Codex, Fourth Edition (1996), National Academic Press, pp. 755-757.