ARSENIC

PRINCIPLE

Arsenic in test solution is converted to arsine, which is evolved and then complexed with silver diethyldithiocabamate. The intensity of the color of the complex is determined with a spectrophotmeter or colorimeter. Arsenic concentration is ascertained by reference to calibration curve prepared with aid of standard arsenic solutions.

SCOPE

The method is applicable to corn syrup and corn sugar.

SAFETY NOTES

Because of extreme toxicity of arsine and optional use of hot concentrated acids in alternate test solution preparation, assemble all apparatus and perform reactions 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 ₮ 24/40 interchangeable joint, a scrubber tube with a ₮ 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).

2. Spectrophotometer: An instrument having a continuously-variable wavelength control in the visible spectrum and equipped with matching 1.0 cm cuvets is recommended (Note 2).

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3. Water Bath: Temperature-controlled at 25 ± 1 °C

REAGENTS (Note 3)

1. Standard Arsenic Solution, 1 µg /mL arsenic:

   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 1*N* sulfuric acid solution, and add 20 mL in excess; dilute to 1-L volume with distilled water and mix.

   Standard Solution: Pipet 10 mL of the stock solution in a 1-L volumetric flask, add 20 mL of 1*N* sulfuric acid, dilute to volume with distilled 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 ($Pb(C_2H_3O_2)_2 \bullet 3H_2O$) in distilled water, dilute to 100 mL volume and mix.

4. Potassium Iodide Solution, 15%: Dissolve 150 g of reagent grade potassium iodide (KI) in distilled water, dilute to 1 L volume and mix.

5. Silver Diethyldithiocarbamate Solution, 0.5%: Dissolve 1.0 g of silver diethyldithiocarbamate [$AgSCSN(C_2H_5)_2$] (Fisher Scientific Company, No. S-666) in 200 mL of reagent grade pyridine (C_5H_5N) and mix. Store in a nonactinic bottle.

6. Stannous Chloride Dihydrate Solution, 40%: Dissolve 40 g of reagent grade stannous chloride dihydrate ($SnC1_2 \bullet 2H_2O$) in concentrated hydrochloric acid, dilute to 100 mL volume with concentrated hydrochloric acid and mix.

7. Zinc Metal: Granular, 20 mesh

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8. Ammonium Oxalate Monohydrate Solution, Saturated: Add 50 g of reagent grade ammonium oxalate monohydrate [$(NH_4)_2C_2O_4 \bullet H_2O$] to 1 L of distilled 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 (Note 4)

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 distilled 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 minutes standing period has elapsed, remove the generator flask from the bath, add 4 g of granular zinc (Note 5), and immediately attach the scrubber tube and absorber tube. Immerse the apparatus in the water bath at 25 °C for 30 minutes. Repeat the above with each assembly.

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 6).

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

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B. Analysis (Note 7): Weigh 5.00 g (± 0.01 g) of sample in a 100-mL beaker, dissolve the sample in 10 mL of distilled water, transfer the solution quantitatively to a generator flask and reserve an empty flask for a reagent blank. To each flask add 5 mL of concentrated hydrochloric acid, 2 mL of 15% potassium iodide solution, and 0.5 mL of 40% stannous chloride solution. Dilute to 40 mL with distilled water, mix, and allow to stand in a 25 °C water bath for 15 minutes.

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 minutes. standing period has elapsed, remove the generator flask from the bath, add 4 g of granular zinc (Note 5), and immediately attach scrubber tube and absorber tube. Immerse the apparatus in the water bath at 25 °C for 30 minutes.

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 6).

CALCULATION

Determine arsenic content of the sample solution by reference to the standardization curve.

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

NOTES AND PRECAUTIONS

1. Alternatively, a photoelectric colorimeter or a color comparator may be used for color determination or color matching.

2. Reagents 2-12 must be arsenic free.

3. Small zinc granules adhering to the neck (24/40 Ts 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

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granules through a small funnel, with a 0.5-in. I.D. by 2.5 in. 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.

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, carry-over 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. Alternate preparation of test solution by oxidative digestion: Weigh 5.00 g (± 0.01 g) of sample in a 100-mL beaker, and dissolve by adding 10 mL of water. Transfer quantitatively to a 800-mL Kjeldahl flask with a minimum amount of water. Add cautiously 50 mL of concentrated nitric acid; then, add cautiously 10 mL of concentrated sulfuric acid while swirling the flask gently.

   Support the flask at an angle of about 60 degrees on an asbestos mat 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 saturated ammonium oxalate solution to assist in expelling oxides of nitrogen from solution. Evaporate again to the point where SO_3 fumes appear in neck of flask.

   Cool, transfer quantitatively with distilled water to a 100-mL volumetric flask, dilute to volume, and mix. Titrate a 25.0-mL aliquot with the 50%

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sodium hydroxide solution to a bromophenol blue indicator end point. Pipet a 25.0-mL aliquot of the digest into generator flask, add the determined amount of 50% sodium hydroxide solution to neutralize the excess sulfuric acid, then follow procedure for arsenic determination. Run a complete blank determination, without sample, using all reagents and steps in the procedure. Multiply the observed arsenic result by 4 to correct for dilution.