CALCIUM (EGTA-Titrimetric)

PRINCIPLE

Organic matter in the sample is destroyed by ignition in a muffle furnace. After dissolution of the residue in dilute acid and following additions of potassium hydroxide and triethanolamine to prevent interference by iron, magnesium and other cations, the solution is titrated with ethylene glycol bis-(∃-aminoethyl ether)-N,N'-tetraacetic acid (EGTA) using hydroxynaphthol blue for end point detection.

SCOPE

This method is applicable to commercial starches and their modifications (Note 1).

SPECIAL APPARATUS

1. Platinum, VYCOR, or Silica Dishes: About 100 mL capacity

2. Muffle Furnace: Equipped with pyrometer and capable of operating at controlled temperatures up to 525 °C

REAGENTS

1. Standard Calcium Solution, 40 µg calcium per mL:

   Stock Solution: Dissolve 1.001 g of reagent grade calcium carbonate ($CaCO_3$) in 25 mL of purified water containing 3 mL of concentrated hydrochloric acid. Transfer quantitatively to a 1 L volumetric flask, dilute to volume with purified water and mix well.

   Standard Solution: Transfer 10.0 mL of the stock solution to a 100 mL volumetric flask, dilute to volume with purified water and mix well. This solution must be prepared fresh daily.

2. Standard Ethylene Glycol Bis-(∃-aminoethyl ether)-N,N'-tetraacetic acid (EGTA) Solution, 0.002 *M*:

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Stock Solution: Dissolve 19.0 g of reagent grade ethylene glycol bis-(-aminoethyl ether)-N,N'-tetraacetic acid ($(HOOCCH_2)_2N$-$(CH_2)_2O(CH_2)_2O(CH_2)_2N(CH_2COOH)_2$), in 400 mL of purified water containing 100 mL of 1.0 *N* sodium hydroxide (NaOH) solution. Transfer to a 1 L volumetric flask, dilute to volume with purified water and mix well.

Standard EGTA Solution: Transfer 20.0 mL of the stock solution to a 500 mL volumetric flask, dilute to volume with purified water and mix well. This solution must be prepared fresh daily.

To standardize, pipet 10.0 mL of the standard calcium solution into a 150 mL beaker and dilute to approximately 50 mL. Then, proceed with the remainder of the titration as directed under Procedure, beginning with the third paragraph (Note 2).

3. Hydrochloric Acid, Concentrated: Reagent grade (37% HCl, sp g 1.19)

4. Hydrochloric Acid Solution, 0.1 *N*: Dilute 8.3 mL of reagent grade concentrated hydrochloric acid with purified water to 1 L volume.

5. Triethanolamine Solution, 30% (V/V): Dilute 300 mL of triethanolamine to 1 L volume with purified water and mix well.

6. Magnesium Chloride Solution, 0.002 *M*: Dissolve 0.407 g of reagent grade magnesium chloride hexahydrate ($MgCl_2 \bullet 6H_2O$) in purified water and dilute to 1 L volume.

7. Potassium Hydroxide Solution, 8 *N*: Dissolve 528 g of reagent grade potassium hydroxide (KOH, 85%) in 500 mL of purified water, cool, dilute to 1 L volume and mix well.

8. Hydroxynaphthol Blue Indicator: For calcium analysis.

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PROCEDURE

Weigh an amount of sample containing approximately 10 g of dry substance in a platinum, VYCOR or silica dish (Note 3). Char the sample on a hot plate or over an open flame. Ignite the sample during this charring process. Place in a muffle furnace at 525 °C until the residue is free from carbon (Note 4).

Cool the dish containing the ash residue, add 5 mL of concentrated hydrochloric acid, swirl to dissolve the residue, and evaporate to dryness on a steam bath. Add 10 mL of 0.1 *N* hydrochloric acid solution, cover with a watch glass and heat on a steam bath for 15 mins. Transfer the solution and any insoluble residue to a 150 mL beaker and dilute to approximately 50 mL (Note 5).

Add 10 mL of 30% triethanolamine solution and 10 mL of 0.002 *M* magnesium chloride solution (Note 6) followed by 5 mL of 8 *N* potassium hydroxide solution. Add 0.2 to 0.3 g of hydroxynaphthol blue indicator and wait for at least 1 min. for maximum pink color to develop. Using a well-illuminated white background, titrate with standard EGTA solution using a rapid delivery until the pink color begins to fade. Continue the titration using a rapid dropwise addition until the pink color of the calcium-indicator complex disappears, and only the blue color of the indicator remains.

CALCULATION

Calculate the calcium equivalent of the EGTA solution from the standardization titer.

$$K = \mu g \text{ of calcium per mL} = \frac{(40\,\mu g \text{ per mL})(10\text{ mL})}{\text{EGTA Standardization Titer, mL}}$$

Calculate the calcium content of the sample:

$$\text{Calcium, ppm (as is)} = \frac{(\text{Sample Titer, mL})(K)}{\text{Sample Wt., g}}$$

NOTES AND PRECAUTIONS

1. Starches containing relatively significant quantities of cations that form stable EGTA complexes cannot be analyzed without method validation.

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2. The 0.002 *M* EGTA solution need not be standardized every day if the stock solution is diluted quantitatively.

3. Evaporate slurries to dryness on a steam bath prior to charring on a hot plate or over an open flame.

4. If the sample is difficult to ash, the dish may be removed from the muffle furnace, cooled, and the residue moistened with a few drops of purified water, and carefully evaporated to dryness. Ignition is then continued until the ash is white.

5. Corn starch may contain added calcium salts. If so, dilute the solution to volume in a 100 mL volumetric flask and transfer an aliquot containing 200 to 2000 µg of calcium to the beaker and dilute to 50 mL volume. Include dilution factor in calculation.

6. The color change at the end point is improved by the addition of 10 mL of 0.002 *M* magnesium chloride solution to the ash solution before addition of the 8 *N* potassium hydroxide solution.