CALCIUM (EGTA-Titrimetric)

PRINCIPLE

Organic matter in the sample is destroyed by ignition in the presence of sulfuric acid. 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-(β-aminoethyl ether)-N,N'-tetraacetic acid (EGTA) using hydroxynapthol blue for end point detection.

SCOPE

The method applies to commercial starches and their modifications, crude and refined sugars (Note 1), corn syrups and other starch hydrolyzates.

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-(β-aminoethyl ether)-N,N'-tetraacetic acid (EGTA) Solution, 0.002 *M*:

CALCIUM (EGTA – Titrimetric) — continued

Stock Solution: Dissolve 19.0 g of reagent grade ethylene glycol bis-(β-aminoethyl ether)-N,N'-tetraacetic acid ($(HOOCCH_2)_2N(CH_2)_2O(CH_2)_2N(CH_2COOH)_2$), 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 fifth 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 and dilute to 1 L volume and mix well.

8. Hydroxynaphthol Blue Indicator: For calcium analysis.

CALCIUM (EGTA – Titrimetric) — continued

9. Sulfuric Acid Solution (1:3): Cautiously pour 100 mL of concentrated reagent grade sulfuric acid (96% H_2SO_4; sp g 1.84) into 300 mL of purified water and mix.

PROCEDURE

Weigh an amount of sample containing approximately 10 g of dry substance (Note 3) in a platinum, VYCOR or silica dish.

For corn sugars and syrups only.
Add 6 mL of 1:3 sulfuric acid solution and warm gently to obtain a homogeneous mixture (Note 4).

For all samples.
Heat carefully over an open flame or on a hot plate until the sample is thoroughly carbonized (Note 5). Ignite the sample during this charring process (Notes 6 and 7). Place the dish in the muffle furnace at 525 °C and ignite until the residue is free from carbon (Note 8).

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.

Add 10 mL of 30% triethanolamine solution and 10 mL of 0.002 *M* magnesium chloride solution (Note 9) 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.

CALCIUM (EGTA – Titrimetric) — continued

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

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. Crude and refined sugars include dextrose (anhydrous and hydrate), dextrose solutions, concentrated and refined hydrolyzates, greens liquors (Corn Sugar Molasses) and hydrol (Feeding Corn Sugar Molasses).

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

3. Selection of a representative sample of cast sugar is difficult. It is recommended that a large sample (e.g., 100 g) be diluted with an equal weight of hot purified water (near the boiling point). Sample and water are shaken in a closed container until solution is complete (15 mins. usually sufficient). After cooling to near room temperature, 25 g of solution, equivalent to about 10 g of dry substance, is taken for analysis.

4. Additional 1:3 sulfuric acid solution or purified water may be added to refined sugar samples to facilitate solution and to obtain a homogeneous mixture. Excess acid or water should be avoided.

5. Evolution of noxious fumes requires that this operation be carried out in a hood.

6. Special attention should be given during the preliminary carbonization since excessive foaming may cause loss of sample.

7. An alternative procedure for carbonizing the sample is more rapid and described under method E-6a. It is best to operate at solution concentrations of 60-70% in order to control the reaction mixture concentration.

CALCIUM (EGTA – Titrimetric) — continued

8. 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.

9. 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.

METHOD HISTORY

Combined the Calcium methods for Corn Starch (Unmodified) (B-11), Corn Syrup (E-11) and Corn Sugar (F-8) on 4-15-2010.

Corn Starch (Unmodified), Calcium (B-11), Date of Acceptance 11-09-1973, Revised 10-7-1996.

Corn Syrup, Calcium (E-11), Date of Acceptance 11-09-1973, Revised 10-07-1996.

Corn Sugar, Calcium (F-8), Date of Acceptance 11-09-1973, Revised 10-07-1996.