Method 5.9 – Syrup: calcium and magnesium by EDTA titration

1. Rationale

The method is applicable to all syrups and uses two separate direct EDTA titrations to determine the amount of calcium (Ca) and of calcium and magnesium (Mg) in solution respectively. The amount of magnesium is determined through the difference in titres of the two titrations.

2. Principle

Calcium and magnesium ions in solution form relatively stable complexes with EDTA and can be quantified using complexation titrations. HHSNNA or Eriochrome Black T indicators are used to determine calcium or calcium and magnesium mixtures respectively. Since the former indicator is not stable two separate titrations are necessary when standardising the EDTA solution and when determining the calcium concentration in solution.

3. Apparatus

3.1 **Analytical balance** readable to 0.0001 g

3.2 **Pipettes**: 4, 5, 10 and 25 cm^3

3.3 **Volumetric flasks**: 250, 500 and 1 000 cm^3

3.4 **Burette**: 50 cm^3

3.5 **Conical flasks**: 4 × 250 cm^3

3.6 **Measuring cylinders**: 10 and 50 cm^3

3.7 **Boiling water batch**

3.8 **Funnel**: 100 mm ϕ

3.9 **Glass mortar and pestle**

3.10 **Porcelain dish**

3.11 **Filter paper**: Whatman No. 1 or equivalent, 185 mm ϕ

3.12 **Litmus paper**

4. Reagents

4.1 Ethylene diamine tetra acetic acid, disodium salt dihydrate (0.01 M)

Ethylene diamine tetra acetic acid (EDTA), disodium salt dihydrate is mildly irritating to the skin, eyes and respiratory tract. Work in a fume cupboard while wearing gloves and safety glasses.

Weigh 1.8612 g EDTA, dissolve in distilled water and dilute to 500 cm^3 in a volumetric flask.

4.2 Hydrochloric acid (concentrated, 32%)

Hydrochloric acid (HCl) is a corrosive acid and should only be handled in a fume cupboard while wearing gloves and safety glasses.

4.3 Hydrochloric acid solution (1 M)

Measure 98 cm^3 concentrated hydrochloric acid and add to approximately 700 cm^3 distilled water in a beaker. Always add the acid to the water and not the other way around. This acid dilution is exothermic and the solution will therefore heat. Allow the solution to cool down, transfer to a 1 000 cm^3 volumetric flask and make to the mark.

4.4 Sodium hydroxide solution (1 M)

Sodium hydroxide (NaOH) is a corrosive base and contact with the skin and eyes should be avoided. Wear gloves and safety glasses during use.

Weigh 40.0 g sodium hydroxide pellets and dissolve in some distilled water. This dissolution is exothermic and the solution will therefore heat. Allow the solution to cool and dilute to 1 000 cm^3 in a volumetric flask.

4.5 Calcium solution (0.01 M)

Weigh 0.500 g anhydrous calcium carbonate accurately. Add 1 M hydrochloric acid drop wise until effervescence ceases or the solution is clear. Neutralise with 1 M sodium hydroxide solution using a pH meter. Transfer quantitatively to a 500 cm^3 volumetric flask and make to the mark with distilled water.

4.6 Potassium hydroxide solution (8 M)

Potassium hydroxide (KOH) is a corrosive base and contact with the skin and eyes should be avoided. Wear gloves and safety glasses during use.

Dissolve 448 g potassium hydroxide pellets in distilled water. The dissolution is exothermic and the solution will therefore heat up. Cool and dilute to 1 000 cm^3 in a volumetric flask. The solution will etch glass containers over a period of time and should be stored in a plastic bottle.

4.7 Potassium chloride (KCl) or sodium chloride (NaCl)

4.8 Eriochrome Black T indicator

Mix 0.1 g of Eriochrome Black T with 30 g potassium chloride or sodium chloride. Grind the mixture with a glass mortar and pestle.

4.9 Sodium sulphate (anhydrous)

Sodium sulphate (Na_2SO_4) is irritating to the skin and eyes.

4.10 HHSNNA indicator

HHSNNA $(C_6H_4)(C_4HCOOHOH)N_2(C_6HOHSO_3H)(C_4H_4)$ is a corrosive. Handle with gloves while wearing safety glasses.

Mix 0.5 g HHSNNA with 50 g of solid anhydrous sodium sulphate.

4.11 Triethanolamine (50% v/v)

Triethanol amine ($C_6H_{15}NO_3$) is toxic and severely irritating to the eyes and mildly irritating to the skin. Wear safety glasses and gloves during handling.

Measure 50 cm^3 triethanolamine with a graduated cylinder and dilute to 100 cm^3 with distilled water in a volumetric flask. Since direct sunlight will decompose the amine, store in an amber bottle.

4.12 Ammonium chloride

Ammonium chloride (NH_4Cl) is a corrosive base and contact with the skin and eyes should be avoided. Wear safety glasses and gloves during handling.

4.13 Ammonia buffer solution (pH 10)

Ammonia (NH_4OH) is a corrosive base and contact with the skin, eyes and through inhalation should be avoided. Work in a fume cupboard while wearing gloves and safety glasses.

Add 142 cm^3 concentrated ammonia to 17.59 g ammonium chloride and dilute with distilled water to 250 cm^3 in a volumetric flask.

5. Procedure

5.1 Standardisation of the EDTA solution

Fill the burette with the EDTA solution.

Pipette two 25 cm^3 portions of calcium solution into two separate 250 cm^3 conical flasks. Add 25 cm^3 of distilled water to each flask. Add 4 cm^3 of the 8 M potassium hydroxide solution to the first flask. Add 0.2 g HHSNNA indicator mixture and titrate with the EDTA solution until the colour changes from red to blue. Record the titre.

Add the volume of this titre minus 1 cm^3 from the EDTA burette into the second flask. Add 4 cm^3 of the 8 M potassium hydroxide solution and 0.2 g of the HHSNNA indicator mixture and titrate with the EDTA until the colour changes from red to blue. Record the titre.

The second titration is necessary since the indicator is not stable under alkaline conditions. Repeat the second titration. The repeat titres should agree to within 0.1 cm^3. Use the average titre to calculate the exact concentration of the EDTA solution as indicated in 6.1.

5.2 Sample preparation

Weigh 50.00 ± 0.01 g of syrup into a porcelain dish. Add 10 cm^3 concentrated hydrochloric acid from a graduate cylinder and place on the boiling water bath until dry. Repeat this twice by each time using 10 cm^3 concentrated hydrochloric acid.

Dissolve the residue in 10 cm^3 hydrochloric acid and transfer quantitatively to a beaker using 90 cm^3 of distilled water. Filter the mixture through filter paper placed inside the funnel to remove any insoluble substances and wash the residue with distilled water. Transfer the filtrate to a 250 cm^3 volumetric flask and make to the mark with distilled water.

5.3 Calcium determination

Pipette 10 cm^3 aliquots of the sample solution into two 250 cm^3 conical flasks and neutralise with potassium hydroxide using litmus paper to monitor the pH. Dilute the samples to 50 cm^3 with distilled water and add 5 cm^3 of the 50% triethanolamine solution.

Add 4 cm^3 of the 8 M potassium hydroxide solution to the first flask. Add 0.2 g HHSNNA indicator mixture and titrate with 0.01 M EDTA until the colour changes from red to blue. Record the titre.

Add the volume of this titre minus 1 cm^3 from the EDTA burette into the second flask. Add 4 cm^3 of the 8 M potassium hydroxide solution and 0.2 g of the HHSNNA indicator mixture and titrate with the EDTA until the colour changes from red to blue.

Repeat the titration. Duplicate titrations should agree to within 0.1 cm^3.

5.4 Calcium and magnesium determination

Pipette a 10 cm^3 aliquot of the sample solution into a 250 cm^3 conical flask and neutralise with potassium hydroxide using litmus paper to monitor the pH. Dilute the sample to 50 cm^3 with distilled water and add 10 cm^3 of the 50% triethanolamine solution and 5 cm^3 of the pH 10 buffer solution.

Add 0.2 g of the Eriochrome Black T indicator mixture and titrate with EDTA to a pure blue endpoint.

Repeat the titration. Duplicate titres should agree to within 0.1 cm^3.

6. Calculations

6.1 EDTA standardisation

$$\text{EDTA concentration (M)} = \frac{V_{Ca}}{V_t} \times C_{Ca}$$

where

V_{Ca}	≡	Volume of the calcium solution (cm^3)
V_t	≡	Volume of the titre (cm^3)
C_{Ca}	≡	Concentration of the calcium solution (M)

The molecular mass of calcium is 40.078 g/mole. Therefore, 1 cm^3 of the 0.01 M calcium solution contains 0.4008 mg calcium.

1 cm^3 of the 0.01 M calcium solution will complex with 1 cm^3 of the EDTA solution. Therefore, 1 cm^3 of a 0.01 M EDTA solution will complex 0.4008 mg calcium.

$$\text{Equivalent mass of calcium (mg)} = 0.4008 \text{ mg} \times \frac{\text{actual EDTA (M)}}{0.01 \text{ M EDTA}}$$

The molecular mass of magnesium is 24.305 g/mole. Therefore, 1 cm^3 of the 0.01 M calcium solution contains 0.2431 mg magnesium.

1 cm^3 of a 0.01 M magnesium solution will complex with 1 cm^3 of the EDTA solution. Therefore, 1 cm^3 of a 0.01 M EDTA solution will complex 0.2431 mg magnesium.

$$\text{Equivalent mass of magnesium (mg)} = 0.2431 \text{ mg} \times \frac{\text{actual EDTA (M)}}{0.01 \text{ M EDTA}}$$

6.2 Calcium determination

$$\text{Calcium (\%)} = \text{titre} \times \frac{250 \text{ cm}^3}{50 \text{ g} \times 10 \text{ cm}^3} \times \frac{\text{calcium (mg)}}{1000} \times 100$$

$$= \text{titre} \times \frac{\text{calcium (mg)}}{20}$$

6.3 Magnesium determination

Titre for Mg (cm^3) = titre for Mg and Ca (5.4) - titre for Ca (5.3)

$$\text{Magnesium (\%)} = \text{titre}_{Mg} \times \frac{250 \text{ cm}^3}{50 \text{ g} \times 10 \text{ cm}^3} \times \frac{\text{magnesium (mg)}}{1000} \times 100$$

$$= \left(\text{titre}_{Mg+Ca} - \text{titre}_{Ca}\right) \times \frac{\text{magnesium (mg)}}{20}$$

where titre_{Mg} ≡ titre for magnesium (cm^3)
titre_{Mg+Ca} ≡ titre for magnesium and calcium (cm^3)
titre_{Ca} ≡ titre for calcium (cm^3)

7. Example

7.1 EDTA standardisation

Titre of EDTA standardisation = 24.60 cm^3

$$\text{EDTA concentration (M)} = \frac{25.00 \text{ cm}^3}{24.60 \text{ cm}^3} \times 0.01 \text{ M}$$

$$= 0.01016 \text{ M}$$

$$\text{Equivalent mass of Ca (mg)} = 0.4008 \text{ mg} \times \frac{0.01016 \text{ M}}{0.01 \text{ M}}$$

$$= 0.4072 \text{ mg}$$

$$\text{Equivalent mass of Mg (mg)} = 0.2431 \text{ mg} \times \frac{0.01016 \text{ M}}{0.01 \text{ M}}$$

$$= 0.2470 \text{ mg}$$

7.2 Calcium determination

Titre of Ca determination = 8.50 cm^3

$$\text{Calcium} = 8.50 \text{ cm}^3 \times \frac{0.4072 \text{ mg}}{20}$$

$$= 0.173\%$$

7.3 Magnesium determination

Titre of Mg determination = 18.35 cm^3

$$\text{Magnesium} = \left(18.35\ cm^3 - 8.50\ cm^3\right) \times \frac{0.2470\ mg}{20}$$

$$= 0.122\%$$

8. References

Jeffery GH, Bassett J, Mendham J and Denney RC (1989). *Vogel's Textbook of Quantitative Chemical Analysis*. 5th Edition, Longman Scientific and Technical, Harlow, 325 - 326.

SASTA (1985). *Laboratory Manual for South African Sugar Factories*. 3rd Edition: 282 - 284.