Determination of Total Calcium and Magnesium Ion Concentration

Introduction

This method, called a **complexometric titration**, is used to find the total calcium and magnesium content of milk, sea water and various solid materials. It can also be used to determine the total hardness of fresh water provided the solutions used are diluted. The combined concentration of calcium and magnesium ions is considered to be the measure of water hardness.

The method uses a very large molecule called EDTA which forms a complex with calcium and magnesium ions. EDTA is short for ethylenediaminetetraacetic acid. A blue dye called Eriochrome Black T (ErioT) is used as the indicator. This blue dye also forms a complex with the calcium and magnesium ions, changing colour from blue to pink in the process. The dye–metal ion complex is less stable than the EDTA–metal ion complex. For the titration, the sample solution containing the calcium and magnesium ions is reacted with an excess of EDTA. The indicator is added and remains blue as all the Ca^{2+} and Mg^{2+} ions present are complexed with the EDTA.

A back titration is carried out using a solution of magnesium chloride. This forms a complex with the excess EDTA molecules until the end-point, when all the excess EDTA has been complexed. The remaining magnesium ions of the magnesium chloride solution then start to complex with ErioT indicator, immediately changing its colour from blue to pink.

The main reaction is:

$$Ca^{2+} + EDTA^{4-} \longrightarrow [Ca\text{-}EDTA]^{2-}$$

Back titration:

$$EDTA^{4-} + Mg^{2+} \longrightarrow [Mg\text{-}EDTA]^{2-}$$

Indicator reaction: Note: ErioT is blue and ErioT-Mg is pink

$$ErioT + Mg^{2+} \longrightarrow ErioT\text{-}Mg$$

Equipment Needed

Burette

20 mL pipette

250 mL conical flasks

100 mL volumetric cylinder

Solutions Needed

EDTA: (ethylenediaminetetraaceticacid) 500 mL of a 0.05 $molL^{-1}$ solution. Weigh 9.31 g of the EDTA salt and dissolve it in 500 mL of distilled water in a volumetric flask.

Buffer: Dissolve 7.0 g of ammonium chloride in 57 mL concentrated ammonia (see safety notes). Dilute to 100 mL with distilled water in a volumetric flask. The pH should be 10.5.

$MgCl_2.6H_2O$: 0.025 $molL^{-1}$ solution. Weigh 2.54 g of magnesium chloride hexahydrate and dilute to 500 mL with distilled water in a volumetric flask.

ErioT indicator: Dissolve 0.2 g of Eriochrome Black T indicator in 15 mL of concentrated ammonia solution (or 15 mL of triethanolamine) (See safety notes) and 5 mL absolute ethanol. Do not store more than one to two days before use. You may be able to get the ErioT indicator from the University of Canterbury, see the contact details at the end.

Method

Sample Preparation

For samples that are already in solution, such as freshwater, seawater and milk, no further preparation is needed.

For solid samples such as eggshells and limestone, the samples must first be dissolved in acid. Accurately weigh about 0.5 g of the solid into a small beaker or conical flask, add about 20 mL dilute hydrochloric acid and allow the solid to completely dissolve (this may take several minutes). Neutralise the unreacted acid with dilute sodium hydroxide solution until the pH of the solution is almost 7 (according to pH indicator paper). For eggshells, the inner membrane will remain undissolved and may be carefully removed from the solution. Transfer the solution to a 100 mL volumetric flask and make up to the mark with distilled water.

Standardisation of the EDTA Solution

1. Pipette a 10 mL sample of the EDTA solution into a conical flask.
2. Add 10 mL of ammonia buffer solution and 1 mL of

Eriochrome Black T indicator solution.

3. Titrate the EDTA with the magnesium chloride solution until the endpoint is reached – a permanent colour change from blue to pink.

4. Having determined the average titre of the magnesium chloride solution, determine the number of moles used.

5. Given the Mg^{2+} : EDTA ratio of 1 : 1, calculate the concentration of your EDTA solution.

Titration Method for Seawater, Milk and Solid Samples

1. Pipette 10 mL of the sample solution into a conical flask.

2. Add 20 mL of 0.05 mol L^{-1} EDTA solution.

3. Add 10 mL of ammonia buffer, 50 mL of distilled water and 1 mL of Eriochrome Black T indicator solution.

4. Titrate the sample with the standard 0.025 molL^{-1} magnesium chloride solution until a permanent pink colour appears.

Titration Method for Fresh or Tap Water Samples

1. Add a 100 mL of the sample solution into a 250 mL conical flask.

2. Prepare a 0.005 mol L^{-1} EDTA solution by diluting the 0.05 mol L^{-1} EDTA solution by a factor of 1/10. Add 20 mL of this diluted EDTA to the sample solution.

3. Add 10 mL of the ammonia buffer and 1 mL of Eriochrome Black T indicator solution.

4. Prepare a 0.0025 mol L^{-1} magnesium chloride solution by diluting the 0.025 mol L^{-1} magnesium chloride solution by a factor of 1/10.

5. Titrate the sample solution with this 0.0025 molL^{-1} magnesium chloride solution until a permanent pink colour appears. Repeat the titration with further samples until concordant results (titres agreeing within 0.1 mL) are obtained.

Result Calculations

1. Calculate the total moles of EDTA added to the sample solution.

2. Calculate the moles of the magnesium chloride solution used in the back titration from your concordant results. From the equation of the titration below, the moles of Mg^{2+} will be equivalent to the moles of excess EDTA.

$$EDTA^{4-} + Mg^{2+} \longrightarrow [Mg\text{-}EDTA]^{2-}$$

3. Given the ratio of $Ca^{2+} + Mg^{2+}$: EDTA = 1 : 1, calculate the moles of Ca^{2+} and Mg^{2+} that must have been complexed with EDTA by subtracting the excess EDTA from the total moles of EDTA added to the sample.

This result is the moles of Ca^{2+} and Mg^{2+} in the sample solution.

Figure 1 Colour changes for magnesium chloride back-titration in clear solution using Eriochrome Black T indicator. Left flask: blue colour well before endpoint (all Ca^{2+}/Mg^{2+} ions complexed by excess EDTA, all indicator molecules uncomplexed). Centre flask: last trace of blue/purple colour just before endpoint (excess EDTA almost totally complexed by added Mg^{2+}). Right flask: pink/red colour at endpoint (all EDTA complexed by added Mg^{2+}, indicator also complexed).

Figure 2 Same colour changes for magnesium chloride back-titration as in Figure 1, but for cloudy (opaque) sample solution, *eg* milk. Left flask: blue colour well before endpoint. Centre flask: last trace of blue/purple colour just before endpoint. Right flask: pink/red colour at endpoint.

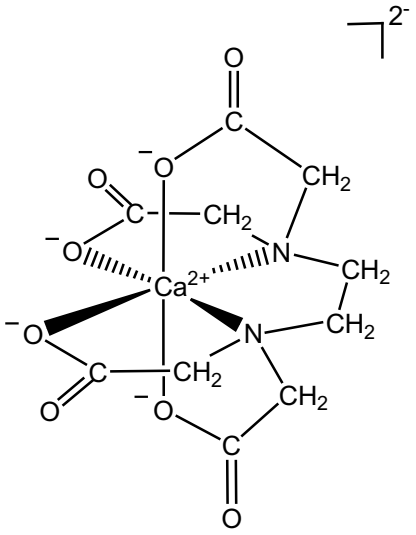
Safety

The concentrated ammonia solution used in preparing the buffer and indicator solutions is highly corrosive and should be handled with care. Wear safety glasses and rubber gloves.

Both the buffer and indicator (and thus also the titration solution) will liberate ammonia gas to some extent. This gas may be harmful if inhaled in large quantities. Work in a fumehood or well ventilated area.

Additional Notes

1. Ethylenediaminetetraacetic acid, EDTA is a large molecule which creates a complex with a metal ion, bonding through six coordination sites.



Complex formed by EDTA and calcium ions

2. The ammonia buffer (pH ~ 10.5) used here is needed as Eriochrome Black T only changes colour in the pH range 7 – 11.

3. The presence of some other metal ions – *eg* copper, iron, cobalt, nickel, zinc, manganese – in high concentrations may introduce error to the determination of calcium and magnesium ions using this method, although this is unlikely.

4. As the concentration of Ca^{2+} and Mg^{2+} in the sample solution may vary considerably depending on the nature and source of the sample it may be necessary vary the concentration of the EDTA(if the titre volume is too low) or to dilute your solutions (if the titre volume is too high). The average titre volume should be in the range of 10 – 30 mL.

Contact Us

If you have any questions or comments relating to this experiment, please contact us:

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