College of Science

UNIVERSITY OF CANTERBURY
Te Whare Wānanga o Waitaha
CHRISTCHURCH NEW ZEALAND

Determination of Calcium Ion Concentration

Safety

Lab coats, safety glasses and enclosed footwear must be worn at all times in the laboratory.
Note that the concentrated (8mol L^{-1}) sodium hydroxide solution used is highly corrosive and should be handled with extra care: ideally wear rubber gloves when preparing and handling it.

Introduction

This method, called a complexometric titration, is used to find the calcium content of milk, the 'hardness' of water and the amount of calcium carbonate in various solid materials.

The method uses a very large molecule called EDTA which forms a complex with calcium ions. EDTA stands for ethylenediaminetetraacetic acid. A blue dye called Patton and Reeder's indicator (PR) is used as the indicator. This blue dye also forms a complex with the calcium ions changing colour from blue to pink/red in the process, but the dye–metal ion complex is less stable than the EDTA–metal ion complex. As a result, when the calcium ion–PR complex is titrated with EDTA the Ca^{2+} ions react to form a stronger complex with the EDTA.

For the titration, the indicator is added to the sample solution containing the calcium ions and forms the pink/red calcium ion-indicator complex (Ca-PR). This solution is then titrated with EDTA. The endpoint occurs when the solution turns blue, indicating that the Ca-PR complex has been completely replaced by the calcium ion-EDTA complex and the PR indicator reverts to its blue colour.

The reaction is:

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

Note: Ca-PR is pink/red and PR is blue.

Equipment Needed

10 and 20 mL pipettes

250 mL conical flasks

100, 250 and 500 mL volumetric flasks

pH indicator paper

10 mL and 100 mL measuring cylinders

burette and stand

Solutions Needed

EDTA: ethylenediaminetetraacetic acid 0.025 mol L–1 solution. If possible, dry 5 g of the disodium salt of EDTA for several hours or overnight at 80°C, allow to cool. Weigh 4.65 g of the dried EDTA salt and dissolve it in 500 mL of distilled water in a volumetric flask.

Patton-Reeder indicator triturate: a small amount may be available from Outreach at the University of Canterbury, see contact details on back page.

Sodium hydroxide solution: (8 molL-1). (See safety notes) Weigh 32 g of solid sodium hydroxide into a 250 mL conical flask and carefully dissolve in 100 mL of distilled water. The solution will get very warm as the NaOH dissolves; the temperature may be controlled by sitting the bottom of the flask in a small basin of cold tap water.

Dilute hydrochloric acid solution: (1-2 mol L^{-1})

Dilute sodium hydroxide solution: (1-2 mol L^{-1})

Method

Sample Preparation

Calcium samples that are already in solution, such as tapwater and milk, do not need any further preparation. Seawater may need to be filtered to remove solid material such as sand and seaweed.

Solid samples, such as limestone and eggshell, must first be dissolved in acid.

1. 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).
2. Neutralise the unreacted acid with dilute sodium hydroxide solution until the pH of the solution is almost 7 (according to pH indicator paper). With eggshells, the inner membrane will not dissolve and should be carefully removed from the solution.
3. Transfer the solution to a 100 mL volumetric flask and make up to the mark with distilled water.

Titration

For undiluted seawater, undiluted milk, eggshell and limestone samples.

1. Pipette a 10 mL aliquot of the sample solution into a conical flask.
2. Add 40 mL of distilled water and 4 mL of 8 mol L^{-1} sodium hydroxide solution (see safety notes), and allow solution to stand for about 5 minutes with occasional swirling. A small of magnesium hydroxide may precipitate during this time. Do not add the indicator until you have given this precipitate a chance to form.
3. Add 0.1 g of Patton-Reeder indicator and swirl the solution to dissolve the indicator.
4. Titrate the sample with the EDTA solution. The endpoint is a colour change from pink/red to blue. Repeat the titration with further samples until concordant results (titres agreeing within 0.1 mL) are obtained.

For tapwater the method is modified due to the much lower Ca^{2+} concentration.

1. Dilute the ETDA standard solution by a factor of 1/50 by pipetting 10 mL into a 500 mL volumetric flask and making up to the mark with distilled water. This will give a 0.0005 mol L^{-1} solution.
2. Pipette a 50 mL aliquot of tapwater into a conical flask. Add 4 mL of 8 mol L^{-1} sodium hydroxide solution, and allow solution to stand for 5 minutes with occasional swirling.
3. Add 0.1 g of Patton-Reeder indicator and swirl the solution to dissolve the indicator.
4. Titrate the sample with the diluted EDTA standard solution to the blue endpoint. Repeat until concordant results are obtained.

Result Calculations

1. Calculate the average volume of EDTA solution used from your concordant titres.
2. Calculate the moles of EDTA required to complex the Ca^{2+} ions in the sample.
3. Using the method ratio Ca^{2+}: EDTA = 1 : 1, calculate the concentration in mol L^{-1} of Ca^{2+} in your sample solution.
4. Calculate the concentration, in mg/L (parts per million or ppm), of Ca^{2+} in your sample solution.
5. In the case of a solid sample which has been dissolved in acid, the concentration of Ca^{2+} in your sample solution may be used to calculate the percentage, by weight, of $CaCO_3$ in the solid sample. This assumes that all the Ca^{2+} found has come from $CaCO_3$.

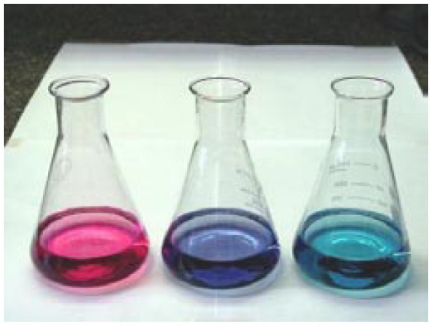
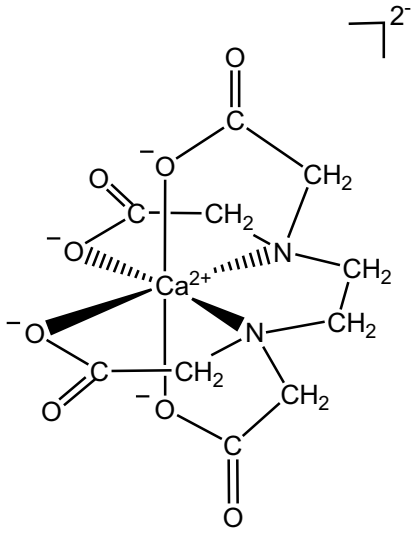


Figure 1 Colour changes for calcium-EDTA titration in clear sample solution using Patton-Reeder indicator. Left flask: pink/red colour well before endpoint (excess Ca^{2+} ions present to complex with indicator). Centre flask: last trace of purple colour just before endpoint (Ca^{2+} ions almost all complexed by EDTA). Right flask: blue colour at endpoint (all Ca^{2+} ions complexed by EDTA, indicator completely uncomplexed).

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

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 Patton-Reeder indicator is used here in the form of a "triturate". Trituration is the dilution of a very strong solid compound with an inert powder (called a diluent) in a definite proportion by weight. This practice is used extensively in pharmaceutical chemistry. Because the undiluted compound is so strong, only a very small portion is required and this is difficult to weigh accurately. The dilution makes it possible to accurately weigh a portion of the mixture containing the correct amount of the compound. This triturate consists of 0.5 g of the pure Patton-Reeder indicator, 2-hydroxy-1-(2-hydroxy-4-sulfo-1-naphthylazo)-3-naphthoic acid, and 50 g of sodium sulfate ground together to a fine powder. Thus addition of 0.1 g of the triturate actually corresponds to the addition of just 0.001 g of the Patton-Reeder indicator compound.
3. This method for determining Ca^{2+} concentration in the presence of Mg^{2+} relies on the fact that the pH of the solution is sufficiently high to ensure that all magnesium ions precipitate as magnesium hydroxide before the indicator is added. (The pH will be approximately 12.5 due to the addition of concentrated NaOH solution). The Patton-Reeder indicator is a suitable indicator in this case as it produces a clear colour change from pink/red to blue in the pH range of 12 – 14.
4. The presence of some metal ions, such as copper, iron, cobalt, nickel, zinc or manganese in high concentrations may cause errors using this method. However, this is unlikely for the solutions and solids suggested.
5. This method for determining the concentration of Ca^{2+} in a sample may be used with the method for measuring total Ca^{2+} and Mg^{2+} concentration using Eriochrome Black T indicator to determine, by difference, the concentration of Mg^{2+} ions in the sample. Note that this method requires a 0.025 mol L^{-1} EDTA solution while the total Ca^{2+} and Mg^{2+} method requires a 0.05 mol L^{-1} EDTA solution.
6. The precise concentration of Ca^{2+} in the sample solution may well vary considerably depending on the nature and source of the sample. To obtain good results, the average titre volume should ideally be between 10 and 30 mL. It may be necessary to vary the concentrations of the EDTA solution used in order to obtain appropriate titre volumes.

Contact Us

If you have any questions or comments relating to this experiment, please contact us. Please note that this service is for senior school chemistry students in New Zealand only. We regret we are unable to respond to queries from overseas.

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