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})

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:

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

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

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

Additional Notes

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

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.

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