Estimation of the total hardness of a water sample using edta

Theory

Ethylenediaminetetraacetic acid (edta) is a reagent that forms edta-metal complexes with many metal ions (**but not with alkali metal ions such as Na^+ and K^+**). In alkaline conditions (pH›9) it forms **stable complexes** with the alkaline earth metal ions **Ca^{2+} and Mg^{2+}**. The edta reagent can be used to measure the total quantity of dissolved Ca^{2+} and Mg^{2+} ions in a water sample. Thus the total hardness of a water sample can be estimated by titration with a standard solution of edta.

Suitable conditions for the titration are achieved by the addition of a buffer solution of pH 10. The buffer solution stabilises the pH at 10. There are H^+ ions produced as the reaction proceeds, and without the buffer solution the pH would decrease.

The edta reagent cannot under these conditions distinguish between the hardness caused by Ca^{2+} and Mg^{2+}, or (directly) between temporary and permanent hardness. Therefore the results of this experiment are usually expressed in terms of the quantity of insoluble $CaCO_3$ that would have to be converted into soluble salts to give the same total number of moles of dissolved Ca^{2+} and Mg^{2+} ions. This enables the total hardness of water from different sources to be compared easily.

Because it is a primary standard, and is also more soluble in water, the disodium salt of edta is more commonly used as the reagent rather than edta itself. If Na_2H_2Y represents this salt, it ionises in aqueous solution to H_2Y^{2-}, which complexes in a 1:1 ratio with either Ca^{2+} or Mg^{2+} ions (which are represented as M^{2+}). The reaction can be represented as follows:

$$H_2Y^{2-} + M^{2+} \rightarrow MY^{2-} + 2H^+$$

The indicator Eriochrome Black T is used to detect the end point. This is an indicator that has a different colour when complexed to metal ions than when it is a free indicator. The reaction between the red indicator-metal complex and the edta reagent at the end point can be represented as follows:

$$MIn^- + H_2Y^{2-} \rightarrow HIn^{2-} + MY^{2-} + H^+$$

Wine blue

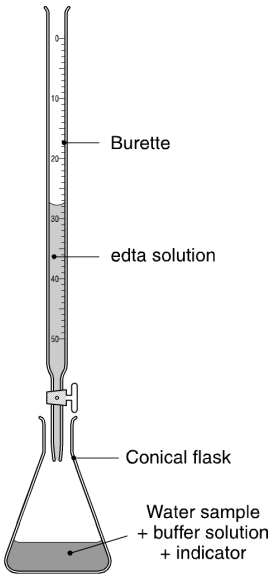
Red

Procedure

NB: Wear your safety glasses.

Wash the pipette, burette and conical flask with deionised water. Rinse the burettemwith the edta solution and the pipette with the hard water.

Using the funnel, fill the burette with the edta solution. Open the tap briefly to fill the part below the tap. Remove the funnel. Adjust the level of the solution to the zero mark. Make sure that the burette is vertical.



Use the pipette to transfer 50 cm^3 of the hard water sample to the conical flask. Add 2-3 cm^3 of the buffer (pH 10) solution (measured out using the graduated cylinder).

Add 0.03 g of the solid indicator to the contents of the flask in the following manner: Add gradually to the flask, swirling after each addition. A deep wine red colour is obtained

Carry out one 'rough' titration to find the approximate end point, followed by a number of accurate titrations until two titres agree to within 0.1 cm^3. At the end point, the colour should be dark blue, with no tinge of wine-red colour.

The water sample could contain metal ions other than Ca^{2+} and Mg^{2+}.

From the data, calculate the total hardness of the water sample.

Table of Results

Volume of hard water sample	=	cm^3
Molarity of edta solution	=	M
Rough titre	=	cm^3
Second titre	=	cm^3
Third titre	=	cm^3
Average of accurate titres	=	cm^3
Total hardness	=	mol/l Ca^{2+}
Total hardness	=	g/l $CaCO_3$
Total hardness	=	p.p.m. $CaCO_3$

Industrial, Environmental & Social Links

Industrial

The hardness of a water supply in industry is critical whenever water is to be heated. This is because heating water with temporary hardness in the water will result in carbonate precipitates forming on the insides of pipes and boilers. This considerably reduces their efficiency. Hence industries, particularly chemical industries, often locate where soft water is available, e.g. Cork Harbour.

Environmental

Some areas of Ireland have geological formations that are largely limestone, e.g. the Burren, an area that is also of outstanding environmental and ecological interest. The water in this area would be expected to have high temporary hardness levels.

Social

There has been a huge upsurge in the popularity of drinking mineral waters because of their taste and calcium content.

Some of the new bathroom cleaners contain edta to help remove scale.

Specimen Results

Rough titre	= 22.4 cm^3
Second titre	= 22.2 cm^3
Third titre	= 22.1 cm^3
Average of accurate titres	= 22.15 cm^3
Volume of hard water sample	= 50 cm^3
Molarity of edta solution	= 0.01 M

Specimen Calculations

$$V_A \times M_A \times n_B = V_B \times M_B \times n_A$$

$50.0 \times M_A \times 1 = 22.15 \times 0.01 \times 1$

$M_A = 22.15 \times 0.01 \times 1 / (50.0 \times 1)$

= 0.00443 moles/litre of Ca^{2+} and Mg^{2+}

= 0.00443 x 100 g/l $CaCO_3$

= 0.443 g/l $CaCO_3$

= 0.443 x 1000 p.p.m. $CaCO_3$

= 443 p.p.m. $CaCO_3$

= total hardness of water sample.

Student Questions

Why is it important that the reaction between the edta and the metal ions in solution is (i) rapid and (ii) go to completion?

These are general requirements of any titrimetic reaction. If the reaction is not almost instantaneous the colour change of the indicator will lag behind the end point and too large a titre would be recorded. If the reagents do not react completely, no conclusion about the concentration of one of the solutions can be obtained from the volume of it that reacts with a known concentration and volume of the other.

How would the reliability of the result be affected if this were the case? Suggest two other metal ions that could be present in the water.

Since alkali metal ions such as sodium or potassium ions do not complex with edta reagent, the results would be unaffected by their presence in the water sample. If, however, there were, for example, iron or aluminium ions present, the value recorded for total hardness by this method would be expected to be too high.

This reagent cannot distinguish between temporary and permanent hardness, List the compounds of calcium and magnesium that cause hardness, and indicate those which cause temporary hardness.

$MgSO_4$, $MgCl_2$, $Mg(HCO_3)_2$, $CaSO_4$, $CaCl_2$ and $Ca(HCO_3)_2$ are the water-soluble compounds of magnesium and calcium that cause hardness. $Mg(HCO_3)_2$ and $Ca(HCO_3)_2$ cause temporary hardness.

Suggest a method of establishing the amount of permanent hardness in a water sample.

A known volume of hard water is boiled to precipitate the temporary hardness-causing hydrogencarbonate compounds as carbonates. These are removed by filtration. The filter paper is washed with deionised water. The filtrate is made up to an exact volume with deionised water and the edta titration carried out again, The result is used to calculate the permanent hardness of the water sample.

What is the function of the buffer solution?

The buffer solution keeps the pH at about 10 thus ensuring that the necessary conditions for the effective operation of the indicator are maintained.