Exercise no. 7

Determination of water hardness

Determination of Ca^{2+} and indirect determination of Mg^{2+}

Introduction

The ions involved in **water hardness**, i.e. Ca^{2+} and Mg^{2+}, can be determined by titration with a chelating agent, ethylenediaminetetraacetic acid (EDTA), usually in the form of disodium salt (H_2Y^{2-}). Eriochrome Black T (Ind) is commonly used as indicator for the above titration. At pH 10, Ca^{2+} and Mg^{2+} ions first complex with the indicator as Ca-Ind and Mg-Ind which is **wine red**. As the stronger ligand EDTA is added, Ind from complexes is replaced by the EDTA, the colour is **blue**. The endpoint of titration is indicated by a sharp colour change from wine red to blue.

PART A: Titration using **Eriochrome Black T** (buffer solution) as indicator determines **total hardness due to $Ca^{2+}$and Mg^{2+} ions.**

PART B: Hardness due to Ca^{2+} ion is determined by a separate titration at a higher pH, by adding NaOH solution to precipitate $Mg(OH)_2\downarrow$, using **murexide** as indicator.

Experimental Procedures

Dilute the analytical sample with distilled water in a measuring flask to the mark (100 mL) and mix completely. The solution in the measuring flask should be treated as 100 mL of the water sample.

Part A: Determination of total hardness

Pipette 10 mL of the solution into the conical flask and add 5 mL of the ammonia buffer solution (pH=10). Swirl to mix. Do not add deionized water to the solution! Add one small pinch of Eriochrome Black T indicator, immediately prior to titrating a sample. Swirl to mix. The solution should be a pale pink. **Do not add more indicator to make the solution darker as this can cause problems with the endpoint**. Titrate the solution immediately with EDTA (0.01M) against a white background until the **light wine red** solution turns a **light sky blue**. Read the final volume (save the solution for colour comparison). Repeat the titration to obtain three concordant results (not differing more than 0.2 mL).

Part B: Determination of concentration of Ca^{2+} ions

Pipette 10 mL of the water sample (from 100 mL) to the Erlenmeyer flask and add 10 mL of 1 M NaOH. Swirl to mix. Do not add deionized water to the solution! Add one small pinch of **murexide** indicator, immediately prior to titrating a sample. Swirl the solution and wait for a one minute to completely precipitate the magnesium ions as $Mg(OH)_2\downarrow$. The solution should be a pale pink-red. **Do not add more indicator to make the solution darker as this can cause problems with the endpoint**. Titrate the solution immediately with EDTA (0.01M) against a white background until the **light pink-red** solution turns a **light blue-violet**. Read the final volume (save the solution for colour comparison). Repeat the titration to obtain three concordant results (not differing more than 0.2 mL).

Calculation

1. From the results in **Part A**, calculate the hardness in ^{o}dH (German hardness unit, equivalent to CaO):

$$^{o}\mathbf{dH} = v_1 \cdot c_{EDTA} \cdot 56.08/10 \cdot 10$$

v_1 – volume of EDTA used in the presence of Eriochrome Black T indicator [mL]

2. From the results in **Part B**, calculate the concentration of Ca^{2+} ions in the water sample in mg/100mL:

$$\mathbf{m_{ca} = v_2 \cdot c_{EDTA} \cdot 0.04008 \cdot 10}$$

v_2 – volume of EDTA used in the presence of murexide indicator [mL]
c_{EDTA} – concentration of EDTA [mmol/mL]
0.040008 – mass of a millimole of Ca^{2+} [g/mmol]

3. Hence, calculate the concentration of Mg^{2+} ions in the water sample in mg/100mL:

$$\mathbf{m_{Mg} = (v_1 - v_2) \cdot c_{EDTA} \cdot 0.02432 \cdot 10}$$

v_1 – volume of EDTA used in the presence of Eriochrome Black T indicator [mL]
v_2 – volume of EDTA used in the presence of murexide indicator [mL]
c_{EDTA} – concentration of EDTA [mmol/mL]
0.02432 – mass of a millimole of Mg^{2+}[g/mmol]