Experiment 47 - Determination of Water Hardness

Goal: To determine the [Ca\(^{2+}\)] in a water sample. The units of [Ca\(^{2+}\)] are \textbf{ppm = parts per million}, where:

\[
1\ \text{ppm} = 1\ \text{g}\ \text{CaCO}_3/1\ \text{million g H}_2\text{O} \text{ or } 1\ \text{mg}\ \text{CaCO}_3/1\ \text{L H}_2\text{O}
\]

We will titrate with EDTA (ethylenediaminetetraacetic acid)

\[
\begin{align*}
\text{HOOC-CH}_2 & \quad \text{N-CH}_2-\text{CH}_2-\text{N} \\
\text{CH}_2-\text{COOH} & \quad \text{HOOC-CH}_2
\end{align*}
\]

It contains 6 donor atoms (underlined) that form a complex ion with Ca\(^{2+}\). One Ca\(^{2+}\) reacts with one EDTA.

Normal lab procedures would call for two basic steps:

1. Standardize EDTA (determine the concentration of EDTA using a known sample of CaCO\(_3\))
2. Use the standardized EDTA to determine the [CaCO\(_3\)] in an unknown water sample

In this experiment, EDTA will be placed in a buret (long tube with graduations, and stopcock to let liquids out) and the hard water sample in an Erlenmeyer flask. To the Erlenmeyer flask, we will add Calmagite - and indicator that will tell us when enough EDTA has been added. This is called the \textbf{endpoint}. At the endpoint the color will change from red to blue, indicating that the molar ratio of Ca\(^{2+}\) to EDTA is 1 to 1. Ideally, EDTA is added to the hard water sample until ONE drop turns the color from blue to red.

Sample calculations:

Objectives:

1. Prepare a standard sample of CaCO\(_3\)

ex. 0.3139 g of CaCO\(_3\) is dissolved in 6 M HCl, and diluted to 250.0 mL in a volumetric flask.

(a) How many mol of CaCO\(_3\) are in the sample?

\[
0.3139\ \text{g CaCO}_3 \times \frac{1\ \text{mol CaCO}_3}{100.1\ \text{g}} = 3.136 \times 10^{-3}\ \text{mol CaCO}_3
\]

(b) What is the molarity of the CaCO\(_3\)?

\[
3.136 \times 10^{-3}\ \text{mol CaCO}_3 = 1.254 \times 10^{-2}\ \text{M CaCO}_3
\]

(c) How many moles of Ca\(^{2+}\) are in a 25.00 mL aliquot?

\[
0.02500\ \text{L} \times \frac{1.254 \times 10^{-2}\ \text{mol}}{1\ \text{L}} = 3.136 \times 10^{-4}\ \text{mol Ca}^{2+}
\]
Objective 2: Standardize EDTA

ex. 25.00 mL aliquot from above example is titrated with EDTA. 32.83 mL of EDTA was required.

(a) How many moles of EDTA were used?

\[
\text{mole EDTA} = \frac{\text{mol Ca}^{2+}}{25.00 \, \text{mL}} \quad \text{(recall rxn is 1 Ca}^{2+} \text{ to 1 EDTA)} \\
\text{mole EDTA} = 3.136 \times 10^{-4} \, \text{mol EDTA}
\]

(b) What is the molarity of EDTA?

\[
\frac{3.136 \times 10^{-4} \, \text{mol EDTA}}{0.03283 \, \text{L EDTA}} = 9.552 \times 10^{-3} \, \text{M EDTA}
\]

Objective 3: Determine [Ca\(^{2+}\)] in unknown water sample.

ex. A 100.0 mL sample of H\(_2\)O was titrated with 26.93 mL of the EDTA in the example above.

(a) How many moles of EDTA were used?

\[
\frac{0.02693 \, \text{L}}{1 \, \text{L}} \left( \frac{9.552 \times 10^{-3} \, \text{mol}}{1 \, \text{L}} \right) = 2.572 \times 10^{-4} \, \text{mol EDTA}
\]

(b) How many mol Ca\(^{2+}\) are in a 100.0 mL water sample?

\[
\text{mol Ca}^{2+} = \frac{\text{mol EDTA}}{2.572 \times 10^{-4}}
\]

(c) How many moles CaCO\(_3\) are in 1.000 L the sample? Grams CaCO\(_3\) in 1.000 L of the sample?

there are \(2.572 \times 10^{-4}\) mol Ca\(^{2+}\) in 0.1000 L of water (one tenth of a liter)

therefore, there are \(2.572 \times 10^{-3}\) mol Ca\(^{2+}\) in 1.000 L of water

\[
\text{mol CaCO}_3 = \frac{\text{mol Ca}^{2+}}{2.572 \times 10^{-3}} = \frac{2.572 \times 10^{-3} \, \text{mol CaCO}_3}{100.1 \, \text{g}} = 2.574 \times 10^{-4} \, \text{g/L CaCO}_3
\]

(d) Concentration of CaCO\(_3\) in ppm.

\[
\frac{2.574 \times 10^{-1} \, \text{g CaCO}_3}{1.000 \, \text{L H}_2\text{O}} \left( \frac{1000 \, \text{mg}}{1 \, \text{g}} \right) = 257.4 \, \text{ppm}
\]
experiment date: 3

ASA: do all questions

Procedure: We will not do standardization of EDTA. Modifying the procedure in the book is very difficult. Therefore, write your procedure from the procedure below.

You will need the following glassware: a 50-mL buret, 250- and 400-mL beakers, at least one 125-mL or 250 mL Erlenmeyer flask, a 25-mL pipet and bulb, a funnel, and a 10-mL graduated cylinder.

Use a dry 250-beaker to obtain about 120 mL of stock EDTA solution, and take this to your desk. If your buret is wet, use a few mL of the EDTA solution to rinse the buret. EDTA rinsates can be poured down the drain with plenty of water. Repeat the rinse twice. Fill the buret full of EDTA. Always use a funnel to pour solutions into a buret. Remove the funnel before reading the volume on the buret. Record the volume on p. 246, beside "Initial buret reading".

Use a dry 400-mL beaker to obtain about 100 mL of an unknown hard water sample, and take this to your desk. Use a 25-mL pipet to measure out exactly 25 mL of the unknown hard water sample and deliver it into an Erlenmeyer flask. Add 5 mL of pH 10 buffer, and 8 drops of Calmagite indicator, which will cause the solution to turn red.

Begin adding the EDTA from the buret to the hard water sample in the flask. Be sure to stop and swirl the contents of the flask regularly to ensure adequate mixing. Near the end-point the color may appear to fade, and will become more violet. The end-point occurs when the last tinge of red disappears and the solution becomes sky blue in color. Record the final volume reading on the buret. Keep your titrated solution as a reference for your next titration.

Refill your buret and titrate two more 25-mL aliquots of the unknown hard water sample.

All solutions and samples can be poured down the drain with plenty of water, at the end of lab or when the samples are no longer needed.

Calculations: Calculations on the data page have been modified from those on the ASA.

Average volume of EDTA per liter of water = \(\frac{\text{average volume of EDTA (in mL)}}{0.02500 \text{ mL H}_2\text{O}}\)

Number of moles EDTA per liter water = 
\[\text{[average volume of EDTA in L (convert above number)]x[molarity of EDTA (on bottle)]}\]

The rest should be straightforward.