Water Hardness

Background

The presence of metal ions in water, particularly calcium, magnesium and sometimes iron cations, cause what is known as “hard water.” The term hard water results from the fact that these metal ions will precipitate soap molecules from water making it "hard" to get things clean. The calcium in hard water will precipitate out as calcium carbonate (lime scale), if the water is boiled. This is sometimes referred to as temporary hardness and causes problems when hard water is used in boilers.

Water hardness is usually determined by measuring the total amount of calcium and magnesium present. The accepted practice for reporting hardness is to report it as milligrams \(\ce{CaCO3}\) per liter, as if all of the hardness were from calcium carbonate. There are several methods used for measuring hardness. We will titrate using ethylene diamine-N,N,N',N'-tetraacetic acid (EDTA). EDTA is a chelating agent that can donate electrons, thereby forming a complex with metal ions. The EDTA will complex first with the \(\ce{Ca^2+}\) and then with the \(\ce{Mg^2+}\).

As with any titration, we will need an indicator to determine when all of the \(\ce{Ca^2+}\) and \(\ce{Mg^2+}\) have complexed with the EDTA (i.e. the endpoint). The indicator will be Eriochrome Black T. At pH 10, the indicator will be in the form HInd2- (Ind stands for indicator), which is blue. The indicator reacts with \(\ce{Mg2+}\) as follows:

\[\ce{HInd^2- (blue) + Mg^2+ -> H+ + IndMg- (red)}\]
The general procedure for this experiment starts with a sample of hard water that contains calcium and magnesium. Then, to insure that all cations stay in solution and that the indicator works properly, a buffer is used to adjust the pH to 9.9 - 10.1. After the pH is adjusted and the indicator is added, the EDTA titrant is added via a buret.

First, the EDTA will complex with the calcium ions:

\[\ce{ EDTA + 2Ca^2+ -> EDTA(Ca^2+)2 }\]
Next, the EDTA will complex with the free magnesium ions:

\[\ce{ EDTA + 2Mg^2+ -> EDTA(Mg^2+)2 }\]
Finally, at the endpoint, the EDTA will complex with the magnesium that is tied up with the indicator:

\[\ce{ EDTA + 2H+ + 2IndMg- (red) -> EDTA(Mg^2+)2 + 2HInd^2- (blue) }\]

Procedure

Samples

Use the samples provided in lab.

Prepare the EDTA Titrant

Prepare 500 mL of EDTA titrant by weighing 1.8615 g disodium ethylenediaminetetraacetate dehydrate, also called (ethylenedinitrilo)tetraacetic acid disodium salt (EDTA). Carefully transfer the EDTA solid to a 500 mL volumetric flask, being careful not to spill any of your sample. Dilute to 500 mL with distilled water, mixing well to dissolve the EDTA. This is the solution you will use for the following titrations.

Blank Determination

Most hardness is caused by the presence of calcium. Some water may be quite hard, yet contain no magnesium at all. If there is no \(\ce{Mg2+}\), then reactions 2 & 3 above will not occur. Without reaction 3, it will not be possible to detect an endpoint. For this reason, the buffer used to adjust the pH contains a small amount of \(\ce{Mg2+}\). Of course, this \(\ce{Mg2+}\) should not be reported as hardness since it is not from the water sample. Thus, it is necessary to run a blank and to subtract the volume of EDTA titrant used for the blank from all future titrations.

1. Measure approximately 50 mL of deionized water into a 250 mL flask.
2. Add 2.0 mL of the buffer solution. The remainder of the titration must be completed within 15 minutes of the time when the buffer is added.
3. Add 4 drops of Eriochrome Black T indicator solution.
4. Titrate using the EDTA titrant. At the end point, the color should change from red to blue.
5. Repeat this procedure at least two additional times.
6. Average the volume of EDTA titrant used for the 3 blank determinations. Subtract this volume from all future titrations.

Standardize the EDTA Solution

Before using the EDTA to titrate water samples, we must know its exact concentration. We will use a solution of calcium carbonate (1.00 mg \(\ce{CaCO3}\)/mL) as the primary standard to determine the exact concentration of EDTA solution.

1. Measure exactly 20.0 mL of the \(\ce{CaCO3}\) standard solution into a 250 mL flask. Add approximately 30 mL of deionized water to the flask.
2. Add 2.0 mL of the buffer solution. The remainder of the titration must be completed within 15 minutes of the time when the buffer is added.
3. Add 4 drops of Eriochrome Black T indicator solution.
4. Titrate using the EDTA titrant. At the end point, the color should change from red to blue.
5. Repeat this procedure at least two additional times.
6. Use this data and the data from part A to calculate exactly how much EDTA titrant is needed to react with 1.00 mg of \(\ce{CaCO3}\). You will use this value in your calculations to determine the water hardness.

Titrate Your Samples

Freshwater or Tap Water

1. Measure exactly 50 mL of the water sample into a 250 mL flask.
2. Add 2.0 mL of the buffer solution. The remainder of the titration must be completed within 15 minutes of the time

when the buffer is added.

3. Add 4 drops of Eriochrome Black T indicator solution.
4. Titrate using the EDTA titrant. At the end point the color should change from red to blue.
5. Repeat this procedure at least two additional times.
6. Use this data and the data from parts A and B to calculate the hardness of your water sample in milligrams of \(\ce{CaCO3}\) per liter.

Hard Water Sample

1. Measure exactly 5.0 mL of the ocean water sample into a 250 mL flask. Dilute the ocean water 1:10 by adding 45 mL of deionized water to the flask. Because the ocean water has a significantly higher concentration of \(\ce{Ca^2+}\) ions, this dilution will decrease the amount of EDTA titrant required to reach the endpoint.
2. Add 2.0 mL of the buffer solution. The remainder of the titration must be completed within 15 minutes of the time when the buffer is added.
3. Add 4 drops of Eriochrome Black T indicator solution.
4. Titrate using the EDTA titrant. At the end point the color should change from red to blue.
5. Repeat this procedure at least two additional times.
6. Use this data and the data from parts A and B to calculate the hardness of your water sample in mg \(\ce{CaCO3}\) per L. Make sure you take into account the 1:10 dilution of your ocean water sample. (The hardness of the ocean water will actually be 10 times the value you calculate because of the 10-fold dilution of the water sample.)

What to Turn In

1. Turn in your scanned lab notebook pages before leaving lab.
2. Turn in your Excel worksheet before the due date.
