Name ____________________________ Section_________________________

Partner(s) ______NONE___________ Date ___________________________

ANALYSIS OF CALCIUM BY EDTA TITRATION TO ASSESS WATER HARDNESS

PRE-LAB QUERIES

1. What properties of a metal ion might be useful for the analysis of that ion?

2. We often speak of water samples as being "hard" or "soft". What does this mean?

OBJECT

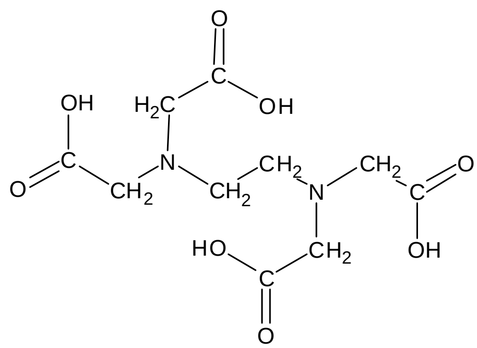
In this activity, you will perform a titrimetric analysis of Ca^{2+} in a standard solution and water samples using the complexometric reaction of EDTA with metal ions.

INTRODUCTION

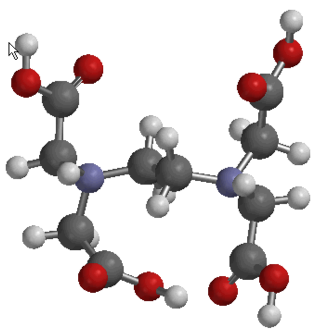
One measure of water quality is "hardness" which is defined by the amount of Mg^{2+} and Ca^{2+} (and sometimes Fe^{3+}) ions in a given amount of water. The presence of calcium and magnesium ions poses no health hazard but water hardness is of particular concern because the reaction of these ions with "soap" (sodium salt of a large fatty acid) produces an insoluble product we know as "soap scum". This scum is abrasive and may weaken clothes fibers as they move against each other when worn. It will also be deposited on hair and skin when soap is used as a cleaner in hard water. Modern detergents do not produce the same degree of insoluble product and have effectively replaced soap for most products including hand cleansers, bars, shampoos, and laundry products.

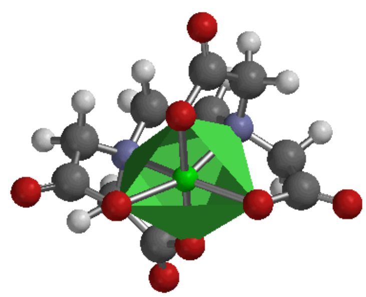
The most common source for Mg^{2+} and Ca^{2+} in water is carbonate compounds in Earth materials. As a result, hardness is often expressed as parts per million of $CaCO_3$ (ppm) by mass. A hardness of 100 ppm would be equivalent to 100 g of $CaCO_3$ in 1 million grams of water (10^3 L) or 0.1 g in 1.0 L or 100 mg in 1.0 L.

Titration procedures provide relatively inexpensive means for the analysis of different substances. These titrations are based on chemical reactions with completion points that can be monitored by some visible change in the reaction systems. As you are aware, the most common system involves acids and bases with the use of an indicator that changes color as the system moves from an acidic to basic composition. Calcium and magnesium ions can be measured through reaction with a chelating agent EDTA (ethylenediaminetetraacetic acid). This molecule has four carboxylic acid (~COOH) group sites and two nitrogens, all of which have lone pairs of electrons. The EDTA molecule can form a complex with as many as six sites on a particular cation like Ca^{2+}. These EDTA complexes are generally very stable are always in 1:1 (metal:EDTA) molar ratios.



Structure of EDTA in acid form





Structure of EDTA

Structure of EDTA Complex

In this activity you will be titrating Ca^{2+} in a standard Ca^{2+} solution or water samples with EDTA. Both Ca^{2+} solutions and EDTA are colorless so an indicator is needed to signal the reaction completion. The indicator of choice is Eriochrome Black T which forms a wine-red complex with Mg^{2+}. A very small amount Mg^{2+} will be bound to the indicator through most of the titration. When all of the Ca^{2+} has reacted with EDTA, the Mg^{2+} in the indicator will react with the EDTA. The indicator then returns to its acidic form which is a sky-blue and signals the end of the process.

To maximize the EDTA-Ca (or Group IIA ion) complex formation and minimize formation of other metal complexes, the pH for the reaction system is set at 10 using an NH_3-NH_4^+ buffer. This keeps EDTA (H_4Y) mostly in a half-neutralized form, H_2Y^{2-}. Below are the reactions that occur during the titration where H_3In is the general formula for the Eriochrome Black T.

During titration:	H_2Y^{2-} (aq) + Ca^{2+} (aq)	→	CaY^{2-} (aq)	+	$2\ H^+$ (aq)		
	H_2Y^{2-} (aq) + Mg^{2+} (aq)	→	MgY^{2-} (aq)	+	$2\ H^+$ (aq)		
At end point	H_2Y^{2-} (aq) + $MgIn^-$ (aq) Wine-red	→	MgY^{2-} (aq)	+	HIn^{2-} (aq) sky-blue	+	H^+

The indicator reaction has to occur after the free Ca^{2+} or any free Mg^{2+} react. Why?

What would happen if the indicator reaction occurred before this point?

The equilibrium constant for the formation of Ca-EDTA has a larger value (~ x100) than for the production of Mg-EDTA. Therefore, the Ca^{2+} is titrated first and then the Mg^{2+} reacts.

A small amount of magnesium ion will be added to the calcium solutions you use to generate the indicator changes. This amount is so small that it does not impact the analysis of the calcium.

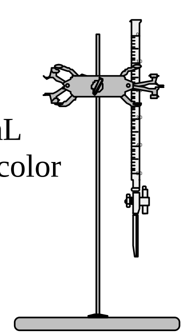
PROCEDURE

Standardization of EDTA

1. Mass a sample of $CaCO_3$ between 0.30 and 0.32 g to the nearest milligram. Record the mass. Quantitatively transfer the $CaCO_3$ to a 250 mL beaker. Add 25 mL of distilled water. CAREFULLY and SLOWLY add 2 mL of 6 M HCl to the mixture in the beaker and mix. If the solution remains cloudy, add another drop of HCl and mix. Repeat if necessary until the solution is clear.

   Cover the beaker with a watch glass and heat the solution to boiling to remove CO_2. When cool, carefully transfer the solution, using a funnel, to a 250 mL volumetric flask. Rinse the beaker several times with small portions of distilled water and transfer the rinse to the volumetric flask. Rinse the funnel in the same manner several times. Fill the volumetric flask with distilled water until the meniscus just rests on the mark on the flask neck. Seal the flask and mix the contents by inverting 10-15 times and shaking over a period of several minutes.

2. Obtain a ring stand with buret clamp and one buret. Clean the buret with a small amount of EDTA solution and drain. Fill the buret with EDTA.



3. Pipet a 25 mL aliquot of Ca^{2+} solution into a 250 mL Erlenmeyer flask. Add 5 mL of pH 10 buffer and 2 drops of Eriochrome Black T indicator. Mix well. What color should the solution be at this point?

4. Titrate the sample in the flask with the EDTA, slowing additions as you near the endpoint. Record the volume required to titrate the calcium sample. Keep the first sample as a color reference.

5. Prepare a second 25 mL portion of Ca^{2+} solution and repeat the titration recording all data. If the volumes of EDTA agree to within 0.4 mL, proceed to the next section. If they do not agree, repeat the titration procedure until you have two sets of EDTA volumes that agree to within 0.4 mL.

Determination of Water Hardness

1. Pipet exactly 50.00 mL of a water sample provided into a 250 mL Erlenmeyer flask. Add 5 mL of pH 10 buffer and 2 drops of Eriochrome Black T indicator. Mix well. Titrate the sample with the same EDTA used in the previous section. Record all volumes.

2. Prepare and titrate 2 additional water samples recording the volume of EDTA used to just reach the end point.

Calculations

1. Determine the moles of $CaCO_3$ (moles Ca^{2+}) in the volumetric flask and each 25.00 mL aliquot titrated.

2. Using the volume of EDTA required to react with Ca^{2+}, calculate the molarity of EDTA and the average EDTA molarity. Use the best two trials to determine the average.

3. Using the volume and average molarity of EDTA required to titrate each water sample, determine the moles of Ca^{2+} in each sample.

   Use these results to compute the moles of Ca^{2+} per liter and grams of $CaCO_3$ per liter.

   From the g $CaCO_3$/L, determine the hardness in ppm (mg $CaCO_3$/L of water).

DATA AND RESULTS

Preparation of Ca^{2+} Solution

Mass of $CaCO_3$ ________________________________

Moles of $CaCO_3$ ________________________________

Moles of Ca^{2+} in 25.00 mL aliquot ________________________________

Standardization of EDTA

	Trial 1	Trial 2	Trial 3
Initial buret reading			
Final buret reading			
Volume of EDTA			
Molarity of EDTA			
Average EDTA molarity			

Work:

Water Hardness

Unknown Code ______________________

	Trial 1	Trial 2	Trial 3
Volume of water			
Initial buret reading			
Final buret reading			
Volume EDTA used			
Moles EDTA			
Moles Ca^{2+} in sample			
Moles Ca^{2+}/ L			
Grams $CaCO_3$ / L			
Hardness (ppm)			
Average hardness			
% CV			

Work:

CONCLUSION

How do your results compare with at least two other students? Who has the best precision? Explain with justification.

POST-LAB QUESTIONS

1. What is the geometry of the Ca^{2+} in its EDTA complex?

2. The $CaCO_3$ used to standardize the EDTA was a primary standard (very high purity). How would the results for the molarity of EDTA be influenced if the $CaCO_3$ was impure? Explain.

3. Hardness is traditionally expressed in mg $CaCO_3$/L of water. Suppose that a water sample you analyzed contained mainly Mg^{2+}, how would the calculation of hardness be affected? Explain.

4. A 0.4005 g sample of $CaCO_3$ is dissolved in HCl and diluted to 250 mL in a volumetric flask. A 25.00 mL aliquot of the sample requires 22.22 mL of an EDTA solution for titration.

   What is the molarity of the EDTA? Show work.

   If a 100.00 mL well water sample requires 20.75 mL of the EDTA solution above, what is the water hardness of the well water? Show work.

5. Go to http://water.usgs.gov/owq/map1.jpeg and describe a region in the United States with a low water hardness and one with a high water hardness.