Experiment 7

EDTA DETERMINATION OF TOTAL WATER HARDNESS AND CALCIUM

3 lab periods

Reading: Chapter 11, Quantitative Chemical Analysis, 8th Edition, Daniel C. Harris (7th Edition: Chapter 12).

Objective

This lab will introduce you to the concept of complexometric titrations. You will learn how to standardize a solution of ethylenediaminetetraacetic acid (EDTA) and how to determine the calcium and magnesium content of water. You may bring a tap water sample from home to analyze. You will also be given a performance evaluation sample.

Suggested Schedule

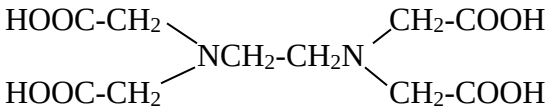
Lab 1 Prepare and standardize your calcium carbonate and EDTA solutions.
Lab 2 Analyze your water samples for total hardness and for calcium.
Lab 3 Finish your analyses.

Water quality is evaluated using a number of parameters, including total ionic content, pH, total dissolved solids, organic compounds, and *water hardness*. Water hardness is a measure of the concentration of all the polyvalent cations dissolved in the water. The most common such cations are calcium and magnesium, although iron, strontium, and manganese may contribute to water hardness. Water hardness is often defined as the sum of the concentrations of Ca^{2+} and Mg^{2+} in water. "Hard" water typically contains high concentrations of Ca^{2+} and Mg^{2+}, which react with the fatty acids in soap, causing them to precipitate. "Soft" water, such as rainwater or water that has passed through a water softener, has very little Ca^{2+} and Mg^{2+}.

Most waters contain more calcium than magnesium. The calcium usually comes from the dissolution of calcium carbonate. Thus, water hardness is usually reported as milligrams of calcium carbonate per liter of solution. The U.S. Geological Survey (www.usgs.gov) provides the following general guidelines for classification of waters:

Soft: 0 to 60 mg/L hardness as $CaCO_3$
Moderately hard: 61 to 120 mg/L hardness as $CaCO_3$
Hard: 121 to 180 mg/L hardness as $CaCO_3$
Very hard > 180 mg/L hardness as $CaCO_3$

Both Ca^{2+} and Mg^{2+} can be determined by titration with ethylenediaminetetraacetic acid (EDTA) at pH 10.



Ethylenediaminetetraacetic Acid (EDTA, or H_4Y)

The EDTA molecule can be represented as H_4Y, where the four acidic hydrogen atoms are those at the "ends" of the molecule. Approximately half of the EDTA dissolved at pH l0 is in the form of HY^{3-} and half is in the form of Y^{4-}. The complexation reaction of EDTA with either Ca^{2+} or Mg^{2+} can therefore be represented in either of the following ways, where M^{2+} represents the metal ion:

$$M^{2+} + HY^{3-} \equiv MY^{2-} + H^{+}$$

$$M^{2+} + Y^{4-} \equiv MY^{2-}$$

Standard EDTA solutions can be prepared directly from either disodium EDTA (Na_2H_2Y) or disodium EDTA dihydrate (($Na_2H_2Y \bullet 2H_20$).

The endpoints of EDTA titrations of Ca^{2+} and Mg^{2+} can be located with the metallochromic indicator, Calmagite. This indicator forms a red complex with either Ca^{2+} or Mg^{2+}. The uncomplexed indicator can exist in the ionic forms H_2In^{-}, HIn^{2-}, and In^{3-} (red, blue, and orange, respectively). At a pH in the range 8.1 - 12.4, the blue HIn^{2-} form predominates; this form is in equilibrium with the red MIn^{-} form when the metal M^{2+} is present:

$$\underset{\text{(blue)}}{M^{2+} + HIn^{2-}} \equiv \underset{\text{(red)}}{MIn^{-} + H^{+}}$$

Before the endpoint of the titration, the solution is red because of the excess metal ion. As the EDTA titrant complexes more and more metal, the above equilibrium shifts to the left. At the endpoint, the solution turns blue. The formation constants for the Calmagite-magnesium and Calmagite calcium complexes are:

Calmagite-magnesium complex	$\log K_f = 5.69$
Calmagite-calcium complex	$\log K_f = 3.67$

EDTA forms a more stable complex with calcium ($\log K_f = 10.65$) than with magnesium ($\log K_f = 8.79$). Thus, in solutions (such as natural water samples) that contain both metals, EDTA reacts first with Ca^{2+}, and, when all the Ca^{2+} ions have been complexed, with Mg^{2+}. When all the free Mg^{2+} has been complexed by EDTA, the remaining free (uncomplexed) EDTA displaces the Calmagite from the red $MgIn^{-}$ complex. At the endpoint, just enough EDTA has been added to displace all the Calmagite and the solution turns blue because of the presence of HIn^{2-} in solution.

In an EDTA titration of natural water samples, the two metals are determined together. To determine the concentration of each metal separately, we need to do an additional measurement that is selective for one of the two metals. This can be done by raising the pH to 12, which precipitates the magnesium as its hydroxide:

$$Mg^{2+} + 2OH^- \equiv Mg(OH)_2\,(s) \qquad pK_{sp} = 9.2$$

The solid $Mg(OH)_2$ is not titrated, but the Ca^{2+}, which remains in solution, is. To perform this titration, Calcon, aka Eriochrome Blue Black R, is used as the indicator. Calcon retains color better at pH 12 than does Calmagite. The endpoint is less precise, however, so your estimate of Ca^{2+} in the water will not be as reliable as your estimate of the total Mg^{2+} and Ca^{2+} present.

The results of the first titration give the total moles of Mg^{2+} and Ca^{2+} in the sample. The second titration gives the moles of Ca^{2+} present in the sample. Obviously, the difference between the two results is the moles of Mg^{2+} present in the sample.

Prelaboratory Assignment

A 100.00-mL water sample was adjusted to pH 10 and titrated to the calmagite endpoint with 10.87 mL of 0.0125 M EDTA solution. Then the pH of another 100.00-mL water sample was adjusted to pH 12 and titrated with EDTA to the calcon endpoint. In this second titration, 2.63 mL of titrant was required. Calculate the concentration of Mg^{2+} and Ca^{2+} in the water. Express your answers in mg/L of $CaCO_3$ and $MgCO_3$, respectively.

Apparatus

- 250- and 500-mL volumetric flasks
- 50 mL buret
- 3 to 4 250-mL Erlenmeyer flasks
- 10-mL graduated cylinder
- 25- or 50-mL volumetric pipet
- Weighing bottle
- 250-mL plastic bottle
- 1 L plastic bottle
- One or more types of pH indicator paper: need indicator paper that can be used to indicate pH 2, pH 7, pH 10, and pH 12
- Beakers of various sizes.
- Droppers

Chemicals

- A sample of water from your home, or another source (~ 1 L).
- pH 10 ammonia/ammonium chloride buffer *(may be prepared by Lab Services)*
  Dissolve 16.9 g NH_4Cl in 143 mL of ammonium hydroxide solution containing at least 28% wt/wt NH_3. Add 1.25 g magnesium salt of EDTA. Dilute to 250 mL with DI water. Prepare this solution in the hood.
- The following indicator solutions will be prepared for you:
  Calmagite solution (0.1 g dissolved in 100 mL of water). **This indicator must be prepared fresh, as the quality rapidly deteriorates (within one day).**
  Calcon (Eriochrome Blue Black R) solution (0.2 g dissolved in 50 mL of methanol). **This indicator must be prepared fresh for this lab.**
- Disodium salt of EDTA or disodium EDTA dihydrate
- Calcium carbonate primary standard ($CaCO_3$)
- Sodium hydroxide solution, 3 M. Prepare from a 50% wt/wt NaOH solution.
- Sodium sulfide solution (5% wt /vol) in water *(freshly prepared by Lab Services).* This step helps alleviate Fe interference.
- Concentrated HCl
- HCl solution (3 M). Prepare from concentrated (12 M) HCl solution.
- Ice is useful to help cool your solutions after boiling.

Procedure

A Preparing a standard EDTA solution

1. *Preparing the calcium carbonate primary standard.*
   Obtain ~ ~~0.1~~ 1.0 g of calcium carbonate standard and dry at 110°C for ~1 hr, or to constant weight. While you are waiting for it to dry, prepare your EDTA solution, as in step 2. Once the calcium carbonate standard has dried and cooled, weigh 0.3 to 0.4 g (to the nearest 0.1 mg) by difference into a clean, dry, short-stemmed funnel set in the mouth of a 500 ml volumetric flask. Tap the funnel gently to force the $CaCO_3$ into the flask. Wash any remaining $CaCO_3$ into the flask using DI water. With the funnel in place, add a small amount (< 2 mL) of concentrated HCl to the flask, washing any remaining $CaCO_3$ into the flask with the HCl (**Do this in the hood**). Rinse the funnel thoroughly with DI water and remove it from the flask. Swirl the flask until all the $CaCO_3$ has dissolved. Dilute to the mark with DI water. Note: you are making a lot of solution. You may wish to share this with others in your class.

2. Preparing your EDTA solution.
   You will be using either the disodium salt of EDTA or disodium EDTA dihydrate (M.W. 372.24 g/mol). Weigh ~ 0.9 g of EDTA. Transfer this into a 250 mL volumetric flask (or Erlenmeyer flask, as you are going to standardize this solution) and fill the flask ~halfway with DI water. Add 3-4 mL of the 3 M NaOH solution and swirl to dissolve. This process might take ~15 minutes. You may warm the solution gently to help the process along. Once the EDTA has dissolved, dilute to the mark with DI water and mix thoroughly. Store in a 250 mL plastic bottle. Keep solution capped when not in use.

3. *Standardizing your EDTA solution*
   a. Pipet 25.00 mL of your $CaCO_3$ standard solution into each of three 250 mL Erlenmeyer flasks. Add ~1 ml of buffer solution using a 10 mL graduated cylinder. The pH of your solution should be ~10 after the addition of buffer. Add ~2-3 drops of calmagite indicator solution. Titrate the solution until the last trace of red color disappears upon addition of just a fraction of a drop of EDTA. The final color change should be from a violet color to a pale blue. The change should be fairly sharp. If it is not, it could mean that the indicator is old. Record each endpoint volume to the nearest 0.01 mL.
   b. Prepare a sample for a blank titration as follows:
   Pipet a 25.00 mL sample of DI water into a clean 250 mL Erlenmeyer flask. Add ~ 1-2 mL of the buffer. Add a few drops of calmagite indicator solution. If the solution turns blue, there is no measureable magnesium or calcium in the solution and you will not have a blank correction. If the solution stays red or violet, titrate with the EDTA solution until there is no trace of red or violet in your solution.

The color change on reaching the endpoint is very subtle. Ask the TA to help you determine if you are near your endpoint. One thing that might help is to carry your solution over to the window and look at it in natural light. The fluorescent lights may make the solution have a pinkish tinge to your eye, even at the endpoint. Also, try to reach the same color for each titration of your standards and unknowns. The consistency of your technique will improve the precision of your measurements.

B Performance Evaluation

1. You will have a performance evaluation sample given to you by your TA or by Lab Services. This sample will have a total volume of 300 mL and should be well shaken. **If you take more than 300 mL your lab grade will be decreased by 50%.**
2. Use a volumetric pipet (either 2 x 50.00 mL or 4 x 25.00 mL) to place 100.00 mL of your water sample in each of three 250-mL Erlenmeyer flasks. Add 5 - 10 drops of 3 M hydrochloric acid to each flask, or until the pH is ~2 (test using indicator paper), and gently boil the solution for about 5 min. Dissolved carbon dioxide is removed from the solutions during the boiling. The acid is added to convert dissolved carbonate to carbon dioxide. Also prepare a solution for a blank titration.
3. Cool each solution to near room temperature. Use ice to speed things up. Add 3 M sodium hydroxide solution dropwise to each flask until the pH is ~7 (use indicator paper to test the pH). This may take anywhere from 5-15 drops of 3 M NaOH solution. The hydrochloric acid which was added in step 2 is neutralized in this step.
4. Add 1 or 2 mL of pH 10 buffer and about 2-3 drops of calmagite indicator. The pH should be ~10. Use indicator paper to check the pH. The solutions should themselves be red in color.
5. Fill a 50-mL buret with the standardized EDTA solution and use the solution to titrate each water sample to the endpoint. At the endpoint the titration solution changes from red to blue. Record each endpoint volume to the nearest 0.01 mL.
6. Carry out a blank titration. Proceed as in steps 2 - 6, but using 100 mL of DI water as a sample.

Calculations (use report form provided)

1. Using your data from Part A, calculate the molarity of Ca^{2+} for each replicate of the performance evaluation sample. Find the average molarity and the standard deviation for each sample.

Questions

Find the latest City of Moscow Annual Water Quality Report (https://www.ci.moscow.id.us/pub_works/water/WaterQuality2010.pdf) to help you answer the following questions:

1) Describe the source of your water sample. Use the USGS classification system to describe the hardness of your water sample. Where does Moscow's drinking water come from? Based on the source of the water, explain the presence of the magnesium and calcium ions in the water. If your sample is not Moscow tap water, then explain the source of the hardness you determined in that water sample.
2) What is a maximum contaminant level (MCL)? What is a maximum contaminant level goal (MCLG)? What is an action level (AL)? Did any of the regulated substances monitored by the City of Moscow exceed the MCL?

Experiment 7 Name: _____

EDTA Determination of Total Water Hardness Unknown #_____

Purpose

Results

Concentration of EDTA solution:_____*M*

PERFORMANCE EVALUATION SAMPLE, (ID number:_____)
CALCIUM

Replicate	1	2	3
EDTA Volume, mL			
$[Ca^{2+}]$, *M*			
Hardness, expressed as mg/L of $CaCO_3$			

Average Hardness: _____ Standard Deviation: _____

Include sample calculations for all three experiments, and answer all questions. Check your calculations carefully! Don't forget to include copies of your lab notebook pages for this experiment.