Determination of Water Hardness using Complexometric titration

You will use EDTA *complexometric titration* to determine the hardness of a sample of water brought from your home. Both the total hardness and the individual calcium and magnesium hardnesses will be measured. EDTA and the metallochromic indicators used are involved in complexation reactions with the magnesium and calcium ions that are responsible for water hardness. A colour change is observed when EDTA replaces the indicator molecule as the ligand in the divalent ion complex. *Solubility products* will be used to our advantage when determining the calcium hardness. You are encouraged to bring your own water sample to study.

Required Reading

D.C. Harris, *Quantitative Chemical Analysis* (6th ed., W. H. Freeman, NY, 2003) pp. 259–64, 272–7, 104–5.

PreLab Quiz Topics

In addition to being able to explain the purpose of your experiment, the general procedure steps, the use of all chemicals in this experiment and any specific hazards, your prelab quiz may include explanations of any of the following terms: chelating ligand, complexometric titration, formation constant, masking agent, water hardness, and solubility product. Know the chemical reactions relevant to the titrations. (You do not have to know the chemical reactions for all the test-tube reactions. Yet.) Describe the chemical and/or physical processes that will occur when you reach the endpoint of your titration.

In nature, water is hardened by the passage of rainwater containing dissolved carbon dioxide through layers of stone such as chalk, gypsum, or limestone. Hard water contains multiply charged ions such as calcium, magnesium, and heavy metal ions, which replace sodium and potassium ions in soaps and detergents to form precipitates. These precipitates interfere with cleaning action and leave bathtub rings and scum. Calcium carbonate ($CaCO_3$) is the most common precipitate. It is water insoluble and is the main component of the scale that clogs pipes. Concentrations of Mg^{2+} and Ca^{2+} are much higher than any other ions responsible for hardness, and *total water hardness* is defined as the sum of the calcium and magnesium concentrations. Total water hardness is usually expressed as the milligrams of $CaCO_3$ equivalent to the total amount of calcium and magnesium present in one liter of water (mg/liter, i.e., ppm). Water hardness may range from zero to hundreds of ppm, depending on the source. The classification of degree of water hardness according to the US Geological Survey is as follows:

Soft	0 – 60	ppm $CaCO_3$ equivalents
Moderately hard	61 – 120	ppm $CaCO_3$ equivalents
Hard	121 – 180	ppm $CaCO_3$ equivalents
Very hard	> 181	ppm $CaCO_3$ equivalents

Complexometric titration is based on the formation of a complex ion. Ethlyenediaminetetraacetic acid (EDTA or H_4Y, where $\mathbf{Y = C_{10}H_{12}N_2O_8}$) is a complexing agent designed to bind metal ions quantitatively, forming stable, water soluble complexes with a 1:1 stoichiometry for most metal ions (i.e., 1 EDTA binds to 1 metal ion). EDTA binds to both calcium and magnesium, but binds more tightly to calcium, thus:

$$Ca^{2+} + Y^{4-} \rightarrow CaY^{2-}$$
$$Mg^{2+} + Y^{4-} \rightarrow MgY^{2-}$$
$$Ca^{2+} + MgY^{2-} \rightarrow CaY^{2-} + Mg^{2+}$$

As a sample is titrated with EDTA, the calcium ions in the sample are preferentially complexed by the EDTA, while magnesium complexes with the indicator. EDTA-metal complexes are generally uncolored; however, metallochromic indicators change colour depending on whether they are bound or unbound. After all the free calcium and magnesium are bound by EDTA, additional EDTA extracts the magnesium ions from the Eriochrome Black T indicator, restoring it to its uncomplexed blue colour, and an endpoint is observed. Comparison of the following reaction to Eqn 13–19 in your textbook can be confusing. Your textbook uses "In" to mean indicator. If you look in Table 13–3 in your textbook, you will see that at pH 10, the Eriochrome Black T indicator will be predominantly in the form HIn^{2-}.

$$MgIn^{-}\text{ (PURPLE-RED)} + H^{+} + Y^{4-}\text{(CLEAR)} \rightarrow MgY^{2-}\text{(CLEAR)} + HIn^{2-}\text{(BLUE)}$$

Eriochrome Black T does not give a sharp colour change for water containing calcium, but no magnesium. To make sure that there is some magnesium present in your sample, we add a small amount of Mg-EDTA (Magnesium already complexed with EDTA). Since we add the same amount of EDTA as Mg^{2+}, the addition of Mg-EDTA to the sample has no net effect on the subsequent titration.

Both EDTA and the metallochromic indicators are weak acids and their actions are very pH dependent; thus we use a pH 10 buffer to hold the solutions at an appropriate pH for both the EDTA and the Eriochrome Black T indicator to work well. Note that the chemical reactions given above are not the full story. In fact, from Fig. 13–6 in your text, you can see that the predominant form of EDTA at this pH is HY^{3-}, it's just easier to write out the reactions that are occurring with Y^{4-} at the same time. Some metal ions interfere with this titration by causing indistinct endpoints, or by complexing with EDTA and/or the indicator more strongly than the metals of interest. We will look at an example of a chemical *masking agent* that is used to counteract such occurrences.

Chemicals and their Location

Above/on/beside lab bench

- Eriochrome Black T, 0.5% wt/vol. in Ethanol
- Hydrochloric acid, 0.1 M
- Magnesium chloride, 0.01 M
- Magnesium-EDTA, 0.01 M
- Nickel sulfate, 0.1 M
- Potassium cyanide, 5%
- Sodium hydroxide, 0.1 M
- Sodium hydroxide, 1 N
- Sodium hydroxide, 50%

Balance Room

- Murexide

You supply it

- 500 mL unknown water sample

In the Hood

- Ammonia/ammonium chloride buffer, pH 10

We encourage you to bring your own unknown water sample, especially if you have access to well or bore water. Otherwise, you may take a water sample from the sink. **DO NOT** attempt to measure the hardness of distilled water, nor bottle water unless it is clear from the label that it has calcium and/or magnesium in it (e.g., spring water).

Equipment and its Location

Stockroom	*TA Bench*
Burette	Glass stirring rods
One 250 mL volumetric flask, acid washed	
One 50 mL volumetric pipette, acid washed	
Three 250 mL Erlenmeyer flasks, acid washed	
Seven acid washed test tubes & rack	

Safety Issues and Chemical Hazard Information

	Physical Hazards	*Health Hazards*
Ammonia	Corrosive	toxic
Ammonium chloride	None	irritant
EDTA dihydrate, disodium salt	None	irritant
Eriochrome Black T	None	irritant
Hydrochloric acid	water-reactive, corrosive	toxic
Magnesium chloride	None	irritant
Murexide	None	irritant
Nickel sulfate	None	toxic, sensitizer, carcinogen, mutagen
Nitric acid	strong oxidizer, water-reactive, corrosive	toxic
Potassium cyanide	corrosive	**extremely toxic**, corrosive
Sodium chloride	none	irritant
Sodium hydroxide	water-reactive, corrosive	toxic, irritant

Potassium cyanide is a **swift acting, highly toxic poison**. You will be using very small amounts of a weak solution, but you still must take extreme care. Poisoning may occur from ingestion, skin absorption or inhalation. **UNDER NO CIRCUMSTANCES ALLOW CYANIDE AND ACID TO COME INTO CONTACT.** The mixture of these two chemicals will create hydrogen cyanide, a very deadly gas. Some of these chemicals are corrosive. Wear gloves and take care not to breathe the vapor when working with these chemicals.

Procedure

> **Important Note**: Any metal ions present in your glassware will react with EDTA and lead to incorrect results. All glassware coming in contact with your EDTA solution has been cleaned for you by the Stockroom by rinsing with 50% nitric acid followed by a distilled water rinse.

At least one week before Lab

Standard EDTA Solution

1. The disodium salt of EDTA dihydrate $Na_2H_2Y{\cdot}2H_2O$ (the free acid is practically insoluble) is a primary standard. It is predried and kept in desiccators in the balance room. To minimize contamination, use the spatula provided in the desiccator. Using a clean dry weighing bottle, weigh accurately, **by difference**, ~0.25 g of disodium EDTA, into an acid-washed 250 mL volumetric flask. Use a clean dry funnel to ensure all of the accurately weighed solid is quantitatively transferred into the flask. Use a small amount of distilled water to carefully rinse the funnel to transfer any solid adhering to the funnel into the flask. Add ~200 mL of distilled water and swirl periodically until the EDTA has dissolved.

2. After the EDTA has dissolved, dilute to the mark and shake thoroughly. Rinse your clean polyethylene 500 mL bottle with three **small** portions of your EDTA solution, swirling to ensure the entire inner surface of the bottle has been rinsed, (to remove metals from the bottle's inner surface), and transfer the rest of your EDTA solution to the bottle for storage. (Polyethylene is preferable to glass for storage because EDTA solutions leach metal ions from glass containers, resulting in a change in the concentration of free EDTA.)

Week of Lab

Test-tube Reactions

Your TA introductory lecture will be after completing this section of the experiment. You will work in groups of two or three on this part of the experiment only. Perform the titrations on your own, not in a group. Do not take too long to do this section because everyone else will be waiting on the last group to finish.

You will carry out a number of test tube reactions to investigate the various reactions with their associated colour changes involved in this experiment. The expected colour changes are mentioned in this procedure, but you must record your own observations after you add each chemical. Swirl each test-tube, or use a clean glass stirring rod to mix, in between adding each chemical, to fully mix the solutions. The amount of water used is not critical — use distilled water to wash down the inner walls of the test tubes where necessary. Keep all your test tubes for colour comparisons during your titrations.

3. *pH Effects on Eriochrome Black T indicator*: Place 4 drops of Eriochrome Black T into each of 3 test tubes. Half fill each tube with distilled water. The contents of all three test tubes should be the same colour. If any of the tubes is a different colour, it isn't clean enough. If necessary, return to the stockroom for a newly acid washed test tube.
   Tube #1: Add 1 drop of 0.1 M HCl (pink-red).
   Tube #2: Add 1 drop of 0.1 M HCl. Add 0.1 M NaOH dropwise until the colour changes (blue).
   Tube #3: Add 1 drop of 50% NaOH (orange-red). Do not discard these solutions.

4. *Eriochrome Black T indicator complexation with metals:*
   Add 5 drops of pH = 10 buffer to Tube #2 (blue). Add 1 drop of 0.01 M magnesium chloride solution to Tubes #1, 2, & 3 (acid and base solutions show no change, pH = 10 solution changes to purple-red).

Note that the Ammonia/ammonium chloride pH 10 buffer has a very strong odour and should be kept in the hood with the lid on at all times when not being transferred.

5. *Eriochrome Black T indicator action:* Place 5 drops of pH = 10 buffer into each of three more test tubes (# 4, 5, & 6). Half fill each tube with distilled water.
   Tube #4: Add 4 drops of Eriochrome black T and 5 drops of your EDTA solution (blue).
   Tube #5: Add 5 drops of EDTA and 1 drop of 0.01 M magnesium chloride (colourless).
   Tube #6: Add 4 drops of Eriochrome black T (blue), 1 drop of 0.01 M magnesium chloride (purple-red) and then 5 drops of EDTA (blue).

6. *Masking:* Place 5 drops of pH = 10 buffer into a test tube (# 7). Half fill with distilled water.
   Add 4 drops of Eriochrome black T (blue) and 1 drop of 0.1 M nickel sulfate (purple-red).
   Add ~ 15 drops of EDTA — notice that the indicator is "blocked". Add several drops of 5% KCN (blue).

Total Hardness Determination

7. Clean your burette. Rinse it out with a small aliquot of your EDTA solution to remove any metals from the glass. Shake your EDTA solution well, and then fill the burette with your EDTA solution.

8. Take your three 250 mL Erlenmeyer flasks to the Stockroom and exchange them for three acid-washed Erlenmeyer flasks. Using the supplied acid-washed 50 mL volumetric pipette, transfer a 50.0 mL aliquot of your water sample into an acid-rinsed 250 mL Erlenmeyer flask. Add 2 mL pH = 10 buffer, 0.5 mL of Mg-EDTA solution, and 5 drops of Eriochrome Black T indicator (purple-red) and mix well.

9. Titrate your water sample with EDTA until the colour changes to the clear blue of the uncomplexed indicator. The reaction is slow at the endpoint, so add your titrant slowly (3 – 5 seconds between drops near the end) and swirl your mixture well to avoid over-shooting. The colour first changes from purple-red to purple. One more drop will change it to clear blue. **If your endpoint took < 10 mL, double the volume of sample for the remaining titrations to increase the precision of your determination.** (If you do not get a colour change after 50 mL of EDTA, you may have metals in your water blocking the indicator. If so, talk to your TA. You may have to use a masking agent. If this is the case, add 1 mL of the 5% potassium cyanide to each flask before titrating. Remember the hazards of potassium cyanide and dispose of it appropriately in the cyanide waste container.)

10. Repeat the titration on two more aliquots of your water sample to accurately determine the total hardness. Clean your Erlenmeyer flasks and return to the stockroom to switch for three more acid-rinsed flasks for the second round of titrations.

Individual calcium Hardness (using Murexide indicator)

11. Transfer three more 50 mL aliquots of your water into three acid-rinsed 250 mL Erlenmeyer flasks. Add 2 mL of 1N sodium hydroxide to each flask, mix. Use pH paper to confirm that the pH is 12 – 13. If not, add some more NaOH.

12. Use a weighboat to measure ~1.2 g Murexide/NaCl mixture. Add approximately a third of this indicator to one of your flasks. Titrate with your EDTA solution to the endpoint, which will be marked by a colour change from pink to purple. Check your endpoint by adding 1 to 2 drops of titrant in excess to make certain that no further colour change occurs.

13. Repeat with the other two flasks, adding Murexide/NaCl indicator just before you start each titration.

Shutdown procedures

Important Note: You may dispose of your NaOH solution now in the Base Waste container.

14. Put all waste in the appropriate waste containers. Clean and dry all glassware. Clear up your work area. Return items to the Stockroom.

15. Make sure you have recorded information on the sample you studied, in this case, list the source of your water sample and anything about the source that may affect the expected hardness of your sample.

Waste Disposal

Waste Chemicals	Waste Container	Location
Cyanide containing waste	Cyanide	Hood
All other waste	EDTA	Waste cabinet

Data Analysis

1. Calculate the molarity of your EDTA solution (recall that you used $Na_2H_2Y{\cdot}2H_2O$ Hint: Y is not Yttrium).

2. Recalling that one EDTA molecule binds to one metal ion (i.e., Ca^{2+} or Mg^{2+}), calculate the number of moles of metal ions in your water sample, from your results from the total hardness titration.

3. Total hardness is expressed in "ppm $CaCO_3$ equivalents" (meaning that we just want to know how many metal ions are bound, either calcium or magnesium, because they both have the same effect on water hardness). Calculate the total hardness of your water sample as mg/liter (ppm) of $CaCO_3$ equivalents, using the molecular weight of $CaCO_3$ in your calculation.

4. Use the results of your individual calcium hardness titrations to calculate the calcium content of your water sample in mg/liter (ppm) of $CaCO_3$ equivalents. Convert this to mg/liter (ppm) of calcium, using the atomic weight of calcium.

5. Combine your answers to data analysis steps 3 & 4 (in ppm of $CaCO_3$ equivalents) to find the difference between total hardness and the hardness due to calcium, which will give you the magnesium hardness of your water sample in mg/liter (ppm) of $CaCO_3$ equivalents. Convert this to mg/liter (ppm) of magnesium using the atomic weight of magnesium.

Discussion Questions

1. Consider the set of test-tube reactions (procedure steps 3–6). For each of these test-tube procedures, summarize what you observed and explain the science behind your observations.

2. Explain why we used a pH 10 buffer for our total water hardness titrations.

3. Considering solubility products, explain the function of the sodium hydroxide when you analyzed for calcium ions. Why didn't we use Eriochrome Black T for the calcium determination (Hint: think of another effect of adding NaOH to the mixture.)?

4. Find out and explain the chemistry behind the water softening process in a home water purifier. (Note we are talking about a water softener not a water filter.)

5. EDTA or other chelating agents can be found many products such as in shampoos, soaps, cleaning products, plant foods, salad dressings, canned foods, etc. Choose such a product and suggest the function of EDTA in that product.

Conclusions

If you studied local Austin water, you can find out the current City of Austin readings of water hardness, calcium and magnesium on the web at `<http://www.ci.austin.tx.us/water/waterreports.htm>` and `http://www.ci.austin.tx.us/water/waterreports.htm`. As part of your conclusions for this experiment, compare your results to the results on the website, or to any relevant information (e.g., off a label) you may have on your sample. Use the USGS classification to describe the hardness of your water sample. Describe the source of your sample, and any explanation you may have for the hardness you determined for that sample.