

## Determination of Hardness of Water of Several Local Sources

**Objective:** You will determine the hardness of water using two different methods, EDTA titration, and cation exchange chromatography followed by NaOH titration.

**Background:** One factor that establishes the quality of a water supply is its degree of ‘hardness’. This is generally defined in terms of its concentration (in M or ppm) of calcium ( $\text{Ca}^{2+}$ ) and magnesium ( $\text{Mg}^{2+}$ ) ions, although ions such as  $\text{Fe}^{3+}$  also contribute to hardness of water. These ions are not generally considered a health threat, but they can cause many other domestic problems. As you learned earlier in the term, many ions can form insoluble salts. This is precisely the problem with hard water. Hard water ions form insoluble salts with soap leaving soap scum, bathtub rings, and reducing the lather of the soap. For this reason, we now wash our clothes in detergents, which differ from soap because detergents do not form these insoluble salts. Hard water also causes more annoying/critical problems like plugged steam lines, blocked showerheads and damaged hot water heaters. Particularly in the Midwest where there is a lot of limestone ( $\text{CaCO}_3$ ), this tends to be a greater problem and you may actually find two water taps in homes, a tap for drinking (hard water) and the other taps for use with soap (soft water).

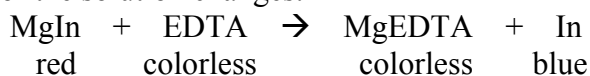
Hardness of water is reported as the amount of calcium, specifically calcium carbonate, in the water because calcium is usually the major problem ion. This can be misleading, however, because other ions do contribute to the measured hardness. Down south where the soil is red,  $\text{Fe}^{3+}$  is the major culprit. Most analyses do not distinguish between calcium and magnesium; many do not distinguish between calcium and most other metal ions.

The units generally used in water chemistry are ppm (mg solute/L  $\text{H}_2\text{O}$  - because one liter of water has a mass of 1000 g, a concentration of 1 mg/L is equivalent to 1 g solute per  $10^6$  g water, or *one part solute per million parts water*); however, most scientists report water hardness not as  $\frac{\text{mg Ca}^{2+}}{\text{L H}_2\text{O}}$  but instead as mg  $\text{CaCO}_3$  per L water. You will calculate the concentration in molarity of  $\text{CaCO}_3$  and in mg  $\text{CaCO}_3/\text{L}$ .

### EDTA Titration

The disodium salt of ethylenediaminetetraacetic acid (EDTA) is a chelating agent of divalent and trivalent cations. This means that it binds with high affinity (very tightly) to cations such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{3+}$ , etc. This binding is pH dependent. EDTA binds to these cations in a 1:1 ratio forming a very stable complex and releasing two protons. In this titration, we will use EDTA as the titrant, adding small amounts of EDTA until all of the metal ions are bound to it instead of being free in solution.

You need to have a detection method for determining when all of the metal ions are bound to EDTA. To do this, you use a metal ion indicator, a chemical whose color changes when bound to a metal ion. An example of this reaction is shown below using an Eriochrome Black T indicator (In) and Magnesium. This is the indicator you will use in the experiment and interestingly, it does not bind calcium. Rather, Eriochrome Black T will bind Magnesium ion until all of the calcium and magnesium ions are removed from the solution. Then EDTA will ‘steal’ the magnesium ions from the indicator itself. At this time, the color of the solution changes.



### Cation Exchange Chromatography

Cation exchange chromatography is a method for removing positively charged ions (hard) from a solution. The solution is passed through a resin comprised of small beads which have anionic groups covalently bound to them (**A** in Figure 1). If the hard cations in the solution bind with higher affinity than the cation already bound to the resin, the resin cations will ‘exchange’ with the hard cations in the solution and the hard cations will bind to the resin (**B** in Figure 1). The cations that were bound to the resin will flow through the column.

You can measure the concentration of hard cations in the original solution by measuring the displaced ions from the resin. In your experiment, you will pass hard water through a cation resin. Calcium and magnesium ions will bind tightly to the resin and displace protons ( $\text{H}^+$  (aq)). You can then titrate the eluate with NaOH to determine the number of protons displaced using a colored pH indicator to tell you when the NaOH has reacted with all of the free protons.

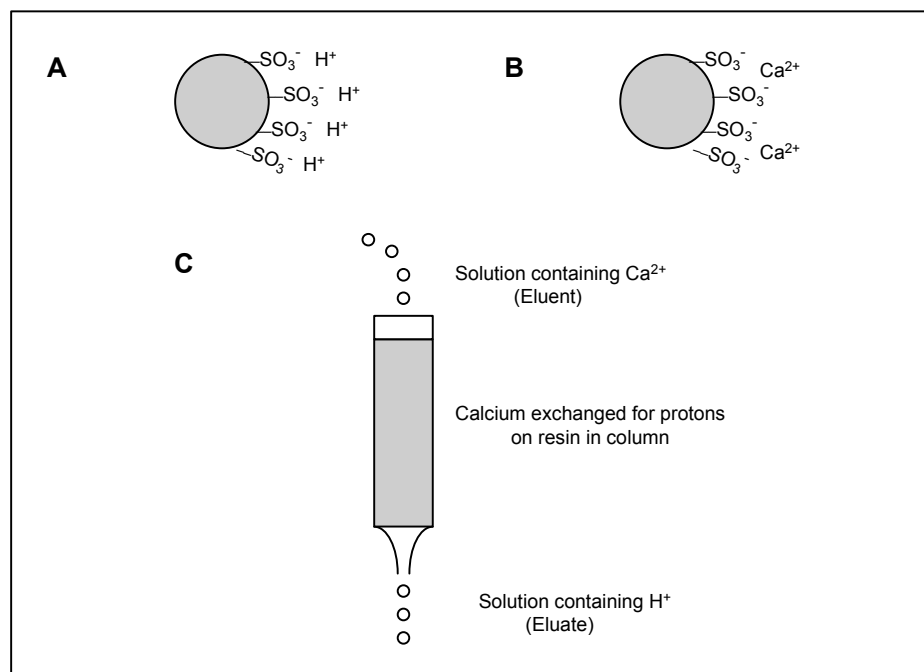


Figure 1: Cation Exchange. A. A resin bead that has protons bound to it before the experiment. B. A resin bead that has Calcium ions after displacing the protons. C. A schematic of the entire process.

## Procedure:

### I. EDTA Titration

#### A. Test the indicator Eriochrome Black T.

1. It is important that you know what color change to expect. This simple test will allow you to see what the color of the indicator is with and without bound  $\text{Mg}^{2+}$ .
2. In separate wells of a well plate, add the following:
  - a. 2 drops pH buffer + 10 drops hard water
  - b. 2 drops pH buffer + 10 drops deionized water
3. Add 1 ‘grain’ sized portion of Eriochrome Black T indicator to each well. If the well with deionized water is not a clear blue, add a drop of EDTA solution to the well.

#### B. Titration

1. Fill a buret with EDTA solution. **Be sure to note the concentration of EDTA in your notebook.** You need not fill to exactly ‘0’, but you do need to note the exact level of the EDTA. How many significant figures should you use?

2. Pipette 20 mL hard water, 5 mL of ammonia buffer, one 'pea' sized portion of Eriochrome Black T indicator, and a magnetic stirring bar into a 125 mL Erlenmeyer flask. Place the flask under the buret, on top of a stirring plate.
3. You are now ready to begin your titration. You do not know how much titrant will be necessary on your first titration, perhaps a milliliter, perhaps many milliliters. To speed the process, you can do one of two methods:
  - a. Method 1: Add EDTA solution very quickly until you see the color change. Note approximately where the color change occurs (the endpoint). Now, in your next three titrations, you can add titrant quickly until you get close to the endpoint. Then slow down to note the exact amount added to get the color change.
  - b. Method 2: Add EDTA solution quickly until you see "flashes" of color change, then slow down so that you can note the exact amount of titrant needed to get to the endpoint.
4. Repeat the titrations until you have three good (similar value of titrant added) titrations. If you use method 1 above, this means you must do the titration at least four times. Remember to **write down your starting and ending volumes in the buret so that you can determine the volume of titrant added.**

## II. Cation Exchange Chromatography

### A. Conditioning the resin

1. Before using the resin for ion exchange, it may be necessary to make sure that all of the beads have  $H^+$  ions attached rather than  $Ca^{2+}$  or  $Mg^{2+}$  from previous experiments. If this is the case then go to step 2.
2. Add 5 mL 6 M HCl to the top of the column. This is a very high concentration of protons that will overwhelm and displace the metal ions, regenerating your column. During this process (steps a – c below), you should never allow the column to run dry (always keep a slight amount of water above the resin). To do this, when flushing the column through with 3 x 25 mL washes of DI water, always keep the level of fluid in the column above that of the beads. Check that the pH of the final flush is between 5 and 7. Your instructor may tell you that your column has already been flushed with acid. If so, then start on (c) below.
  - a. Allow the liquid level to drop near the top of the resin.
  - b. Carefully add the HCl to the column.
  - c. Allow the liquid level to drop near the top of the resin.
  - d. Carefully add at least 25 mL of deionized water. Continue to add water until the eluate is at a pH of 5 to 6 ( $CO_2$  is dissolved in the water making the water slightly acidic – remember the 1<sup>st</sup> experiment?) Check the acidity with pH paper.

### B. Ion Exchange of hard water sample

1. Allow the liquid level to drop near the top of the resin.
2. Place a clean 250 mL Erlenmeyer flask under the column.
3. Add 20.0 mL of your hard water to the column, collecting all eluate.
4. Allow the liquid level to drop near the top of the resin.
5. Add 30 mL of deionized water to the column, collecting all eluate.

### C. Repeat ion exchange two more times using fresh hard water sample.

### D. Determination of $H^+$ ions in eluate.

1. Add 3 drops of Bromocresol Green to each flask of eluate
2. **Slowly** titrate with NaOH (**note the concentration in your lab book**)
3. Remember to **write down your starting and ending volumes in the buret so that you can determine the volume of titrant added.**

### E. **Recondition the resin** (as described above in steps 2a-2c) before leaving the lab.

**Write Up**

Complete the write up sheet posted at the web page.

**Questions:**

1. Using your EDTA titration data, determine the 'hardness' (mean and standard deviation) of water in all of your samples, expressing them in the appropriate units (Molarity of  $\text{CaCO}_3$ ). What is the Molarity of  $\text{Ca}^{2+}$ ? Remember however that this is the concentration of all the hard water species, not just  $\text{Ca}^{2+}$ . If you are unsure of how to calculate the mean and standard deviation, see the Statistics page on the web site.
2. Using your ion exchange data, determine the 'hardness' of water (mean) in all of your samples, expressing them in the appropriate units (Molarity of  $\text{CaCO}_3$ ).
3. Do you get the same total 'hardness' values from each experiment? Why/Why not?
4. If a sample of water was found to have 50 ppm  $\text{CaCO}_3$ . What is the molarity of  $\text{CaCO}_3$  in this water?

**References:**

1. Brown, T. L., LeMay H. E., and Bursten B. E. *Chemistry: The Central Science*, 8<sup>th</sup> ed. Prentice Hall, 2000; chapters 18,24.
2. American Chemical Society. *Chemistry in Context*, 3<sup>rd</sup> ed. Wm. C. Brown, 2000; chapter 5.