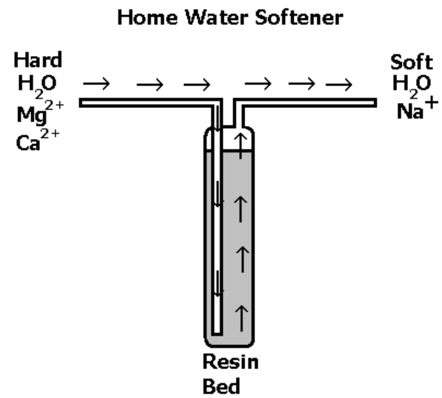
Water Hardness and Softening *(Bring a water sample from home)*

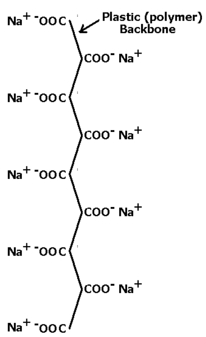
Minneapolis Community and Technical College
Principles of Chemistry II, C1152
v.2.16

I. Introduction

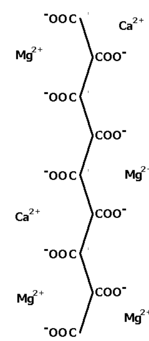
Hard Water and Water Softening



Water that contains dissolved Mg^{2+} and Ca^{2+} cations is known as "hard water" and the presence of these ions leads to the problems often associated with hard water. When solid $CaCO_3$ formation within pipes it reduces the inside diameter of the pipe and consequently the rate of water flow. In some extreme cases, enough $CaCO_3$ can even completely plug the pipe. Hard water also reduces the cleaning effectiveness of soaps causing them to precipitate as soap scum and bath tub ring.



"Softened" water has been treated in order to remove the Mg^{2+} and Ca^{2+} cations. In the household water softener, hard water is passed over plastic or polymer beads known as the "resin bed" (*upper right figure*). On a molecular level, the beads are coated with COO^- groups covalently bonded to a polymer backbone (*figure at left*). Na^+ cations are attached to the COO^- group via ionic bonds. As the hard water passes over the resin bed, dissolved Ca^{2+} and Mg^{2+} ions displace the Na^+ ions that are then released into the flowing water stream. , Having been removed from the water, the Ca^{2+} and Mg^{2+} ions stay attached to the COO^- groups (*figure at right*) until the water softener is recycled.



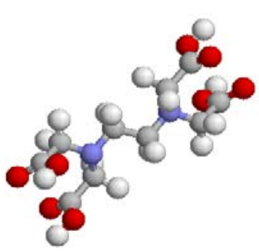
Recycling or recharging the water softener involves flushing the resin bed with highly concentrated $NaCl_{(aq)}$ solution whereby Na^+ ions displace the Ca^{2+} and Mg^{2+} ions returning the resin bed to its previous state.

Water softening via this method releases replaces Ca^{2+} and Mg^{2+} ions in the water with Na^+ ions. Some individuals suffering from hypertension (high blood pressure) can be sensitive to sodium in their diet and may choose to avoid consuming softened water and the additional sodium ions it contains.

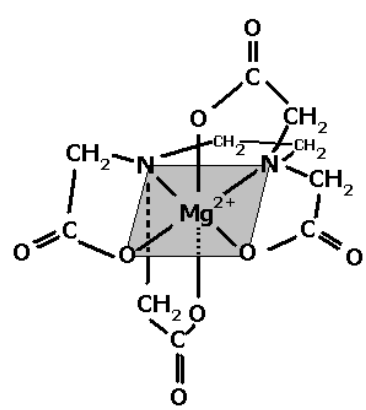
EDTA titration: Determining the Ca^{2+} and Mg^{2+} concentrations via titration

The total ion concentration is determined via a titration technique that cannot distinguish between the Mg^{2+} and Ca^{2+} ions. Consequently, the water hardness concentration represents the sum of the Mg^{2+} and Ca^{2+} cation concentrations. However, the Mg^{2+} ion concentration can be determined by subtracting from the total ion concentration the concentration of the Ca^{2+} ion determined via the A.A. technique (above).

Initially, the water hardness ions, Mg^{2+} and Ca^{2+}, are reacted with a commercially available Calmagite indictor solution whose molecules form complex ions with the metal cations. Complex ions are formed when the metal ion attaches itself to the other molecular species via lone pair electrons it donates. The bond that forms is referred to as a *coordinate covalent bond* since the bonding electrons come from one species. The color of the Calmagite/metal ion complex ion that initially forms is **red**.



As the titration proceeds, **E**thylene**D**iaminete**T**raacetic **A**cid (a.k.a. EDTA) is added to the indicator/water solution. This molecule (figure at left) possesses 2 nitrogen atoms and 4 oxygen atoms that have available lone pairs making it possible for six coordinate covalent bonds to form. The six lone pairs on the EDTA molecule are so effective that they completely lure the metal ions away from the indicator molecules.



The complex that forms (figure at right) shows how the EDTA molecule essentially surrounds the metal ion (octahedral geometry) with 6 coordinate covalent bonds (top, bottom and 4 in the shaded plane).

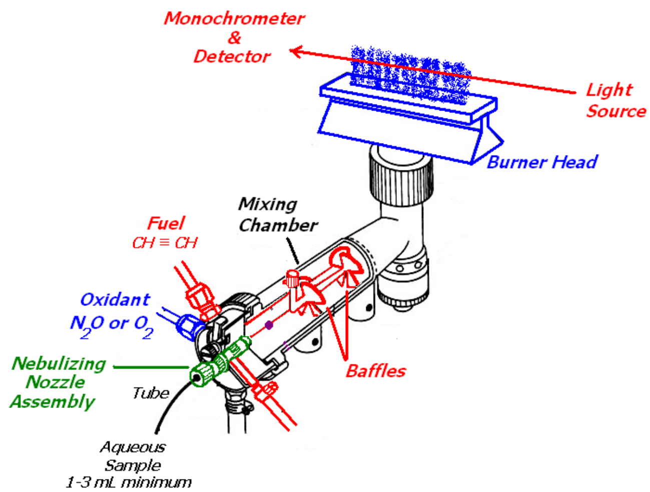
When enough EDTA has been added to the reaction mixture, the Calmagite indictor is no longer connected to the metal ions. The color then changes from that of the Calmagite indicator/metal ion complex **(red)** to the color of the unbound Calgamite molecule **(blue)** signaling the endpoint of the titration.

By knowing the volume and concentration of the added EDTA solution, we can calculate the number of moles of EDTA used. The mole ratio that relates EDTA to metal cations is 1:1 since one metal ion is captured by one EDTA molecule.

Atomic Absorption Spectroscopy: Detecting Ca^{2+} concentrations with light.

The concentration of calcium ions present in a water sample can be determined using the atomic absorption spectrophotometer (A.A.S.). The device, shown at right, mixes the aqueous sample with combustible acetylene and air. This mixture is then injected into the burner's flame where the water rapidly vaporizes leaving the calcium ions suspended in the flame.

A monochromatic light source is positioned at one side of the flame. If calcium ions are present in the water sample (and therefore in the flame), they absorb some of the incident light. The light detector on the opposite side of the flame measures the reduced light intensity of the transmitted light and displays the result as an absorbance or transmittance on a display panel.



The sample's absorbance reading is compared to a previously prepared solutions of known concentration via a calibration graph (absorbance vs. Ca^{2+} concentration) to determine the actual concentration of calcium ions in the sample.

Concentration Units

Several different systems are used when reporting concentration levels of solids dissolved in water. The first, ***molarity (M)***, is already familiar to us:

$$\text{Molarity} = \text{moles}_{\text{solute}}/\text{Liters}_{\text{solution}}$$

The second, ***parts per million (ppm)***, refers to the amount of solute *in milligrams* dissolved in 1 *million mg (1L)* of water.

That is, 1 ppm = $1\ \text{mg}_{\text{solute}}/1\ \text{Liter}_{\text{solution}} =\sim 1\ \text{mg}_{\text{solute}}/1\ \text{Liter}_{\text{water}}$.

II. Pre Lab Exercise *Clearly answer these questions in INK in your lab notebook before coming to lab.*

1. Mg^{+2} and Ca^{+2} ions bind to either Calmagite or EDTA via a "*coordinate covalent bond*."
   a. What is a coordinate covalent bond?
   b. What species serves as the Lewis acid in this experiment? What species serves as the Lewis base?

2. A 75.00 mL sample of tap water is titrated with 0.0100 M EDTA following the procedure outlined below. If 38.54 mL of EDTA is required, what is the total ion concentration in the original tap water sample in molarity units? (Note that EDTA can't distinguish between Ca^{+2} and Mg^{+2} ions. Therefore, you are determining the total contribution of these ions).

3. Following the procedures outlined below, the friendly chemist finally adds 10 drops of Calmagite indicator to her reaction mixture whereupon the solution instantly turns blue; even before the EDTA is added. What is the significance of her result?

III. Word processed report

Page 1:

- **Upper right corner:** Your name, Your lab section number, Date of experiment
- **Data table:** Obtain a copy of the data table from the lab-handout web site and fill in your values.

Page 2:

Answers to the following questions:

1. Show all of the calculations for your first tap water titration.
2. What is the percentage of Ca^{2+} and Mg^{2+} (total) removed from the hard water by the softening process. Based on this result, how would you judge the success of the water softening process used in this experiment?
3. Why is softened water better for cleaning applications?
4. In your own words describe how distilled water is made in the laboratory and how the process softens the water.
5. What is the maximum Pb^{+2} level allowed in drinking water (ppb)? How many times smaller is this than the Mg^{+2} concentration you determined for Minneapolis drinking water)?

IV. Procedure

You will be working individually today

A. Water softening

a. Place approximately 150 mL of hard water (laboratory tap water) in a clean, dry 250 mL beaker.

b. Add approximately 5 grams of dry, sodium cation exchange resin (10 grams if wet) to the hard water in the beaker.

c. Swirl the beaker's contents for approximately 10 minutes

d. Decant the softened water into another clean beaker.

e. Place the used softening resin in the "Used Resin" container. (Don't return it to the unused container). The used resin will be rejuvenated with saturated NaCl solution for later use.

f. Put the softened sample aside for later use.

B. Atomic Absorption Determination of Ca^{2+} concentration in your water sample.

a. Obtain a centrifuge tube from the laboratory instructor.

b. Fill the centrifuge test tube approximately ¾ full of your home water sample.

c. Label the vial with your first and last name using the water soluble pen provided.

d. Return the centrifuge tube to your instructor for placement in the AAS instrument.

e. When the A.A.S. analysis is complete, your instructor will call out your name and the calcium ion concentration of your water sample in ppm units.

C. EDTA Titration

You will be determining water hardness for the following four samples:

i. *Lab tap water*	*(2 titrations)*
ii. *Lab distilled water*	*(1 titration)*
iii. *Softened lab water*	*(1 titration)*
iv. *A home water sample*	*(2 titrations).*

Note: Be sure the samples you get from home are fresh and stored in clean glass or plastic containers.

a. Obtain a clean 25 mL buret and rinse it twice with ~1-2 mL portions of 0.0100 EDTA solution already prepared for you.

b. Fill the buret and eliminate any bubbles that may be lodged in the valve assembly and tip.

c. In a clean, 250 mL Erlenmeyer flask, add the following in order:
   - i. 50.0 mL water sample
   - ii. 10 mL 1.5 M NH_3-0.3M NH_4Cl buffer.
   - iii. 2-3 mg of ascorbic acid (*analytical balance*)
   - iv. 10 mL of 0.01 M MgEDTA/0.1 M NH_3 solution
   - v. 10 drops of Calmagite indicator.
   - vi. Magnetic stirring bar

d. Record the initial burette reading.

e. Position the 250 mL Erlenmeyer flask on a stir plate and stir thoroughly (NO HEAT). ***Avoid splashing the liquid onto the sides of the flask.***

f. Titrate the contents of the flask with the 0.0100 EDTA solution until the solution turns from the initial red to **blue.** (Purple will be observed along the way.)

Suggestion: *As you get close to the titration's endpoint, keep a record in your note book of buret readings and the solution's color. This will help you decide exactly when the color change occurred.*

g. Record the final buret reading in your lab notebook and calculate the amount of EDTA solution used.

h. Dispose of all waste solutions in the sink.

i. Repeat the above procedure a second time for the laboratory tap water sample and verify the results are within approximately 0.5 mL. Repeat the tap water trial as necessary in order to achieve consistent results.

j. Repeat the above procedure once for the softened water sample and once for the distilled water samples.

k. Repeat the above procedure twice for your home water sample.

V. Data Table: Cut and paste this data table into your lab notebook using glue and transparent tape.

		Laboratory Tap Trial 1	Laboratory Tap Trial 2	Laboratory Distilled	Laboratory Tap Softened	Home Sample Trial #1	Home Sample Trial #2
EDTA	**Initial Buret Reading (mL)**						
	Final Buret Reading (mL)						
	Vol. dispensed (mL)						
	Moles (#)						
Water Sample	**Water Sample Volume (mL)**	**50.0**	**50.0**	**50.0**	**50.0**	**50.0**	**50.0**
	Ca^{+2}/Mg^{+2} Total Moles (1:1 ratio)						
	Total Ion Concentration in H_2O Sample (M)						
A.A.	**[Ca^{2+}] (ppm = mg/L)**	!	!			!!	!!
	[Ca^{2+}] ** (M)						
	[Ca^{2+}] + [Mg^{2+}] (same as * above)						
	[Mg^{2+}] (M)						
	[Mg^{2+}] * (ppm)**						

******Calculate using the molar mass of calcium: 40.078000 g/mol.
*******Calculate using the molar mass of magnesium 24.305000 g/mol
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! Results of A.A.S. analysis of Minneapolis Laboratory Tap Water. Announced by instructor.
!! Results of A.A.S analysis of your water sample. Announced by instructor.