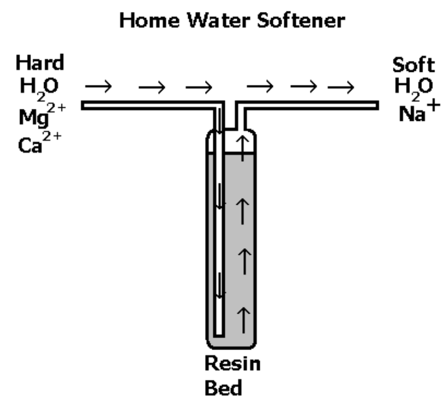
Water Hardness and Softening *(Bring a water sample from home)*

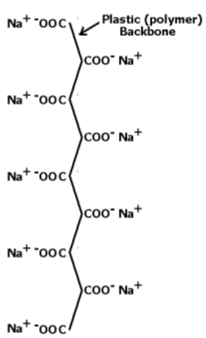
Minneapolis Community and Technical College
Principles of Chemistry II, C1152
v.5.10

I. Introduction

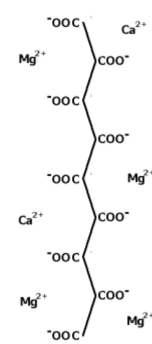
A. Hard Water and Water Softening



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.



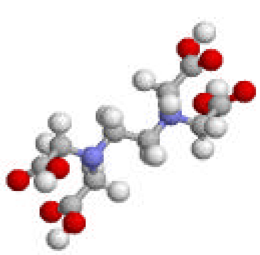
Recycling the water softener involves flushing the resin bed with highly concentrated $NaCl_{(aq)}$ solution whereby Na^+ ions now displace the Ca^{2+} and Mg^{2+} ions returning the resin bed to its previous state.

Additional note: 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.

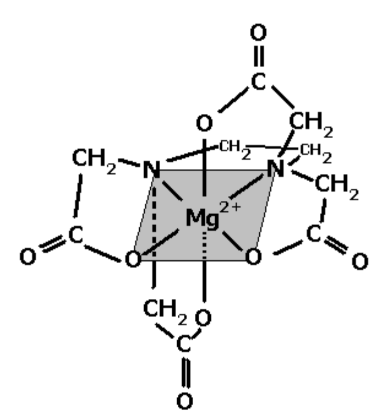
B. EDTA titration: Determining the Ca^{2+} and Mg^{2+} concentrations via titration

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.



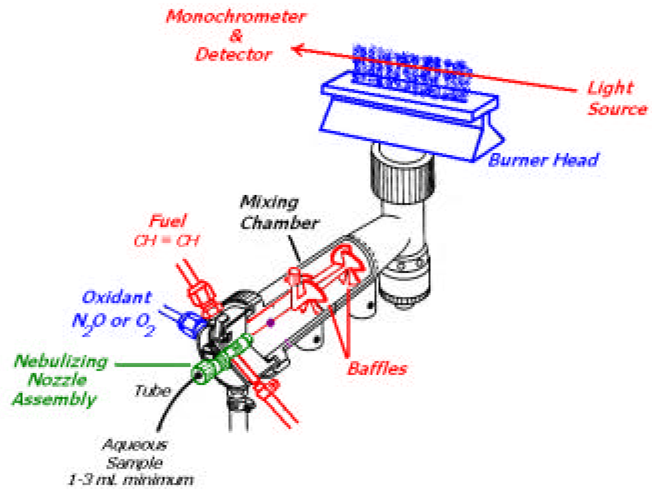
The complex that forms (figure at right) shows how the EDTA molecule essentially surrounds the metal ion (octahedral geometry) with 6 coordinate covalent bonds (top, bottom and 4 in the shaded plane).

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.

C. 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 absorbtion 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 for a short time 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.

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

II. MSDS: Chemical Information

EDTA

CAUTION! MAY BE HARMFUL IF SWALLOWED. MAY CAUSE IRRITATION TO SKIN, EYES, AND RESPIRATORY TRACT.
Health Rating: 1 - Slight Flammability Rating: 1 - Slight Reactivity Rating: 0 - None Contact Rating: 1 - Slight
Lab Protective Equip: GOGGLES; LAB COAT
Storage Color Code: Orange (General Storage)
Potential Health Effects
Inhalation: Mild irritant. Can cause sore throat and coughing.
Ingestion: Substance has low toxicity by ingestion. Large amounts may cause gastrointestinal upset due to osmotic imbalance caused by its ability to sequester metal ions.
Skin Contact: Can cause redness and pain.
Eye Contact: Can cause redness and pain.
Chronic Exposure: No information found.
Aggravation of Pre-existing Conditions: No information found.

Calmagite

The toxicological properties of this material have not been fully investigated.
Potential Health Effects
Eye: May cause eye irritation.
Skin: May cause skin irritation.
Ingestion: Ingestion of large amounts may cause gastrointestinal irritation.
Inhalation: May cause respiratory tract irritation.
Chronic: No information found.

III. 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 an NaCl solution for later lab sections to use.
f. Put the softened sample aside for later use.

B. EDTA Titration

You will be determining water hardness for the following four samples: ***i.*** *Lab tap water,* ***ii.*** *Lab distilled water,* ***iii.*** *softened lab water,* ***iv****. an additional sample brought from home. Note: Be sure the samples you get from home are fresh and stored in clean 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 (*weigh on 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 buret reading in your lab notebook
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 **blue.**

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 (tap water only) and verify the results are within approximately 0.2 mL. Repeat the tap water trial as necessary in order to achieve consistent results.
j. Obtain two consistent trials for the water sample you brought from home and use these in your calculations.

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

1. Fill the centrifuge test tube approximately ¾ full of your home water sample.
2. Label the vial with your initials using the water soluble pen.
3. Your instructor will collect a small amount of your home water sample to be used in the A.A.S. analysis
4. 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.

Data Table:

		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 (moles/liter) *						
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.
*******Calculate using the molar mass of magnesium.
! Results of A.A.S. analysis of Lab Tap Water. Announced by instructor.
!! Results of A.A.S analysis of your water sample. Announced by instructor.

V. Individual Reports

<u>Page 1:</u>

- **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.

<u>Page 2:</u>

Answers to the following questions:

a. Show below your calculation for the conversion of the AAS calcium ppm concentration into molarity units.

b. Show below your calculation for the conversion of molar $[Mg^{2+}]$ concentration into ppm units.

c. What is the percentage of Ca^{2+} and Mg^{2+} (total) removed from the hard water by the softening process.