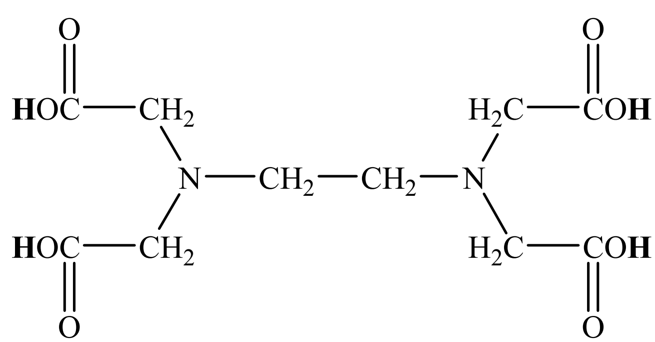
Determination of the Hardness of Water

One of the factors that establishes the quality of a water supply is its degree of hardness. Hardness is defined as calcium and magnesium ion content. Since most analyses do not distinguish between Ca^{2+} and Mg^{2+}, and since most hardness is caused by carbonate mineral deposits, hardness is usually reported as parts per million (ppm) of calcium carbonate (by weight). A water supply with a hardness of 100 ppm contains the equivalent of 100 g of $CaCO_3$ in 1 million g of water or 0.1 g in 1 L of water (or 1000 g of water since the density of water is about 1 g/mL).

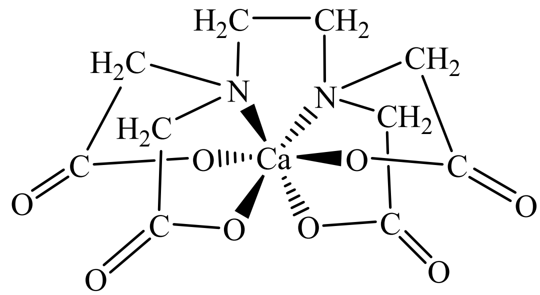
Water Hardness	
calcium carbonate (ppm)	**designation**
0-43	Soft
43-150	Slightly Hard
150-300	Moderately Hard
300-450	Hard
450	Very Hard

Water hardness is usually noticed because of difficulty in lathering soap and the formation of a scum in the bathtub. Ca^{2+} and Mg^{2+} form **insoluble salts** with soaps causing precipitation of the soap scum. Another effect of hard water is "boiler scale". When hard water comes into contact with dissolved carbonates, a precipitate of insoluble calcium carbonate forms. This "scale" can build up on the inside of water pipes to such a degree that the pipes become almost completely blocked.

Water hardness can be readily determined by titration with the chelating agent (Greek **χηλή**, *chelè*, meaning claw) EDTA (ethylenediaminetetraacetic acid). This reagent is a weak acid that can lose four H (in bold) on complete neutralization; its structural formula is:



The four acid oxygen sites and the two nitrogen atoms have unshared electron pairs, which can form bonds to a metal ion forming a **complex ion** or **coordination compound**. The complex is quite stable, and the conditions of its formation can ordinarily be controlled so that it is selective for a particular metal ion.



In a titration to determine the concentration of a metal ion, the added EDTA combines quantitatively with the cation to form the complex. The endpoint occurs when essentially all of the cation has reacted.

In this experiment a solution of EDTA will be standardize by titration against a standard solution made from calcium carbonate, $CaCO_3$. The EDTA solution can then be used to determine the hardness of an unknown water sample. Since both EDTA and Ca^{2+} are colorless, it is necessary to use a special indicator to detect the end point of the titration. The indicator most often used is called Eriochrome Black T, which forms a very stable wine-red complex, $MgIn^-$, with the magnesium ion. A tiny amount of this complex will be present in the solution during the titration. As EDTA is added, it will complex free Ca^{2+} and Mg^{2+} ions, leaving the $MgIn^-$ complex alone until essentially all of the calcium and magnesium have been converted to chelates. At this point EDTA concentration will increase sufficiently to displace Mg^{2+} from the indicator complex; the indicator reverts to its uncombined form, which is sky blue, establishing the end point of the titration.

The titration is carried out at a pH of 10, in a NH_3/NH_4^+ buffer, which keeps the EDTA (H_4Y) mainly in the form HY^{3-}, where it complexes the Group 2 ions very well but does not tend to react as readily with other cations such as Fe^{3+} that might be present as impurities in the water. Taking H_4Y and H_3In as the formulas for EDTA and Eriochrome Black T, respectively, the equations for the reactions which occur during the titration are:

Titration reaction: $HY^{3-}(aq) + Ca^{2+}(aq) \longrightarrow CaY^{2-}(aq) + H^+(aq)$ (also for Mg^{2+})

End point reaction: $HY^{3-}(aq) + \underset{\textbf{wine red}}{MgIn^-(aq)} \longrightarrow \underset{\textbf{sky blue}}{MgY^{2-}(aq) + HIn^{2-}(aq)}$

Since the indicator requires a trace of Mg^{2+} to operate properly, a little magnesium ion will be added to each solution. The effect of the added Mg^{2+} can be subtracted by titrating a blank.

Experimental Procedure

1. Place about half a gram of calcium carbonate in a sample vial and weigh the vial on the analytical balance. **Carefully** pour between 0.20 to 0.25 g of the carbonate to a 250-mL beaker and weigh the vial again. Determine the mass of the $CaCO_3$ sample to **0.1 mg** by difference.

2. Add about 25 mL of distilled water to the beaker and slowly add ~40 drops of 6 M HCl. Allow the reaction to proceed until all of the solid carbonate has dissolved. Rinse the walls of the beaker with distilled water from a wash bottle and heat the solution until it just begins to boil. Be sure not to be confused by the evolution of CO_2 which occurs with the boiling. Add 50 mL of distilled water to the beaker and **carefully** transfer the solution to a 250-mL volumetric flask. Rinse the beaker several times with small portions of distilled water and transfer each portion to the flask. All of the Ca^{2+} originally in the beaker should then be in the volumetric flask. Fill the volumetric flask to the horizontal mark with distilled water, adding the last few mL with a disposable pipet. Stopper the flask and mix the solution thoroughly by inverting the flask at least 20 times over a period of several minutes.

3. Rinse a 50-mL buret thoroughly with a few mLs of ~0.01 M EDTA solution. Drain through the stopcock and then fill the buret with the EDTA solution.

4. Make a blank by adding 25 mL distilled water (pipet) and 5 mL of pH 10 buffer (graduated cylinder) to a 250-mL Erlenmeyer flask. Add a small amount of solid Eriochrome Black T indicator mixture from the container. You need only a small portion, about 25 mg, just enough to cover then end of a small spatula. The solution should turn blue; if the color is weak, add a bit more indicator. Add 15 drops of 0.03 M $MgCl_2$, which should contain enough Mg^{2+} to turn the solution wine red. Read the buret to 0.01 mL and add EDTA to the solution until the last tinge of purple just disappears. The color change is rather slow, so titrate slowly near the end point. Only a few mLs will be needed to titrate the blank. Read the buret again to determine the volume required for the blank. This volume must be subtracted from the total EDTA volume used in each titration. Save the solution as a reference for the end point in all your titrations.

5. Pipet three 25 mL portions of the Ca^{2+} solution in the volumetric flask into three clean 250-mL Erlenmeyer flasks. To each flask add 5 mL of the pH 10 buffer, a small amount of indicator (as with the blank), and 15 drops of 0.03 M $MgCl_2$. Titrate the solution in one of the flasks until its color matches that of your reference solution; the end point is a reasonably good one, and you should be able to hit it within a few drops if you are careful. Read the buret. Refill the buret, read it, and titrate the second solution, then the third.

6. Obtain a sample of water for hardness analysis. Since the concentration of Ca^{2+} is probably lower than that in the standard calcium solution you prepared, pipet 50 mL of the water sample for each titration. As before, add some indicator, 5 mL of pH 10 buffer, and 15 drops of 0.03 M $MgCl_2$ before titrating. Carry out as many titrations as necessary to obtain two volumes of EDTA that agree within about 3%. If the volume of EDTA required in the first titration is low due to the fact that the water is not very hard, increase the volume of the water sample so that in succeeding titrations, it takes at least 20 mL of EDTA to reach the end point.

Questions

1. Water is usually softened by using an ion exchange resin to replace each Ca^{2+} (and Mg^{2+}) ion with 2 Na^+ ions. What must be true of the Na^+ salt of soap?

2. A 0.2431 g sample of $CaCO_3$ is dissolved in 6 M HCl and the resulting solution is diluted to 250.0 mL in a volumetric flask. Titration of a 25.00 mL sample of the solution requires 28.55 mL of EDTA to reach the Eriochrome Black T end point. A blank containing the same amount of Mg^{2+} requires 2.60 mL of EDTA. What is the molarity of the EDTA solution?

3. A 50.00 mL sample of hard water is titrated with the EDTA solution in Problem 2. The same amount of Mg^{2+} is added as previously, and the volume of EDTA required is 22.44 mL. What is the water hardness in ppm $CaCO_3$?

Data Treatment

1. The **molarity** (M) of the EDTA solution is the mass of the calcium carbonate sample divided by the titration volume (minus the blank) in mL. Find the average for your three samples. We will then calculate a class average.

2. The hardness of the water sample, in ppm of $CaCO_3$, is the class average molarity of EDTA times the volume titrated (in mL) times 2000.

3. In the laboratory, we will calculate the class average of the water hardness (ppm) and demonstrate indeterminate error with a statistical analysis of the data. In particular, we will calculate the **estimate of standard deviation**, **s**:

$$\mathbf{s} = \sqrt{\frac{\sum d_i^2}{N-1}}$$

Where:
Σ means "the sum of"
$d_i = | x_i - \bar{x} |$
N = number of measurements
$\bar{x}$ = average of the *i* measurements