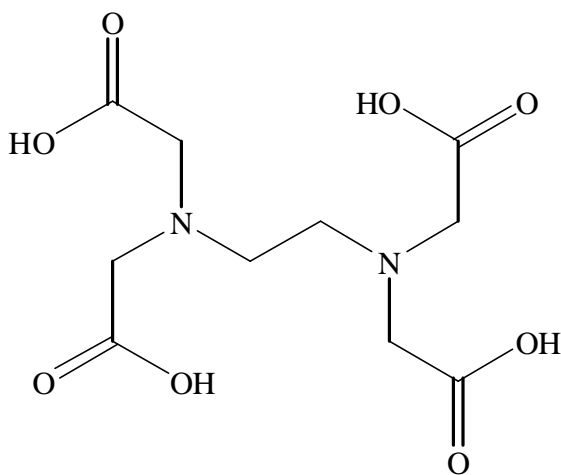


One of the factors that establishes the quality of a water supply is its degree of hardness. The hardness of water is defined in terms of its content of calcium and magnesium ions. Since an analysis does not distinguish between  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , and since most hardness is caused by carbonate deposits in the earth, hardness is usually reported as total parts per million calcium carbonate by weight. A water supply with a hardness of 100 parts per million would contain the equivalent of 100 grams of  $\text{CaCO}_3$  in 1 million grams of water or 0.1 gram in one liter of water. In the days when soap was more commonly used for washing clothes, and when people bathed in tubs instead of using showers, water hardness was more often directly observed than it is now, since  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  form insoluble salts with soaps and make a scum that sticks to clothes or to the bath tub. Detergents have the distinct advantage of being effective in hard water, and this is really what allowed them to displace soaps for laundry purposes.

Water hardness can be readily determined by titration with the chelating agent EDTA (ethylenediaminetetraacetic acid). This reagent is a weak acid that can lose four protons on complete neutralization; its structural formula is below.



The four acid sites and the two nitrogen atoms all contain unshared electron pairs, so that a single EDTA ion can form a complex with up to six sites on a given cation. The complex is typically quite stable, and the conditions of its formation can ordinarily be controlled so that it contains EDTA and the metal ion in a 1:1 mole ratio. In a titration to establish the concentration of a metal ion, the EDTA that is added combines quantitatively with the cation to form the complex. The end point occurs when essentially all of the cation has reacted.

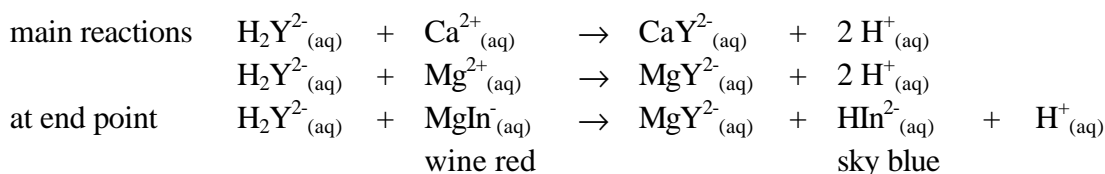
In this experiment you will standardize a solution of EDTA by titration against a standard solution made from calcium carbonate,  $\text{CaCO}_3$ . You will then use the EDTA solution to determine the hardness of an unknown water sample. Since both EDTA and  $\text{Ca}^{2+}$  are both colorless, it is necessary to use a rather special indicator to detect the end point of the titration. The indicator you will employ is called Eriochrome Black T, which forms a rather stable wine-red complex,  $\text{MgIn}^-$ , with the magnesium ion. A tiny amount of this complex will be present in the solution during the titration. As

## General Chemistry II Lab

## #4 - Determination of the Hardness of Water

EDTA is added, it will complex free  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions leaving the  $\text{MgIn}^-$  complex alone until essentially all of the calcium and magnesium has been converted to chelates. At this point, the EDTA concentration will increase sufficiently to displace  $\text{Mg}^{2+}$  from the indicator complex; the indicator reverts to an acid form, which is sky blue, and this establishes the end point of the titration.

The titration is carried out at a pH of 10, in an  $\text{NH}_3\text{-NH}_4^+$  buffer, which keeps the EDTA ( $\text{H}_4\text{Y}$ ) mainly in the half-neutralized form,  $\text{H}_2\text{Y}^{2-}$ , where it complexes the Group IIA ions very well but does not tend to react as readily with other cations such as  $\text{Fe}^{3+}$  that might be present as impurities in the water. Taking  $\text{H}_4\text{Y}$  and  $\text{H}_3\text{In}$  as the formulas for EDTA and Eriochrome Black T respectively, the equations for the reactions that occur during the titration are as follows.



Since the indicator requires a trace of Mg to operate properly, you will add a little magnesium ion to each solution and titrate it as a blank.

This experiment requires that you recall the concepts of stoichiometry, molarity and dilutions. You may need to refresh your memory before you begin the prestudy and the experiment.

### EXPERIMENTAL PROCEDURE

Obtain a 50 mL buret, a 250 mL volumetric flask and 25 and 50 mL pipets.

Using weighing paper, accurately weigh between 0.390 g and 0.410 g of  $\text{CaCO}_3$ . Transfer it quantitatively to a 250 mL beaker. (That is, make sure that every bit of the  $\text{CaCO}_3$  gets from the paper into the beaker.) Add 25 mL of distilled water to the beaker and then slowly, about 20 drops of 12 M HCl. (**CAUTION:** 12 M HCl will burn flesh and clothing.) Cover the beaker with a watch glass and allow the reaction to proceed until all of the solid carbonate has dissolved. Rinse the walls of the beaker down with distilled water from your wash bottle and heat the solution until it just begins to boil. (Be sure not to be confused by the evolution of  $\text{CO}_2$  which occurs with the boiling.) Add 50 mL of distilled water to the beaker and carefully transfer the solution, using a clean funnel, to the 250 mL volumetric flask. Rinse the beaker several times with small portions of distilled water and transfer each portion to the flask through the funnel. Rinse the funnel several times also. All of the  $\text{Ca}^{2+}$  originally in the beaker should now be in the volumetric flask; the solution is one of slightly acidic  $\text{CaCl}_2$ . Fill the volumetric flask with distilled water, adding the last few mL a drop at a time with your wash bottle or an eye dropper. When the bottom of the meniscus is just even with the horizontal mark on the flask, stopper the flask and mix the solution thoroughly by inverting the flask at least a dozen times and shaking at intervals over a period of five minutes.

Clean your buret thoroughly. Draw about 300 mL of the stock EDTA solution from the carboy into a clean, dry beaker. Rinse the buret with 5 mL of the solution three times. Make sure the tip of the buret is full before continuing with the titration. Don't forget to check the tip for air bubbles.

Determine a blank by adding 25 mL distilled water and 5 mL of the pH 10 buffer to a clean but not necessarily dry 250 mL Erlenmeyer flask. Add two drops of Eriochrome Black T indicator. The solution should turn blue. Read the buret to the nearest 0.01 mL and titrate the solution with EDTA until the last tinge of purple just disappears. 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.

Pipet four 25 mL portions of your  $\text{Ca}^{2+}$  solution from the volumetric flask into clean but not necessarily dry 250 mL Erlenmeyer flasks. To each flask add 5 mL of the pH 10 buffer and 2 drops of indicator. Titrate each solution 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 other solutions. Use the best three titrations for your calculations.

Your instructor will furnish you with a sample of water for hardness analysis. Since the concentration of  $\text{Ca}^{2+}$  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 2 drops of indicator and 5 mL of pH 10 buffer before titrating. Carry out as many titrations as necessary to obtain three good trials. 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. Use the best three of these titrations for your calculations.

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**General Chemistry II Lab**

**#4 - Determination of the Hardness of Water**

**DATA AND CALCULATIONS**

Mass of  $\text{CaCO}_3$  \_\_\_\_\_

Moles of  $\text{CaCO}_3$  \_\_\_\_\_

Molarity of  $\text{Ca}^{2+}$  (equal to molarity of  $\text{CaCO}_3$ ) \_\_\_\_\_

Moles  $\text{Ca}^{2+}$  in each 25 mL aliquot titrated \_\_\_\_\_

**STANDARDIZATION OF EDTA**

**Blank**                                      **Trial 1**                                      **Trial 2 (if needed)**

*Initial buret reading*                      \_\_\_\_\_                                      \_\_\_\_\_

*Final buret reading*                        \_\_\_\_\_                                      \_\_\_\_\_

Volume of EDTA\*                            \_\_\_\_\_                                      \_\_\_\_\_

\*Use below

**Standard  $\text{Ca}^{2+}$  solution (25.00 mL aliquots)**

Check box to right if trial used to calculate the average molarity	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	Trial 1	Trial 2	Trial 3	Trial 4

*Initial buret reading*                      \_\_\_\_\_                      \_\_\_\_\_                      \_\_\_\_\_                      \_\_\_\_\_

*Final buret reading*                        \_\_\_\_\_                        \_\_\_\_\_                        \_\_\_\_\_                        \_\_\_\_\_

Volume of EDTA                            \_\_\_\_\_                            \_\_\_\_\_                            \_\_\_\_\_                            \_\_\_\_\_

Volume for blank\*                        \_\_\_\_\_                        \_\_\_\_\_                        \_\_\_\_\_                        \_\_\_\_\_

Volume of EDTA used                      \_\_\_\_\_                      \_\_\_\_\_                      \_\_\_\_\_                      \_\_\_\_\_

Molarity of EDTA                            \_\_\_\_\_                            \_\_\_\_\_                            \_\_\_\_\_                            \_\_\_\_\_

Average molarity of EDTA \_\_\_\_\_

NAME \_\_\_\_\_

**General Chemistry II Lab**

**#4 - Determination of the Hardness of Water**

UNKNOWN DETERMINATION

*Unknown Number* \_\_\_\_\_

Check box to right if trial  
used to calculate the  
average ppm

Trial 1

Trial 2

Trial 3

Trial 4

*Volume of water used*

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

*Initial buret reading*

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

*Final buret reading*

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

Volume of EDTA

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

Volume for blank\*

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

Volume of EDTA

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

Moles EDTA

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

Moles  $\text{Ca}^{2+}$  in sample

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

Moles  $\text{Ca}^{2+}$  per liter

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

Grams  $\text{CaCO}_3$  per liter

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

Water hardness (ppm,  
mg  $\text{CaCO}_3/\text{L}$ )

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

Average water hardness (ppm) \_\_\_\_\_

Instructor's Stamp \_\_\_\_\_

NAME \_\_\_\_\_

**General Chemistry II Lab**

**#4 - Determination of the Hardness of Water**

**PRESTUDY**

1. A 0.4505 g sample of  $\text{CaCO}_3$  was dissolved in HCl and the resulting solution was diluted to 250.0 mL in a volumetric flask. A 25.00 mL aliquot of the solution required 24.25 mL of an EDTA solution (after subtracting out the amount of EDTA for the blank) for titration to the Eriochrome Black T end point.

a. How many moles of  $\text{CaCO}_3$  were used?

b. What is the concentration (molarity) of  $\text{Ca}^{2+}$  in the 250.0 mL of  $\text{CaCl}_2$  solution?

c. How many moles of  $\text{Ca}^{2+}$  are contained in a 25.00 mL sample?

d. How many moles of EDTA are contained in the 24.25 mL used for the titration?

e. What is the concentration (molarity) of the EDTA solution?

2. If 100.00 mL of a water sample required 23.24 mL of EDTA of the concentration found in part e of problem 1, what is the hardness of the water in terms of ppm  $\text{CaCO}_3$  (ppm = mg/L)?