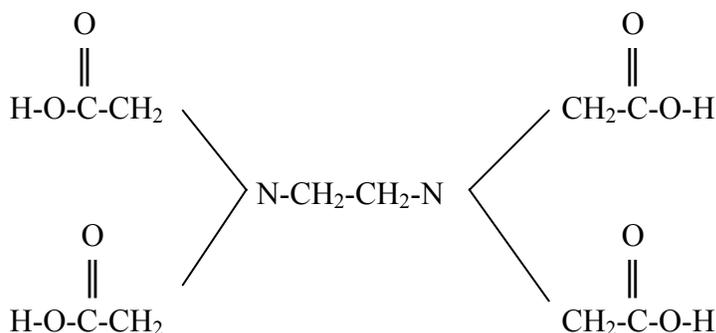


## Calcium Analysis by EDTA Titration

One of the factors that establish 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. Calcium in water will be analyzed this week by EDTA titration and next week by atomic absorption analysis and the results compared.

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.

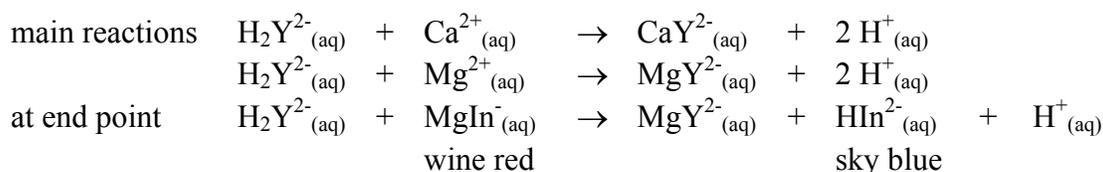


The four acid sites and the two nitrogen atoms all contain unshared electron pairs, so that a single EDTA ion can form a complex with up to six sites on a given cation. The complex is typically quite stable, and the conditions of its formation can ordinarily be controlled so that it contains EDTA and 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 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.



A little magnesium ion is already present in the solutions you will be using to form the initial red complex with the indicator.

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 0.3120 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.) If the solution is not clear add a few drops more of the HCl. Cover the beaker with a watch glass and allow the reaction to proceed until all of the solid carbonate has dissolved. 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.) 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. **This solution will contain 499.7 ppm of calcium ion needed for use in next week's AA experiment.**

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.

Pipet 25 mL portions of your  $\text{Ca}^{2+}$  solution from the volumetric flask into two 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. The initial color should be red and the endpoint color blue with no purple tint to it. **Reference solutions will be available for color comparison.** Be sure to read the buret to 0.01 mL. Refill the buret, read it, and titrate the second solution. Do a third titration if there is poor agreement between the first two. Use your best two values in 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 into two clean 250 mL Erlenmeyer flasks. As before, add 2 drops of indicator and 5 mL of pH 10 buffer and titrate to a blue endpoint. 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 endpoint. As above two titrations must be reported, do a third titration if necessary.

**Be sure to save about 50 mL of your standard calcium solution in a bottle for next week's experiment and label it "500 ppm calcium".**

**Be sure to save about 50 mL of your unknown solution in a bottle for next week's experiment and label it "unknown calcium".**

**Be sure to save the unknown number and the ppm  $\text{CaCO}_3$  calculated in this experiment for use in next weeks AA experiment.**

Name: \_\_\_\_\_

### Data and Calculations

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

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

Molarity of the 250 mL of standard  $\text{Ca}^{2+}$  solution \_\_\_\_\_

### STANDARDIZATION OF EDTA

(EDTA Molarity is Approximately 0.01M)

	Trial 1	Trial 2	Trial 3 (If Needed)
<i>Volume of <math>\text{Ca}^{2+}</math> Titrated</i>	_____	_____	_____
<i>Moles <math>\text{Ca}^{2+}</math> Titrated</i>	_____	_____	_____
<i>Moles EDTA</i>	_____	_____	_____
<i>Initial buret reading</i>	_____	_____	_____
<i>Final buret reading</i>	_____	_____	_____
Volume of EDTA	_____	_____	_____
Molarity of EDTA	_____	_____	_____

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

Name: \_\_\_\_\_

### UNKNOWN DETERMINATION

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

	Trial 1	Trial 2	Trial 3 (If Needed)
<i>Volume of water sample used</i>	_____	_____	_____
<i>Initial buret reading</i>	_____	_____	_____
<i>Final buret reading</i>	_____	_____	_____
Volume of EDTA Used	_____	_____	_____
Moles EDTA	_____	_____	_____
Moles Ca <sup>2+</sup> in sample	_____	_____	_____
Moles Ca <sup>2+</sup> per liter	_____	_____	_____
Grams CaCO <sub>3</sub> per liter	_____	_____	_____
Water hardness (ppm, mg CaCO <sub>3</sub> /L Sample )	_____	_____	_____

Average water hardness (ppm CaCO<sub>3</sub>) \_\_\_\_\_

**Save this value and place in page 4 question 6 of the next experiment, Calcium Analysis by Atomic Absorption, for comparison purposes. Also save the unknown number and place in the table on page 3 of next week's experiment.**

