**EDTA Determination of Total Hardness and Determination of Individual Calcium and Magnesium**

Read about EDTA and its titration on pp. 310-318; 325-328; 853e in your text.

**Background**

The presence in water of salts of calcium and magnesium is spoken of as *hardness.* The salts causing hardness are principally bicarbonates Ca(HCO3)2 and Mg(HCO3)2 and sulfates (CaSO4 and MgSO4).

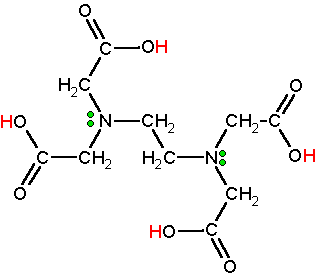
When boiling water, the bicarbonates are decomposed with carbon dioxide being expelled and the normal carbonates precipitating.

Because of this, the hardness caused by calcium and magnesium bicarbonates is known as *temporary* or *carbonate hardness.* Boiling produces no change in a solution of sulfates and hardness caused by sulfates is known as *permanent* or *non-carbonate hardness.*

**Ca(HCO3)2 🡪 CaCO3 + H2O + CO2**

**Mg(HCO3)2 🡪 MgCO3 + H2O + CO2**

The total hardness of water varies greatly with locality and source. Water with total hardness less than 100 parts per million (ppm) of calcium carbonate is generally considered soft; water with total hardness above 300 is considered very hard. The determination of total hardness of water can be made quickly and accurately by titration with ethylenediaminetetraacetic disodium salt (EDTA).



Ethylenediaminetetraacetic acid is insoluble in water, but the disodium dihydrogen salt is soluble. It is a tetrabasic acid and for convenience is frequently represented by H2Y. The disodium salt is marked as the dihydrate and is used for the preparation of standard solutions for titrametric work. In solution, disodium salt is almost completely dissociated according to the reaction.

**Na2H2Y 🡪H2Y2- + 2Na+**

A solution of the disodium salt is thus in effect a solution of the ion H2Y2-. This is the solution generally referred to as “EDTA”. Basically the reactions employed for the determination of calcium and magnesium are:

**Ca2+ + H2Y2- 🡪 CaY2- + 2H+**

**Mg2+ + H2Y2- 🡪 MgY2- + 2H+**

To make the reactions go completely to the right it is necessary to remove the hydrogen ion formed. The pH should be about 10 during the titration and such a pH is readily obtained by adding a buffer consisting of a mixture of ammonia and ammonium chloride.

**Procedure**

**Standardization of EDTA**

Prepare 0.01 M EDTA solution by dissolving about 3.75-4.0 g of the EDTA disodium salt and 0.1 g MgCl2 **∙** 6H2O in about 400 mL 18 MΩ H2O. Dilute the solution to 1L after all the solid has dissolved. Some heating may be done to help dissolve the EDTA. Prepare your calcium standard by weighing 1.00 g dried primary standard CaCO3 to the nearest 0.1 mg into your 1 L volumetric flask. Add 400 mL of 18 MΩ H2O and 6 mL conc. HCl to dissolve the CaCO3. Dilute the solution to the 1L mark after all of the solid has dissolved and mix. Calculate the molarity of this solution using the exact weight for CaCO3.

Standardize your EDTA solution by using a 25 mL volumetric pipet to measure the calcium carbonate standard solution into a 250 mL Erlenmeyer flask. Add 10 mL of pH 10 NH4/NH4OH buffer and 10 mg of ascorbic acid just before titrating. Check the pH of the solution, and if necessary, adjust the pH of the solution to a minimum of pH 10 by adding concentrated NH4OH drop wise to the solution and checking the pH on pH paper. Add 4 - 5 drops of calmagite indicator and titrate with your EDTA solution to a deep blue endpoint with no violet present. Perform four replicate titrations to standardize your EDTA. Calculate the molarity of the EDTA solution using the relation

**Determination of Total Hardness by Titration with Standardized EDTA**

Determine the total hardness (Ca2+ and Mg2+) by using a volumetric pipet to pipet 25 mL of the unknown solution into a 250 mL Erlenmeyer flask. Add 10 mL of pH 10 NH4/NH4OH buffer and 10 mg of ascorbic acid just before titrating. Check the pH of the solution, and if necessary, adjust the pH of the solution to a minimum of pH 10 by adding concentrated NH4OH drop wise to the solution and checking the pH on pH paper. Add 4 - 5 drops of **calmagite indicator** and titrate with your EDTA solution to a deep **blue endpoint** with no violet present. Report your total hardness in ppm. Perform four replicate titrations.

**calmagite-metal complex, red color** 🡺 **At pH=10 indicator is blue when un-complexed**

**Analysis of a the Unknown via Ion Chromatography**

Chromatography is a useful analytical technique for the separation, identification, and quantification of mixtures. Ion chromatography (IC) as used in this lab will allow you to separate the components of the unknown to quantify the individual components as well as the total hardness as determined from titration.

The column utilized for ion chromatography must be oppositely charged for the species of interest. As this lab is concerned with positively charged species, the column used contains covalently bound, negatively charged sites that attract cations. As the sample is introduced to the column, the analyte binds to the column as a result of charge attraction. Elution of the compounds of interest is then done using a weekly acidic solution. For the purposes of this lab an isocratic gradient is used. This means that the same concentration of eluent is always pumped through the column. The charged species in the eluent will displace those which were in the sample and these will flow to the detector. Detection is done using a conductivity detector. The resulting analysis can be visualized on a chromatogram of conductivity versus time. From the chromatogram it is possible to get the area under the curve which is directly related to the concentration of the analyte. An analysis done on a series of samples with known concentrations is utilized to build a calibration curve. Thus one simply needs to determine the area under the curve of the unknown and use the calibration curve to find the unknown concentration.

The same unknown which was titrated will be analyzed by IC. You will work in partners as determined by which unknown was chosen. Obtain a small volume of your unknown and make a 10x dilution of the unknown. Submit for analysis. Your TA will give you further information on how you will obtain your data. From the data you will determine the calcium and magnesium concentrations as well as total hardness.