**EDTA Titration: Determination of Total Hardness of an Unknown**

**Ion Chromatography: Individual Quantification of Calcium and Magnesium, Total Hardness of an Unknown**

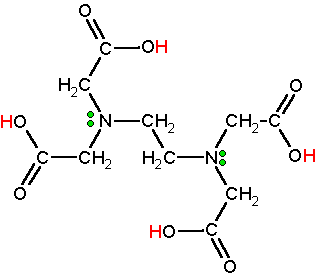
**Background**

In water, the presence of salts of calcium and magnesium is referred to as *hardness.* Salts contributing to the hardness of water are principally calcium bicarbonate, Ca(HCO3)2, and magnesium bicarbonate, Mg(HCO3)2, as well as both calcium and magnesium sulfate, CaSO4 and MgSO4, respectively. When boiling water, the bicarbonate compounds decompose: carbon dioxide (CO2)) is expelled and carbonates precipitate. Because of this, hardness caused by calcium and magnesium bicarbonates is known as *temporary* or *carbonate hardness.* Boiling produces no change in the sulfate compounds contributing to water hardness; so hardness caused by sulfates is called *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 while water with total hardness above 300 ppm is considered very hard. Determination of the total hardness of water is completed quickly and accurately via a titration with ethylenediaminetetraacetic disodium salt (Na2 – EDTA). For every 1 mole of metal ion present in solution, one mole of EDTA reacts and forms a complex.



Ethylenediaminetetraacetic acid (EDTA) is insoluble in water. However, the disodium dihydrogen salt (Na2 – EDTA) is soluble and therefore used in this experiment. Na2EDTA is a tetrabasic acid and for convenience is frequently represented as H2Y. In solution, the disodium salt, represented as Na2H2Y, almost completely dissociates according to the following reaction:

**Na2H2Y ⇄ H2Y2- + 2Na+**

A solution of the disodium salt is thus in effect a solution of the ion H2Y2-. This solution is generally

referred to as “EDTA.” The predominate form of EDTA present in solution is strictly governed by pH. At low pH, EDTA is protonated in various forms (see lecture text for pKa values), while at higher pH deprotonated EDTA is the main species. The form of EDTA present is important for the stability of the EDTA-metal bond that forms, essential for quantitative calculation of metal ions present in solution.

The reactions employed for the determination of calcium (Ca2+) and magnesium (Mg2+) ions in a solution include the following:

**Ca2+ + H2Y2- ⇄ CaY2- + 2H+**

**Mg2+ + H2Y2- ⇄ MgY2- + 2H+**

To force the above reactions completely to the right (products), it is necessary to remove the hydrogen ion formed. Therefore, the pH of the solution in the reaction vessel during titration should be around 10. The pH is controlled by adding a buffer consisting of a mixture of ammonia and ammonium chloride or ammonium hydroxide. If pH during the titration is too low, the EDTA-metal complex is not stable and unreliable in a quantitative sense. The excess H+ ions in solution compete with the metal ions to form a bond with EDTA. On the other hand, a pH too high [well above 10] may cause metal hydroxides (M-OH) to precipitate out. Both situations negatively affect results as quantitative determination relies on knowing how many moles of EDTA complex to the unknown number of moles of metal ions in the unknowns.

Also important in terms of pH is the color of indicator. Calmagite, a metal ion indicator, change colors based on whether it is bound (or unbound) to a metal. The color of unbound calmagite is dependent on the pH of the reaction mixture. For a metal ion indicator to work, its affinity to a metal must be weaker than that of the metal to EDTA. When the reaction mixture is wine red, calmagite is bound to a metal. When blue (no violet present), calmagite has released the metal, is unbound. If a reaction mixture is violet, then proper pH of the reaction mixture was not achieved and the titration is not reliable.

**Procedure**

**Preparation and Standardization of EDTA Solution**

Prepare ~0.01 M EDTA solution by dissolving 3.750-4.000 grams of EDTA disodium salt and 0.1000 grams of magnesium chloride hexahydrate (MgCl2 **∙** 6H2O) in about 400 mL of Nanopure H2O in a 600 mL beaker. Use a watchglass as the weighing vessel for solid EDTA; it is easier than weighing paper in this instance. Heating may be utilized to aid in dissolving the EDTA OR add one Pasteur pipet-full of concentrated ammonium hydroxide (NH4OH). Transfer the contents of the beaker to a 1 Liter glass storage bottle. Add ~600 mL of Nanopure H2O so the final volume of solution is approximately 1 Liter. It is better to prepare this solution in a storage bottle as *volumetric flasks cannot be heated*!

Prepare a calcium standard solution by weighing 0.2500 grams of dried *primary standard* calcium carbonate (CaCO3) to the nearest 0.1 mg using an analytical balance. Use proper quantitative transfer technique to transfer the solid into a 250 mL volumetric flask. Add ~150 mL of Nanopure H2O and 1.6 mL of concentrated (12.0 M) HCl to the flask to dissolve the solid CaCO3. *Solution should be clear when all solid has dissolved!* Dilute the solution to volume in the flask with Nanopure H2O. Parafilm and invert flask to mix. Calculate the molarity of this solution [to four significant digits] using the weight of CaCO3 that was measured using the analytical balance. Un-parafilm the volumetric flask and pour some of the standard CaCO3 solution into a beaker [*because you never pipet directly out of a volumetric flask*]. Obtain a 25.00 mL volumetric pipet and pipet bulb. Remember to clean the volumetric pipet before use!

Using a 25.00 mL volumetric pipet, transfer an aliquot of the calcium carbonate standard solution into a 250 mL Erlenmeyer flask. Add 10.0 mL of pH 10 NH4/NH4OH buffer to the flask using a graduated cylinder. Then add 10 mg of ascorbic acid just before titrating. Ascorbic acid is added to reduce any other species present in solution, Cu2+ or Fe3+ for example, to prevent their binding to EDTA. Anything complexing to EDTA other than the analytes (Ca2+ and Mg2+) will negatively affect results. Check the pH of the solution using pH paper and proper technique. When available, a pH meter may be used. If necessary, adjust the solution’s pH to a minimum of pH 10 by adding concentrated NH4OH drop wise via a Pasteur pipet. Re-check the pH to ensure it is a minimum of 10. Add 4 - 5 drops of *calmagite indicator* to the Erlenmeyer flask. Prepare the buret (clean and rinse), and fill it with the EDTA solution. Titrate with EDTA until the reaction mixture reaches a deep blue endpoint with no violet present. Perform at least 3 titrations. Calculate EDTA molarity for *each* titration. Calculate the average EDTA molarity, standard deviation, and ppt to ensure results are precise.

**Determination of Total Hardness (Ca2+ and Mg2+) of an Unknown Sample**

Using a volumetric pipet, transfer 25.00 mL of an unknown solution into a 250 mL Erlenmeyer flask. Add 10.0 mL of pH 10 NH4/NH4OH buffer to the flask using a graduated cylinder. Then add 10 mg of ascorbic acid just before titrating. Check the pH of the solution using pH paper and proper technique. When available, a pH meter may be used. If necessary, adjust the pH of the solution to a minimum of pH 10 by adding concentrated NH4OH drop wise via a Pasteur pipet. Re-check the pH of the solution to ensure it is pH 10. Add 4 - 5 drops of *calmagite indicator* and titrate with EDTA to a deep blue endpoint with no violet present. Perform at least 3 replicate titrations. Report total hardness of the unknown in parts per million (ppm). Calculate average, standard deviation, and ppt of total hardness in the unknown sample.

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

**Sample calculation for total hardness:**

An unknown solution required 40.00 mL of standardized 0.01000 M EDTA titrant to reach the endpoint.

(0.01000 M EDTA) x (0.04000 L EDTA) = 4.000 x 10-4 moles EDTA

4.000 x 10-4 moles EDTA x = 4.000 x 10-4 moles Ca/Mg

4.000 x 10-4 moles Ca/Mg ÷ 0.02500 L = **MCa & Mg unknwn soln** = 0.01600 M

Calculated **M** then needs to be adjusted to report as total Ca2+:

0.01600 x x = 641.0 mg / L = 641.0 ppm Ca  
  
Note: 40.078 grams/mole is the M.W. of Ca; total hardness is reported in terms of calcium even though both Mg and Ca are present in the sample. In a typical water sample, more calcium salts are present than magnesium salts.

**Analysis of Unknown via Ion Chromatography (IC)**

**Background**

Chromatography is a useful analytical technique for the separation, identification, and quantification of mixtures. Ion chromatography (IC), as used in this experiment, will allow separation of the components of an unknown to quantify the ions individually, as well as, compute total hardness. In other words, this instrumental method will individually quantify the concentration of Ca2+ and Mg2+. This could be useful if speciation of salts contributing to hardness is necessary. Total hardness can then be calculated from these individual results. The IC total hardness value can then be compared to total hardness as determined via titration. Ideally, two different methods (titration and IC) should yield the same result. So in effect, this experiment is showing you a classical method of analysis (titration) compared to an instrumental method (IC). There are pros and cons to both methods which you should identify.

The separation column utilized in IC must be oppositely charged for the species of interest. This experiment is concerned with positively charged species (Ca2+ and Mg2+), so the separation column contains covalently bound, negatively charged sites that attract cations. As the unknown sample is introduced to the column, the analyte ions bind to the column as a result of charge attraction. Separate elution of the ions of interest is achieved by using a weakly acidic solution for the mobile phase. In this experiment, an isocratic gradient is used, which means that the same concentration of eluent (mobile phase) is always pumped through the IC system. The charged species in the eluent will displace those of which were in the unknown sample and as consequence the analyte ions will flow, post-column, to a conductivity detector. The result of IC analysis is called a chromatogram, a graph of conductivity versus time. From the chromatogram, it is possible to obtain the area under the curve, which is directly related to an analyte’s concentration. Analyses completed on a series of samples with known concentrations facilitates constructing a calibration curve. Thus, one simply needs to determine the area under the curve [via analysis] of the unknown and use the calibration curve to determine the unknown’s concentration.

**Prepare Unknown for IC Analysis**

Use the same unknown as the titration portion of the experiment. Prepare a 10x dilution of the unknown in a volumetric flask via a volume dilution technique (variable volume pipettor) or mass technique (using an analytical balance). Instructor and TA will discuss these methods. Label the volumetric flask with name and unknown #. Instructor and TA will assist student use of the Metrohm 883 Basic Ion Chromatograph (IC) and give further information on how to obtain & process results. Once unknowns are analyzed, determine the individual calcium and magnesium ion concentrations in the unknown as well as total hardness (as Ca) in parts per million (ppm).