Introduction

A 0.03 M solution of EDTA is prepared in order to analyze the calcium in both a known and an unknown sample. First, the 0.03 M EDTA solution is standardized using a primary standard, CaCO$_3$. This is done using a substitution reaction in which a small, but reproducible amount of a MgEDTA solution is added. The chemical reactions employed in this experiment will be explained in a laboratory briefing. In this titration with EDTA, first the calcium ion and then the displaced Mg ion are titrated in a complex-forming titration which uses Eriochrome Black T to indicate the end point. The percentage of calcium in the unknown sample is then similarly determined using the standardized EDTA solution. As an illustration of the practicality of this analysis, the widely used EDTA titration for the “total hardness” (both free calcium and magnesium ion) in drinking water, using the Eriochrome Black T indicator end point, will be conducted. In this analysis the total hardness is reported in parts per million CaCO$_3$ and reflects how the EDTA titrant is conveniently standardized.

Solutions and Chemicals Required:

- Solid, reagent grade Na$_2$EDTA
- Solid, primary standard CaCO$_3$, previously dried at 110°C
- Unknown calcium sample, to be dried for 1 hour at 110°C

EACH STUDENT is to bring in about 500 ml. of their “home” tap water. (Make sure that you checkout from the stockroom an appropriate plastic bottle to collect and transport the sample. The instructor will discuss proper sampling procedure).

- 5 M NaOH
- 1 M NaOH
- 1 M HCl
- Methyl red indicator
- pH 10 ammonia buffer
- Mg$^{2+}$-EDTA complex
- Eriochrome Black T indicator- keep in the refrigerator or on ice
- Toluene used to preserve the aqueous calcium solution
- Special 10 ml buret, checked out from the stockroom

Procedure

A. Preparation and Standardization of a 0.03 M EDTA Solution

Into a clean weighing bottle, weigh approximately 5.6 grams of the reagent grade, Na$_2$EDTA-dihydrate (fw. = 372.25). Store in the dessicator. Please do not waste this sodium EDTA; as it is expensive. Return all unused sodium EDTA solid and any unused EDTA solution to the appropriately labeled bottles for recovered liquid or solid EDTA.
Into a 250 ml Erlenmeyer flask, accurately weigh by difference to the nearest 0.0001 grams, 5.6 grams of the reagent Na$_2$EDTA. Add about 80 ml of deionized water to the 250 ml flask and gently warm the solution on the hot plate (not with a Bunsen Burner) to a temperature no higher than 60 °C. It is necessary to heat the solution to dissolve the Na$_2$EDTA, but the Na$_2$EDTA will permanently break down over 80 °C. Transfer the solution with several deionized water rinsings through a regular funnel to your 500 ml volumetric flask. Quickly cool this solution by running cool tap water around the side of the 500 ml volumetric flask. When the solution has reached near room temperature, carefully dilute the solution with more deionized water to the flask’s calibration mark. Since EDTA can extract ions from the glass container, the EDTA solution needs to be transferred to a 500 ml plastic bottle on the same day that it is made. A 500 ml plastic bottle may be signed out from the stockroom.

**Preparation of the Known Concentration Calcium Standard**

Weigh about 2.2 grams of primary standard CaCO$_3$ into a dry weighing bottle. In your laboratory notebook, record the purity factor of the pure CaCO$_3$ from the bottle’s label. Into a 250 ml Erlenmeyer flask, accurately weigh by difference 1.0 to 1.3 grams of the dry CaCO$_3$ known to the nearest 0.0001 grams.

To dissolve the sample, add about 20 ml of deionized water followed by dropwise addition of concentrated HCl (found in several of the hoods) until the effervescence (loss of CO$_2$) stops. Swirl and gently boil the solution using a Bunsen burner flame to expel the CO$_2$ until the solution’s volume is about one fourth of its original volume. Do not heat to dryness. If a solid precipitate appears, add enough deionized water to re-dissolve it. It should re-dissolve! If it does not, add three more drops of concentrated HCl and continue heating. If the precipitate persists, notify the laboratory instructor. Rinse down the sides of the flask with deionized water. Add enough deionized water so the total volume is about 50 ml.

If you have insufficient time (about 1 hour is needed) to titrate this calcium solution during the present laboratory period, stopper the Erlenmeyer flask with a clean rubber stopper, leaving the calcium solution in the acidic state until the next laboratory period. The reason for this is that a (harmless-to-humans) water mold tends to grow in non-acidic calcium solutions in our building’s deionized water supply. If this happens, the calcium solution must be discarded and a new one made.

When ready to begin the titrations of the standard calcium solution with the EDTA solution, carefully neutralize the strongly acidic solution as follows so that later additions of the pH 10 buffer will be effective. First, add two drops of methyl red indicator to the calcium solution. Then, slowly add 5 M NaOH solution (provided in a dropping bottle) until the red color of the indicator just turns yellow. Bring the color back to red using a few drops of 1 M HCl. Then very carefully add 1 M NaOH until the solution just turns yellow again. Do not add a large excess of NaOH or a white precipitate of Ca(OH)$_2$ will form which is difficult to re-dissolve with acid. With deionized water, carefully transfer the entire calcium solution through a funnel to your calibrated 250 ml volumetric flask. Add a drop of toluene to inhibit the growth of the water
mold. Carefully dilute the solution to your 250 ml volumetric tape calibration mark from GA/1. Shake well, usually 10 times, end-over-end.

Determination of the Indicator Blank

An appreciable indicator blank exists for the titration of calcium with EDTA in the presence of free Mg ion. Usually from 0.30 to 0.60 ml. of the EDTA is needed to just change the indicator. To determine this indicator blank proceed as follows:

Take 50 ml of distilled water, measured with a graduated cylinder, 5.0 ml of the pH 10 buffer, 2.0 ml of the Mg-EDTA solution and the specified number of drops of Eriochrome Black T indicator. (The number of drops of indicator needed depends on the batch of indicator used, which will be announced in the lab briefing). Titrate with the EDTA titrant from a color change of red through purple to an end point of a pure “royal” blue with no reddish tinge. Repeat at least two times. Agreement in the ml of EDTA titrant should be within 0.03 ml. The average value of this blank must be subtracted from the volume of EDTA delivered from subsequent titrations.

Standardization of the 0.03 M EDTA

Carefully pipet exactly one 25 ml aliquot of the standard calcium solution into a 250 ml Erlenmeyer flask. Add 5.0 ml of the pH 10 buffer, and 2.0 ml of the Mg-EDTA solution (pipets will be provided for these solutions). Then add the Eriochrome Black T indicator. For precise results, it is very important to be consistent in delivering the same number of indicator drops as was used for the Indicator Blank! Titrate the calcium solution with the 0.03 M EDTA solution to the same color change from red through purple to an end point of pure “royal” blue with no reddish tinge. (This end point will be demonstrated in a laboratory briefing). Since the change in the indicator’s color is slow, the EDTA should be added slowly and the solution swirled well. Repeat the determination at least three more times. Stop your experimental work and calculate the molarity of the EDTA solution now! Results should be within 3.0 parts per thousand. If not, you should probably perform another two calibration runs, perhaps use a q-test to reject the most outlying result(s) and check your new precision. This is not an easy end point!

B. Determination of the Calcium in an Unknown Sample and in a Water Sample

Unknown Calcium Sample

Dry the unknown calcium sample for one hour at 110 °C. Note, before this part is started, the standardization of EDTA with standard calcium solution must be successfully completed since it is necessary to discard the standard calcium standard and to reuse the calibrated 250 ml volumetric flask. Discard the standard calcium solution and carefully rinse your 250 ml volumetric flask, first with tap water and then with deionized water.

Into a 250 ml Erlenmeyer flask, accurately weight 1.0 to 1.2 grams, known to the nearest 0.0001 grams, of the unknown calcium sample. Solubilize this calcium sample exactly as the standard
CaCO₃ was solubilized in the previous part. Continue following the procedure, performing all steps through the final dilution of the solution to 250 ml but now with your unknown calcium sample. Titrate the unknown calcium solution following the same procedure as for the standard calcium solution. Do at least four trials. The indicator blank need not be repeated as long as the same batch of indicator is used, but do not forget to subtract the volume of the indicator! All the equations needed for the calculation will be given in a laboratory briefing. The results should be reproducible to within 3.0 parts per thousand.

**Water Sample**

It is expected that each student will bring in his’ or her’s own “home” drinking water sample. The laboratory water is the same as most dormitories’ tap water. All of UCONN’s water supply is taken from below the Fenton River. There will be certain other real drinking water samples also available. Be sure to record in your laboratory book the source of your tap water. Checkout from the stockroom a 10 ml buret and small plastic funnel, used for filling the buret. Using a 100 ml pipet (several will left in the hoods in the laboratory) transfer a 100 ml aliquot of the tap water into a clean 250 ml Erlenmeyer flask. Acidify the water sample with two drops of concentrated HCl and gently boil the solution to remove the CO₂. Rapidly cool the sample by running tap water around the outside of the Erlenmeyer flask. Add two drops of methyl red indicator. Neutralize the solution with 1 M NaOH until the yellow color just appears. Add 5.0 ml of the pH 10 buffer and the usual number of drops of the Eriochrome Black T indicator. But do not add the 2.0 ml of Mg-EDTA. (This analysis of total hardness involves titrating both the free magnesium as well as calcium in drinking water. Using the 10 ml buret, titrate the water sample with the standard 0.05 M EDTA solution to the same pure blue end point. If the color change is very sluggish, it could be because of the absence of free Mg ion in the water. In that case, add 2.0 ml of the Mg-EDTA complex. Repeat at least twice more. Note if the Mg-EDTA solution is used, then the previously determined indicator blank needs to be subtracted from the total volume of EDTA delivered. The results should be reproducible to within 3.0 ppt.

Carefully rinse the 10 ml buret after use because EDTA solution, when dried, tends to clog the finer tip of these 10 ml burets.

**Calculations**

**A. Standardization of EDTA**

1. Calculate the average molarity of the EDTA solution. Also, calculate the standard deviation and relative standard deviation in ppt of the value for the molarity of EDTA solution.

2. Calculate the CaCO₃ titer of the solution, reported as mg CaCO₃/ml EDTA. Calculate the standard deviation of the titer (using propagation of error rules).

**B. Calculate the Percentage of Calcium in the Unknown Sample**
1. Calculate the percentage of calcium the unknown sample. Also, calculate the standard deviation and the relative standard deviation in ppt. of the percentage of calcium in the unknown sample (remember to use propagation of errors).

2. Calculate the ppm CaCO$_3$ (mg CaCO$_3$/liter) in the water sample using the CaCO$_3$ titer of the EDTA calculated in Part A, Section 2.