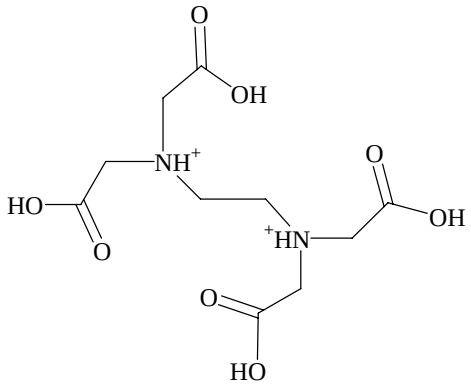
Chemistry 120: Experiment 2

EDTA Titration of Calcium^{II} and Magnesium^{II}

Calcium and magnesium ions are the primary contributors to "hardness" of water and they are important components of limestone. Calcium is also of biological importance and is contained in teeth and bone. The determination of these two elements by classical procedures (i.e. by non-instrumental procedures) usually requires gravimetric analysis because the ordinary titration methods (acid-base, redox) are not applicable since neither ion has useful acid-base or oxidation-reduction properties. The development of multidentate complexing agents such as EDTA (named either ethylenediaminetetraacetic acid or ethylenedinitrilotetraacetic acid) allowed the creation of practical titrimetric or complexometric methods for determination of calcium and magnesium.



H_6Y^{2+}

EDTA has six titratable protons, two from the nitrogens and four from the carboxylate groups. It can be designated as H_6Y^{2+} because it is a hexaprotic acid that can lose six protons to form Y^{4-}, the fully deprotonated form. At neutral pH, the dominant form of EDTA in solution is HY^{3-}. The complexation reaction with calcium ions occurs through the unprotonated form of EDTA, Y^{4-}.

$$Ca^{2+} + Y^{4-} = CaY^{2-} \qquad (1)$$

The acid-base properties of the EDTA ligand will cause the reaction (1) to be very dependent on pH, with lower pH giving a smaller fractional amount of Y^{4-}, called α_{Y4-} , forcing the equilibrium to the left toward Ca^{2+}. In practice, calcium (and magnesium) are titrated at pH near 10, where α_{Y4-} is large, and calcium (but not magnesium) can be titrated at pH as high as 12, where α_{Y4-} is ~ 1.

As in other titrimetric procedures, visual indicators have been developed for EDTA titrations. This task was made easier by the fact that none of the species involved here (EDTA, calcium ions, magnesium ions or the complexes) is colored. The indicators are dye molecules, added in minute quantities, that have a different color when complexed to metal ions as compared to the free, uncomplexed dye molecule. In the present experiment we will use hydroxynaphthol

blue as an indicator for titration of calcium at pH 12 and eriochrome black T for titrating the sum of calcium and magnesium at pH 10.

Solid EDTA is available in a form (the disodium salt) which is sufficiently pure to be used as a primary standard. However, in this experiment, in which the highest possible level of accuracy is desired, we will standardize the EDTA solution with primary standard solid calcium carbonate. This will also provide useful practice in detecting the end point before analysis of your unknown solutions.

Apparatus

250-mL Erlenmeyer flask, three
50-mL buret
25-mL pipet
250-mL volumetric flask
100-mL volumetric flask
weighing bottle
pH meter

Chemicals

$CaCO_3$ for standard calcium solution
About 25 L of 0.01 M EDTA solution, prepared from $Na_2H_2Y \cdot 2H_2O$ and stored in the large polyethylene carboy marked "EDTA"
Eriochrome Black T and hydroxynaphthol blue indicators as powdered mixtures of dye and KCl
1-M NaOH
Buffer: 1.3-M NH_4Cl, 8.5-M NH_3
pH paper
Unknown calcium and magnesium solution

Procedure

1. A large polyethylene storage bottle containing 0.01 M EDTA will be used by all students in the laboratory. Glass storage bottles are not used because calcium can be leached from the glass by EDTA.

2. Dry primary standard calcium carbonate in a weighing vial (dried at 110 °C overnight and transferred to a desiccator). To prepare a standard calcium solution, weigh accurately about 0.25 g of calcium carbonate and transfer to a clean 250-mL volumetric flask (it need not be dry). Dissolve the solid in a minimum (about 5-8 mL) of 1 M HCl, dilute to the mark and MIX WELL. Compute the molar concentration of your standard calcium stock solution.

3. Pipet 25.00 mL of the standard calcium stock solution into a clean 250-mL Erlenmeyer flask and add about 50 mL of distilled water. Place a square of pH paper in the flask, **GO TO THE HOOD**, add 1-M NaOH dropwise to bring to about pH 10, then add 1-2 mL of 1-M NaOH which will bring the pH to 12 and offer reasonable buffer capacity to absorb protons liberated in the reaction of Ca^{2+} with H_2Y^{2-} (1 mL of 1-M NaOH diluted to 100 mL gives 0.01 M OH^-, or pH ~ 12). Normally, one would have added KCN to complex any iron, which would interfere. However, no KCN is added because the samples are known to have negligible iron.

4. Add a small amount of hydroxynaphthol blue indicator (a powdered mixture of dye and KCl) and titrate with the EDTA solution until the pale red color changes to blue. Use fractional drops near the endpoint.
5. Carry out in triplicate the titration of the standard calcium solution (steps 3 and 4) and calculate the average molarity of the EDTA titrant and its standard deviation. The EDTA has now been standardized.

6. Determination of the hardness of an unknown bottled water. As practice, we will titrate an unknown bottled water and report the water hardness as ppm $CaCO_3$. Adjust the pH of 100 mL (4 deliveries from a 25-mL pipet) to about 10 by addition of 3 mL of the ammonia buffer; check with a pH meter. If needed, a few drops of 1-M NaOH can be added to bring the pH to 10. Note that this would normally be the point where you would add KCN to complex the iron, but this step is skipped because there is negligible iron in the samples. Using eriochrome black T (wine red to blue), titrate with EDTA and report the total water hardness as ppm $CaCO_3$ (the sample may contain both Ca^{2+} and Mg^{2+} but they are titrated together).

7. Analysis of an unknown mixture of calcium and magnesium. Carefully transfer 10.00 mL of your unknown solution (you will receive only 100 mL) into a 250-mL Erlenmeyer titration flask. Add 3 mL of the ammonia buffer to bring the pH to about 10; check with the pH meter. If needed, a few drops of 1-M NaOH can be added to bring the pH to 10. Titrate with the standardized EDTA solution using eriochrome black T as indicator. Under these conditions, both calcium and magnesium are titrated so the end point volume along with the EDTA concentration will give the **sum** of the number of moles of calcium and magnesium in the 10-mL aliquot.

8. Calcium is determined at pH 12 where magnesium is quantitatively precipitated as the hydroxide and will not react with EDTA. A scout titration is performed to determine the approximate calcium content. Transfer a 10.00-mL aliquot of sample to a titration flask, adjust the pH with 1-M NaOH until the pH is about 10 (pH paper or meter) and add 1-2 mL of excess 1-M NaOH to bring the pH to about 12 (as in step 2). The magnesium will form a white precipitate. Titrate the calcium with your standardized EDTA solution using hydroxynapthol blue to determine the approximate calcium content. The result is approximate because some calcium always co-precipitates with magnesium.

9. Accurate determination of calcium. Using another 10.00 mL aliquot of sample, add only enough NaOH to reach pH near 10 (pH paper) then add (using your buret) enough EDTA titrant to be within 2-3 mL of the anticipated end point (based on the result in step 8). Then add the 1-2 mL of excess 1-M NaOH (to precipitate the magnesium after most of the calcium has been protected by complexation), add the indicator and complete the titration.

10. In this case, report the results as ppm Ca and ppm Mg.

Acknowledgment: This experiment has been adapted in part from laboratory procedures authored by Professor S. D. Brown and Emeritus Professor W. H. McCurdy, Jr. Last updated Feb 2005 by TPB.