

EDTA Titrations

Introduction

In these times of environmental awareness and concern, it is very important that you become experienced with water analysis. As you know, Davis is not known for the exceptional quality of its water. In fact, let's face it, the water here tastes pretty bad! What is in it? That would be a good question to try to answer if we had lots of time and if we wanted to spend it doing an experiment in qualitative analysis. However, for now we want to learn more about *quantitative analysis*. It is well known that ground water commonly contains a large amount of two metal ions, calcium and magnesium. The term "hard water" refers to the presence of these two metals. As you may know, these metals give the water a rather harsh taste and will also cause the white deposits often observed on faucets or as "lime" deposits in bathtubs. These white deposits are generally metal carbonates. In addition, these two metal ions will precipitate soaps, leaving the unsightly bathtub scum that you may have observed. Perhaps you have had the experience of living or visiting a residence where the water has been "softened". Softening refers to a process whereby the water is passed through a column in which the calcium and magnesium ions are removed. This makes the water feel "softer" when taking a bath or shower, because the soap precipitates do not form.

In this experiment, you will determine the amount of calcium carbonate present in an unknown solid sample the stockroom has prepared. To do this you will use a hexadentate ligand called ethylenediaminetetraacetic acid (EDTA). This ligand, due to its six donor atoms and to its size and shape, has the exceptional ability to complex or chelate with a variety of metal ions. The equilibrium constant for the formation of each metal/EDTA complex is different, and the kinetic rate at which each metal complexing agent forms is different as well. Thus, the ligand can be used to complex one metal ion in the presence of another. For example, calcium-EDTA is given as an antidote for mercury ion poisoning. Once the EDTA is ingested, it will selectively bind to the free mercury ions, effectively removing them and not allowing them to bind to enzymes and cytochromes. Thus the poison is removed and passes innocuously through the physiological system. For our analysis, we will use disodium EDTA to bind to calcium and magnesium ion as is shown below:

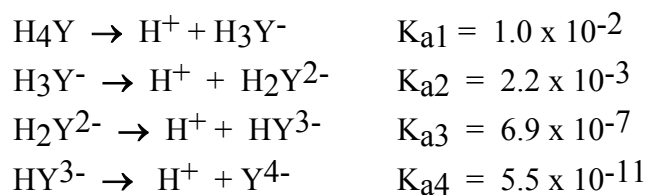


However, we need something to indicate when the reaction is complete. We need an indicator. The indicator will need to be another ligand and it must have a different color when it is free than when bound to a metal ion. One such ligand is Calmagite that binds to alkaline earth metals producing a color change as follows:



The reaction of EDTA with metals ($K \sim 10^8$) is greater than that of Calmagite ($K \sim 10^9$). Thus, if a small amount of indicator is added to a solution of magnesium and calcium, a red or pink colored complex will result. If EDTA is then added via a buret, the color will change when the metal is stripped from the Calmagite and binds to the EDTA; the solution will turn blue. If we have carefully measured the amount of EDTA that we have added, then we can determine the total amount of calcium and/or magnesium in the sample.

It is important that you appreciate that EDTA has acid/base properties. It has four acid constants, as is shown below (Note: $Y = \text{EDTA}^{4-}$)



For this reason, analyses must be done at a constant pH and one that will enable the ligand to bind successfully with the metal. These determinations will be conducted at pH 10 via the addition of a $\text{NH}_4\text{OH}/\text{NH}_4\text{Cl}$ ($\text{p}K_a = 9.24$) buffer.

Safety: The pH 10 buffer is 10 M ammonia. Keep it under the fume hood as much as possible and avoid breathing its vapors. Wear your goggles!

Procedure

Work individually on this experiment.

Pre-Laboratory Preparation

During the laboratory period **before** beginning this experiment (Electrochemical Cells) you were instructed to dry a sample of pure calcium carbonate and an unknown sample.

Part I. Preparation and Standardization of an EDTA Solution

1. Prepare approximately 500 mL of a 0.03 M Na_2EDTA solution by filling the 1-L bottle with approximately 300 mL of deionized water. Add the necessary mass of solid $\text{Na}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$. Stir to dissolve. Since solid EDTA dissolves slowly, go on to weigh your CaCO_3 samples for the standardization. After your solid $\text{Na}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$ has dissolved, TAKE YOUR SOLUTION TO THE FUMEHOOD and add about 20 mL of the pH 10 buffer.

NOTE: 1) DO NOT USE THE BUFFER SOLUTION FOUND ON THE SHELVES IN THE LAB. ADD THE 10 M AMMONIA BUFFER FOUND IN THE FUMEHOOD.

2) ONLY ADD THE 10 M AMMONIA BUFFER TO YOUR SOLUTION IN THE FUMEHOOD.

2. Mix well and add another 180 mL of deionized water to make approximately 500 mL of solution
3. Standardize the EDTA solution by using dry calcium carbonate. Here are some tips to make your titration smooth and successful.

In preparing for the lab, you should have calculated the approximant mass of the primary standard, CaCO_3 , necessary for the titration. Weigh your 3 samples of your primary standard by difference being careful not to touch the vial containing the calcium carbonate with your fingers. Use a small piece of folded paper wrapped around the vial to handle the sample. Find the initial mass of vial; dispense the solid in a 250 mL Erlenmeyer flask; and reweigh the vial. Record the precise masses in your notebook. Calcium carbonate is insoluble in water. To dissolve the sample, add about 20 mL of deionized water to it and then slowly add 6 M HCl drop-wise. You will observe the evolution of CO_2 gas as the carbonate reacts with

the HCl. It will take approximately 6-15 drops of HCl to neutralize the sample and dissolve it. DO NOT OVER ACIDIFY.

Question A: Write the balanced chemical equation for the standardization of EDTA solution.

It is absolutely essential that the pH of the calcium carbonate solution remain 10 throughout the titration. To ensure that the pH remains at 10, IN THE FUMEHOOD add an additional 5 mL of the ammonia buffer (FOUND IN THE FUME HOOD) and another 30 mL of water to the calcium carbonate solution. Check the pH of the solution using Alkacid paper. You may also want to check the pH of the solution a couple of times during the titration.

NOTE: 1) BE SURE TO USE ONLY THE AMMONIA BUFFER LOCATED IN THE FUMEHOOD. DO NOT USE ANY OTHER BUFFERS THAT MAY BE FOUND ELSEWHERE IN THE LABORATORY.

2) ONLY ADD THE AMMONIA BUFFER TO YOUR SOLUTION IN THE FUMEHOOD.

3 – 4 drops of Calmagite indicator is sufficient to show the color change at the endpoint. It is best if you add this just before you reach the endpoint. In addition, one can sharpen the endpoint by adding about 1 mL of the solution labeled Na₂MgEDTA. The magnesium ion is approximately 40 times more strongly bound to the indicator Calmagite than is the calcium ion. In addition, the calcium ion is approximately 200 times more tightly bound to the ligand EDTA. Thus when EDTA is added to the solution it will preferentially bond to the calcium ion. When the calcium ion has completely reacted, the EDTA will then pull the magnesium ion away from the indicator and the solution will then change color. Note that adding one mL of this solution does not affect the stoichiometry of the titration as the solution contains an equal molar amount of magnesium and EDTA. Be sure to titrate all the way to the **blue color endpoint** and not stop titrating when the solution is the purple color. Keep the flask of your first trial titration to use as a reference color for subsequent trials. Be sure you have 3 acceptable trials before moving on to Part B. To determine if a trial is acceptable, calculate the molarity of the EDTA solution based on your volumes and mass of CaCO₃ for each trial and then perform the Q-test. For more details regarding the Q-test calculation, see page 7 in the introductory section of your laboratory manual.

Question B: Write the balanced chemical equation for the reaction between the EDTA solution and the indicator, MgIn(aq).

Perform the analysis with three samples. Calculate the molarity of the EDTA solution for each sample. Calculate an average molarity and the standard deviation. The post-lab exercises will guide you through these calculations.

Part II. Determination of Calcium in an Unknown

1. Clean three 125 mL, 250 or 300 mL Erlenmeyer flasks. It is very important that the flasks be extremely clean and well rinsed with deionized water. Accurately weigh three samples of your dry unknown into the three Erlenmeyer flasks. The unknown samples should weigh between 0.150 - 0.180 grams.
2. Titrate the unknown samples using the same procedure that you used for the standardization of your EDTA solution. Be sure you have 3 acceptable trials before cleaning up. To determine if a trial is acceptable, calculate the percent mass CaCO_3 in the sample for each trial based on your volumes of EDTA and mass of CaCO_3 for each trial and then perform the Q-test. Report the average percent by mass of CaCO_3 in your unknown along with both a relative and standard deviation, and a 90% confidence limit. The post-lab exercises will guide you through these calculations.

Clean-up. Rinse all glassware with deionized water. Return all chemicals and equipment to the proper location. Rinse the bench with your sponge and water.

In order for the on-line program to identify the unknown that you were assigned to analyze, you will need to know the hyphenated number embossed on your locker in your laboratory room. For example, in room 0435 Chemistry Annex one of the locker's hyphenated number reads, 0435-6-24; in room 66 Chemistry one of the locker's hyphenated number reads, 66-4-1.

Your locker's hyphenated number is _____ - _____ - _____.

Post-Laboratory Exercise Questions

In the standardization of the sodium EDTA solution using the solid calcium carbonate primary standard, we must examine each of three acceptable trials. Enter the precise mass in **GRAMS** of the dry primary standard, calcium carbonate, used for each of 3 acceptable trials in the standardization titration. Your mass precision should be reported to a thousandth of a gram.

In the standardization of the sodium EDTA solution using the solid calcium carbonate primary standard, your titration volumes of the sodium EDTA solution should be approximately 20 - 30 mL. For each of the 3 acceptable trials used in the titration of your calcium carbonate samples, enter the precise volume in **milliliters** of EDTA solution (e.g. 20.34 mL). Be sure to enter your volumes in the corresponding order that you entered your masses of calcium carbonate previously. For instance, the mass of calcium carbonate you entered for entry #1 above should correspond to the volume of EDTA solution that you enter for entry #1 here.

Using the volumes of sodium EDTA solution you just entered and the corresponding calcium carbonate masses entered earlier, calculate the molarity of the sodium EDTA solution for each trial. Enter your calculated molarity of the EDTA solution for each trial. Be sure to enter your calculated molarities in the corresponding order that you entered your EDTA volumes previously. For instance, the EDTA volume you entered for entry #1 above should correspond to the molarity that you enter for entry #1 here.

The molarity of the EDTA solution is taken as the average of the three trials. Please enter the average molarity.

Please enter the standard deviation of the EDTA molarity.

The following series of questions pertains to Part II of the EDTA Titration Experiment, where you are to calculate the percent mass of calcium carbonate in your dry unknown sample.

In the titration of the dry unknown sample with the secondary standard solution, sodium EDTA, we must examine each of three acceptable trials. Enter the mass of your dry unknown sample in **GRAMS**, for each your 3 acceptable trials. Your mass precision should be reported to a thousandth of a gram.

In the titration of the dry unknown sample with the secondary standard solution, sodium EDTA, your titration volumes of the sodium EDTA solution should be approximately 20 - 30 mL. For each of the 3 acceptable trials, enter the precise volume in **milliliters** of EDTA solution used in the titration of your dry unknown samples (e.g. 20.34 mL). Be sure to enter your trial volumes in the corresponding order that you entered your masses of the samples previously. For instance, the dry unknown sample mass you entered for entry #1 above should correspond to the EDTA volume you enter for entry #1 here.

Using the volumes of EDTA solution you just entered and the corresponding dry unknown sample masses entered earlier, calculate the percent mass of calcium carbonate in the unknown sample mixture. Enter the calculated percent mass of calcium carbonate in the dry unknown sample for each of the 3 acceptable trials. Be sure to enter your mass percentages to the correct number of significant digits and in the corresponding order that you entered your masses of your dry unknown samples and volumes of your EDTA previously. The dry unknown sample mass you entered for entry #1 above should correspond to the percent mass of calcium carbonate you enter for entry #1 here.

The percent mass of calcium carbonate in the dry unknown sample is taken as the average of the three trials. Enter the average mass percent of calcium carbonate in the dry unknown samples.

Please enter the standard deviation of the average mass percent of calcium carbonate in your dry unknown samples.

Please enter the calculated 90% confidence limit for the average percent mass of the calcium carbonate in your dry unknown samples.

Please enter your room number, locker series and locker number which is the hyphenated numbers embossed on your locker. For example, if the hyphenated numbers read, 0435-6-24, your room number is 0435, your locker series is 6, and your locker number is 24. If the hyphenated numbers are 66-4-1, your room number is 66, your locker series is 4, and your locker number is 1.