**Analysis of Sulfate via Precipitation and Back Titration**

This lab utilizes principles and techniques from the Gravimetric Analysis of Sulfate and the EDTA Titration labs.

Typically when one thinks of a titration, it is assumed it is an acid/base titration or a titration to determine cationic species such as in labs that you have already completed. In this lab, you will be determining the anionic sulfate content of your unknown by back titration as anions are not directly analyzable via a titration.

There are three basic titration techniques. The first is a direct titration. In a direct titration one determines the concentration of an analyte by adding a titrant that reacts or complexes directly with that analyte. This is the type of titration that was done with the EDTA titration for calcium and magnesium.

The second type of titration is an indirect titration. This is accomplished by determining the concentration of a different species present in solution whose concentration is related to the concentration of the desired analyte. For example, one can determine the concentration of chloride in a calcium chloride solution by titrating with EDTA for calcium. The concentration of chloride can then be determined from that as for every mole of calcium present there will be two moles of chloride in solution.

The third type of titration is a back titration. This type of titration involves adding an excess of a species that reacts with the analyte and then measuring the excess amount of the added species added via titration. This is what will be done in this particular lab.

In this lab, the unknown will be reacted with an excess of reagent (BaCl2) which will allow the sulfate to precipitate out of solution as BaSO4. The excess barium in the solution will then be titrated with EDTA. The EDTA will bind to barium allowing you to determine exactly how much excess barium was added to the solution initially. Simple stoichiometric calculations follow allowing you to determine the amount of sulfate that was initially in the unknown. An example of such calculations follows.

Suppose an indirect EDTA titration was performed on a water sample to determine the sulfate content. To a 50.00 mL aliquot of the water sample, 10.00 mL of 0.0100 M BaCl2 was added so that all of the SO42- was precipitated out as BaSO4. The excess Ba2+ was then titrated with 0.00500 M EDTA. If it took 8.58 mL of EDTA to reach the endpoint, what is the molarity of SO42- in the water sample?

It is necessary to first calculate the number of moles of Ba2+ that were added to the solution.

(0.0100 M BaCl2) / (0.01000 L) = 1.00 × 10-4 moles Ba2+ total.

Now we find how many moles of Ba2+ were left after the precipitation. We know that EDTA complexes in a 1-to-1 ratio with barium so the calculation is as follows:

(0.00500 M EDTA) (0.00858 L EDTA) = 4.29 × 10-5 moles EDTA

= 4.29 × 10-5 excess moles Ba2+

This excess amount of barium is then subtracted from the total number of moles added to find the number of moles of barium that reacted with the sulfate. Again, the reaction occurs in a 1:1 ratio so the difference between the number of moles of barium is the number of moles of sulfate:

(1.00 × 10-4 moles Ba2+ total) – (4.29 × 10-5 excess moles Ba2+) = 5.71 × 10-5 moles SO42-

Finally one can use the volume of the sample to determine the concentration of sulfate in the original solution:

[SO42-] = 5.71 × 10-5 moles/(0.05000 L) = 1.14 × 10-3 M

Modifications can be made to the above calculations for determining the percent composition in a solid unknown as well.

**Procedure for the Precipitation of Sulfate**

Weigh out three 0.3 g (0.1 mg) dried unknown sulfate samples into separate beakers (250-400 mL beakers will work will). Add about 50 mL distilled water to the beaker and dissolve the sample. Record the exact volume of water added. Add 50 µL of concentrated HCl to adjust the pH to 3-4. Heat the solution to 90°C with a watch glass on top of each beaker. While stirring, slowly add 28 mL of 0.125 MBaCl2 over a 3-5 minute period with low heat. This is best accomplished by delivering the BaCl2 solution via buret. Record the exact volume of BaCl2 solution that you added. Once all the BaCl2 has been added, keep the solution hot (DIGEST) for 1.5 hours.

After the above BaSO4mixture has been heated for 1.5 hours, let it cool to room temperature. Add about 50 mL of distilled water and record the exact volume added. Cover the solution and store it in your cabinet until the next lab period.

The following steps may not need to be done if the student has saved the standardized EDTA solution from the lab titrating calcium and magnesium.

**Preparation and Standardization of EDTA**

While the above solution is digesting, prepare and standardize a 0.01 M EDTA solution. Place about 300 mL of water in a 600 mL beaker and begin heating. Weigh out about 1.86 g of EDTA and add it to the warm water. When the EDTA is fully dissolved, let the solution cool and transfer it to a 500 mL volumetric flask. Dilute the solution to volume using MilliQ water.

Prepare a calcium standard by weighing 1.0 g dried primary standard CaCO3 to the nearest 0.1 mg. Remember to record the exact mass of CaCO3 that was used. Quantitatively transfer this to a clean 1 L volumetric flask. Add about 400 mL of MilliQ water and 6 mL of concentrated HCl to dissolve the CaCO3. After the solid is completely dissolved, dilute the solution up to the 1 L mark. Calculate the molarity of this solution using the mass weighed out 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 dropwise to the solution and checking the pH. Add 4 - 5 drops of calmagite indicator and titrate with your EDTA solution to a deep blue endpoint with no violet present. Perform at least three replicate titrations to standardize your EDTA maintaining good precision. Calculate the molarity of the EDTA.

**Titration of Excess Ba2+**

In this part of the experiment you will measure the amount of excess Ba2+ that did not react with SO42- in the water sample. You will titrate the samples that were treated with BaCl2 with your standardized EDTA solution, determine the concentration of Ba2+ in excess, and finally use this value to determine the concentration of sulfate and the percent SO3 present in the unknown.

Carefully transfer 25 mL of the supernatant to a 250 mL Erlenmeyer flask. Be very careful that you do not transfer over any of the precipitate as this will make the endpoint more difficult to observe. 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 dropwise to the solution and checking the pH. Add 4 - 5 drops of calmagite indicator and titrate with your EDTA solution to a deep blue endpoint with no violet present. Titrate the remaining samples in the same manner.

From the results of the back titration, calculate the percent of sulfur trioxide in the sample. The unknown percentages are 40-60% SO3.

**Warning: Soluble barium salts are toxic! Handle BaCl2 carefully and wash your hands thoroughly when you complete this laboratory. Dispose of excess BaCl2 as instructed.**