4

Gravimetric Analysis

Gravimetric Determination of Aluminum

Goal:

This experimental technique demonstrates one of the most precise and accurate techniques that the student will encounter this semester. It is also the only standardless method that will be used. In this experiment, a chelating agent, 8-hydroxyquinoline, will be used to bind the aluminum in an unknown sample. The complex will be isolated and then weighed to yield the % Al in the unknown. Throughout the semester, the student will be exposed to a variety of titrimetric and instrumental techniques which will, in most cases, demonstrate more rapid analysis. However, it will be difficult to replicate the precision and accuracy that it is possible to obtain from a gravimetric technique.

Reading Assignment:

Chapter 27 in Harris (6th ed.), especially sections 27-1, 27-2, 27-3.

Prelab: Questions & Calculations:

1. Calculate the formula weight of the Al $[C_9H_6ON]_3$ complex that will be formed in this experiment.

2. A solution is prepared by dissolving 4.0115 g of a solid unknown in a 250 mL volumetric flask. A 10.00 mL aliquot of this solution is pipetted into a beaker for gravimetric determination using 8-hydroxyquinoline. If the precipitate, after subtracting

the crucible and microfilter, weighed 1.2176 g, what is the % Al in the original soli sample?

3. A mixture containing only Al_2O_3 (MW 101.96) and Fe_2O_3 (MW 159.69) weighs 2.01 When heated under a stream of H_2, the Al_2O_3 is unchanged, but the Fe_2O_3 is converte metallic Fe plus $H_2O_{(g)}$. If the residue weighs 1.774 g, what is the weight percent of Fe_2O the original mixture?

BACKGROUND

In gravimetric analysis, the mass of a product is used to calculate the quantity of original analyte.[1] Gravimetric analysis is one of the oldest, most precise, and accur techniques that you will encounter in this course. A gravimetric determination usu involves a quantitative conversion of the constituent of interest and the subsequ separation and isolation of a product, of known composition, that is suitable for weighing. Historically, gravimetric analysis is significant because it was used to determine the ato masses of Ag, Cl and N to a six-figure accuracy.[2-4] Today gravimetric analysis is still wid used, typically to measure C, H, N, S, and halogens in organic compounds.[1]

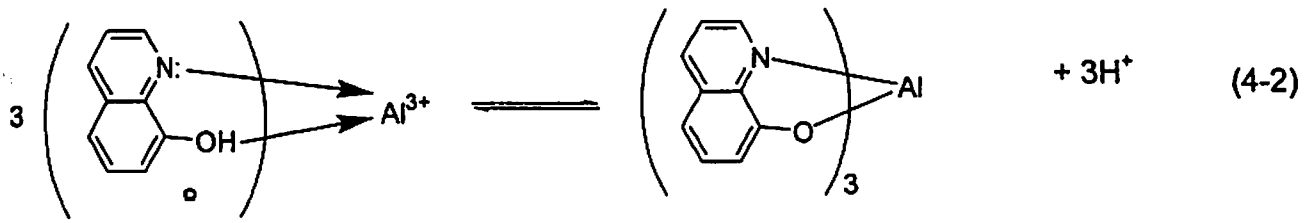
Gravimetric analyses are fairly inexpensive and require relatively simple equipmen carry out. Gravimetry is a standardless method in that no reagents need to be standardi nor is there a need for the use of a standard reference, only a calibrated balance necessary. In addition, a multitude of methods have been developed over the last cent which allow for the analysis of a large portion of the elements in the periodic tab Gravimetry also has the advantage of providing tangible results in the form of an isola product whose purity and identity can be tested if necessary.

The excellent sensitivity and accuracy of gravimetric methods is based on the dev used for the analytical measurement- - the analytical balance. With a suitable balance, i possible to obtain the weight of a few micrograms of material to within a few parts thousand, and for higher weights one can expect the weighing uncertainty to decrease t few parts per million. Few other analytical methods, especially instrumental ones, c perform up to this level. As this course progresses you will have the opportunity to perfo many analyses utilizing both titrimetric and instrumental methods. In most cases the methods will provide a much more rapid analysis; however, it will be difficult to replicate precision and accuracy that you should obtain from this first experiment.

In this experiment 8-hydroxyquinoline (8-HQ) will be used to complex the alumin in an unknown sample. In the pH range of 4.5 to 9.5, Al^{3+} reacts with 8-HQ to form insoluble chelate (complex), as illustrated by the reaction 4-1.

$$Al^{3+} + 3C_9H_6(OH)N: \rightleftharpoons Al[C_9H_6(O^-)N:]_{3\,(s)} \downarrow + 3H^+ \qquad (4\text{-}1)$$

As can be seen from Equation 4-2 below, the nitrogen atom and the phenoxide oxygen atoms of 8-HQ, which are electron rich, are the ligand atoms in this molecule, and it is these atoms that will bind to Al^{3+} through a Lewis Acid-Base type interaction.



(4-2)

8-HQ - Al Complex

The above complexation allows the aluminum in the unknown sample to be separated from the rest of the mixture, isolated, washed, dried, and then weighed; thus allowing the percent aluminum in the unknown to be accurately determined.

EXPERIMENTAL

This experiment is long if you are not well prepared and not organized you may find it difficult to finish on time. Make sure you are familiar with the procedure before you start. You do not want to make a mistake and have to start over.

- Obtain an unknown from your TA and record the unknown # in your lab notebook.
- Place a powder funnel in a clean 250 mL volumetric flask. The unknown is a fine powder and is not easily introduced into the flask so the funnel helps to facilitate this process.
- Weigh out by difference approximately 3.5 (± 0.2) g of your unknown. It is necessary that you record the exact weight to 5 significant figures. Use your wash bottle to rinse down the funnel with DI water. Remove the funnel and add DI water to the graduated mark. Mix your solution for at least three minutes to make sure all of your unknown is dissolved. Mix it again before you are ready to use this solution.
- Into each of three clean 250 mL beakers add about 90 mL of DI water and 10 mL of your unknown solution.

It is important that you make sure your unknown solution is well mixed and that all of the unknown is dissolved. Hold your solution up to the light and

make sure there are no undissolved particles floating around. In additio make sure you rinse your pipet with some of the unknown solution befo pipetting the 10 mL of your unknown into the beakers.

- While stirring, heat your solutions to around 60 - 65°C. When the temperatu has stabilized add 3.0 mL of the 8-HQ solution to each of the beakers. You ma use a graduated plastic pipet for this.

- Add 2.5 mL of 2 M NaOH to each solution. Now begin to add 2 M NaOH dro wise to each of your solutions using a clean graduated disposable plastic pipe add a few drops at a time of 2 M NaOH to each of your solutions. Continue t add NaOH drop wise until the pH is 8 (bright red on the pH 6.8 to 8.4 paper Initially, the pH may be monitored with broad-range (pH 1-12) paper until pH 6. is reached. At this time you may move to the narrow range pH strip: **Conserve this paper because it is expensive**. With each addition of NaOH check the pH. Repeat this process with all three of your solutions. **Try not t overshoot the pH**. If you do, you may be able to add a few drops of the 8-H solution to bring the pH back to 8, but this is not a guarantee solution.

- Cover your beakers with watch glasses and heat for 40-45 min. Leave th thermometer in one of the beakers to make sure the temperature stay between 60 to 70°C. Note: the temperature will increase some when th watchglass is placed over the beaker, but if you started around 60 - 65°C thi should not be a problem.

- After 25 min of heating you can remove your crucibles from the oven and plac them in your desiccator to cool for at least 20 min. After the crucibles hav cooled down, label each crucible (do not use tape!) and weigh them to four decima points. Make sure that the microfilter is in the crucible when you weigh it.

- After 45 min of heating, remove your solutions and cool them down in an ice batl Do not allow the solutions to cool down below room temperature. Also, coc down a beaker of DI water for use later.

- Securely set up a filtration flask with a crucible holder. Place the first crucible int the holder and apply vacuum. Rinse down the microfilter with DI water. Mak sure the microfilter is lying flat in the bottom of the crucible. In some cases witl smaller crucibles the mats can curl up and can let precipitate through.

- Pour the solution from the first beaker through the gooch crucible, making sur that it is rinsed well to remove all traces of the yellow precipitate. Wash the precipitate with some of the cold DI water. Also, wash any other items that were

in contact with the solution (thermometer, stir bar etc..) as well. Repeat this process for the remaining two crucibles.

- Place all the crucibles in a large covered beaker and place in the oven to dry. Your collected solids will dry at 130°C until your next class period.
- Sometime next class period you will need to remove the crucibles from the oven. Allow the crucibles to cool in your desiccator for at least 20 min. Once the crucibles are cool weigh them.

CALCULATIONS & QUESTIONS

1. Calculate the resultant weight of the $Al(HQ)_3$ compound.

2. From the three trials, calculate and report the mean, standard deviation and % RSD from the calculated weight percent values from each trial.

3. Which step in this procedure do you think contributes the most to any error which might be present in your results?

4. An analyst was using two methods (I and II) to monitor the content of Al in two lots of an aluminum nitride powder (AlN) that his company was producing. Method I involved the use of a gravimetric method to determine the % Al in the AlN. The % Al results from Method II were obtained using an atomic emission spectroscopic method called inductively coupled plasma (ICP).[5] Results were as follows:

Method I:

Lot 1	65.27 %	Lot 2	65.98 %
	65.22 %		65.80 %
	65.44 %		65.67 %
	65.50 %		65.75 %

Method II:

Lot 1	65.5 %	Lot 2	66.0 %
	65.1 %		65.5 %
	65.4 %		66.5 %
	65.8 %		65.7 %

a. Calculate the mean and standard deviation for each lot in each of the two methods.

b. Calculate the pooled standard deviation for Method I and Method II.

c. Calculate the student's t value (t_{calc}) for Method I and II.

d. For each method, is the aluminum content different at the 95% confidence level for the two Lots? Which technique offers the superior precision?

The above comparison was actually carried out by a local lab in Tuscon to compare these two analytical methods used by the analytical laboratory.

REFERENCES

1. Harris, D. C. *Quantitative Chemical Analysis*, 6th ed., W. H. Freeman and Co.: New York, 2003, pp. 680-690.

2. Richards, T. W. *Chem. Rev.* **1925**, *1*, 1.

3. Beck, C. M. *Anal. Chem.* **1994**, 66, 225A.

4. Kolthoff, I. M. *Anal. Chem.* **1994**, *66*, 241A.

5. Harris, D. C. *Quantitative Chemical Analysis*, W. H. Freeman and Co.: New York, 2003, pp. 501-502.