A Gravimetric Analysis for Chloride

In this laboratory exercise we will analyze a solution for its Chloride Ion (Cl\(^-\)) content. In order to do this we will employ a Gravimetric Analysis in which the Chloride is precipitated as AgCl. This precipitate will be collected and weighed, giving us, indirectly, the amount of Chloride originally present.

Analyses in which a given analyte is isolated from the sample and weighed in some pure form are generally known as Gravimetric Analyses. Gravimetric Analysis is one of the most accurate and precise methods of macro quantitative analysis. This method of analysis is also one of the oldest methods known:

The gravimetric methods which had been so effectively used by Bergman, Klaproth, Vauguelin, and Berzelius continued to be popular in the last half of the nineteenth century...

Gravimetric procedures were looked upon with favor because the presence of a weighable precipitate gave the analysis an air of certainty. Actually, the analysis was no more accurate than the state of chemical knowledge permitted. There was, first of all, the completeness of precipitation. This varied with the nature of the precipitates and reactants. Fortunately for early gravimetric analysis, the precipitates selected - BaSO\(_4\), AgCl, and MgNH\(_4\)PO\(_4\), for example - were sufficiently insoluble so as to create no serious difficulties. Another problem involved identifying the precipitate....

The quality of the materials used for filtering improved greatly during the nineteenth century. The term "filter" is derived from *filtrum*, the medieval Latin term for felt. This stems from the fact that felt bags were used by the alchemists for filtration; cotton or linen clothes mounted on wooden frames were also used. Lavoisier, however, concluded that unsized paper was cleaner than cloth. Berzelius introduced the use of very pure absorbent paper. J.H. Munktells, a Swedish papermaker, began to manufacture this paper around 1810.

The Development of Modern Chemistry by Aaron J. Ihde

In a gravimetric analysis, isolation of an analyte may be carried out by:

i) precipitating it in an insoluble form.
ii) depositing it as a pure metal by electrolysis.
iii) converting it to a gas which is absorbed in a suitable reagent.

Of these three typical methods, precipitation is the most common. In order for a gravimetric analysis to work, the precipitate must fulfill the following conditions:

i) Its solubility must not be large enough to cause significant error (very low K\(_{sp}\)).
ii) It form a particulate or large crystal solid.
iii) It must be sufficiently pure and in a form suitable for drying and weighing.
iv) Its stoichiometry, and preferably its Solubility Product, must be known.
Typically, an analysis is carried out by causing the analyte to precipitate from an aqueous solution. The precipitate is then filtered, washed free of impurities, and converted to a product of known composition by suitable heat treatment. This product is then weighed. The amount of analyte originally present is then determined using appropriate stoichiometric ratios.

As an example, to analyze for aqueous Calcium, an excess of Oxalic Acid is added to the analyte solution. The subsequent addition of Ammonia, which raises the pH and deprotonates the Oxalic Acid, causes essentially all the Calcium to precipitate as Calcium Oxalate:

\[
\text{Ca}^{2+} (\text{aq}) + C_2\text{O}_4^{2-} (\text{aq}) \rightarrow \text{CaC}_2\text{O}_4 (\text{s})
\]

The precipitate is collected in a weighed filtering crucible, dried, and ignited at a Red Heat. This process converts the precipitate entirely to Calcium Oxide.

\[
\text{CaC}_2\text{O}_4 (\text{s}) \rightarrow \text{CaO} (\text{s}) + \text{CO}(\text{g}) + \text{CO}_2(\text{g})
\]

The crucible and precipitate are cooled, weighed, and the mass of the Calcium Oxide determined by difference. The following stoichiometry is then applied to determine the Calcium content of the original sample:

\[
\text{# mole Ca}^{2+} = (\text{# mole CaO}) \times \left(\frac{1 \text{ mole CaC}_2\text{O}_4}{1 \text{ mole CaO}}\right) \times \left(\frac{1 \text{ mole Ca}^{2+}}{1 \text{ mole CaC}_2\text{O}_4}\right)
\]

Some commonly employed gravimetric analyses are given below:

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Precipitate Formed</th>
<th>Product Weighed</th>
<th>Interferences</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>Fe(OH)$_3$</td>
<td>Fe$_2$O$_3$</td>
<td>Many, Al, Ti, Cr, etc.</td>
</tr>
<tr>
<td>Al</td>
<td>Al(OH)$_3$</td>
<td>Al$_2$O$_3$</td>
<td>Many, Al, Ti, Cr, etc.</td>
</tr>
<tr>
<td>Ca</td>
<td>CaC$_2$O$_4$</td>
<td>CaCO$_3$</td>
<td>All metals except Alkalis and Mg.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CaO</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>MgNH$_4$PO$_4$</td>
<td>MgP$_2$O$_7$</td>
<td>All metals except Alkalis.</td>
</tr>
<tr>
<td>Zn</td>
<td>ZnNH$_4$PO$_4$</td>
<td>ZnP$_2$O$_7$</td>
<td>All metals except Mg.</td>
</tr>
<tr>
<td>Ba</td>
<td>BaCrO$_4$</td>
<td>BaCrO$_4$</td>
<td>Pb</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>BaSO$_4$</td>
<td>BaSO$_4$</td>
<td>NO$_3^-$, PO$_4^{3-}$, ClO$_3^-$</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>AgCl</td>
<td>AgCl</td>
<td>Br$^-$, I$^-$, SCN$^-$, CN$^-$, S$^{2-}$, S$_2$O$_3^{2-}$</td>
</tr>
<tr>
<td>PO$_4^{3-}$</td>
<td>MgNH$_4$PO$_4$</td>
<td>MgP$_2$O$_7$</td>
<td>MoO$_4^{2-}$, C$_2$O$_4^{2-}$, K$^+$</td>
</tr>
</tbody>
</table>

The ideal gravimetric precipitation will have only a very small amount of sample remaining in solution. Since an analytical balance, with a typical precision of 0.1mg, is used for the weighings, the precipitation should leave less than 0.1 mg of the sample in solution. In most cases a slight excess of the precipitating reagent is usually added to help drive the precipitation reaction toward completion. This excess has the effect of further reducing the solubility of the desired species by the Common Ion Effect, causing more of the precipitate to form.

Interfering chemical equilibria may also have an effect on the precipitation. Ions in equilibrium with the precipitate may be involved in other equilibria, reducing their effective concentration.
For instance, in the precipitation of Chloride Ion with Silver Ion, the presence of a slight excess of Ammonia will prevent the precipitation of Silver Chloride through the formation of Silver-Ammonia complexes.

Co-precipitation of other salts having a low solubility in the presence of the precipitating agent will increase the quantity of precipitate; generating a systematic error in the analysis. Likewise, adsorption of other chemical species from the analyte solution onto the surface of the precipitate will increase its mass and lead to another possible systematic error in the analysis. This is more likely when the surface area of the precipitate is large; i.e., the particle size is small.

There are two types of “particles” that can form during precipitation; crystalline (tend to be larger particles) and colloidal (smaller particles, frequently too small to be filtered). So that the precipitate may be efficiently filtered and collected, it must have a sufficiently large particle size. Precipitation always begins with nucleation; a process of particle formation from the homogenous solution. This is dependent on a solution that is supersaturated with material. Subsequent particle growth results from the continuing deposition of material onto these initial nuclei. To ensure that large filterable crystals are obtained the number of nucleation sites must be limited so that particle growth can dominate the precipitation process. This is achieved by mixing the reagents slowly so that the level of supersaturation is never too high. In addition, if the temperature is raised the solubility is increased and the level of supersaturation is also reduced. Larger crystals are then formed through growth as the solution cools. If nucleation dominates the precipitation process, many small colloidal particles will result. If this should occur, there are methods for forming colloidal precipitates via the coagulation of the colloidal particles.

To reduce the adsorption of other ions onto either type of precipitate, the precipitate is typically washed after filtration. If the precipitate is simply washed with deionized Water, colloidal precipitates could disperse and pass through the filter. To prevent this from happening, the wash solution is typically composed of a volatile electrolyte such as Nitric Acid. The high concentration of the electrolyte keeps the colloidal precipitate from dispersing. The volatile electrolyte exchanges with contaminant ions on the surface of the precipitate and is then driven off during drying.

In this laboratory, we will analyze a solution for Chloride Ion content. Silver Nitrate (AgNO₃) will be added to the Sample Solution, causing the precipitation of Silver Chloride (AgCl).

\[
\text{Ag}^+(aq) + \text{Cl}^-(aq) \rightarrow \text{AgCl(s)}
\]

This precipitate is then filtered, dried, and its mass determined. From the mass of the Silver Chloride, the mass of Chloride in the Solution can be determined.

Silver Chloride is a particularly insoluble salt, so we do not expect much of a reverse reaction:

\[
\text{AgCl(s)} \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq) \quad K_{sp} = 1.82 \times 10^{-10}
\]

Hence, essentially all the Chloride Ion will precipitate and can be collected.
Pre-Lab Questions

1. The Unknown Sample Solution will contain between 40% and 70% soluble Chloride Ion. Assuming a mass of about 0.2 grams of unknown sample and 0.2 M solution of Silver Nitrate precipitating agent, estimate the volume of Silver Nitrate solution that should be added to insure "complete" precipitation of the Chloride. \( \text{MW}_{\text{AgCl}} = 143.32 \text{ g/mol}; \text{MW}_{\text{Cl}} = 35.4527 \text{ g/mol}. \)

2. Suppose that a 0.2045g Unknown sample is analyzed using the procedure for this lab experiment. If the initial crucible weight is 3.0531g and the final crucible weight is 3.5016g, what is the %Cl by mass of the Unknown sample? Show all work. (Ans. 54.25% Cl by mass)
Procedure

Week 1

Prepare Crucibles
Each crucible should be cleaned and rinsed thoroughly with distilled water. If there are still stains on them, they will need to be cleaned with acid. (Consult your instructor.) Each crucible needs to be marked in some manner that will not be rubbed off, removed by heating, or change in mass. To dry, place the clean crucibles in a beaker and place in the oven. Remove the crucibles with tongs (never touch crucibles with your hands or paper for the duration of the experiment) and allow them to cool for a few minutes before placing them in a dessicator to cool to room temperature (20-30 min). Weigh crucibles to the nearest 0.0001g. Return them to the oven for 2 hours or longer and repeat weighing procedure. This procedure should be repeated until two consecutive masses agree to within $\pm 0.0003g$. It is extremely important that the crucibles be treated exactly the same way during this procedure as they will be treated when they contain the precipitate.

NOTE: You need to use the same balance throughout the course of this experiment. Switching balances when weighing the crucibles will introduce an error into your calculations and is a common cause of crucibles not coming to a constant mass. Indicate which balance you used in this experiment in your lab notebook.

Prepare and Precipitate the Unknown Sample
Record the unknown number on the assay sheet and in your notebook. Failure to do so will result in no credit being given for the completion of this experiment. Weigh three individual portions of the dried unknown sample into three separate clean 400 mL beakers. Each sample of unknown should weigh about 0.2 g, recorded to 4 decimal places. Add approximately 100 mL of distilled water to each beaker to dissolve the sample. (The exact volume is not important.) Working in the fume hood, carefully add, with the aid of a stirring rod, 1 mL of concentrated Nitric Acid to each solution. A separate stirring rod should be used with each solution and the stirring rod should be kept in the solution for the duration of the experiment. Heat the solution to about 80° C. Add 30 mL of 0.2M Silver Nitrate slowly in 8-10 portions. Use the stirring rod to pour the solution down the side of the beaker. Stir the solution carefully after each addition of the Silver Nitrate solution. Any solution or precipitate lost during any of these steps will cause large errors in the final value.

Allow for Crystal Growth
After completing the addition of Silver Nitrate, cover the beaker (and stirring rod) with a watch glass and store in your cabinet until the following week.
Between Week 1 and Week 2

Test for Completeness of Precipitation
After the precipitate settles, test the clear supernatant solution for remaining Chloride Ions by adding a few drops of Silver Nitrate solution. If additional precipitate does not form, the precipitation is complete. If precipitate does form, more Silver Nitrate solution must be added and the test for completeness must be repeated. Perform this test some time during the week between lab classes.

Week 2

Filter Precipitate
Working in the fume hood, make a precipitate wash solution by diluting ~ 2 mL of concentrated Nitric Acid to ~ 250 mL in Water. Assemble a suction flask and trap for filtration. There are only a few of these, so you may need to wait until one is available. Insert the crucible into the crucible holder on the suction flask and apply a gentle suction to the filter assembly. To begin filtration, hold the beaker at an angle so that the precipitate “nestles” in the lower corner of the beaker and decant the supernatant solution into the crucible. It is best to pour the solution along the glass stirring rod to avoid missing the crucible or loss of drops of solution. Never allow the level in the crucible to reach above 2/3 full as the solution tends to creep upward and particles may be lost over the side of the crucible. When almost all of the supernatant is decanted through the crucible, wash the AgCl precipitate in the beaker with 3 or 4 -20 mL portions of the precipitate wash solution. Add the wash solution, swirl the precipitate gently about the flask, and pour solution to crucible.

Test Filtrate for Silver Ions
Collect a few mL of the last portions of wash liquid coming through the crucible in a test tube. Add one or two drops of dilute HCl to this filtrate to test for remaining Silver Nitrate. If no turbidity (cloudiness) is observed, the filtrate is adequately washed. If cloudiness is observed, wash the precipitate further. The filtrate can be discarded down the drain with plenty of water.

Dry and Weigh Precipitate
Place the crucibles in a beaker and watch glass assembly as before and allow them to dry in the oven for several days. Weigh the crucibles as you did earlier. Repeat heating, cooling and weighing until the mass of each crucible is constant to within ± 0.0003g. Once a constant mass is reached, discard the solid in the waste container provided.

Calculate Percentage Chloride
On the basis of the three separate results, calculate and report:

i) mean percent chloride in the unknown.
ii) standard deviation
iii) 95% confidence interval.
Eliminate data using the Q-test if needed. Turn in the assay sheet one week after the crucibles-with-precipitate reach a constant mass.