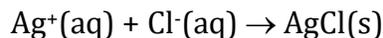


## Gravimetric Determination of Chloride

### Introduction

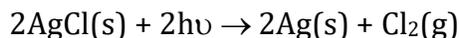
The chloride content of a soluble salt, or of an aqueous solution, can be determined by precipitation of the chloride ion as silver chloride:



The silver chloride precipitate initially forms as a colloid, which is coagulated with heat. Nitric acid and a small excess of silver nitrate aid coagulation by providing a relatively high electrolyte concentration. The solution is kept slightly acidic during the precipitation step to eliminate possible interference from anions of weak acids (for example,  $\text{CO}_3^{2-}$ ). These anions form slightly soluble silver salts in neutral solution. Nitric acid is added to the wash liquid to maintain a high electrolyte concentration and to prevent peptization during the washing step. (Peptization is the formation of a colloid by dispersion of a precipitate. Colloids pass through filter crucibles while precipitates don't.) The excess acid is volatilized during the subsequent heat treatment. Finally, the precipitate is collected in a previously weighed filtering crucible, washed, and brought to constant mass at 105 °C.

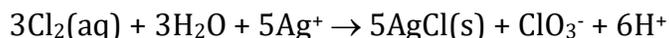
Several situations can cause significant increases or decreases in precipitate mass, and therefore poor results.

Silver chloride slowly photodecomposes by the following reaction:



Since chloride is lost as chlorine gas, the above reaction causes the results to be low. The silver metal produced during photodecomposition is responsible for the violet color that develops in the precipitate.

If photodecomposition occurs in the presence of excess silver ion, the following reaction occurs:



This causes the analytical results to be too high.

Dry silver chloride is virtually unaffected by exposure to light. As the analysis is performed, it is almost impossible to prevent photodecomposition of the wet silver chloride precipitate. Generally, the effect is small and can be ignored provided that exposure to direct sunlight, or extended exposure to fluorescent lights, is avoided. The simplest way to minimize photodecomposition is to store the silver chloride in a dark space (desk drawer).

The presence of other halides (iodide, bromide) and thiocyanate ion will cause the results to be high due to coprecipitation. Other interferences in the analysis are tin and antimony, which precipitate as oxychlorides under the analysis conditions.

Silver nitrate, like other silver salts, is relatively expensive. Use the amount of silver nitrate solution that you need for the experiment, but try to avoid wasting significant amounts of silver nitrate solution.

Solutions needed for this experiment:

Solutions prepared by the student	Solutions provided by the instructor
6 F nitric acid	Concentrated nitric acid
6 F ammonium hydroxide	0.2 F silver nitrate
	Concentrated hydrochloric acid
	Concentrated ammonium hydroxide

Specialized equipment needed:

You will need filtering crucibles and a crucible holder. These are shown in the figure below. The filtering crucible has a porous bottom.

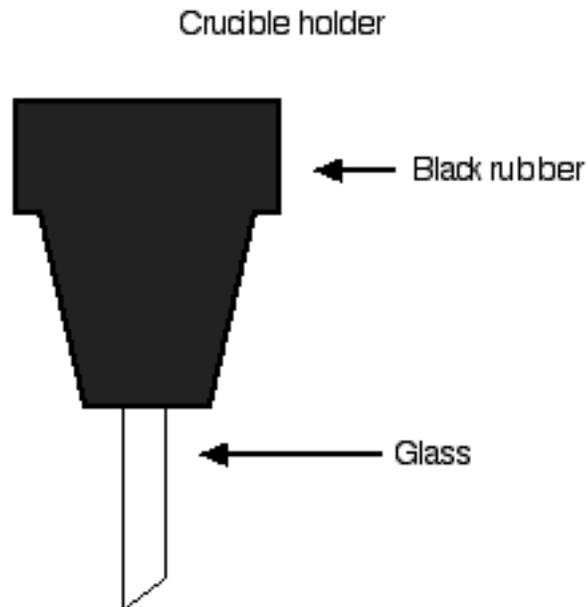
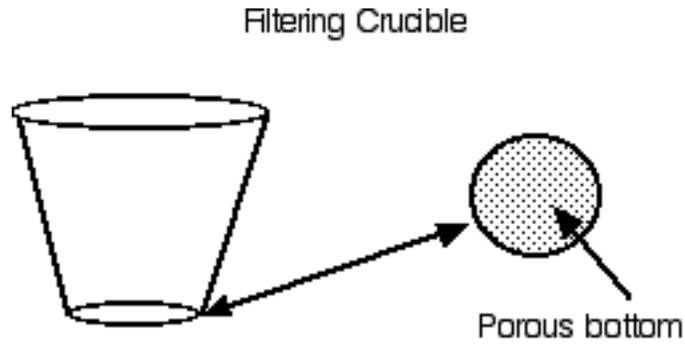


Figure 1. Filtering crucible and crucible holder.

## Experimental Procedure

1. Clean three sintered-glass crucibles using the following procedure.
  - a. Pour 5 mL of concentrated nitric acid into each crucible and let the crucibles soak for a few minutes.
  - b. Using vacuum, draw the nitric through the crucible. Then draw 3 portions of tap water through each crucible.
  - c. Discontinue vacuum and add 5 mL of 6 F ammonium hydroxide to each crucible. Let the crucibles soak for a few minutes.
  - d. Draw the ammonium hydroxide through each crucible, using vacuum. Rinse the crucible six to eight times with deionized water.
  - e. Mark each crucible with your initials and a number, and dry each crucible to constant mass by heating at 110 °C for at least 1 hour.
2. Record the unknown number, and transfer the unknown to a weighing bottle. Dry the unknown in the oven for at least 2 hours at 105 – 110 °C. After drying, store the unknown in the weighing bottle in your desiccator and allow it to cool.
3. Wash 3 beakers (600 mL) using soap and water, and rinse them with 3 portions of deionized water (25 mL portions). Clearly label these beakers so that you can tell them apart!
4. Using the analytical balance, weigh 3 individual samples of your unknown, and put each individual sample into its own clean 600 mL beaker. You must weigh the samples to 4 decimal places, and each sample should be between 0.15 and 0.20 grams. Samples slightly above 0.20 grams, or below 0.15 grams, will work. Samples significantly outside the indicated range should be avoided.
5. Dissolve each sample in about 100 mL of deionized water containing 2 – 3 mL of 6 F nitric acid.
6. Slowly, with stirring, add 0.2 F silver nitrate to each solution until the AgCl is observed to coagulate (see Notes 1 and 2 at the end of the experimental procedure). Then add 3 – 5 mL additional silver nitrate.
7. Heat the solutions almost to boiling, and digest the solid for about 10 minutes. Alternately, you can digest the precipitate at room temperature, overnight, in your locker.
8. Check for completeness of precipitation by adding a few drops of silver nitrate to the supernatant liquid. If further precipitation occurs, add 3 mL of silver nitrate, digest the solution for an additional 10 minutes, and test for completeness of precipitation. Repeat this step as often as necessary until no

further precipitation occurs. **Pour any unused silver nitrate solution into the waste container, DO NOT RETURN UNUSED SILVER NITRATE TO THE REAGENT BOTTLE!** Cover each beaker with a watch glass and store for at least 2 hours, or preferably until the next day.

9. Decant the supernatant liquid through a weighed filtering crucible. Wash the precipitate, while it is still in the beaker, with a cold solution (wash liquid) containing 2 – 5 mL of 6 F nitric acid per liter of deionized water. Decant these washings through the filtering crucible.
10. Using a stream of wash liquid and a rubber policeman, transfer all of the precipitate to the filtering crucible. Once all of the precipitate is transferred, wash it with 20 mL of wash liquid.
11. Using additional wash liquid, wash the precipitate and collect a few milliliters of the used wash liquid in a test tube. Add 2 – 3 drops of hydrochloric acid to the test tube. If a precipitate forms (indicating the presence of free silver ion), continue washing until no precipitate is formed using this test.
12. Dry the precipitates at 105 – 110 °C for at least 2 hours. Cool the crucibles in the desiccator. Determine the mass of the crucibles and their contents with the analytical balance. Repeat the cycle of heating, cooling, and weighing until consecutive weighings agree within 0.2 mg. Calculate the percentage of chloride in the sample.

After the experiment has been completed, remove the precipitates from the filtering crucibles and transfer them to the silver chloride waste container located in the waste hood. Clean the crucibles as described at the beginning of the procedure.

### Lab report

A sample lab report is shown at the end of this experiment.

### Notes:

1. Determine the approximate volume of silver nitrate solution needed by calculating the volume of silver nitrate required IF the unknown was pure sodium chloride.
2. Use a separate stirring rod for each sample and leave it in the beaker throughout the analysis.

**WASTE DISPOSAL:** Put solid silver chloride in the solid waste container. Put unused silver nitrate solution in the aqueous metals containers. Your instructor will show you the location of these containers. Liquid wastes (other than silver nitrate)

can go down the sink. Solid wastes (other than silver chloride) can go in the trashcan.

SAMPLE REPORT:

ALL VALUES ARE FICTIONAL AND ARE USED FOR ILLUSTRATION ONLY!!

STUDENTS ARE RESPONSIBLE FOR REPORTING FINAL VALUES WITH THE CORRECT NUMBER OF SIGNIFICANT FIGURES!

Gravimetric Chloride

Unknown #88

T.A. Lee ← Your name goes here, not mine!

	1 <sup>st</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>
Mass unknown, g	0.1876	0.1693	0.1932
Mass crucible, g	22.1986	20.2955	19.2289
Mass, crucible + precipitate, g	22.5279	20.6149	19.5033
Mass, precipitate, g	0.3293	0.3194	0.2744
Mass chloride, g	0.08145757	0.079008653	0.067877189
% chloride in unknown	43.42088	46.66783	35.13312

Average % chloride: 41.74

Standard deviation: 5.95

Sample calculations:

$$\begin{aligned}\text{Mass chloride} &= \text{precipitate mass} \times (\text{A.W. Cl} / \text{F.W. AgCl}) \\ &= 0.3293 \text{ g} \times (35.45 / 143.31) \\ &= 0.08146 \text{ g}\end{aligned}$$

$$\begin{aligned}\% \text{ chloride} &= (\text{mass chloride} / \text{mass unknown}) \times 100 \\ &= (0.08146 / 0.1876) \times 100 \\ &= 43.42\%\end{aligned}$$