## Gravimetric Analysis of Chloride

In this experiment you will conduct a gravimetric analysis of the chloride ion ($Cl^-$) mass percentage in an unknown solid. The method makes use of the very low solubility of silver halides. Gravimetry has the distinct advantage of being an extremely straightforward and direct method. The analyte of interest is converted into a known chemical form that is purified and weighed. This is as direct a measurement as is used in quantitative analysis, and as such, the precision and accuracy of these determinations is usually very good.

The precipitate will be filtered and weighed in Gooch crucibles, ceramic containers with a fritted bottom that can be used as a filter. You will clean the crucibles one lab period, make and filter the precipitate the following period, and weigh it (after drying for the intervening time) during the third period, requiring three weeks (overlapping other experiments) during the regular term.

### Cleaning the crucibles

**You need to do this part the period before the lab period when you are to do the experiment according to the schedule**

1. The TA will show you the vacuum filtration apparatus used for cleaning. Add 2 pumps of Conc. $HNO_3$ from the dispenser to your Gooch crucible and set it aside for 5 min. Then use the vacuum to drain the acid, making sure that all the conc. acid gone goes into the **concentrated acid wash flask**. Then stop the vacuum.

2. Transfer the crucible to the general wash flask, turn on the vacuum and rinse with DI water, filling and vacuuming each crucible 3 times with DI water.

3. Stop the vacuum; bring the crucibles back to the hood.

4. Add 5-ml of 6 M $NH_3$ and set the crucible aside for 5 min. Then use the vacuum to drain the $NH_3$ into the **general wash flask.**

5. Rinse with 6-8 portions of DI, trying to get rid of the $NH_3$ residue.

6. Dry the crucibles in the oven (in a beaker) until the next lab period. Due to limited space in the oven, you may need to share a beaker with other people, please follow your TA's advice. (Generally it's a good idea to team up with 3 or 4 other people in a big beaker, using a pencil to write your initials and the sample number on your crucibles.) DON'T USE OTHER PEOPLE'S CRUCIBLES!!! Anyone caught doing this will clean ALL of the crucibles at the end of the experiment.

***Concentrated nitric acid is very corrosive and is a strong oxidant. Be sure to wear gloves and goggles and be very careful when handling it. And recycle all the concentrated acid wash in the designated waste container.***
***To avoid acid dripping onto the floor, please have a piece of paper towel underneath the crucible when you bring it to the vacuum station. When doing the filtration, having a piece of paper underneath the crucibles to avoid discoloring the bench top, wipe the bench top after you finish at the filtration station.***
***Keep an eye on the general wash flask, if it is full, it won't function properly; discard the waste from the general wash to the gravimetric waste jar after finishing the filtration.***
***The 6 M ammonia has a pungent odor; you may wish to place the crucibles in the hood during the step where it is used.***

## Bringing the crucibles to constant mass

Dry the crucibles to constant mass by heating at 110°C while the other steps in the analysis are being carried out. The first drying took place between the two periods, so you can obtain a mass near the beginning of the class; subsequent heating periods can usually be shorter (30 to 40 min). Cool the crucibles in your desiccator before weighing and be careful that you don't handle the crucibles with your bare hands, since they will absorb water and oils from your fingers. This process of heating and drying should be repeated until the mass becomes constant to within 0.2 to 0.3 mg. The same procedure will be used for weighing the crucible with the pure silver chloride precipitate during the next experimental period.

## Preparing the silver chloride precipitate for filtering

Transfer the unknown (which should have been drying in the oven at 110°C) to your vial and allow the contents to cool to room temperature in a desiccator. Weigh individual 0.1 g (to the nearest 0.1 mg) samples and transfer them to 400-mL beakers (Note 1). Dissolve each sample in about 100 mL of distilled water to which 2 to 3 mL of 6 M $HNO_3$ have been added.

Prelab calculation: Assume that your unknown is NaCl and calculate the volume of 0.2 M $AgNO_3$ required to react completely with the chloride.

Slowly, and with continuous vigorous stirring, add 0.2 M $AgNO_3$ to each of the sample solutions until AgCl is observed to coagulate (Note 2), and then introduce an additional 3 to 5 mL of silver nitrate. Heat all of the sample solutions almost to boiling, and digest the solids for 10 min. To *digest* means to heat an unstirred precipitate in the **mother liquor** (the solution from which it was formed).

Add a few drops of $AgNO_3$ to confirm that precipitation is complete. If more precipitate forms, add about 3 mL of $AgNO_3$, digest, and again test for completeness of precipitation. Pour any unused $AgNO_3$ into the waste container (*not* into the original reagent bottle). Cover each

beaker and store in a dark place for as long as is practical - at least 2 hr. During this period, colloidal silver chloride agglomerates, producing particles that are large enough to be filtered efficiently.

## Filtering the agglomerate (precipitate)

Be sure you have labeled your crucibles. *Ask your TA if you aren't sure of the procedure for filtering precipitates.* Decant the supernatant liquids through your Gooch crucibles, using the vacuum to pull the liquid through the fine frit on the bottom of the crucible. Wash the precipitates several times (while they are still in the beaker) with a dilute $HNO_3$ solution (provided – or use 2 to 5 mL of 6 M $HNO_3$ per liter of DI water); decant these washings through the Gooch crucibles. Quantitatively transfer the AgCl from the beakers to the individual crucibles with fine streams of the dilute nitric acid wash solution; use rubber policemen to dislodge any particles that adhere to the walls of the beakers. Continue washing with the dilute nitric acid solution until the filtrates are essentially free of $Ag^+$ ion (Note 3).

Place the crucibles with the silver chloride in the beakers and back in the oven. Dry the precipitate at 110°C until the next laboratory period. During the next laboratory period, obtain a constant mass for the crucible plus silver chloride: transfer the crucibles to your desiccator while they cool; determine the mass of the crucibles and their contents; repeat the cycle of heating, cooling, and weighing until consecutive weighings agree to within 0.2 mg.

When the analysis is complete, remove the precipitates by gently tapping the crucibles over a piece of glazed paper. Transfer the collected AgCl to a container for silver wastes. Remove the last traces of AgCl by filling the crucibles with 6 M $NH_3$ and allowing them to stand for 15 min. and then use the vacuum to pull the ammonia through the frit into a catch flask (put the ammonia wash in the waste container).

## REQUIRED MEASUREMENTS

As with all of the previous labs, the PreLab calculation spreadsheet is due before you can start your work.

You will present the results for % chloride in your solid unknown (be sure to provide the unknown # as well) to your lab TA during week 8. As always, your results include the mean and relative standard deviation of your replicate determinations. You should expect the precision to be very good (ppth level) in this case.

**Sample Results Table**

| Unknown # | %Cl | Stdev | RSD (‰) |
|---|---|---|---|
| | | | |

## NOTES

**1.** Consult with the TA concerning an appropriate sample size.

**2.** Use a separate stirring rod/rubber policeman for each sample and leave it in its beaker throughout the determination.

**3.** To test the washings for $Ag^+$, collect a small volume in a test tube and add a few drops of HCl. Washing is judged complete when little or no turbidity develops.

You have to be conscious of time to get the procedure done (including the 2 hours of dark agglomeration) during the middle lab period. One suggestion is to start the period by moving your crucibles from the oven to your desiccator so that they can begin cooling. There are “down times” later in the lab when you can do the weighing.

If you are unsure of how to set up the filtration with the Gooch crucible, be sure to ask the TA for help. There isn't enough time for you to spend it figuring it out on your own.

After the digestion, you may not have enough time to allow the samples to sit in the dark for two hours. One hour should be sufficient, but if you can go longer, you will probably get better results. Use your best judgment, but leave yourself at least 40 min. for the filtering and washing steps. The goal is to have the filtered and washed silver chloride in the crucibles in the oven when you leave from the middle period (nothing to report to the TA that day, but you do have to be cleaned up).