

## EXPERIMENT 2

### Gravimetric Analysis of a Soluble Chloride

#### SAFETY AND LABORATORY TECHNIQUE NOTE

Throughout this experiment, avoid getting silver nitrate solution on your hands (or any other part of your body that you slop it on). If you do, rinse it off immediately. If you don't and then expose your body to light, the skin will turn black and might peel off in a couple of days. Essentially this is due to the photographic process; the black material coloration due to tiny silver metal particles:  $\text{AgCl} + h\nu \rightarrow \text{Ag} + \text{Cl}$ . [When very finely powdered, all metals appear black.] Don't worry, you won't die or lose the limb. This is rather more evidence of sloppy technique than it is of a health hazard. However, if you are at all concerned, seek medical advice and/or treatment.

#### UNKNOWN

Submit a clean, *dry*, labeled glass weighing bottle to the instructor so that your solid unknown chloride sample can be issued. Your name, section number, and your locker number should be written legibly on this flask with a fine-point permanent marker pen. The bottle must be dry inside and out. ***The bottle must be turned in immediately after you have checked into the laboratory, because you will have to dry the unknown for at least 1 hour in a 110° oven and cool it in your desiccator prior to use.*** Drying overnight or for several days will not harm the unknown. The solid unknown should be a free-flowing powder. If it is not, *very carefully* crush the lumps with a heavy rod or your spatula prior to putting it into the oven. Place the weighing bottle into a clean, dry, labeled 250-mL beaker with its lid tipped sideways. Cover the beaker with a watch glass and place in a drying oven.

#### TIME REQUIRED FOR COMPLETION

Three to four laboratory periods.

#### BACKGROUND

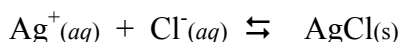
Gravimetric analysis is based on the *quantitative* isolation of the desired constituent – the *analyte* of interest – from the sample in highly pure form or in some combined form and weighing the isolated constituent. The desired constituent is usually isolated or separated by precipitation. From the weights of sample and precipitate, the percentage of the constituent in the original sample can be calculated.

Precipitation is effected by inorganic or organic precipitating agents. Two common inorganic precipitating agents are silver nitrate, which is used to precipitate halide ions such as chloride, and barium chloride, which is used to precipitate sulfate ion. Potassium, ammonium, rubidium, and cesium ions can be precipitated by sodium tetraphenylborate. In all of these precipitation reactions, the product is a salt because it is formed by reactions between cations and anions. Thus the bonding is ionic or *electrovalent*.

Organic precipitating reagents contain functional groups that combine with inorganic ions to form insoluble salts. The organic reagent may contain groups such as carboxyl or hydroxyl that ionize to form anions that combine with cations to form insoluble salts. In this reaction, the bonding is also electrovalent. Some organic reagents contain nitrogen or oxygen that can combine with metal ions by forming covalent or coordinate bonds. Other organic reagents may contain two or more functional groups that can combine with a single cation to form a ring structure. Such a reagent would be called a *bidentate ligand* if it contained two functional groups, a *tridentate ligand* if it contained three, and so forth. The product formed between a cation and some *multidentate ligand* to form a ring structure is called a *chelate*.

The three major requirements for a good gravimetric analysis are that (a) the reagent will react only with the analyte of interest to form a precipitate, (b) it forms one and only one product with the analyte and (c) that the analyte precipitates quantitatively from solution, that is, >99.99%

In aqueous solution silver ion undergoes the following reaction with chloride:



Silver chloride is a relatively insoluble compound with a solubility product  $K_{sp} = [\text{Ag}^+][\text{Cl}^-] = 1.8 \times 10^{-10}$ .

An excess of silver ion is added so that the chloride concentration at equilibrium will be negligible. If enough silver nitrate solution is not used, the precipitation will be incomplete, resulting in a substantial error and a low value for the % Cl in the sample.

## PROCEDURE

### Preparation of Filter Crucibles

1. Clean and dry three porcelain filter crucibles (see note below). Make sure crucibles are marked so they can be distinguished from one another. Use a permanent marker, not a paper or tape label.
2. Dry crucibles in the oven at 100-110 °C for one hour or overnight. The crucibles should be put in a labeled beaker and covered with a watch glass when in the oven.
3. Cool the crucibles in a desiccator for 20 minutes and weigh.

- Repeat Steps 2 and 3, this time oven-drying for only 20 minutes.
- Repeat this procedure until the mass of each crucible agrees to within 0.3 mg between weighings.

***Note: Cleaning Procedure for Porcelain Filter Crucibles***

- Scrape any large amount of gray or purplish precipitate in the crucible into the waste container for ***Solid AgCl***.
- Thoroughly wash the inside and outside of the crucible with a test tube brush and a small amount of soapy water. ***Soak off and remove all paper or tape labels.***
- If there is a gray or white residue in the crucible, add about 100 mL of water to a filter flask to dilute the rinse acid or base when it comes through. Mount the filter crucible in the filter flask, add 1-2 mL of concentrated  $\text{NH}_3$ , let it sit for a few of minutes, then apply a gentle vacuum to pull the resulting solution through the fritted bottom. Follow by rinsing with large amounts of distilled water from a wash bottle. You may need to repeat this procedure 2 or 3 more times. **NOTE: Always break the vacuum first before you turn off the aspirator water.**
- If a dark stain remains, empty the contents of the filter flask in the appropriate waste container and add a few mL of conc.  $\text{HNO}_3$  to the crucible. Let it sit for a few minutes, apply a gentle vacuum as before, and rinse the crucible thoroughly with distilled water.
- If there is a reddish stain in the crucible, empty it and add a few drops of conc.  $\text{HCl}$ . This should remove it nicely. Proceed as with  $\text{HNO}_3$  above. If the crucible does not filter rapidly (1-2 drops per second) after this cleaning, repeat the entire procedure. If it still does not drain rapidly under vacuum, consult with a TA.
- After you are completely done. Rinse the vacuum flask and crucible holder thoroughly with distilled water. Turn on the vacuum and squirt some distilled water down the rubber hose. Place the vacuum flask, crucible holder, and rubber hose back in their proper drawers.

***Hazardous Waste Note:*** The  $\text{NH}_3$  waste (basic) container is housed in a separate hood from the  $\text{HNO}_3$  and the  $\text{HCl}$  waste (acidic) containers.

**Preparation of the Chloride Unknown Samples**

- Dry the sample in an oven at 110 °C for 1-2 hours or overnight.
- Weigh out ***accurately***, by difference, three portions of the dried sample of about 0.5 to 0.7 g each to within  $\pm 0.1$  mg. **NOTE: NEVER transfer chemicals inside the balance.**
- Dissolve each portion in a clean, separate, labeled 400-mL beaker, using 150 mL of distilled water to which about 1 mL of concentrated nitric acid has been added.

4. Place a watch glass cover on each beaker.

### Precipitation of Chloride with Silver Ion

1. Heat the chloride solutions to gentle simmering on a hotplate and keep each one hot until the AgCl is fully precipitated. **Precipitate the chloride from one unknown solution at a time.**
2. Go to the hood containing the stock silver nitrate solution and carefully **pour about 80 mL of the solution into a 100-mL graduated cylinder.** [Each unknown will require about 50-70 mL to precipitate the Cl<sup>-</sup> completely. **DO NOT FILL ANY CONTAINER LARGER THAN 100 mL with the stock silver nitrate solution. Owing to severe wastage of very expensive silver nitrate in the past, any student caught filling a larger container with the stock solution will be penalized severely.**
3. Stirring constantly **with a glass stirring rod** (do NOT use a magnetic stirrer and stir bar), add the silver nitrate from the graduated cylinder in approximately 5 mL increments to your first unknown solution until the precipitation of the silver chloride is complete. To check for complete precipitation, silver nitrate must be added in small quantities and vigorously stirred. Allow the precipitate to settle a bit and add some more silver nitrate solution (no stirring yet). If the solution becomes cloudy, keep adding. If the solution remains clear, then add a total of about 5% more silver nitrate solution than you have added to that point.
4. Now place the beaker (covered) *in your locker* for at least one hour to “digest” before filtering. This minimizes exposure of the AgCl to light and consequent decomposition.
5. Repeat this precipitation and digestion for your other unknown solutions, one at a time. If you have used a graduated cylinder to monitor the volume of silver nitrate solution used for your first unknown solution, then you can then estimate about how much you need to add to the remaining samples. Simply ratio the volume to be used based on the masses of the two unknown samples that you weighed out.

### Filtration and Final Weighing

This procedure should be done separately for each sample in turn.

1. After the solution has digested for a *minimum of 1 hour*, filter the supernatant liquid through a labeled, weighed filter crucible with suction, keeping most of the precipitate in the beaker. *NOTE: Always break the suction on the flask before turning off the water flow on the aspirator.*
2. Test the filtrate in the suction flask for complete precipitation by again adding a few drops of silver nitrate solution. If your filtrate remains clear, dispose of the filtrate in the appropriate waste container.

3. Wash the precipitate with three 25-mL portions of 0.01 M nitric acid (2 drops of concentrated  $\text{HNO}_3$  per 100 mL of water) using your washing bottle. [A standard-sized washing bottle will hold about 500 mL.] The washings are poured through the filter crucible and the precipitate is left in the beaker. If any of the precipitate has dried on the sides of the beaker or the glass stirring rod, scrape them down with a rubber policeman and rinse with small amounts of the wash solution during this process to ensure that 100% of the precipitate will be filtered off into the filter crucible.
4. Stir the bulk of the precipitate up in a small volume of 0.01 M  $\text{HNO}_3$  and quantitatively transfer the precipitate to the crucible.
5. After filtering, place the crucibles in a large beaker covered with a watch glass and dry at 120-140 °C for 2 hours. You can leave the crucibles overnight, if you return the next day and put them in your desiccator.
6. Cool in a desiccator and weigh.
7. Return them to the oven for 20 minutes. Then cool in the desiccator for 20 minutes and reweigh. Repeat this step until the mass of a crucible with the precipitate agrees to within 0.4 mg.

## CALCULATIONS

Calculate the % chloride in the sample. The *gravimetric factor* is given by

$$m_{\text{Cl}} / m_{\text{AgCl}} = 35.453 \text{ g Cl}^- \text{ mol}^{-1} / 143.321 \text{ g AgCl mol}^{-1} = 0.247368 \text{ g Cl}^- / \text{g AgCl}$$

where  $m$  = the mass in grams. The mass of chlorine in each sample is therefore

$$m_{\text{Cl}} = m_{\text{AgCl}} \times \text{gravimetric factor} = m_{\text{AgCl}} \times 0.247368$$

Finally, the percent  $\text{Cl}^-$  in each sample is:

$$\% \text{ Cl}^- = (m_{\text{Cl}} / m_{\text{sample}}) \times 100\%$$

Use the  $Q$ -test if you suspect that you have an *outlying* or *spurious* value. If so, run at least one more sample through the entire procedure. Retest to see if the spurious value can be rejected. Finally report the average value for your 3 or 4 results and its standard deviation.

Remember, you can always throw out one or more values *for cause* – a specific, known reason that you have documented in your notebook. Example: “There were lots of black specks that looked like dusts belched from the air duct in replicate #2.”

## HAZARDOUS WASTE DISPOSAL

*Each of the following is to be placed in its proper, labeled Hazardous Waste Container in the hoods. If you are unsure about the container, ASK.*

*Solid AgCl Precipitate.*

*NH<sub>3</sub> Washings.*

*HNO<sub>3</sub> Washings.*

*Filtrate from Filtration of Precipitated AgCl.*

## TEST REFERENCE

D. A. Skoog, D. M. West, F. J. Holler, and S. R. Crouch, *Analytical Chemistry: An Introduction*, 7th ed., Chapter 8, pp. 179-201.

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