Experiment 1

Gravimetric Methods of Analysis

General aspects, calculations, and typical applications of gravimetric analysis are discussed in Chapter 27, pages 628-641.

GRAVIMETRIC DETERMINATION OF CHLORIDE IN A SOLUBLE SAMPLE

Introduction

The chloride content of a soluble salt can be determined by precipitation of the chloride anion as silver chloride according to the reaction:

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s) \qquad [1.1]$$

If fully precipitated, the mass of the chloride (m_{Cl}) in the AgCl(s) precipitate (m_{AgCl}) will be equal to the mass of chloride in the unknown sample (m_{unk}). From these data, the mass % of chloride in the unknown can be calculated using:

$$\%Cl = \frac{m_{AgCl} \times \dfrac{M_{Cl}}{M_{AgCl}}}{m_{unk}} \times 100\% \qquad [1.2]$$

where M_{Cl} and M_{AgCl} are the molar masses of Cl and AgCl, respectively.

Experimentally, the AgCl precipitate is collected in a weighed filtering crucible and washed; its weight is determined after it has been dried to constant weight at 110 °C.

The solution containing the sample is kept somewhat acidic during the precipitation to eliminate possible interference from anions of weak acids (such as CO_3^{2-}) that form sparingly soluble silver salts in a neutral environment. A moderate excess of silver ion is needed to diminish the solubility of silver chloride, but an excess is avoided to minimize co-precipitation of silver nitrate.

Silver chloride forms first as a colloid and is subsequently coagulated with heat. Nitric acid and the small excess of silver nitrate promote coagulation by providing a moderately high electrolyte concentration. Nitric acid in the wash solution maintains the electrolyte concentration and eliminates the possibility of peptization during the washing step; the acid subsequently decomposes to give volatile products when the precipitate is dried.

In common with other silver halides, finely divided silver chloride undergoes photodecomposition:

$$2\ AgCl(s) \rightarrow 2\ Ag(s) + Cl_2(g) \qquad [1.3]$$

The elemental silver produced in this reaction is responsible for the violet color that develops in the precipitate. In principle, this reaction leads to low results for chloride ion. In practice, however, its effect is negligible provided direct and prolonged exposure to sunlight is avoided. If photodecomposition of silver chloride occurs before filtration, the additional reaction

$$3\ C1_2(aq) + 3\ H_2O(l) + 5\ Ag^+(aq) \rightarrow 5\ AgCl(s) + ClO_3^-(aq) + 6\ H^+(aq) \qquad [1.4]$$

tends to cause high results. Some photodecomposition of silver chloride is inevitable as the analysis is ordinarily performed. It is worthwhile to minimize exposure of the solid to intense sources of light as far as possible.

Iodide, bromide, and thiocyanate, if present, precipitate along with silver chloride and may cause high results. Additional interference can be expected from tin and antimony, which are likely to precipitate as oxychlorides under the conditions of the analysis.

Experimental Procedure

Week 1: Preparation

Clean three or four sintered-glass or porcelain filtering crucibles (in a hood) by placing the crucibles in a petri dish bottom and allowing about 5 mL of concentrated HNO_3 to stand in each for about 5 min. Use a vacuum to draw the acid through the crucible. Rinse each crucible with three portions of water by drawing it through the crucible, and then discontinue the vacuum. Dump the filtrate and rinse the filter flask in the hood sink. If concentrated HNO_3 seeped onto the petri dish dilute it carefully by pouring it off into a beaker of water and then rinsing the petri dish with a wash bottle. Once dilute the HNO_3 may be poured down the hood sink.

Next, add about 5 mL of 6 M NH_3 and wait for about 5 min before drawing it through the filter. Finally, rinse each crucible with six to eight portions of distilled or deionized water, pulling the water through the filter with the vacuum. Dump the filtrate and rinse the filter flask in the hood sink before cleaning your next crucible.

After cleaning each of the crucibles, place them all in a 600-mL beaker. Write your name on a piece of paper and put it in the beaker. Cover the beaker with a watch glass supported by drying hooks and place it into an oven at 110 °C to dry until next week.

Transfer the unknown to a weighing bottle and dry it at 110 °C by leaving it in the oven until next week. Leave the weighing bottle open!

Week 2

Take out your unknown from the oven and place the weighing bottle and its contents in a desiccator. Leave the weighing bottle open until it cools down to room temperature, then close it. Close the desiccator and allow the bottle to cool to room temperature (this may take 30 min).

Thoroughly clean four 400-mL beakers with soap, rinse with tap followed by deionized water.

Weigh (to the nearest 0.1 mg) individual unknown samples into these 400-mL beakers. (Do not weigh the 400-mL beakers on analytical balances; you will have to weigh the bottle containing your unknown, tap out some amount of unknown in the first beaker and determine the mass of the unknown by difference.) Use sample sizes of approximately 0.3 - 0.4 g, but know the values to the nearest .1 mg. Read pp. 22-25 for hints on weighing.

Dissolve each sample in about 100 mL of distilled water to which 2 to 3 mL of 6 M HNO_3 have been added (first pour water, then add 6 M HNO_3).

Determine the approximate volume of 0.2 M $AgNO_3$ needed for precipitation by calculating the amount that would be required if the unknown were pure NaCl.

Slowly add this amount of 0.2 M $AgNO_3$ to each of the cold sample solutions with continuous stirring; then introduce an additional 3 to 5 mL portion. *Adding an additional 3 to 5 mL of $AgNO_3$ (source of*

Ag^+) serves *to push the precipitation equilibrium (Eqn. [1.1]) as far to the right as possible (this is an application of Le Chatelier's principle). Any Cl^- not precipitated as AgCl will not be weighed and thus, not measured, which will cause a systematic error in your measurement.*

Heat almost to boiling, and digest the solids for about 10 min with frequent vigorous stirring. *This step is necessary in order to increase the particle size of the precipitate, so it will filter more easily next week.* Add a few drops of 0.2 M $AgNO_3$ to confirm that precipitation is complete (i.e. no cloudiness develops upon addition of the $AgNO_3$). If additional precipitate forms, add about 3 mL of 0.2 M $AgNO_3$, heat almost to boiling, digest, cool down and again test for completeness of precipitation.

Pour any unused $AgNO_3$ into a waste container (NOT into the original reagent bottle). Cover each beaker and store in a dark place until the next laboratory period.

If the crucibles have been in the oven for at least a week, allow them to cool in a desiccator for at least 30 minutes, label them (a graphite pencil usually works) and THEN obtain their weight. These crucibles should be dry and at constant weight so further heating and weighing is not required. [If, for some reason, you end up cleaning your crucibles just before you need to use them, you still must dry them to a constant weight. The first drying should be for at least 1 h; subsequent heating periods can be somewhat shorter (30 to 40 min). After each heating allow the crucibles to cool in a desiccator then obtain their weight until constant weight is achieved, until consecutive weighings agree to within 0.3 mg (indicating completely dry crucibles).]

Week 3

Read the instructions for filtration in the Harris textbook (pp 30). Decant the supernatant liquids through weighed filtering crucibles – know which solution is being filtered into which crucible! Wash the precipitates (while they are still in the beaker) with a wash solution consisting of 2 to 5 mL of 6 M HNO_3 per liter of distilled water; decant the washings through the filters; repeat this procedure several times. Quantitatively transfer the AgCl from the beakers to the individual crucibles with fine streams of wash solution; use rubber policemen to dislodge any particles that adhere to the walls of the beakers.

Continue washing until the filtrates are essentially free of Ag^+ ion. To test the washings for Ag^+, collect a small volume in a test tube and add a few drops of HCl. (Don't test old filtrate from the beginning of the filtration. Test only the filtrate from the end of the filtration.) Washing is judged complete when little or no turbidity develops.

Dry the precipitates at 110 °C for at least 1 h (or preferably until next week).

Next week: Take out the crucibles from the oven and store them in a desiccator while they cool. Determine the mass of the crucibles and their contents.

Upon completion of the analysis, remove the precipitates by gently tapping the crucibles over a piece of glazed paper. Transfer the collected AgCl to a container for silver chloride wastes. Rinse out the remaining AgCl with deionized water. Remove the last traces of AgCl by filling the crucibles with 6 M HNO_3 and allowing them to stand.

Calculate the percentage of Cl^- in the sample.

Determine the standard deviation of your measurements and the 95 % confidence interval for the analysis. Hand in the sheet on the following page with your data and results for grading.

Gravimetric Analysis Results Sheet

Name: _____

Unknown Number: _____

Sample #	Unknown Mass (g)	AgCl Mass (g)	Mass % Cl^-

Mean Mass % Cl^- (Your reported result for grading) _____

Actual Mass % Cl^- (to be filled in by grader) _____

Standard Deviation Mass % Cl^- _____

95% Confidence Interval Mass % Cl^- _____

Grade _____