
INTRODUCTION TO ANALYTICAL CHEMISTRY – LAB

EXPERIMENT II GRAVIMETRIC DETERMINATION OF CHLORIDE

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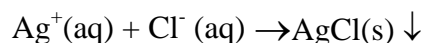
INTRODUCTION

For any given analyte, numerous analytical methods are available in the literature, each having unique advantages and disadvantages. The two most common methods for the determination of chloride ion are based on its quantitative reaction with silver ion to form silver chloride. One method involves the isolation of the silver chloride precipitate by filtration, determining its mass, and using stoichiometry to calculate the percent chloride in the sample, this is termed **Gravimetric Analysis**. Alternately, the chloride ion may be titrated with a standard solution of silver ion and the volume of titrant used to calculate the percent chloride in the sample. This **Volumetric Analysis** is often described as a precipitate-forming titration.

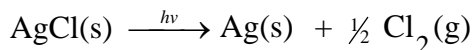
In this experiment you will obtain an unknown sample, containing chloride ion, and you will carry out a gravimetric analysis. Gravimetric methods are among the most accurate and precise methods of quantitative analysis. These advantages are counterbalanced by the fact that they are often time consuming, require considerable attention to detail and are limited to sample size and concentrations which yield a weighable quantity on a conventional analytical balance. While many gravimetric methods have been at least partially replaced by newer, faster techniques, there remain several situations where the only suitable analytical techniques are gravimetric. For these reasons you should become experienced and competent with gravimetric techniques, such as the gravimetric determination of chloride.

THEORY

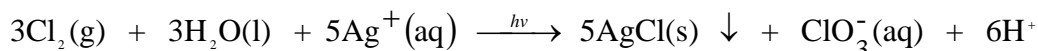
Addition of a solution containing silver ion [usually an aqueous silver nitrate (AgNO_3) solution] to a dissolved sample containing chloride ion will quantitatively precipitate the chloride ion as solid silver chloride (AgCl), due to the small solubility product constant of silver chloride ($k_{\text{sp}} = 1.82 \times 10^{-10}$). The precipitate may be isolated from solution by filtration, the material dried, weighed and the percent chloride (% Cl^-) calculated from the stoichiometry of the reaction:



In addition to possible interferences common to all gravimetric methods, the presence of any other halide will cause high results since they produce a silver halide which is even more insoluble than silver chloride. Also, silver chloride is light-sensitive and excessive photodecomposition will produce erroneous results, according to the reaction:



The precipitate becomes violet-purple, due to the presence of finely divided silver metal, and results will be low. If silver ion (Ag^+) is present, in addition to the above, the following reaction will also occur as a result of the photodecomposition reaction:



If this reaction predominates, the results will be high. To minimize such errors, it is recommended that unnecessary exposure to light be avoided.

PROCEDURE

Preparation of the Sample for Analysis

Obtain approximately 5 g of an unknown sample from your instructor in a **clean, dry**, weighing bottle. Dry the unknown material in the microwave oven at medium power for two minutes. Weigh accurately, after cooling in a desiccator for approximately 30 minutes, triplicate samples of approximately 0.5 g into numbered 400-mL beakers. Dissolve in deionized water and dilute each to approximately 150 mL volume. Add approximately 0.5 mL of reagent-grade concentrated nitric acid (HNO_3).

Preparation of Crucibles

Clean and suitability mark **three** sintered glass crucibles of **medium (M)** porosity. Your instructor will outline for you the best method of cleaning the crucibles, as the method of cleaning is dependent upon their past history. Then place the crucibles in a beaker and bring the crucibles to constant weight in the microwave oven at medium power. The first heating should be at least 30 seconds; let the crucible cool, heat for a further 30 seconds, cool, then finally heat for 4 minutes. Re-heat for 2-minute periods until constant weight is obtained. The weight should become constant to within ± 0.3 mg.

Preparation of Precipitating Reagent

An aqueous solution of 0.5 M silver nitrate (AgNO_3) is available in the laboratory. Assuming the unknown to be pure sodium chloride, calculate the volume of the silver nitrate solution required to just precipitate all the chloride ion in each sample. Include a 10% excess in the final volume to compensate for the fact that the calculation is based on an assumption that could be incorrect.

Precipitation

Add the calculated amount of silver nitrate solution slowly to each sample, preferably from a buret, with adequate stirring, (remember each sample will require a different volume of silver nitrate solution as each sample is of a different weight). Cover each solution with a watch glass (remember to leave the stirring rod in the beaker). Heat each solution, on a hot plate, to nearly boiling to coagulate the silver chloride precipitate. Let each solution cool and settle, then test for complete precipitation as demonstrated by the instructor. Add more precipitating reagent, if necessary, and re-check for complete precipitation. Allow each solution to digest (in the dark) at least 1-2 hours, or, if necessary overnight.

Filtration

Filter each solution through the corresponding sintered glass crucible, adhering to the guidelines for proper filtration, presented by the instructor. Be certain to "police" each beaker to assure quantitative transfer. Wash each precipitate with a solution of 1:500 nitric acid/water (nitric acid is added to prevent peptization) until the washings give a negative test for Ag^+ . After you have a negative test for Ag^+ , place the sintered glass crucible in the filtration apparatus and pull a vacuum on it for several minutes. It is important that you get the filtrate as dry as possible before drying in an oven.

NOTE: *Washings may be tested for their silver ion content by using the following procedure. After you have filtered your precipitate and washed with an initial amount of wash solution, carefully remove the filter crucible and touch the base to the surface of a clean, dry watch glass. Several drops of the residual wash will transfer to the watch glass. If this does not occur, add a small amount (1 or 2 mL) of wash solution to the filter crucible and wait for gravity to cause the transfer of some of the wash solution. Add 2-3 drops of 12 M HCl to the wash solution on the watch glass. The formation of a cloudy white solution indicates the presence of Ag^+ in the wash solution. If this occurs, reassemble and wash with ~10 mL of wash solution and retest. Repeat until a negative test for Ag^+ is obtained.*

Drying the Crucibles

Place the crucibles in a beaker covered with a ribbed watch glass (as with the empty crucibles). Dry in the oven for 1 hour; cool in a desiccator and weigh. Reheat for 15 minute periods until constant weight is obtained.

Cleaning the Crucibles

After completion of the analysis, remove carefully, without damaging the sinter, the cake of silver chloride from the crucible(s) and place the cake in the silver waste bottle. Place the crucibles in a beaker and fill each crucible with concentrated aqueous ammonia solution (**Do this in a hood**). Allow the crucibles to sit until all the silver chloride has been dissolved by the ammonia. Rinse each crucible with several portions of deionized water and air dry in a microwave oven at medium power for 4 minutes or until dry.

CALCULATION OF RESULTS

Report your results as the % CI in your sample. Be certain to report each individual value, the mean value, the absolute deviation of each value from the mean, the relative average deviation in parts per thousand, the standard deviation and the confidence interval at an appropriate confidence level. A relative average deviation of > 5 ppt (5) parts per thousand should be considered unsatisfactory.