

Precipitation Titration: Determination of Chloride by the Mohr Method

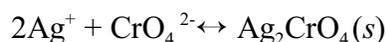
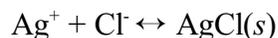
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Introduction

Titration is a process by which the concentration of an unknown substance in solution is determined by adding measured amounts of a standard solution that reacts with the unknown. Then the concentration of the unknown can be calculated using the stoichiometry of the reaction and the number of moles of standard solution needed to reach the so called end point.

Precipitation titrations are based upon reactions that yield ionic compounds of limited solubility. The most important precipitating reagent is silver nitrate. Titrimetric methods based upon silver nitrate are sometimes termed argentometric methods. Potassium chromate can serve as an end point indicator for the argentometric determination of chloride, bromide and cyanide ions by reacting with silver ions to form a brick-red silver chromate precipitate in the equivalence point region.

The Mohr method uses chromate ions as an indicator in the titration of chloride ions with a silver nitrate standard solution. After all the chloride has been precipitated as white silver chloride, the first excess of titrant results in the formation of a silver chromate precipitate, which signals the end point (1). The reactions are:



By knowing the stoichiometry and moles consumed at the end point, the amount of chloride in an unknown sample can be determined. This report describes experiments aimed at determining the concentration of chloride in a solid sample.

Materials and Methods

Equipment and Reagents:

The solid reagents used in this experiment were NaCl, CaCO₃, NaHCO₃, K₂CrO₄ and AgNO₃. The equipment used is listed below:

A buret	Transfer pipette 25 mL and pipette pump
Erlenmeyer flasks 250 mL	Desiccator
Volumetric flask 500 mL	Amber bottle
Graduated cylinder 100 mL	Wash bottle

Methods:

Preparation of 5% K₂CrO₄(indicator): 1.0 g of K₂CrO₄ was dissolved in 20 mL of distilled water.

Preparation of standard AgNO₃ solution: 9.0 g of AgNO₃ was weighed out, transferred to a 500 mL volumetric flask and made up to volume with distilled water. The resulting solution was approximately 0.1 M. This solution was standardized against NaCl. Reagent-grade NaCl was dried overnight and cooled to room temperature. 0.2500 g portions of NaCl were weighed into Erlenmeyer flasks and dissolved in about 100 mL of distilled water. In order to adjust the pH of the solutions, small quantities of NaHCO₃ were added until effervescence ceased. About 2 mL of K₂CrO₄ was added and the solution was titrated to the first permanent appearance of red Ag₂Cr₂O₄.

Determination of Cl⁻ in solid sample: The unknown was dried at 110° C for 1 hour and cooled in a desiccator. Individual samples were weighed into 250-mL Erlenmeyer flasks and dissolved in about 100 mL of distilled water. Small quantities of NaHCO₃ were added until effervescence ceased. About 2 mL of K₂CrO₄ was introduced and the solution was titrated to the first permanent appearance of red Ag₂Cr₂O₄. An indicator blank was determined by suspending a small amount of chloride free CaCO₃ in 100 mL of distilled water containing 2 mL of K₂CrO₇.

Presentation and Interpretation of Data

Standardization of AgNO₃

<i>Replicate</i>	<i>Sample, g NaCl</i>	<i>Volume of AgNO₃ used, mL</i>	<i>Concentration of AgNO₃, M</i>
Blank	-	0.20	
1	0.2500	42.90	0.1002
2	0.2750	47.20	0.1001
3	0.2500	42.80	0.1004

Calculations for Replicate 1 of standardization :

Molecular mass of NaCl = 58.44 g/mole

$$\text{mmoles of AgNO}_3 = \frac{0.2500 \text{ g NaCl}}{58.44 \text{ g / mole}} \times \frac{1000 \text{ mmoles NaCl}}{1 \text{ mole NaCl}} = 4.278 \text{ mmoles}$$

$$\text{Molarity of AgNO}_3 = \frac{4.278 \text{ mmoles AgNO}_3}{(42.9 - 0.2) \text{ mL AgNO}_3} = 1.002 \text{ M (Reagent volume corrected for blank)}$$

$$\text{Molarity of AgNO}_3 = \frac{0.1002 + 0.1001 + 0.1004}{3} = 1.002 \pm 0.001 \text{ M}$$

Determination of Chloride in Unknown

<i>Replicate</i>	<i>Weight of Unknown, g</i>	<i>Volume of AgNO₃, mL</i>	<i>% (w/w) Cl in unknown</i>
1	0.2000	26.90	47.4
2	0.2500	33.70	47.6
3	0.1800	24.30	47.6

Calculations for Replicate 1 of unknown:

Atomic mass of Cl⁻ = 35.45 g/mole

$$\text{mmoles of Cl}^- = M_{\text{AgNO}_3} \times V_{\text{AgNO}_3} = 0.1002 \frac{\text{mmoles}}{\text{mL}} \times (26.90 - 0.20) \text{ mL} = 2.675 \text{ mmoles}$$

$$\text{mass of Cl}^- = 2.675 \text{ mmoles} \times \frac{35.45 \text{ mg Cl}^-}{1 \text{ mmole}} = 94.83 \text{ mg}$$

$$\%Cl^- (\text{replicate 1}) = \frac{94.83 \text{ mg } Cl^-}{200 \text{ mg sample}} \times 100 = 47.4\%$$

%Cl⁻ in unknown = 47.5 ± 0.1

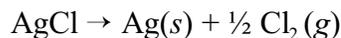
Discussion

The well known Mohr's method in which alkaline or alkaline earth chlorides react with silver nitrate in the presence of a few drops of potassium chromate solution as indicator is a simple, direct and accurate method for chloride determination.

In this experiment, the amount of chloride in an unknown sample was determined by Mohr titration. The titration was carried out at a pH between 7 and 10 because chromate ion is the conjugate base of the weak chromic acid (2, 3). Therefore, when the pH is lower than 7, chromate ion is protonated and the chromic acid form predominates in the solution. Consequently, in more acidic solutions the chromate ion concentration is too low to produce the precipitate at the equivalence point. If the pH is above 10, brownish silver hydroxide forms and masks the end point. A suitable pH was achieved by saturating the analyte solution with sodium hydrogen carbonate.

Since the solubilities of silver chloride and silver chromate depend on temperature, all titrations were carried out at about the same temperature. Good stirring during the addition of the silver nitrate is also required for a sharp and reproducible end point; otherwise, silver chromate that forms locally before the endpoint can become occluded in the silver chloride precipitate instead of redissolving.

Standard silver nitrate solution and the silver chloride precipitates formed were protected from light at all times because silver chloride decomposes according to:



The silver ion concentration at chemical equivalence in the titration of chloride with silver ions is given by:

$$[\text{Ag}^+] = \sqrt{K_{sp}} = \sqrt{1.82 \times 10^{-10}} = 1.35 \times 10^{-5} \text{ M}$$

The chromate ion concentration required to initiate formation of silver chromate under this condition can be computed from the solubility product constant for silver chromate:

$$[\text{CrO}_4^{2-}] = \frac{K_{sp}}{[\text{Ag}^+]^2} = \frac{1.2 \times 10^{-12}}{(1.35 \times 10^{-5})^2} = 6.6 \times 10^{-3} \text{ M}$$

In principle, an amount of chromate to give this concentration should be added, in order to develop the red precipitate after the equivalence point. However, a chromate ion concentration of $6.6 \times 10^{-3} \text{ M}$ imparts such an intense yellow color to the solution that formation of the red silver chromate is not readily detected. Thus, lower concentrations of chromate ion are generally used. An excess of silver nitrate is therefore required before precipitation begins. An additional excess of the reagent must also be added to produce enough silver chromate to be seen over the heavy white precipitate of silver chloride. These two factors create a positive systematic error in the Mohr method that becomes significant in magnitude at reagent concentrations lower than about 0.1 M. A correction for this error was made by a blank determination. In a blank determination, all steps of the analysis are performed in the absence of the analyte. In this experiment, blank was determined by titrating a solution of a small amount of chloride free calcium carbonate and indicator potassium chromate with standard silver nitrate solution. Calcium carbonate was used to imitate the white silver chloride precipitate. Reagent volumes were corrected for blank in the calculations.

References

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3. Kraemer E. O. and Stamm A. J. Mohr's Method for the Determination of Silver and Halogens in other than Neutral Solutions, J. Am. Chem. Soc.; **1924**; 46(12); 2707-2709.