INTRODUCTION

Volumetric methods based upon the formation of sparingly soluble silver salts are among the oldest known. These procedures were and still are routinely employed for the analysis of silver as well as for the determination of ions such as chloride, bromide, iodide and thiocyanate.

A chemical indicator is used in precipitation titration procedures to obtain a visually detectable change (usually of color change or turbidity) in the solution. For example, the formation of a second precipitate such as silver chromate, \( \text{Ag}_2\text{CrO}_4 \), of distinctive color is the basis for end-point detection with the Mohr method. The formation of a colored complex such as Iron(III) thiocyanate, \( \text{FeSCN}^2+ \), is used for the end-point detection of the back-titration with the Volhard method. Adsorption of some organic dyes such as fluorescein can be used in end-point detection with Fajans method.

Most applications of precipitation titrations are based upon the use of a standard silver nitrate solution, and are sometimes called Argentometric methods. Here, all three methods of Argentometric titrations have been discussed but only the determination of chloride ion by Mohr and Fajans methods will be studied experimentally. Generally, standard 0.1 M silver nitrate solution is used as titrant in these methods.

Analysis of Chloride Mixtures

The composition of a solution containing only \( \text{MgCl}_2 \) and \( \text{NaCl} \) can be determined by an indirect titration method by performing a precipitation titration to determine the total amount of chloride present, followed by a complex-formation titration to determine the amount of magnesium ions. A common precipitation titration technique used to determine the amount of chloride ions present in a solution is the Fajans method. On the other hand, the amount of magnesium ions present in a solution can be determined by complexometric titration with ethylenediaminetetraacetic acid, EDTA. Eriochrome Black T (Erio T) is a common indicator used for EDTA titrations. When \( \text{pH}>7 \), Erio T imparts a blue color to the solution in the absence of metal ions and forms a red color when coordinated to metal ions.

In this experiment, chloride content of the solution containing \( \text{MgCl}_2 \) and \( \text{NaCl} \) will be determined by the Fajans method. Magnesium ion concentration will be determined by EDTA titration.

REAGENTS AND APPARATUS

- \( \text{MgCl}_2 \), \( \text{NaCl} \) unknowns (already prepared)
- Standard \( \text{AgNO}_3 \) solution (already prepared, exact concentration will be given)
- \( \text{NaHCO}_3 \), a pinch
- Dextrin, a pinch
- \( \text{CaCO}_3 \), a pinch
- Dichlorofluorescein (already prepared, in droppers)
- 5 % (w/v) K$_2$CrO$_4$ (already prepared)
- buret
- 250mL conical flasks X2
- 100 mL graduated cylinder

**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 articles: $\text{AgCl} + h\nu \rightarrow \text{Ag} + \text{Cl}$. [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.

**PROCEDURE**

A) Determination of Chloride by Mohr Method

1) Take 2 unknown samples from your assistant into 250 mL conical flasks. Add 100 mL of distilled water.
2) Add NaHCO$_3$, a pinch at a time until effervescence ceases.

- The Mohr titration must be performed at a pH of about 7 or 8. If the pH is too low (pH < 6) part of the chromate ion will change into dicromate according to the following equilibrium

$$2\text{CrO}_4^{2-} + 2\text{H}^+ \leftrightarrow \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$$

Therefore the concentration of CrO$_6^{2-}$ will decrease and more Ag$^+$ ions will be required to reach stoichiometric point. In a basic medium, the silver hydroxide or silver oxide forms

At stoichiometric point

$$\text{Ag}^+ + \text{OH}^- \leftrightarrow \text{AgOH}$$
$$2\text{AgOH} \leftrightarrow \text{Ag}_2\text{O} + \text{H}_2\text{O}$$

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

$$[\text{OH}^-] = \frac{\text{K}_{sp}}{[\text{Ag}^+]} = \frac{2.6 \times 10^{-8}}{1.35 \times 10^{-5}} = 1.93 \times 10^{-3}$$

The concentration of (OH$^-$) to start AgOH precipitation will be

so

$$\text{pH} = 14 - \left[ -\log(1.93 \times 10^{-3}) \right] = 11.28$$
Therefore, pH of the solution should not be greater than 11.

3) Introduce ca. 2.0 mL of 5.0 \% (w/v) potassium chromate, K\textsubscript{2}CrO\textsubscript{4} and titrate to the first permanent appearance of a buff color (pale brown) due to silver chromate, Ag\textsubscript{2}CrO\textsubscript{4}.

- The solubility of silver chromate increases with rising temperature; its sensitivity as an indicator in this titration undergoes a corresponding decrease. Satisfactory result using the Mohr method, requires titration at room temperature.

4) Determine an indicator blank by suspending a small amount of chloride free CaCO\textsubscript{3} (white powder) in about 100 mL of distilled water containing 2.0 mL of 5.0 \% potassium chromate, K\textsubscript{2}CrO\textsubscript{4}; use the color developed due to K\textsubscript{2}CrO\textsubscript{4} in this mixture as a standard for judgment of the end point in the actual titrations.

5) Subtract the blank from the total volume used to obtain the net volume for each portion of sample.

6) Report the mg chloride in the unknown sample.

B) Determination of Chloride Ion by Fajans Method

1) Take 2 unknown samples from your assistant into 250 mL conical flasks. Add 100 mL of distilled water.

2) Add a pinch (~0.1 g) of dextrin into the sample.

- In this titration, the anionic form of adsorption indicator dichlorofluorescein is used to locate the end point. With the first excess of titrant, the indicator forms a complex with the silver ions in the counter-ion layer and imparts a red color to the precipitate. The particles of the precipitate should be kept in colloidal state in order to obtain satisfactory color change. Therefore, dextrin is added to stabilize the silver chloride (AgCl) particles against coagulation.

3) Then, add 4-5 drops of dichlorofluorescein indicator.

4) Titrate this solution with a standard AgNO\textsubscript{3} solution till the color of the solution turns to a permanent brown-green color.

- Before the end-point the color of the solution is yellow-green. This is resulted from the repelling of indicator anions by negatively charged surface of silver chloride particles. Before end-point, surface of silver chloride particles are negatively charged due to the adsorption of excess chloride ions in the solution. After all chloride ions are used in the solution by silver ions, excess silver ions are adsorbed on the silver chloride particles immediately. Thus, a positively charged layer is formed and it attracts the dichlorofluoresceinate ion displaying a pink-red color.

5) Record the volume of AgNO\textsubscript{3} solution.

6) Calculate mg of Cl\textsuperscript{-} in the solution.
C) Analysis of Chloride Mixtures (MgCl\textsubscript{2} and NaCl mixture)

\textit{c1) Determination of Total Chloride by Fajans Method}

1) Take unknown solution into a 250 mL Erlenmeyer flask. Add 100 mL of distilled water and then, add 0.1 g of dextrin into the Erlenmeyer flask.
2) Add five drops of dichlorofluorescein indicator solution.
3) Titrate the unknown solution with standard AgNO\textsubscript{3} solution until pink-red color persists.
4) Record the volume of AgNO\textsubscript{3} used in mL.

\textit{c2) Determination of Mg\textsuperscript{2+} by Direct Titration with EDTA}

1) Take the unknown solution into Erlenmeyer flask and add 100 mL of distilled water and then, add 1.0 mL of \textit{pH} 10 buffer.
2) Add 3-4 drops of Erio-T indicator solution.
3) Titrate the unknown solution with standard EDTA solution until the color changes from red to blue.
4) Record the volume standard EDTA solution used in mL.

\textit{c3) Calculations Chloride Mixtures (MgCl\textsubscript{2} and NaCl mixture)}

1) Determine the amount of Cl\textsuperscript{-} ions in millimoles in 100 mL of unknown solution.
2) Determine the amount of Mg\textsuperscript{2+} ions in millimoles in 100 mL of unknown solution.
3) Calculate the concentrations of MgCl\textsubscript{2} and NaCl in the unknown solution, in g/100 mL.

**PRE-LAB STUDIES**

Read pages 407-413 from the textbook (9\textsuperscript{th} Ed)

1) What are the main differences between precipitation titrations and neutralization titrations?
2) What are the applications of precipitation titration?
3) Explain Mohr method by writing related reaction equations.
4) What causes the dark color that forms when AgCl is exposed to light?
5) In what respect(s) Fajans method is superior to the Volhard method for the determination of chloride ion?
6) Explain briefly the working principle of adsorption indicators? Give examples.

**POST-LAB STUDIES**

1) Explain the importance of adjusting the pH of the titration medium in Mohr method. Write the related reaction equations.
2) Blank is used to dissipate the error brought about by impurities. What is the other reason of using blank in Mohr method?
3) In Mohr method, why did we use CaCO\textsubscript{3} in the blank?
4) Explain the working principle of CrO\textsubscript{4}\textsuperscript{2-} and write the importance of the concentration of it in the titration medium.
A. Determination of Chloride by Mohr Method

1st replicate: Volume of 0.10 M AgNO₃, mL=
2nd replicate: Volume of 0.10 M AgNO₃, mL=

B. Determination of Chloride Ion by Fajans Method

1st replicate: Volume of 0.10 M AgNO₃, mL=
2nd replicate: Volume of 0.10 M AgNO₃, mL=

C. Analysis of Chloride Mixtures (MgCl₂ and NaCl mixture)

c1) 1st replicate: Volume of 0.10 M AgNO₃, mL=

1st replicate: Volume of 0.10 M EDTA, mL=

c2) 2nd replicate: Volume of 0.10 M AgNO₃, mL=

2nd replicate: Volume of 0.10 M EDTA, mL=

TRUE VALUES:

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<th>Concentration, M</th>
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<th>Mass, mg</th>
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<tbody>
<tr>
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<td>NaCl (part C)</td>
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<tr>
<td>MgCl₂ (part C)</td>
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TA’s Name and Signature: