FE 211 ANALYTICAL CHEMISTRY

Experiment No. 5

PRECIPITATION TITRATIONS

Volumetric methods based on the formation of a slightly soluble precipitate are called precipitation titration. For example, formation of sparingly soluble silver salts are among the oldest known. Silver nitrate, $AgNO_3$, is the most widely used and most important precipitating reagent which is used for the determination of the halides such as chloride, Cl^-, bromide, Br-, iodide, I^-, and the halide-like anions such as thiocyanate, SCN^-, cyanide, CN^-, and etc.

The end point produced by a chemical indicator usually consists of a color change or, occasionally, the appearance or disappearance of turbidity in the solution being titrated. For example, the formation of a second precipitate of distinctive color is the basis for end-point detection with the Mohr method. Chromate ion, CrO_4^{2-}, in the Mohr method is the indicator. The end point being signaled by the appearance of brick-red silver chromate, Ag_2CrO_4, precipitate.

In the Volhard method iron (III) ion is indicator. The formation of red colored complex $FeSCN^{2+}$ is used for the end-point detection.

DETERMINATION OF CHLORIDE

A) MOHR METHOD

The Mohr method uses CrO_4^{2-} ion as an indicator in the titration of chloride ion with silver nitrate. The first excess of titrant, $AgNO_3$, results in the formation of red silver chromate precipitate, Ag_2CrO_4 (s), which signals the end point. The indicator reaction is

$$2\ Ag^+ + CrO_4^{2-} \ <====>\ \ Ag_2CrO_4\ (s)$$

B) VOLHARD METHOD

The Volhard method, as originally developed for the determination of silver, involves the titration of a solution containing the silver ion with a standard solution of either potassium thiocyanate, KSCN, or ammonium thiocyanate, NH_4SCN, and formation of a deep-red-colored ferric thiocyanate, $Fe(SCN)^{2+}$ complex with the first excess of thiocyanate ion in the titration vessel. The end point is thus marked by the appearance of a colored ion in the solution. The primary reaction in the titration is:

$$Ag^+ + SCN^- \ <====>\ \ AgSCN\ (s)$$

and the indicator reaction is

$$Fe^{3+} + SCN^- \ <====>\ Fe(SCN)^{2+}$$

Although the Volhard procedure is primarily a method for the determination of silver it may be modified to permit the determination of any ion that forms an insoluble silver salt. In principle, two general modifications are possible the direct and indirect methods. In the direct method, the ion being determined is precipitated as the silver salt by the addition of excess silver nitrate the precipitate is coagulated, filtered, washed and redissolved. The liberated silver ion may then be titrated with standard thiocyanate solution. The indirect method is much more commonly used, particularly for determination of chloride and other halides. It involves the addition an amount of standard silver nitrate solution containing the unknown anion, removal of the precipitate formed and titration of the remaining silver ion with standard thiocyanate solution. The removal of silver chloride may be accomplished by titration or, more easily, by shaking the suspension with nitrobenzene.

A) Reagents:

- Iron (III) solution
- Nitrobenzene
- Ammonium thiocyanate, NH_4SCN,
- Silver nitrate, $AgNO_3$, 0.1 M solution prepared by dissolving 8.5 g $AgNO_3$ in water and diluting to 500.0 mL.
- 6 M HNO3
- Sodium chloride, NaCl, analytical reagent grade
- Potassium chromate, K_2CrO_4, solution containing 1.0 g K_2CrO_4 per 50 mL solution.

B) Procedure:

<u>Standardization of Silver Nitrate Solution</u>

-Dry the sodium chloride, NaCl, at 110°C for one hour.

-Weigh accurately 0.2 gram NaCl and dissolve in 50 mL water in 300 mL erlenmeyer flask

-**or Take exactly 10.0 mL of prepared 0.10 M sodium chloride, NaCl, solution into an erlenmeyer flask and dilute to 50 mL**

-Add 2 mL potassium chromate, K_2CrO_4, solution.

-Titrate with the silver nitrate, $AgNO_3$, solution until the first lasting appearance of the colored precipitate which is silver chromate. The background for viewing the titration flask should be white

-Calculate the molarity of the silver nitrate solution.

<u>Determination of Chloride Ion by the Mohr Method</u>

a) If the sample is solid dry it 1 hr at 110°C weigh 0.25.to 0.35 g samples to the nearest 0.1 mg. Dissolve each in about 100 mL of water. or

b**) If the sample is given to you as a solution, take 10.0 mL and dilute it about 100 mL with distilled water.**

- Add 2 mL potassium chromate, K_2CrO_4, solution.

- Titrate with the silver nitrate, $AgNO_3$, solution until the first permanent appearance of the red color of silver chromate precipitate.

-Calculate the percentage Cl in the sample.

Determination of Chloride Ion by Volhard Method

a) If the sample is a solid, dry it at 100°C to 110°C for 1 hour. Weigh 0.25 to 0.35 g samples to the nearest 0.1 mg into 250 mL Erlenmeyer flask. Dissolve each sample in 100 mL of distilled water.

b) **If the sample is given as aqueous solution, take 5.0 mL and dilute it to about 100 mL with distilled water.**
   - Introduce an excess of standard silver nitrate, exactly 30.0 mL.
   - Acidify the solution with 1 mL of 6 M HNO_3 (Note 1).
   - Add 5 mL 0.5 M iron (III) solution and 5 mL chloride free nitrobenzene if chloride is analyzed (Note 2).
   - Shake vigorously. Titrate the excess silver nitrate with 0.1 M standard NH_4SCN until the red color of $FeSCN^{2+}$ is permanent for 1 min.

Note 1. To obtain an approximation of the volume of standard $AgNO_3$ constituting an excess, calculate the amount that would be required for one of the samples, assuming that it contains 100 percent NaCl. When actually adding silver solution to the sample, swirl the flask vigorously and add 3 or 4 mL in excess of the volume required to produce the clear point. Nitric acid, HNO_3, is added to improve observation of the clear point.

Note 2. Thiocyanate ion forms insoluble silver salt with silver ion which has a lower Ksp value than silver chloride. So,

$$AgCl(_s) + SCN^- \quad <===> \quad AgSCN(s) + Cl^-$$

reaction has to be considered and may cause a significant error. This undesired reaction may be prevented by filtering the solution before making the thiocyanate titration or by adding nitrobenzene after precipitation of the silver chloride. The nitrobenzene forms an oily coating on the particles of silver chloride and prevents reaction with the thiocyanate.

FE 211 ANALYTICAL CHEMISTRY DATA SHEET

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PRECIPITATION TITRATIONS

1. **Standardization of Silver Nitrate, $AgNO_3$, solution**

   Volume of 0.1 M $AgNO_3$ used (mL) :……

2. **Determination of Chloride Ion by Mohr Method**

   Volume of standardized $AgNO_3$ used (mL) :……

3. **Determination of Chloride Ion by Volhard Method**

   Volume of NH_4SCN used (mL) : ……

Submitted by: Submitted to:

Date: