**Week 3 :**

**Precipitation titration:**

**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.

**General Principles:**

The major precipitation reaction used is that of silver with a range of anions. These anions include:

* Chloride
* Bromide
* Iodide
* Thiocyanate

Titrations involving silver are termed argentometric, from the old name for silver, argentum.

The reaction ratio is 1:1 and silver salts formed are generally quite insoluble.

Silver nitrate solutions slowly decompose when exposed to light, so they should be kept in dark bottles.

**Chemical Indicators:**

There are three common chemical indicators that are associated with argentometric titrations:

1. The chromate ion, CrO4-2(the Mohr method);

2. The ferric ion, Fe3+ (the Volhard method);

3. Adsorption indicators such as fluorescein (the Fajans method)

**Comparison of silver titration methods:**

Method Advantages Disadvantages

Mohr Simple Alkaline solutions only

 Not suitable for iodide

Volhard Capable of direct silver and Must be 1M nitric indirect halide analyses acid solution

**Mohr method:**

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, End point is signalled by the appearance of the red silver chromate. (1). The reactions are:

Ag ++ Cl - AgCl(*s*)

2Ag+ + CrO4 -2  Ag2 CrO4 (*s*)

By knowing the stoichiometry and moles consumed at the end point, the amount of chloride in an unknown sample can be determined.

Solution during titration should be close to neutral.6-9.

Above this pH, silver starts to react with hydroxide anions, precipitating in form of AgOH and Ag2O.

Below this pH chromate converts to dichromate, a bright orange colour thereby obscuring the endpoint

Mohr’s method is suitable only for titration of chloride, bromide and cyanide

Determination of unknown of Chloride sample.

**Procedure:**

1-Pipette aliquot of chlorides solution into 250 mL Erlenmeyer flask.

2-Add 1 mL of 5% potassium chromate solution.

3-Titrate with silver nitrate solution till the first color change.

4- calculate the Concentration of NaCl

**Volhard method**

**The Theory:**

The Volhard method is based on the precipitation of silver thiocyanate in nitric acid solution with iron (III) ion employed to detect excess thiocyanate ion:

Ag+ + SCN- → AgSCN (s) **(white) Volhard Titration Reaction**

The solution turns red with first slight excess of thiocyanate ion:

Fe+ **+** SCN- → FeSCN2+ (red) **Volhard End Point Reaction**

The titration with thiocyanate is carried out in acidic solution. When the silver (I) has been precipitated as white silver thiocyanate, the excessive titrant will react with the iron (III) indicator and form a soluble red complex. The color change at the end point is not extremely sharp, but it can be detected with a little practice

In the Volhard method for determination of chloride and other anions, a known amount of standard silver nitrate solution is added to the sample solution; the amount of silver nitrate is in excess to react with the halide:

Ag+ **+** X- → AgX(s) + excess Ag+ **Titration Reaction**

The excess silver (I) is then back-titrated with standard thiocyanate

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SCN- + excess Ag+ → AgSCN(s) **Back-Titration Reaction**

SCN- + Fe3+ → Fe(SCN)2+ **End Point Reaction**

procedures:

Part1: ***Determination of unknown silver sample by Volhard method***

1-Pipette 10 ml silver nitrate solutions to a 250 ml conical flask

2-Add 5 ml of 1:1 nitric acid and 1 ml of ferric indicator

3-. Titrate with thiocyanate solution, shaking the solution thoroughly between

additions of drops. The end point is marked by the permanent appearance of the

reddish orange color of the ferricthiocyanate complex.

Part II: ***Determination of unknown KBr sample by Volhard method***

1-Pipette 10 ml of KBr solution to 250 ml conical flask.

2-add 20 ml of AgNO3 ,5 ml of 6N HNO3 and 1ml of ferric indicator

3- titrate the excess of AgNO3 by solution of KSCN from the burette ,shaking will till

reach the end point .

4- make the blank,and calculate the concentration of KBr