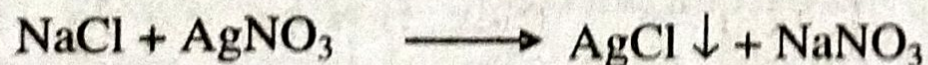


## 2.4. PRECIPITATION TITRATION

In precipitation titrations, chemical reactions result in the formation of a precipitate. In this type of titrations, standard solution and reaction substances react and lead to a slightly soluble salt as the primary reaction product or precipitate. In precipitation titrations, precipitating agents are used to determine many analytes, **for example**,  $\text{AgNO}_3$  is used as a precipitating agent for the determination of  $\text{Cl}^-$ .

Generally, precipitation reactions are not as important as redox and acid-base reactions in volumetric determinations. The reaction between sodium chloride and silver-nitrate solution results in the formation of a precipitate of silver chloride, as given in the reaction below:



**To locate the end point during precipitation titration, potassium chromate ( $\text{K}_2\text{CrO}_4$ ) solution may be used that shows precipitation of red chromate (indicating the end point) as soon as an extra drop of silver nitrate is added after complete precipitation of chloride.**

### 2.4.1. Principle

Formation of an insoluble product by the combination of two ionic species is known as **precipitation**. The completion of reaction is indicated by the precipitation of the product. Precipitation reactions are not frequently used in titration because all the precipitation reactions do not comply with the desired specifications.

In water, silver chloride is slightly soluble having  $1.79 \times 10^{-3}$  g/l at 25°C saturation limit. On adding silver nitrate solution to potassium chloride solution, the concentration of silver chloride exceeds the saturation limit, thus, resulting in the formation of precipitates. The product of the molecule concentration of its ions is constant when the salt is almost insoluble. This product is the **solubility product** of an insoluble salt.

$$SP_{AgCl} = [Ag^+] \times [Cl^-]$$

Where,  $Ag^+$  and  $Cl^-$  = Concentration in moles/l of silver and chloride ions, respectively.

### 2.4.2. Indicators used in Precipitation Titrations

The end point in precipitation titration can be marked by using a reagent, known as **indicator**, responding to the sudden rise in analyte concentration at the equivalence point. Several methods have been developed for marking the end point in precipitation titrations. The better known of these have been developed for titration involving  $Ag^+$ ; they are based on the formation of a coloured precipitate, turbidity, a coloured complex ion, precipitation titrations, and adsorption of dyes onto charged precipitate particles.

#### 2.4.2.1. Adsorption Indicators

There are certain organic dyes which are strongly adsorbed by colloidal precipitates. In a precipitation titration, this adsorption may be greater prior to equivalence point or the indicator may be more strongly adsorbed after the equivalence point. In some cases the dye undergoes a sudden change of colour in the process of being adsorbed. This may act as a means of locating the end point in a precipitation titration. These indicators are employed in Fajan's method. **For example**, sodium salt of fluorescein, sodium fluoresceinate, can be used as an indicator in the titration of chloride with  $AgNO_3$  solution in a neutral or slightly basic medium.

Some of the commonly used adsorption indicators along with their uses and end point colour changes are given in the **table 2.3**:

**Table 2.3: Adsorption Indicators**

Indicator	Use	End Point Colour Change	Experimental Conditions
Fluorescein	$Cl^-$ , $Br^-$ , $I^-$ with $Ag^+$	Yellow green $\rightarrow$ pink	Neutral or weakly basic solution
Dichlorofluorescein	$Cl^-$ , $Br^-$ , with $Ag^+$	Yellow green $\rightarrow$ red	pH range 4.4 to 7
Tetrabromofluorescein (eosin)	$Br^-$ , $I^-$ with $Ag^+$	Pink $\rightarrow$ red violet	Best in ethanoic acid solution
Tartrazine	$Ag^+$ with $I^-$ or $SCN^-$ ; $I^- + Cl^-$ ; excess $Ag^+$ , back titration with $I^-$	Colourless solution $\rightarrow$ green solution	Sharp colour change in $I^- + Cl^-$ , back titration

### 2.4.3. Precipitation Titration Methods

The precipitation titrations using silver nitrate with chlorides, bromides, iodides, and thiocyanates are most widely used. These precipitation titrations are also known as **argentometric titrations**, since silver is always involved during the reaction. Therefore, concluding that these titrations have limited use.

As per the end point detection method, four main procedures are used depending on the type of application. These procedures are as follows:

- 1) Mohr's method,
- 2) Volhard's method,
- 3) Modified Volhard's method, and
- 4) Fajan's method.

#### 2.4.3.1. Mohr's Method

This method is named after **Karl Friedrich Mohr**. In this method, potassium chromate is used as an indicator which produces red coloured silver chromate at the end point when all the chloride ions have reacted.

In Mohr's method, the end point is detected when a coloured precipitate of chloride or bromide is formed. A neutral solution of chloride ions is titrated with silver nitrate solution using a small quantity of potassium chromate solution as an indicator. The chromate ions combine with silver ions at the end point, forming a red coloured and sparingly soluble silver chromate.

#### Preparation and Standardisation of 0.1M Silver Nitrate Solution

- 1) 1.2gm of NaCl or 1.6gm of KCl is dissolved in water contained in a 250ml volumetric flask.
- 2) An aliquot of 50ml from this solution is pipetted out into a clean 250ml conical flask and 2ml of 0.1M potassium chromate indicator is added.
- 3) A burette is filled with  $\text{AgNO}_3$  solution and the initial reading is noted.

- 4) Thereafter,  $\text{AgNO}_3$  solution is added to chloride solution (swirling the titration mixture constantly) till a red colour of silver chromate ( $\text{Ag}_2\text{CrO}_4$ ) appears and spreads throughout the solution, thus, indicating the end point.
- 5) Formation of white curdy  $\text{AgCl}$  lumps also indicates that the end point is near.
- 6) At this point,  $\text{AgNO}_3$  solution is added drop wise till the yellow coloured  $\text{CrO}_4^{2-}$  ions permanently changes to a red coloured silver chromate precipitate.
- 7) If required, an indicator blank is run and then the procedure is repeated in the form of two similar titrations in order to obtain a concordant set of readings.

**Calculations:** Let the weight of  $\text{NaCl}$  taken in a 250ml volumetric flask with 0.1N standard solution be =W gm

$$\therefore \text{Normality of standard NaCl solution} = \frac{4W}{58.5}$$

$$\therefore \text{Normality of AgNO}_3 \text{ solution, } N_{\text{AgNO}_3} = \frac{4W}{58.5} \times 50 \times \frac{1}{V_1}$$

Where,  $V_1$  = Volume of  $\text{AgNO}_3$  solution (burette reading) used.

### 2.4.3.2. Volhard's Method

Volhard's method, named after **Jacob Volhard**, is a type of back titration.

In this method, a soluble coloured compound forms at the end point. Thiocyanate is used to titrate silver ion in an acidic solution using ferric ion as an indicator. Initially, precipitate of silver thiocyanate is formed and after the equivalence point (when all the  $\text{Ag}^+$  ions have been reacted), the excess of thiocyanate added reacts with  $\text{Fe}^{+++}$  giving a reddish brown coloured ferric thiocyanate.

This method is precise and commonly used for determining halides by adding a measured excess of standard silver nitrate to the halide solution of chloride. Silver chloride precipitates completely and excess of  $\text{Ag}^+$  ions are back titrated with standard ammonium or potassium thiocyanate using  $\text{Fe}^{+++}$  as an indicator. A reddish brown coloured ferric thiocyanate is formed at the end point of the back titration.

#### Sources of Error during Volhard's Titration

Following are the sources of error in Volhard's titration:

- 1) A premature end point occurs during the back titration as the  $\text{Ag}^+$  ions get adsorbed on the surface of  $\text{AgCl}$  precipitate. Vigorous shaking of the mixture before back titration overcomes this problem as it causes desorption of  $\text{Ag}^+$  ions. Then the mixture is boiled for a few minutes and the use of potassium nitrate prevents the resorption of  $\text{Ag}^+$  ions.
- 2) The two sparingly soluble salts ( $\text{AgCl}$  and  $\text{AgSCN}$ ) are in equilibrium with the solution, hence:

$$\frac{[\text{Cl}^-]}{[\text{SCN}^-]} = \frac{K_{\text{sp}}(\text{AgCl})}{K_{\text{sp}}(\text{AgSCN})} = \frac{1.2 \times 10^{-10}}{7.1 \times 10^{-13}} = 169$$

The thiocyanate may react with the  $\text{AgCl}$  precipitate when all the excess of  $\text{Ag}^+$  has reached. Silver thiocyanate salt is less soluble until the ratio  $\frac{[\text{Cl}^-]}{[\text{SCN}^-]}$

in solution is 169. Therefore, at the end point of the back titration, excess of  $\text{SCN}^-$  will react with  $\text{Ag}^+$  from  $\text{AgCl}$  instead of the indicator  $\text{Fe}^{+++}$  ions, resulting in a higher end point. The reaction between thiocyanate and silver chloride should be prevented to overcome this problem.

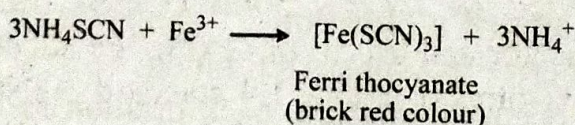
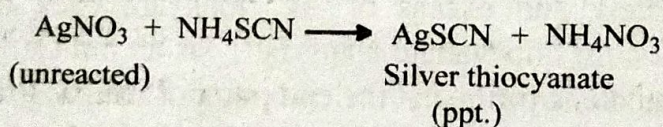
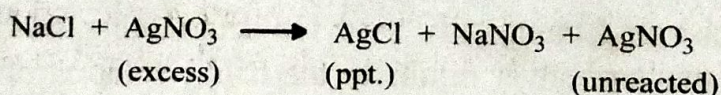
However, this is **affected** in several ways:

- i) The  $\text{AgCl}$  precipitate is boiled for a few minutes, the precipitate is removed by filtration, and then the cold filtrate is back titrated.
- ii) The  $\text{AgCl}$  particles are prevented from reacting with thiocyanate by coating with an immiscible liquid, e.g., nitrobenzene.

### 2.4.3.3. Modified Volhard's Method (I.P. 1985)

The principle of assay by Volhard's method is based on indirect volumetric precipitation titration. In this method, nitric acid solution is used to acidify  $\text{NaCl}$  (or other chloride) solution; and then in the presence of nitrobenzene, this solution is treated with measured excess amount of standard solution of silver nitrate. Some moles of silver nitrate are consumed in the reaction with  $\text{NaCl}$  and the remaining unreacted silver nitrate is determined by titrating with a standard solution of ammonium thiocyanate. In this titration, solution of ferric ammonium sulphate (ferric alum) is used as an indicator.

**Nitrobenzene** forms an organic layer around the precipitate particles of silver chloride, thus, rendering it completely insoluble. This prevents silver chloride to react with ammonium thiocyanate. The **nitric acid** added prevents ferric ammonium sulphate solution (i.e., the indicator) to hydrolyse. Formation of a permanent brick red colour due to the formation of ferric thiocyanate indicates the attainment of end point.



#### Procedure

- 1) Accurately weighed 0.1gm of sodium chloride is dissolved in 50ml of water in a glass stoppered flask.
- 2) In this solution, 50ml of 0.1N silver nitrate, 3ml of nitric acid, 5ml of nitrobenzene, and 2ml of ferric ammonium sulphate are added.
- 3) This mixture is titrated with 0.1N ammonium thiocyanate till a reddish yellow colour is attained marking the end point.

#### Calculations

Eq. wt. of  $\text{NaCl}$  = Mol. wt. of  $\text{NaCl}$  = 58.44gm

Therefore, 1000 ml of 1N  $\text{AgNO}_3$  = 58.44gm of  $\text{NaCl}$

1ml of 1N  $\text{AgNO}_3$   $\equiv$  0.05844gm of  $\text{NaCl}$

#### 2.4.3.4. Fajan's Method

Fajan's method, named after **Kazimierz Fajan**, uses dichlorofluorescein as an indicator and the end point is observed when the green coloured suspension turns pink.

**Kazimierz Fajan** introduced a useful indicator for precipitation titration by studying its nature of adsorption. At the equivalence point, these indicators get adsorbed on the precipitate, resulting in a colour change. These indicators are either basic dyes (e.g., rhodamine series) or acidic dyes (e.g., fluorescein, eosin etc.)

This method uses the property of a colloidal precipitate to adsorb its own ions present in excess amount. When sodium chloride is titrated with silver nitrate, excess of chloride ions get adsorbed on the silver chloride precipitate forming uniform layers. Thus, the primary adsorbed layer of chloride ions holds the secondary adsorbed layer of  $\text{Na}^+$  ions.

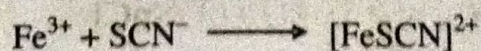
After the equivalence point, the silver chloride adsorbs excess of  $\text{Ag}^+$  ions present as a **primary adsorbed layer** and  $\text{NO}_3^-$  ions as a **secondary adsorbed layer**. If the solution contains sodium salt of fluorescein,  $\text{AgCl}$  will absorb the negatively charged fluorescein ions as the secondary adsorbed layer, instead of  $\text{NO}_3^-$  ions. Due to this adsorption, a pink coloured complex of  $\text{Ag}^+$  and modified fluorescein ions is formed at the end point, turning the solution pink.

Fajan's method has the following applications:

- 1) **Standardisation of the Unknown NaCl Solution:** 25ml of the given NaCl solution (of unknown concentration) is pipetted out in a 250ml conical flask. 10 drops of dichlorofluorescein indicator and 0.1gm of dextrin are added to the solution. The resultant solution is titrated with  $\text{AgNO}_3$  solution and a minimum of three concordant readings are recorded. For further calculations, the volume of  $\text{AgNO}_3$  solution used this time is assumed to be  $V_2$  ml and the strength of NaCl in gm/lit and percentage of chloride in the sample are calculated. Fluorescein or its sodium salt can also be used as an indicator instead of dichlorofluorescein.
- 2) **Standardisation of  $\text{AgNO}_3$  Solution:** Self-prepared 25ml of 0.1N standard NaCl solution is pipetted out in a 250ml conical flask. 10 drops of dichlorofluorescein indicator and 0.1gm of dextrin are added to the solution. The resultant solution is titrated with 0.1N standard  $\text{AgNO}_3$  solution. The titration is performed repeatedly by taking 2-3 aliquots of NaCl solution to get a minimum of two consecutive readings. Therefore, adsorption indicators can be used for standardising  $\text{AgNO}_3$ .
- 3) **Determination of Complexes:** In the presence of nitric acid,  $\text{AgNO}_3$  solution is titrated with KSCN or  $\text{NH}_4\text{SCN}$  solution using iron (III) alum as an indicator. The end point in this case is marked with the formation of a white coloured  $\text{AgSCN}$  precipitate.



As the reaction moves forward to achieve end point where all  $\text{Ag}^+$  ions have reacted completely, a drop of thiocyanate solution is added which produces a reddish-brown colour of  $\text{FeSCN}^{2+}$  complex.



## 2.4.4. Applications of Precipitation Titrations

Following are the pharmaceutical applications of precipitation titrations:

- 1) Precipitation reactions are applicable in removal of salts from water during water treatment, in qualitative inorganic analysis, and also in manufacturing of pigments.
- 2) The products of any reaction can also be isolated during work-up by the precipitation reactions. As the product of a reaction is insoluble in the solvent, it precipitates forming pure crystals.
- 3) Precipitation reactions are also used in metallurgy for **solid solution strengthening process** in which precipitate from a solid solution is used to strengthen alloys.
- 4) When an **anti-solvent** (a solvent in which the product is insoluble) is added, precipitation occurs, thus, reducing the solubility of the desired product. After this, the precipitate formed is easily separated by filtration, decantation, or centrifugation.