



“बेटी बचाओ, बेटी पढ़ाओ”

**JAYOTI VIDYAPEETH WOMEN'S UNIVERSITY, JAIPUR**  
**FACULTY OF PHARMACEUTICAL SCIENCE**

**Faculty Name** : JV'n Dr. Parveen Parihar  
**Course** : B. Pharm (1<sup>st</sup> Sem)  
**Session** : Pharmaceutical Analysis–  
(Precipitation Titration)

**Academic Day starts with–**

- Greeting with saying ‘**Namaste**’ by joining Hands together following by 2-3 Minutes Happy session, Celebrating birthday of any student of respective class and National Anthem

**Precipitation Titration**

**Precipitation titration:**

Precipitation titration is a type of titration which involves the formation of precipitate during the titration technique. In precipitation titration, the titrant reacts with the analyte and forms an insoluble substance called a precipitate. It continues till the last amount of analyte is consumed. It is used to determine chloride by using silver ions.

**Principle :**

The principle of precipitation titration can be shown as follows –

Quantity of added precipitating reagent = quantity of substance being precipitated

### **Precipitation Titration curve:**

precipitation titration curve, a graph is drawn between change in titrant's concentration as a function of the titrant's volume. A precipitation titration curve is given below for 0.05M NaCl with 0.1M AgNO<sub>3</sub>.

**Reaction involves is as follows –**



### **Argentometric Titration**

It is a type of precipitation titration which involves the use of silver ions. The symbol of silver is Ag which is taken from its Latin name Argentum. So, the word argentometric is also taken from the Latin word Argentum.

### **Methods of Argentometric Titration**

#### **Volhard's Method**

#### **Fajan's Method**

#### **Mohr's Method**

#### **Volhard's Method**

German Chemist- Jacob Volhard This method was first given by German Chemist Jacob Volhard in 1874. This method involves the determination of halide (F, Cl, Br, I) ions, anions like phosphate, chromate in acidic medium by using silver ions. This titration must be performed in an acidic medium otherwise iron ion get precipitated as hydrated oxide. Iron ions are used as indicators in Volhard's method. In this method, 1<sup>st</sup> analyte (halide ion solution or any other anionic solution) is titrated with a measured excess of AgNO<sub>3</sub>.

Reaction – If the analyte contains chloride anions. The reaction will be as follows -



Now the unreacted or in excess silver ions are titrated with a standard solution of KSCN using iron ion ( $\text{Fe}^{+3}$ ) as an indicator which gives red color in the end point. Reaction – The reaction can be shown as follows-



Now as the thiocyanate ion will be in excess in the titration mixture, red colour appears which is due to the formation of the  $\text{FeSCN}(\text{II})$  compound. Reaction – Reaction involved can be shown as follows –



It is an indirect method of precipitation.

### **Fajan's Method**

American Chemist – Kazimierz Fajan

This method was given by American chemist Kazimierz Fajan. That's why it is known as fajan's method. This method is also known as the indicator adsorption method because in this method chloride ions present in excess are adsorbed on silver chloride surface. In this method dichlorofluorescein is used as an indicator. The end point is determined by green suspension (of  $\text{AgCl}$  and indication) turning pink (complex of  $\text{AgCl}$  and indicator). Reaction – reaction involved can be written as follows –



It is a direct method of precipitation.

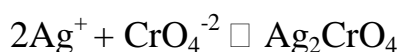
### **Mohr's Method**

Karl Friedrich Mohr

This method was given by Karl Friedrich Mohr, a German Chemist. That's why this method is called Mohr's method. It's a direct titration method. In this method silver nitrate is used as titrant and chloride ion solution as analyte.

Potassium chromate is used as an indicator. At the end point, when all chloride ions are consumed by silver ions, reddish brown colored precipitate is formed by reaction of silver ions and chromate ions. Reaction- Reaction involved can be written as follows –  $\text{AgNO}_3 + \text{Cl}^- \rightarrow \text{AgCl} + \text{NO}_3^-$

At the end point –



### **Applications of Precipitation Titration**

- It is used for the determination of halide ions in the solution.
- It is used to measure salt content in food, beverages and water.
- It is used for Sulphur, thiocyanate, dichromate etc.
- Many drugs such as carbromal, KCl infusion, NaCl infusion etc. can be analysed by precipitation titration.
- It can be used for the determination of concentration of anions in the analyte

### **Significance of Learning the Concept of Precipitation Titration**

Learning the concept of precipitation titration is important for all chemistry students. In this topic, you will learn the various methods of formation of a precipitate using the titration technique. This process is carried out for a number of reasons, such as determining the number of halide ions in a solution, measuring the amount of salt in food items, etc. So, by learning this concept you can improve your understanding of different kinds of reactions involved in the process of precipitation titration. Below are some more reasons why learning the concept of precipitation titration is important for you.

### **Evaluation of Precipitation Titrations**

After the end point, the surface of the precipitate carries a positive surface charge due to the adsorption of excess  $\text{Ag}^+$ . Dichloro fluorescein now adsorbs

to the precipitate's surface where its color is pink. This change in the indicator's color signals the end point.

### **Evaluation of Precipitation Titration :**

The scale of operations, accuracy, precision, sensitivity, time, and cost of a precipitation titration is similar to those described elsewhere in this course such as acid–base, complexation, and redox titrations. Precipitation titrations also can be extended to the analysis of mixtures provided that there is a significant difference in the solubility of the precipitates.

Although precipitation titration is rarely listed as a standard method of analysis, it may still be useful as a secondary analytical method for verifying other analytical methods

In this unit the fundamentals of precipitation titration have been discussed and the calculations for the precipitation titration curves have been investigated . The ideas , advantages and disadvantages of each of Mohr's , Volhard's and Vajan's methods have been studied . The applications of precipitation titration are investigated

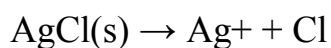
Titration curves for precipitation titrations :

Titration curves are represents : 1) The change in conc. reactants throughout titration . 2) Titration error that is likely occur when using the indicators . 3) The conditions at equivalent point .

### **End point detection precipitation titration :**

- 1) formation of a second colored precipitate (Mohr method): This method depends on formation of second highly colored precipitate for detect end point.

This method has been widely applied to the titration of chloride ion and bromide ion with silver nitrate , and the indicator is chromate ion ( $\text{CrO}_4^{2-}$ ) . the end point being signaled by the appearance of red silver chromate( $\text{Ag}_2\text{CrO}_4$ ) .



$$K_{sp}(\text{AgCl}) = 1.35 \times 10^{-5} \text{ (from previous example)}$$



$$K_{sp}(\text{Ag}_2\text{CrO}_4) = 1.2 \times 10^{-12}$$

$$K_{sp} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}]$$

$$[\text{CrO}_4^{2-}] = 6 \times 10^{-3} \text{ M}$$

The titration is performed in neutral or slightly basic medium  $\text{pH} = (7-10)$  to prevent silver hydroxide formation at  $\text{pH} > 10$  or formation of chromic acid at  $\text{pH} < 7$



The presence of an excess of either sodium hydrogen carbonate or borax in the sol. tends to maintain the hydrogen ion conc. within suitable limits

2) formation of colored complex ( Volhard method ) : Volhard method can be use as a directly method to detect  $\text{Ag}^+$  and an indirectly method to detect halides . To detect silver ion : a standard sol. of thiocyanate is use as a titrant for silver ion . Iron ion (III) is use as an indicator imparting a red coloration to sol. with first slightly excess of thiocyanate.  $\text{Ag}^+ + \text{SCN}^- \rightarrow \text{AgSCN(s)}$   $\text{Fe}^{3+} + \text{SCN}^- \rightarrow \text{Fe(SCN)}^{2+}$  The titration must be done in acidic medium to prevent the precipitate of Iron(III) as hydrated oxide (iron hydroxide) . also , most of ions in neutral or weak acid medium are gives a precipitate with  $\text{Ag}^+$  . It found from the experimental , that the red  $\text{Fe(SCN)}^{2+}$  complex color can detect at  $6.4 \times 10^{-6} \text{ M}$  . 6 To detect halides ions :volhared method can be applicated for the indirect determination of halides by measured the excess of standard silver nitrate sol. that added to the sample (halides) , and the excess of silver ion determine by back-titration with a standard thiocyanate sol.

$\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl} + \text{Ag excess}$

$\text{Ag excess} + \text{SCN}^- \rightarrow \text{AgSCN}$

Complex formation titration :

Complex ions ( coordination compounds) are produced from reaction of many metal ions (electrons acceptor) with electron pair donors . The donor species (or called ligands) must have at least one pair of unshared electrons for bond formation . Metal ions form coordination complexes with anions or molecules :

a) anionic ligands : like ,  $\text{SCN}^-$  ,  $\text{CN}^-$  ,  $\text{OH}^-$  ,.....ect.

b) molecular ligands : like ,  $\text{H}_2\text{O}$  ,  $\text{NH}_3$  ,  $\text{RNH}_2$  , .....ect.  $[\text{Ag}(\text{CN}^-)_2]$  ,  $[\text{Cu}(\text{NH}_3)_4]^{+2}$  ,  $[\text{Zn}(\text{H}_2\text{O})_4]^{+2}$

- **Next Topic-**

- Pharmaceutical Analysis– (Titration Curve for complex titration)

- **Academic Day ends with-**

National Song 'Vande Mataram'