# SHREE H. N. SHUKLA INSTITUTE OF PHARMACEUTICAL EDUCATION AND RESEARCH



## **B.PHRAM**

(SEMESTER –I)

## SUBJECT NAME: PHARMACEUTICAL ANALYSIS -I

## SUBJECT CODE: BP102TP

## **CHAPTER 3(a): PRECIPITATION TITRATION**

## Content

Precipitation titrations: Mohr's method, Volhard's, Modified Volhard's, Fajans method, estimation of sodium chloride.

### THEORY OF PRECIPITATION TITRATION

Those titrations in which chemical reactions between two solutions takes place and they will form a precipitates.

#### Examples:



#### Key points of the precipitation reaction

Precipitation is itself an ionic process, the cations comes from one solution and anion from other solution.

Thus, precipitation of ionic products forces the reaction towards completion.

#### Basic requirements of precipitation reaction useful in titrimetric analysis:

- > The precipitate must be practically insoluble.
- > The reaction should be rapid and quantitative.
- > The equivalence point or end point must be possible to detect during the titration.
- > The titration results should not be hampered by other adsorption effects like coprecipitation.

Precipitation titrations are limited to use of Ag+ ions as a precipitating agent and it will be used to determine anions like Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, SCN<sup>-</sup> etc.

It has limited use because of lack of indicator to detect the end point during the titration.

Another reason behind limited use of precipitation titration is that slow rate of precipitation reaction.

The main precipitation titrations are argentometric titrations in which standard solution of  $AgNO_3$  is used to determine the anions.

#### Theory of precipitation solubility and solubility product

Solubility which is dependent on solvent and temperature. Solubility is the concentration of the dissolved solute in moles per liter when solution is in equilibrium with a solid solute.

Concentration of saturated solution is known as solubility.

In solid state, the solute molecules occupy the space in a fixed repeatating pattern to form crystal of solid. Solute molecule held together by intramolecular forces of attraction.



For dissolving solute molecules, solvent should compete with crystal forces of solute molecules and overcome them. For that solvent environment is similar that of crystal structure. (simple rule-like dissolve like).

During the precipitation, opposite condition occurs, where the intramolecular forces between the molecules of product are high and solute-solvent forces are replaced by solute-solute forces.

**Solubility:** Concentration of saturated solution is known as solubility and no further compound/salt can be dissolved in a specified temperature.

#### Example:

For example 100 gm of water can dissolve 35 gm of NaCl at room temperature. (**Solubility is 35** g). When 36 g is added in 100 g water, then excess 1 g of NaCl cannot be dissolved.

Undissolved 1 gm of Nacl remain ass unionized form. This solution is known as saturated solution.



Here, excess amount NaCl cannot interfere in the concentration of Nacl in the solution. Therefore, concentration of NaCl [NaCl] is constant in saturated solution.

So, K $[NaCl] = Ksp$ (4)	
$Ksp = [Na^+] [Cl^-](5)$	
If $Ksp > [Na^+] [Cl^-]$	No precipitation
If $Ksp = [Na^+] [Cl^-]$	Saturated solution
If $Ksp < [Na^+] [Cl^-]$	Precipitation occurs

Relationship between solubility and solubility product

NaCl  $\longrightarrow$  Na<sup>+</sup> + Cl<sup>-</sup>

If solubility of NaCl = S Mole/L. Then it will produce S mole of Na<sup>+</sup> & S mole of Cl<sup>-</sup> in 1 L water.

 $Ksp = [Na^+] [Cl^-]$ 

 $Ksp = S \times S$ 

$$Ksp = S^2 \quad OR \quad S = \sqrt{Ksp}$$

Unit of  $Ksp = (S mole/L)^2$  where Ksp = Solubility product

S = Solubility

When, in the Case of (Complex case),

 $B_m A_n (s) \longleftarrow [B^{n+}]^m [A^{m-}]^n$ 

Unit of Ksp - (S mole/L)<sup>m+n</sup>

For e.g.  $Ag_2CrO_4 \implies 2 Ag^+ + CrO_4^{2-}$ 

(S mole/L) 2S S

 $Ksp = [2S]^2$  [S]

 $Ksp = 4S^2 \times S$ 

 $Ksp = 4S^3$  — Product of ionic concentration exceeds the Ksp value. Substance will precipitate out. Thus precipitation occurs.

## **Calculation of solubility & Solubility product**



 $Ksp = X^2$ 

 $Ksp = (6.32 \times 10^{-3})^2$  $Ksp = 4 \times 10^{-5}$ 

The solubility product of MgCO<sub>3</sub> is equal to  $4 \times 10^5$ 

## Calculation of solubility of an electrolyte

**Ex:2** Calculate the solubility of Mg(OH)<sub>2</sub> in mg/litre of Ksp (Mg(OH)<sub>2</sub>) is 6 x 10<sup>-10</sup>. Molecular weight of Mg(OH)<sub>2</sub> is 58.33.  $Mg(OH)_2$   $\longrightarrow$   $Mg^{+2}$  +  $2OH^{-1}$ If solubility of  $Mg(OH)_2$  is x. Then concentration of  $Mg^{+2}$  and  $OH^{-1}$  ions will be x. Ksp  $(Mg(OH)_2) = [Mg^{+2}] [2OH^{-}]^2$ Ksp  $(Mg(OH)_2) = [X] [2X]^2$ Ksp  $(Mg(OH)_2) = 4X^3$  $6 \times 10^{-10} = 4X^3$  $X = \frac{6 x \, 10^{-10}}{4}$  $X^3 = 1.5 \times 10^{-3}$  $X = \sqrt[3]{1.5 \times 10^{-3}}$  $X = \sqrt[3]{150 \ x \ 10^{-12}}$  $x = 5.31 \times 10^{-14}$ Solubility = Molar solubility x Molecular weight  $= 5.31 \times 10^{-4 \times 58.33}$  $S = 31.10^{-3} \text{ mg/litre}$ Solubility of Mg(OH)<sub>2</sub> is 31 x 10<sup>-3</sup> mg/litre

Sr. No.	Questions	Answer
1	Titrations in which chemical reactions between two solutions	Precipitation Titration
	takes place and they will form a precipitates is known as	
2	The solubility of precipitate in precipitation titration must be	Practically insoluble

3	In most of precipitation titration precipitating agent used is	AgNO <sub>3</sub>
4	Precipitation titration is also known as	Argentometric titration
5	Precipitation titration is used to determine	Halides like Cl, Br, I, F
		& SCN
6	Concentration of saturated solution is known as	Solubility
7	is the concentration of the dissolved solute in	Solubility
	moles per liter when solution is in equilibrium with a solid	
	solute.	
8	Solubility mainly depends on	Solvent, Temperature
9	$Ksp > [Na^+] [Cl^-]$ indicates the	No precipitation
10	$Ksp = [Na^+] [Cl^-]$ indicates the	Saturated solution
11	$Ksp < [Na^+] [Cl^-]$ indicates the	Precipitation occurs
12	Which precipitates are formed when NaCl is reacted with	AgCl
	AgNO <sub>3</sub> ?	
13	Precipitation is itself an process	Ionic
14	The precipitate must be practically soluble. True or False?	False
15	Limited use of precipitation titration is due to	Lack of indicator,
		Slow rate of
		precipitation reaction
16	The main precipitation titration in which standard solution of	Argentometric
	AgNO <sub>3</sub> is used to determine the anions	Titrations
17	Solute molecule held together by forces of	Intramolecular
	attraction.	
18	What is the effect in concentration of NaCl is occured when	No Change
1.0	excess NaCl than its solubility is added?	
19	Solubility product is denoted by	K <sub>SP</sub>
20	Unit of Ksp is	(S mole/L) <sup>2</sup>
21	When product of ionic concentration exceeds the Ksp value,	True
	substance will precipitate out. True or False?	

### Factors affecting solubility of precipitates

- 1) Acid (pH)
- 2) Temperature
- 3) Solvent
- 4) Common ion effect

#### 1) Effect of Acid (pH):

- If we add precipitating agent (AgNO3) in to the solution containing anion (for e.g. Cl-), it will form slightly soluble salt. (AgCl).
- For sparingly soluble salts of strong acid, addition of acid will not affect.

- If salt is a conjugate base of a weak acid (HA), then acid will generally have a solvent effect upon it.
- If hydrochloric acid is added to an aqueous suspension of such a salt, the following equilibrium will be established.

(If weak acid is HA & salt is a BA)



- Here concentration of A- ion will be increased upon addition of Acid (HA).
- Due to common ion effect, reaction of weak electrolyte (HA  $\longrightarrow$  H+ + A-) moves towards backward. (Dissociation constant of acid is very small & therefore A- will be removed from the solution to form the undissociated acid HA).
- Therefore, equilibrium disturbs and more BA (salt) will be dissociate to give A- (replace the anion (A-) removed.) and this process will continue until equilibrium is established. i.e. until [B+] & [A-] has become equal to the solubility product of BA, or if sufficient hydrochloric is present, sparingly soluble salt has dissolved completely.
- Thus, solubility of sparingly soluble salt BA (precipitate) will be increased with increase in H+ concentration or decrease in pH. (By addition of pH)

#### 2) Effect of Temperature:

- The solubility of precipitates in precipitation titration will increase with rise in temperature.
- With some substances, the influence of temperature is very small, but with others it is quite more.
- As the temperature increases, the solubility of slightly soluble ionogen increases.
- The Ksp value is characteristic for a particular compound at a specific temperature.
- So, as the temperature increases Ksp value will also increases and molar concentration of ions will be less than its Ksp value.

- To maintain equilibrium more amount of ionization occurs. More solid will get dissolved so that molar concentration of ions is equal to Ksp. Solubility increases in this way.
- For e.g. Solubility of BaSO<sub>4</sub> at  $10 \text{ }^{\circ}\text{C} = 2.2 \text{ mg/l}$

Solubility of BaSO<sub>4</sub> at 100 °C = 3.9 mg/lSolubility of AgCl at 10 °C = 1.72 mg/lSolubility of AgCl at 100 °C = 21.1 mg/l

#### 3) Effect of Solvent:

- Most of inorganic compounds are soluble in water but when we add organic solvent like (methyl, ethyl & n-propyl alcohols), solubility of most of inorganic compounds can be reduced.
- For e.g. addition of 20 % alcohol (organic solvent) by volume permits quantitative separation of lead sulphate precipitates by decreasing solubility of the precipitates.

#### 4) Common ion effect:

• By adding an excess of ions of a slightly soluble salt, its solubility can be reduced. The dissociation of slightly soluble salt (precipitates) is

$$BA(s) \longleftarrow B+ + A-Ksp = [B+] [A-]$$

- This is the equilibrium condition. If however, an excess of either B+ or A- are added in the form of another salt (whole solubility) is greater than that of BA.
- Because addition of common salt [B+] or [A-], produces common ion effect and therefore more ion of any one (B+) or (A-) will be in the solution.
- Thus, product of ionic concentration ([B+] [A-]) will exceed (greater than) the solubility product (Ksp).

 $Ksp < [B+] [A-] \longrightarrow Precipitation occurs$ 

- Thus, BA will be precipitate out.
- Thus, common ion effect, decreases the solubility of slightly soluble salt (precipitates).

#### **QUESTION - ANSWER**

Sr. No.	Questions	Answer
1	Which are the factors affecting solubility of precipitates?	<ol> <li>Acid (pH)</li> <li>Temperature</li> <li>Solvent</li> <li>Common ion effect</li> </ol>
2	What is the effect on solubility of sparingly soluble salt (precipitate) with increase in H <sup>+</sup> concentration or decrease in pH?	Solubility will be increased
3	What is the effect of temperature on solubility of precipitates?	Solubility will be increased
4	As the temperature increases Ksp value will also increases and of ions will be less than its Ksp value.	molar concentration
5	What is the effect of addition of organic solvent on solubility of inorganic compounds?	Solubility reduced
6	Solubility of inorganic solvent is more in	Water
7	How much percentage of alcohol permits quantitative separation of lead sulphate precipitates by decreasing solubility of the precipitates?	20 %
8	Product of ionic concentration ([B+] [A-]) will exceed (greater than) the solubility product (Ksp), it leads to	Precipitation
9	What is the effect of common ion effect, on the solubility of slightly soluble salt (precipitates)?	Decreases

## **METHODS FOR END POINT DETECTION**

There are different methods to detect the end point in precipitation titration.

- 1) Mohr's method (Formation of coloured precipitates)
- 2) Volhard's method (Formation of soluble coloured compound)
- 3) Fajan's method (Utilization of absorption indicator)
- 4) Non-precipitation method (Turbidity method)

#### 1) MOHR'S METHOD

- Mohr's method is used to determine chlorides and bromides e.g. Nacl, NaBr, Kcl, KBr.
- It is method of estimation of chloride and bromide ion by titration with silver nitrate. (AgNO<sub>S</sub>).

- It is one of the oldest titration methods.
- In this method AgNO<sub>3</sub> is used as a titrant and 5 % solution of potassium chromate ( $K_2CrO_4$ ) is used as an indicator.
- Titration of 0.1 M NaCl by using 0.1 N AgNO3 in the presence of K<sub>2</sub>CrO<sub>4</sub> (5 % solution).
- This reaction is carried out in neutral media for determination of Cl<sup>-</sup> ions.



#### **PRINCIPLE:**

- Titration of 0.1 M NaCl by using 0.1 M AgNO<sub>3</sub> in the presence of K<sub>2</sub>CrO<sub>4</sub> (5 % solution).
- AgNO<sub>3</sub> (0.1 M standard) will be added from the burette in to the solution containing NaCl and indicator (K<sub>2</sub>CrO<sub>4</sub>).

- As per the Ksp value  $Ag_2CrO_4$  should precipitate out first, but this will not be happen because of concentration of Cl<sup>-</sup> ion is much much higher than  $CrO_4^{2-}$ .
- Therefore, AgNO<sub>3</sub> first reacts with NaCl and gives white precipitates of **AgCl** when NaCl is completely used in reaction with AgNO<sub>3</sub> it will form saturated solution of AgCl.
- After the completion of NaCl in the solution, excess one drop of AgNO<sub>3</sub> from burette leads to formation of reddish brown precipitates of  $Ag_2CrO_4$  because now AgNO<sub>3</sub> reacts with K<sub>2</sub>CrO<sub>4</sub> solution (CrO<sub>4</sub><sup>2-</sup> ions).
- Appearance of reddish brown precipitates after consuming all NaCl (sample) will help to detect end point.

#### Limitations of Mohr's Method:

- It can be carried out only in neutral media.
- It cannot be carried out in basic media because Ag<sup>+</sup> ion precipitated as Silver hydroxide (Ag(OH)<sub>2</sub>) & Ag<sub>2</sub>O in basic media (alkaline media).
- In highly acidic media chromate ion reacts with H<sup>+</sup> ions with the formation of HCrO<sub>4</sub><sup>-</sup> (which is only slightly ionized) thus, decreasing the concentration of chromate ion. It will disturb in detection of end point.

$$2H^+ + 2CrO_4^2 \longrightarrow HCrO4^- \longrightarrow Cr_2O_7^2 + H_2O$$

- This method is only applicable to Cl<sup>-</sup> & Br<sup>-</sup> ions but not applicable to iodide (I<sup>-</sup>) and thiocyanate (SCN<sup>-</sup>) due to AgI and AgSCN absorb chromate ion and gives coloured precipitates with our sample.
- It cannot be carried out in the presence of reducing agent because CrO<sub>4</sub><sup>2-</sup> will be reduce to Cr<sup>3+</sup>.
- It cannot be done in the presence of anions like PO<sub>4</sub><sup>3-</sup>, S<sup>2-</sup> etc. because it will give painted precipitates.

Sr.	Questions	Answer
No.		
1	How many methods are available to detect end point in	4
	precipitation titration?	
2	In which method for detection of end point in precipitation	<b>Mohr's Method</b>
	titration coloured precipitates are formed?	

3	Mohr's method is used to determine	Chlorides and bromides
4	Which method is oldest titration method in precipitation titration?	Mohr's Method
5	What is used as titrant in Mohr's method?	AgNO <sub>3</sub>
6	What is the role of AgNO <sub>3</sub> in Mohr's method?	<b>Titrant or Precipitating</b>
		agent
7	Which precipitating agent is used in Mohr's method?	AgNO <sub>3</sub>
8	Which indicator is used in Mohr's Method?	5 % solution of
		potassium chromate
		$(K_2CrO_4)$
9	In which method of precipitation titration K <sub>2</sub> CrO <sub>4</sub> is used as indicator?	Mohr's method
10	Which type of precipitates will help to detect end point in	Reddish brown ppts of
	Mohr's method?	Ag <sub>2</sub> CrO <sub>4</sub>
11	What is precipitated out first in Mohr's method?	AgCl
12	Which chemical compound is precipitated out as reddish	Ag <sub>2</sub> CrO <sub>4</sub>
	brown colour in Mohr's method?	
13	In which method $Ag_2CrO_4$ is precipitated out as reddish brown colour?	Mohr's method
14	In which media Mohr's method is carried out?	Neutral media
15	After the completion of in the solution, excess one	NaCl
	drop of AgNO <sub>3</sub> from burette leads to formation of reddish	
	brown precipitates of Ag <sub>2</sub> CrO <sub>4</sub> .	
16	Mohr's method is not carried out in basic media due to	$(Ag(OH)_2) \& Ag_2O$
	formation of	
17	If Mohr's method is carried out in acidic media, disturbance	HCrO <sub>4</sub> -
	in detection of end point is due to formation of	
18	It Mohr's method is carried out in acidic media, how	By decreasing the conc.
10	formation of HCrO <sub>4</sub> <sup>-</sup> will disturb in detection of end point?	of chromate ions.
19	Mohr's method is not applicable to iodide $(I)$ and thiocyanate	Chromate ion
	(SUN) due to Ag1 and Ag5UN absorb and gives	
20	Why Mohe's method is not opplicable for L and SON- 9	Cines esterned
20	why wome's method is not applicable for 1 and SCN?	Gives coloured
		precipitates with
		sample

#### 2) VOLHARD'S METHOD (Formation of soluble coloured compound)

- It is also known as **Argentometric Back Titration.**
- It is not always possible to use Mohr's method to determine concentration of chlorides and bromides.

- For e.g. Mohr's method requires neutral solution, but in many cases solution has to be acidic, to prevent precipitation of metal hydroxides.
- In such cases we can use Volhard method which is not sensitive to low pH.
- The Volhard titration is an example of Indirect (back) titration.

In back titration, a known quantity of reagent is added in excess of that required to completely react with analyte. The remaining reagent is then subsequently titrated.

The difference between the total amount of reagent added, and that remaining after reaction with the analyte, is proportional to the number of moles of analyte in the sample.

- This method is used for all halides (Cl<sup>-</sup>, I<sup>-</sup> & Br<sup>-</sup>) except fluoride ion.
- It is also used for pseudohalides (OCN<sup>-</sup>, SCN<sup>-</sup> & CN<sup>-</sup>) from insoluble precipitates with Ag<sup>+</sup>.

#### **Determination of Halides:**

There are two steps for determination of halides (Cl<sup>-</sup>) by Volhard's method.

- 1) Standardization of AgNO<sub>3</sub>
- 2) Titration of reaction mixture with potassium thiocyanate (KSCN) or ammonium thiocyanate (NH<sub>4</sub>SCN)- (Determination of analyte)

Indicators used in the reactions are:

- ➢ Iron Alum
- Ferric ammonium sulphate ( $NH_4$  Fe( $SO_4$ )<sub>2</sub>. 12H<sub>2</sub>O)

#### 1) Preparation and Standardization of AgNO<sub>3</sub>

- Here we use AgNO<sub>3</sub> as a reagent. AgNO<sub>3</sub> (silver nitrate) when exposed to atmospheric air gets darken due to reduction to metallic silver. Hence, AgNO<sub>3</sub> should be standardized.
- Standardization of AgNO<sub>3</sub> is carried out by its titration with primary standard compound NaCl which forms a precipitate of AgCl.
- When all the chloride ion has been titrated the very next drop of silver nitrate (AgNO<sub>3</sub>) reacts with potassium chromate (K<sub>2</sub>CrO<sub>4</sub>). Upon reaction of AgNO<sub>3</sub> with K<sub>2</sub>CrO<sub>4</sub>, reddish brown precipitates of Ag<sub>2</sub>CrO<sub>4</sub> (silver chromate) forms.
- Formation of reddish brown precipitates of silver chromate indicates the end point.

$$NaCl + AgNO_3 \longrightarrow AgCl + NaNO_3$$
  
2 AgNO\_3 + K\_2CrO\_4  $\longrightarrow$  Ag\_2CrO\_4 (Reddish brown ppt) + 2KNO\_3

• The actual molarity of AgNO<sub>3</sub> will be found from above titration.

#### 2) <u>Determination of analyte:</u>



#### **PRINCIPLE:**

- In this method there is a formation of a soluble coloured compound at the end point.
- Silver ion is titrated with thiocyanate in acid solution using ferric ion as an indicator. Initially, Silver thiocyanate (AgSCN) is precipitated.
- After the equivalence point, no Ag<sup>+</sup> is present, the excess of thiocyanate added reacts with Fe<sup>3+</sup> to give reddish brown ferric thiocyanate (Fe(SCN)<sup>+2</sup>) compound.
- Volhard's method is carried out in acidic condition provided by nitric acid (0.5-1.5 M). Because HNO<sub>3</sub> prevents hydrolysis of Fe<sup>+3</sup> to insoluble basic salts and it also prevents colour of Fe<sup>+3</sup> in the indicator solution.
- In Volhard's method, first sample KCl is reacted with AgNO<sub>3</sub>. Once the sample consumed, excess of AgNO<sub>3</sub> will react ammonium thiocyanate (NH<sub>4</sub>SCN) and all excess AgNO<sub>3</sub> is consumed, then NH<sub>4</sub>SCN will react with indicator ion (Fe<sup>+3</sup>). This reaction with indicator gives the reddish brown Fe(SCN)<sup>+2</sup> compound which indicates the end point.

#### **REACTION:**



#### **METHODOLOGY:**

- 0.1 N AgNO<sub>3</sub> solution is taken and standardize first. Excess amount of this standardized AgNO<sub>3</sub> solution is taken as a reagent with sample (KCl) in conical flask.
- Add few drops of Fe<sup>+3</sup> alum indicator.
- Add HNO<sub>3</sub> (nitric acid) for creating acidic media.
- This mixture is being titrated with NH<sub>4</sub>SCN.
- When all AgNO<sub>3</sub> is reacted, NH<sub>4</sub>SCN is react with Fe<sup>+3</sup> from indicator. Formation of coloured compound ferric thiocyanate indicates the end point.
- Repeat above procedure without sample, which is known as blank determination.
- Calculate the amount of KCl from volume of AgNO<sub>3</sub> used to react with our sample (KCl). For that substrate volume of AgNO<sub>3</sub> obtained in normal determination from volume of AgNO<sub>3</sub> obtained in determination without sample (Blank determination).
- This volume of AgNO<sub>3</sub> is a volume required to react with sample.

#### Problems to overcome during Volhard's method:

 During back titration Ag<sup>+</sup> ions get absorbed on AgCl precipitates and gives premature end point.

This is overcome by vigorously shaking the mixture before the back titration in order to desorb the Ag<sup>+</sup> ions.

Alternatively, the mixture is boiled for few minutes and potassium nitrate (KNO<sub>3</sub>) is used to prevent reabsorption of  $Ag^+$ .

2. The two sparingly soluble salts AgCl and AgSCN are in equilibrium with the solution hence.

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

When all the excess of Ag<sup>+</sup> has reached, the thiocyanate may react with AgCl precipitate.

Since, Silver thiocyanate is the less soluble salt until the ratio  $\frac{[Cl-]}{[SCN-]}$  in solution is 169.

So at the end point of the titration, the excess  $SCN^-$  will react with  $Ag^+$  from the AgCl. Instead of the indicator  $Fe^{+3}$  ions, and hence a higher end point than actual results.

- To overcome this it is necessary to prevent the reaction between thiocyanate and silver chloride. This may be effected in several ways.
  - i. The AgCl precipitates is boiled for a few minutes, the precipitate is removed by filtration, and cold filtrate is back titrated.
  - ii. The silver chloride particles are coated with the immiscible liquid. e.g. nitrobenzene and hence protected from reaction with thiocyanate.

#### **<u>Comment</u>**: Why nitrobenzene is used in Volhard's method of nitrogen.

During titration ammonium thiocyanate may react with Ag<sup>+</sup> ion from AgCl precipitates and error may be introduced in the titration.

AgCl (s) + SCN<sup>-</sup>  $\longrightarrow$  AgSCN (s) + Cl<sup>-</sup>

To avoid this problem AgCl precipitates may be filtered off before titration. The other method to avoid this problem is addition of small volume of a heavy organic liquid that is not miscible with water.

(Like nitrobenzene, dibutyl phthalate, chloroform or carbon tetrachloride)

- > These liquid are better from wetting precipitate than water.
- Shaking the precipitates with any one of these liquid coagulates and coats the silver chloride precipitates.
- Once the precipitate is covered with non-polar liquid, it is separated from the water and unable to dissolve.
- > The excess AgNO<sub>3</sub> stays in the aqueous layer and is titrated with standard thiocyanate.

Sr. No.	Questions	Answer
1	Volhard's method is also known as	Argentometric Back Titration.
2	Sometimes acidic solution is required for the detection of halides. Why?	To prevent precipitation of metal hydroxides

3	End point in Volhard's method is detected by	Formation of soluble coloured compound
4	A known quantity of reagent is added in excess of that required to completely react with analyte. The remaining reagent is then subsequently titrated. This titration is known as	Back titration
5	Volhard's method is used for estimation of	Halides like Cl <sup>-</sup> , I <sup>-</sup> & Br Pseudohalides like OCN <sup>-</sup> , SCN <sup>-</sup> & CN <sup>-</sup>
6	Which halide is not detected by Volhard's method?	Fluoride ion
7	Indicators used in the Volhard's method are	<ol> <li>Iron Alum</li> <li>Ferric ammonium sulphate (NH<sub>4</sub></li> <li>Fe(SO<sub>4</sub>)<sub>2</sub>. 12H<sub>2</sub>O)</li> </ol>
8	Why standardization of AgNO <sub>3</sub> is required?	Due to reduction of metallic silver
9	AgNO $_3$ (silver nitrate) when exposed to atmospheric air gets darken due to	Reduction to metallic silver
10	Which primary standard is used for standardization of AgNO <sub>3</sub> solution?	NaCl
11	In Volhard's method, which compound is precipitated out?	Silver thiocyanate (AgSCN)
12	Which compound will be formed at the end point of Volhard's method?	Ferric thiocyanate Fe(SCN) <sup>+2</sup>
13	Colour of ferric thiocyanate is	<b>Reddish brown</b>
14	Which compound is used to prevent reabsorption of Ag <sup>+</sup> on AgCl precipitates?	Potassium nitrate (KNO3)
15	What is the role of potassium nitrate in Volhard's method?	To prevent reabsorption of Ag <sup>+</sup>
16	Which heavy organic liquids are used in Volhard's method to prevent reaction of ammonium thiocyanate with Ag <sup>+</sup> from AgCl instead of with Ag <sup>+</sup> from AgNO <sub>3</sub> .	Nitrobenzene, Dibutyl phthalate, Chloroform or Carbon tetrachloride
17	What is the role of nitrobenzene in Volhard's method?	Coating agent for precipitates
18	What is the role of Dibutyl phthalate in Volhard's method?	Coating agent for precipitates
19	What is the role of Chloroform in Volhard's method?	Coating agent for precipitates
20	What is the role of Carbon tetrachloride in Volhard's method?	Coating agent for precipitates

21	Why coating of AgCl precipitates is required by water immiscible liquids?	To prevent reaction of Ag <sup>+</sup> with NH4SCN from AgCl
22	Which method other than water immiscible liquids is used to avoid reaction of ammonium thiocyanate with Ag <sup>+</sup> from AgCl?	Filtration of AgCl precipitates before titration
23	What should be used to provide acidic media in Volhard's method?	Nitric Acid
24	How much concentration of nitric acid is preferable to provide acidic media in Volhard's method?	0.5 to 1.5 M
25	Why acidic media provided by HNO <sub>3</sub> is required in Volhard's method?	To prevents hydrolysis of Fe <sup>+3</sup>
26	During back titration Ag <sup>+</sup> ions get absorbed on AgCl precipitates. What is the effect of that on end point?	Gives premature end point

#### 3) FAJAN'S METHOD (Use of adsorption indicator)

- This method is used to determine chloride, bromides and iodides.
- In Fajan's method, end point is observed by colour change of precipitates by adsorption of indicator on the surface of precipitates.
- K. Fajan through his study, introduced a useful type of indicator for precipitation titrations. For e.g. fluorescein, eosin, dichloro-fluorescien etc. These indicators are either acid dyes or basic dyes of rhodamine series.
- The property of a colloidal precipitate to adsorb its own ions which are in excess, is applicable in this method.



- In this method, solution of silver chloride (NaCl) is titrated with silver nitrate (AgNO<sub>3</sub>) standard solution by using fluorescein as an indicator.
- In this reaction silver chloride (AgCl) precipitates will be formed and these precipitates will absorb chloride ions (**Cl**<sup>-</sup>,**its own ion**) which are initially in excess before equivalence point. (Initially, NaCl is in excess before addition of AgNO<sub>3</sub> and till equivalence point)
- Thus, chloride ions form the primary adsorbed layer. Chloride ions are anions and thus repulses the indicator anion (In<sup>-</sup>) and more loosely held secondary (counter) layer of adsorbed ions is of cations, such as Na<sup>+</sup>.

Colour of precipitate is yellow-green due to unabsorbed indicator

After the equivalence point Ag<sup>+</sup> will be in excess and thus surface of the precipitates adsorb positively charge Ag<sup>+</sup> (its own ion) from the AgNO<sub>3</sub> and this will form primary absorbed layer and NO<sub>3</sub><sup>-</sup> forms secondary layer. Now if the Na<sup>+</sup> salt of fluorescein is also present in the solution then the negatively charge fluorescein ions (In<sup>-</sup>) would be adsorbed instead of NO<sub>3</sub><sup>-</sup> as secondary adsorbed layer.

AgCl 
$$\bullet$$
 Ag<sup>+</sup>  $\bullet$  In<sup>-</sup>



• This adsorption of indicator occurs with change to pink or red colour due to formation of a pink/red coloured complex of Ag<sup>+</sup> and modified fluorescein ions.

### **The factors which must be considered during selection or choice of an adsorption** <u>indicator.</u>

- The indicator ion should have a charge (In<sup>-</sup>) opposite to that of the ion of the precipitating agent.
- The solution should be concentrated enough to give sharp colour change.
- The indicator should be secondarily adsorbed only after the equivalence point.
- Precipitates particle should be of colloidal dimension to maximize quantity of indicator adsorbed on these particles.
- Multivalent ions and other factors which have a coagulating effect should be avoided as a colloidal state of the precipitate is desired.
- At equivalent point, the formation of AgCl precipitate should be slow to retain adsorptive property.
- Improper selection of indicator results into long time for adsorption which results into error in the titration.

#### **b pH of the titration mixture**

• The pH of the titration mixture must be adjusted to pH 7-10 if fluorescein is used as an indicator and if dichlorofluorescien is used as an indicator then pH should be adjusted to 4-10.

#### **Exposure to sun-light**

• Silver halides are sensitized to the action of light by layer of adsorbed dye stuff (indicator) such as fluorescein and hence precipitation titration of halides using argentometry and adsorption, indicator should be carried out with minimum exposure to light.

#### Limitations of Fajan's Method:

- Low background levels of non-reacting ions to ensure that coagulation does not occur. [If non-reacting ion level is high coagulation occurs, which is not desired.]
- It cannot work with very low levels as there will not be enough precipitate to allow the colour change to be observed.

[If very low levels of reagents- precipitate formation not enough-adsorption of indicator less- colour change not properly observed.]

#### **4** Advantages of Fajan's Method:

• Titration using adsorption indicator are rapid, accurate and reliable with their application limited only by the relatively few precipitation reactions in which colloidal precipitate is formed quickly.

Sr.	Questions	Answer
No.	<b>Zuchtoni</b>	
1	Which halides are determine by Fajan's Method?	Cl <sup>-</sup> , I <sup>-</sup> & Br <sup>-</sup>
2	In which method of precipitation titration, adsorption indicator is used?	Fajan's method
3	In which method of precipitation titration, end point is observed by colour change of precipitates by adsorption of indicator on the surface of precipitates.	Fajan's method
4	In Fajan's method, end point is observed by colour change of precipitates by	Adsorption of indicator
5	Which indicators are useful in Fajan's method as adsorption indicator?	Fluorescein, Eosin, Dichloro-fluorescien
6	What is the role of Fluorescein in Fajan's method?	Indicator
7	Nature of the indicator used in Fajan's method which is responsible for end point detection	Adsorption indicator
8	What is the type of indicators used in Fajan's method?	Acidic or Basic dyes
9	Which type of precipitate has ability to adsorb its own ions which are in excess?	Colloidal
10	Which type of property of precipitate particle is preferred to maximize quantity of indicator adsorbed on these particles?	Colloidal nature
11	Colloidal precipitates have tendency to adsorb on the surface of precipitates.	Its own ion
12	The pH of the titration mixture must be adjusted to pH if fluorescein is used as an indicator.	7-10
13	The pH of the titration mixture must be adjusted to pH if dichlorofluorescien is used as an indicator.	4-10
14	What is used as titrant in Fajan's method?	AgNO <sub>3</sub>
15	In Fajan's method, which ions are adsorbed on the surface of	Cl
16	In Faian's method, which ions formed the primary advarhad	Cŀ
10	layer when NaCl is in excess?	U

17	In Fajan's method, which ions are adsorbed on the surface of	Cl <sup>-</sup>
10	AgCl precipitates before equivalent point?	
18	In Fajan's method, which ions formed the secondary adsorbed	Na
10	layer when NaCl is in excess?	<b>X7 11</b>
19	In Fajan's method, what is the colour of precipitates before	Y ellow-green
• •	equivalent point due to unabsorbed indicator?	<b>.</b>
20	In Fajan's method, Y ellow-green colour of precipitates before	Unabsorbed indicator
• 1	equivalent point is due to	
21	In Fajan's method, which ions are adsorbed on the surface of	$Ag^+$
	AgCl precipitates after equivalent point?	
22	In Fajan's method, which ions formed the primary adsorbed	$Ag^+$
	layer after equivalent point?	
23	In Fajan's method, which ions formed the secondary adsorbed	Fluorescein ions
	layer after equivalent point?	(Indicator ions)
24	In Fajan's method, what is the colour of precipitates after	Pink/Red
	equivalent point due to absorbed indicator?	
25	The indicator ion should have a charge (In-) same to that of	False
	the ion of the precipitating agent. True or False?	
26	The solution of indicator should be concentrated enough to	Sharp colour change
	give	
27	The indicator should be secondarily adsorbed only after the	True
	equivalence point. True or False?	
28	Colour of the precipitates after equivalent point is pink or red	Adsorption of indicator
	in Fajan's method is due to	
29	pH of the solution is adjusted to 7-10 if	Fluorescein
	indicator is used.	
30	pH of the solution is adjusted to 4-10 if	Dichlorofluorescien
	indicator is used.	
31	Coagulation of the precipitates is desired for adsorption	No
	indicator method or not?	
32	High background levels of non-reacting ions are not desired	Coagulation
	in Fajan's method because it may lead to of	
	precipitates.	
33	Silver halides are sensitized to the action of light by layer of	True
	adsorbed dye stuff (indicator). True or False?	

#### 4) Non-Precipitation Method (Turbidity Method or Gay Lussac's method)

- It is an indicator free method as there is no use of indicator in this method.
- In this method end point is detected by occurrence of turbidity.(turbidity produced at end point)



#### **Titration of NaCl with AgNO3**

- Weigh accurately 0.12 g of NaCl. Dissolve NaCl into 100 ml of distilled water.
- Add few drops of HNO<sub>3</sub> to provide an acidic media. (reaction better takes place in acidic media)
- Add Ba(NO<sub>3</sub>)<sub>2</sub> as coagulating agent to coagulate the precipitates. (As the coagulation occurs, clear solution obtained)



- This mixture of the flask is titrated with 0.1 M AgNO<sub>3</sub> which start reaction of NaCl and AgNO<sub>3</sub>.
- First add 20 ml of 0.1 M AgNO<sub>3</sub> (at once) from burette to the mixture present in the conical flask.
- Reaction between NaCl and AgNO<sub>3</sub> takes place.

#### $NaCl + AgNO_3 \longrightarrow AgCl + NaNO_3$

- AgCl precipitate will be coagulated by the effect of barium nitrate (Ba(NO<sub>3</sub>)<sub>2</sub>).
- After coagulation of AgCl precipitate, supernated liquid will be clear.
- Add 1 ml of AgNO<sub>3</sub>, if chloride ion (Cl<sup>-</sup>) will be present then again AgCl will be formed and coagulated.
- Again add 1 ml of AgNO<sub>3</sub> no precipitation (turbidity) occurs.
- Thus, 20 ml is taken as pilot reading.
- Again take 0.12 g NaCl. Dissolve in 100 ml of distill water, add few drops of HNO<sub>3</sub>. Add Ba(NO<sub>3</sub>)<sub>2</sub>.
- Add 20 ml of 0.1 M AgNO<sub>3</sub> at once.
- AgCl will be coagulated.
- Add AgNO<sub>3</sub> dropwise, again precipitation will take place.
- After 21 ml, if we add 22.1 ml- precipitation occurs

22.2 ml- precipitation occurs

22.3 ml- turbidity observed.

- 22.2 ml is a reading which is end point. Above this result NaCl is no more in solution. All NaCl will will be consumed and therefore precipitates will not be formed after 22.2 ml.
- Above this addition of 0.1 ml cause turbidity & therefore this method is known as turbidity method.

Questions	Answer
Which method of precipitation titration is indicator free	Non-Precipitation
method?	Method
In Non-pecipitation method end point is detected by	Occurrence of turbidity
Non-pecipitation method is also known as	<b>Turbidity Method or</b>
	Gay Lussac's method
Which agent is used as a coagulating agent to coagulate the	<b>Barium Nitrate</b>
precipitates in non-precipitation method of precipitation	$(Ba(NO_3)_2)$
titration?	
What s the role of Barium Nitrate in non-precipitation method	Coagulating agent
of precipitation titration?	
What is used to provide acidic media in Non-precipitation	HNO <sub>3</sub>
method?	
	QuestionsWhich method of precipitation titration is indicator free method?In Non-pecipitation method end point is detected byNon-pecipitation method is also known asWhich agent is used as a coagulating agent to coagulate the precipitates in non-precipitation method of precipitation titration?What s the role of Barium Nitrate in non-precipitation method of precipitation titration?What is used to provide acidic media in Non-precipitation method?

7 In turbidity method of precipitation titration, clear media is observed in the solution is due to precipitates

#### **Estimation of Sodium Chloride**

**PRINCIPLE:** (By Volhard's Method)

- Volhard's precipitation titration method (argentometric back titration) is used for the estimation of sodium chloride.
- NaCl, sodium chloride (sample) is reacted with excess quantity of AgNO<sub>3</sub> (precipitating agent).
- Precipitates of AgCl formed.
- The intereference of AgCl precipitates are removed by coagulating the precipitates by adding nitrobenzene or dibutylphthalate.



• Excess silver nitrate is back titrated by ammonium thiocyanate using ferric ammonium sulphate as an indicator.

$$NaCl + AgNO_3 \longrightarrow AgCl + NaNO_3$$

Excess AgNO<sub>3</sub> + NH<sub>4</sub>SCN 
$$\longrightarrow$$
 AgSCN + NH<sub>4</sub>NO<sub>3</sub>  
Fe<sup>+3</sup> + SCN<sup>-</sup>  $\longrightarrow$  Fe(SCN)<sup>+2</sup> (Reddish brown compound)

- When all excess AgNO<sub>3</sub> is reacted with NH<sub>4</sub>SCN, after that NH<sub>4</sub>SCN reacts with indicator ion Fe<sup>+3</sup> which gives the coloured amount of (Fe(SCN)<sup>+2</sup>).
- End point is detected by formation of reddish brown coloured compound ferric thiocyanate (Fe(SCN)<sup>+2</sup>).
- This determination gives the volume of AgNO<sub>3</sub> used.
- Take blank determination. Blank determination gives the volume of AgNO<sub>3</sub> reacts with NH<sub>4</sub>SCN.
- Now substrate result of normal determination from the result of blank determination.

Blank Determination	Normal Determination	
Whole AgNO <sub>3</sub> reacts with NH <sub>4</sub> SCN	AgNO <sub>3</sub> first reacts with NaCl	
due to absence of sample.	(sample) After sample consumed	
(A)	remaining AgNO3 reacts with	
	$\rm NH_4SCN.$	
	<b>(B</b> )	
$\underline{A-B}$ = gives the volume of AgNO <sub>3</sub> required to react with our sample (NaCl).		

- Thus, this reaction is known as Argentometric Back Titrationn. It is also known as Volhard's method.
- Thus, estimation of NaCl is done by Volhard's method/ Argentometric back titration method.

#### **PROCEDURE:**

- Weigh accurately about 0.1 g of sample (sodium chloride), dissolve in 50 ml of water in glass stoppered flask.
- Add 5 ml of 2M Nitric acid (HNO<sub>3</sub>), 2 ml of dibutyl phthalate and 50 ml of 0.1 M AgNO<sub>3</sub>.
- Shake vigorously for 2 minutes.
- Add 2 ml of ferric ammonium sulphate (indicator) titrate with 0.1 M NH<sub>4</sub>SCN until reddish brown colour appears.
- Perform blank titration.

• Each ml of 0.1 M AgNO<sub>3</sub> is equivalent to 0.00584 gm of NaCl.

Sr.	Questions	Answer
No.		
1	Which method of precipitation titration is best for estimation of sodium chloride?	Volhard's method
2	In estimation of sodium chloride, nitrobenzene is used as	Coating agent