



# PRECIPITATION TITRATION



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# Precipitation Titration Definition

- It is a Titrimetric method which involves the formation of precipitates during the experiment of titration.
- The titrant reacts with the analyte and forms an insoluble substance.
- The titration is continued till the last drop of the analyte is consumed.
- When the titrant is excess it reacts with the indicator and signals to terminate the titration process.



# Precipitation Titration Example

- Here we have discussed an example of precipitation titration.
- Example –
- To determine the concentration of **chloride ion** in a certain solution we can titrate this solution with **silver nitrate** solution (**whose concentration is known**). The chemical reaction occurs as follows:



- AgCl in the form of a white precipitate can be seen settled at the bottom of the flask during titration.
- The quantity of **silver ion used to equivalence point is equal to the quantity of chloride ion** which was originally present.
- To calculate the number of moles of chloride ion or silver ion we **can use  $n = cV$  ... (molarity definition)**

# PRECIPITATION

- The formation of a solid inside another solid or a solution during a chemical reaction or by diffusion in a solid ,is known as a precipitation.
- The solid formed is said to be a precipitate.
- It the reaction occurred in a liquid whereas it is said to be a pellet if compacted by centrifugation .
- Supernant is the liquid that remains above the precipitate.





# PURITY OF PRECIPITATION

- After chemical reaction, the precipitate formed from the solution is not as pure as required.
- A precipitate contamination with the substance present in mother liquor is said to be a co-precipitate.
- And this process of contamination is known as co-precipitation.
- This process involves the adsorption of foreign substance at the surface of the particles in the solution.
- Many errors can also be introduced during the titration by the process of post precipitation, in which the precipitation takes place after the formation of the first ppt on its surface.

# PROBLEMS DURING THE PRECIPITATION

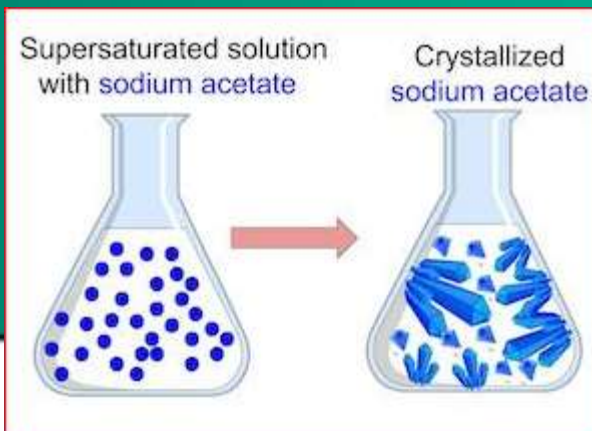
## 1) FLOCCULATION:

- Flocculation refers to the process by which fine particulates are caused to clump together into a floc .
- The floc may then float to the top of the liquid (creaming), settle to the bottom of the liquid (sedimentation), or be readily filtered from the liquid.



## 2) SUPER SATURATION

A supersaturated solution is a more solute solution than can be dissolved by the solvent





# PRINCIPAL

- It is also known as **Argentometric Titration**.
- It is type of titrimetric procedure involves the formation of precipitate during the course of Titration.
- Formation of the insoluble product by the combination of two ionic species is known as precipitation.







# Requirements for precipitation titrations

- Precipitate must be practically insoluble.
- Precipitation reaction must be rapid and quantitative
- Co precipitation must not occur
- It must be possible to detect equivalence point during titration
- The precipitation reaction undergoes in aqueous solutions or medium in an ionic state.
- The reaction takes place between ions present in the aqueous solutions, forming the product
- The products formed at the end of precipitation reaction are the precipitates which are insoluble in aqueous solutions
- Precipitation reactions are known as ionic reactions since the ions actively take part in the reaction and form the product.
- These reactions depend on the temperature, concentration of the solution, buffer solution, etc.



## Example of precipitation titration

- $\text{AgNO}_3(\text{aqueous}) + \text{KCl}(\text{aqueous}) \longrightarrow \text{AgCl}(\text{precipitate}) + \text{KNO}_3(\text{aqueous})$
- $2\text{KOH}(\text{aqueous}) + \text{CaCl}_2(\text{aqueous}) \longrightarrow \text{Ca}(\text{OH})_2(\text{aqueous}) + 2\text{KCl}(\text{aqueous})$
- $\text{AgNO}_3(\text{aqueous}) + \text{NaCl}(\text{aqueous}) \longrightarrow \text{AgCl}\downarrow + \text{NaNO}_3(\text{aqueous})$
- $\text{Mg}(\text{OH})_2(\text{s}) + 2\text{HCl}(\text{aqueous}) \longrightarrow \text{MgCl}_2(\text{aqueous}) + 2\text{H}_2\text{O}(\text{l})$





# SOLUBILITY AND SOLUBILITY PRODUCT

- Solubility
- Concentration of saturated solution is known as solubility and no further compound salt can be dissolved in a specific temp.
- 40 gm of Nacl dissolve in approximately 100 ml of the water at RT.(40gm of solubility)
- $\text{Nacl} \rightleftharpoons \text{Na}^+ + \text{cl}^- \text{ -----1}$
- $K = \frac{[\text{Na}^+ + \text{cl}^-]}{[\text{Nacl}]} \text{ -----2}$
- $K \times [\text{Nacl}] = [\text{Na}^+] + [\text{cl}^-] \text{ -----3}$
- $\text{So } K \times [\text{Nacl}] = K_{SP} \text{ -----4 Solubility product}$



- **Conc of [Nacl] will always be constant become present in solid form and no affect of temp in solubility of solid Nacl.**
- **$K_{SP} = [Na^+] + [Cl^-] \text{ -----} 5$**
- **$K_{SP} > [Na^+] + [Cl^-] = \text{No ppt}$**
- **$K_{SP} = [Na^+] + [Cl^-] = \text{Saturated solution}$**
- **$K_{SP} < [Na^+] + [Cl^-] = \text{Precipitation occurs}$**



# Relation between Solubility (s) & solubility product

- $\text{NaCl} \longrightarrow \text{Na}^+ + \text{Cl}^-$
- If the solubility of NaCl = s mol/L
- Then, it will produce S mole of  $\text{Na}^+$  and S mole of  $\text{Cl}^-$
- $\text{KSP} = [\text{Na}^+] + [\text{Cl}^-]$
- $\text{KSP} = \text{S} + \text{S}$
- $\text{KSP} = \text{S}^2$  <sup>SO</sup>, KSP is a solubility product and S is solubility.
  - $\text{Ag}_2\text{CrO}_4 \longrightarrow [2\text{Ag}^+] + [\text{CrO}_4^-]$
  - S mole/ L  $\longrightarrow$  2 S                      S
  - $\text{KSP} = [2\text{Ag}^+] + [\text{CrO}_4^-]$ 
    - $\text{KSP} = [2\text{S}]^2 + [\text{S}]$
    - $\text{KSP} = 4\text{S}^2 + \text{S}$
    - $\text{KSP} = 4\text{S}^3$



# Factors affecting solubility

## 1. Common ion effect

- The solubility of any slightly soluble salt can be decreased by adding an excess of either of its ions.



- If excess of either  $B^+$  or  $A^-$  are added in form of another salt whose solubility is greater than that of  $BA$ , then the product of  $[B^+][A^-]$  will exceed the solubility product and hence  $BA$  will precipitate out.



## 2. Effect of PH on solubility:

(a) For the salt whose anion is a conjugate base of a weak acid:



On adding  $\text{H}^+$ , pH is decreased,



- In presence of  $\text{H}^+$ , concentration of acetate ions is lowered, hence according to Le Chatelier's principle the equilibria of equation 1 will shift toward right, thus increasing the solubility of the salt.
- Hence for the salt whose anion is a conjugate base of weak acid, the solubility will increase with an decrease in pH or increase in  $\text{H}^+$  concentration.





**(b) For the salt whose cation is a conjugate acid of weak base:**



- If  $\text{OH}^-$  ions are added to the solution, i.e. pH is increased, concentration of ammonium ions will be lowered as ammonium ions will combine with  $\text{OH}^-$ .



- Hence according to Le Chatelier's principle, the equilibria of equation (1) will shift toward right, thus increasing the solubility of the salt.
- Hence for the salt whose cation is a conjugate acid of weak base, the solubility will increase with an increase in pH or decrease in  $\text{H}^+$  concentration.



### **3. Effect of temperature:**

- Solubility of precipitates increases with increase in temperature. The influence of temperature may be small or appreciable.
- For exothermic reactions, solubility decreases with increasing temperature. This situation is not very common where an increase in temperature produces a decrease in solubility.

### **4. Effect of solvent on solubility:**

- Solubility of a solute in a solvent depends on the nature of both solute and solvent.
- Polar solute dissolves in polar solvent, while non polar solute dissolves in non polar solvents.



# METHODS IN PRECIPITATION TITRATION

## Detection of end point:

- Chemical -
  - Precipitation Type - Mohr's method
  - Adsorption – Fajan's method
  - For silver analyses – Volhard method
  - Sensors – Potentiometric or amperometric
- **The chemical types are also classified into:**
  - 1. Indicators reacting with titrant forming specific colour.
  - 2. Adsorption indicator



## 1. Mohr's Method:

- This method was described by K. F. Mohr in 1865 for estimation of halides (mostly chloride) using silver ions (silver nitrate) as titrant.
- The end point detection depends on formation of coloured precipitates.
- This method uses potassium chromate as an indicator.
- Initially the titrant (silver nitrate) forms precipitates with the analyte (e.g.: chloride).
- After completion of precipitation reaction between the analyte and titrant, titrant forms precipitate with the indicator-potassium chromate.





Figure 1 Before the addition of any silver nitrate the chromate indicator gives the clear solution a lemon-yellow colour.



- The precipitates of silver chromate are of brick red colour. Hence, the end point is marked by formation of brick red precipitates.
- Mohr's method should be applied only to neutral or slightly alkaline solution, i.e. pH 6.5-9, because in acidic solution, chromate ions form dichromate ions.





- In alkaline solution, silver hydroxide may be precipitated.
- Acidic solution can be made neutral by adding calcium carbonate or sodium hydrogen carbonate.
- Alkaline solution can be made neutral by adding acetic acid and then calcium carbonate.
- Titration of iodide and thiocyanate is not successful because  $\text{AgI}$  and  $\text{AgSCN}$  adsorb chromate ions strongly, hence a false, indistinct end point result.



## 2. Volhard's Method

- This method uses a back titration with potassium thiocyanate to determine the concentration of chloride ions in a solution.
- Before the titration an excess volume of a silver nitrate solution is added to the solution containing chloride ions, forming a precipitate of silver chloride.
- The term 'excess' is used as the moles of silver nitrate added are known to exceed the moles of sodium chloride present in the sample so that all the chloride ions present will react.







- The indicator  $\text{Fe}^{3+}$  (ferric ion) is then added and the solution is titrated with the potassium thiocyanate solution.
- The titrate remains pale yellow as the excess (unreacted) silver ions react with the thiocyanate ions to form a silver thiocyanate precipitate.



- Once all the silver ions have reacted, the slightest excess of thiocyanate reacts with  $\text{Fe}^{3+}$  to form a dark red complex.





- The concentration of chloride ions is determined by subtracting the titration findings of the moles of **silver ions that reacted with the thiocyanate** from the total moles of silver nitrate added to the solution.
- This method is used when the pH of the solution after the sample has been **prepared is acidic**.
- If the pH is **neutral or basic**, **Mohr's method** or the gravimetric method should be used.
- The method is illustrated below by using the procedure to determine the concentration of chloride (from sodium chloride) in neutral or basic, Mohr's method or the gravimetric method should be used.
- The method is illustrated below by using the procedure to determine the **concentration of chloride (from sodium chloride) in cheese**.



## Equipment Needed:

- 500 mL volumetric flask
- 10 mL and 100 mL measuring cylinders
- conical flasks
- Bunsen burner,
- tripod and gauze burette and stand
- 50 mL pipette (if possible)



## Solutions Needed:

- **Silver nitrate solution:** If possible, dry 5 g of  $\text{AgNO}_3$  for 2 hours at  $100^\circ\text{C}$  and allow to cool. Accurately weigh about 4.25 g of solid  $\text{AgNO}_3$  and dissolve it in 250 mL of distilled water in a conical flask. Store the solution in a brown bottle.
- **Potassium thiocyanate solution:** Weigh 2.43 g of solid  $\text{KSCN}$  and dissolve it in 250 mL of distilled water in a volumetric flask.
- **Potassium permanganate solution:** (5%) Add 1.5 g  $\text{KMnO}_4$  to 30 mL of distilled water.
- **Ferric ammonium sulphate solution:** (saturated) Add 8g of  $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  to 20 mL of distilled water and add a few drops of concentrated nitric acid (see safety notes)



## Method Sample Preparation:

- The salt sodium chloride is added during the manufacture of cheddar cheese.
- In this method, the cheese is 'digested' to release this salt to obtain the concentration of chloride ions.
- To carry out this digestion, the cheese is reacted with nitric acid and potassium permanganate.
- The chloride ions are then 'free' to form a precipitate with the added silver ions.
- Cut or grate the cheese into fine pieces and accurately weigh about 6 g into a 500 mL conical flask.



- Precisely add 50 mL of 0.1 mol L<sup>-1</sup> silver nitrate solution (by pipette if possible), 20 mL of concentrated nitric acid, (very carefully – see safety notes), 100 mL of distilled water and a few boiling chips, and heat the solution in fume hood .
- As the solution boils add 5 mL of 5% potassium permanganate solution.
- This addition will cause a very smelly reaction and should be done in a fumehood.
- Keep boiling until the purple colour disappears, then add another 5 mL of potassium permanganate solution.



- Continue this process until 30 mL of potassium permanganate solution has been added and the cheese particles are completely digested (or as close as possible).
- To find out when digestion is complete, remove the flask from heat and allow it to stand for a few moments.
- Undigested cheese particles will float upon the surface of the clear liquid, while the white precipitate of silver chloride will sink to the bottom.
- If there is still too much undigested cheese, the boiling.
- and addition of 5 mL of potassium permanganate should be continued, checking each time until there is a satisfactory level of digestion.



- Cool the solution and filter it. Wash the solid residue with a few mL of distilled water. Make the filtrate up to 500 mL in a volumetric flask.
- **Titration:** Use a volumetric cylinder to measure 100 mL of the cheese extract solution (be as precise as possible) and pour it into a conical flask.
- Add 1 mL of saturated ferric ammonium sulphate solution as indicator.
- Titrate the unreacted silver ions with the 0.1 mol potassium thiocyanate solution.
- The end point is the first appearance of a dark red colour due to the ferric thiocyanate complex .
- Repeat the titration with 100 mL samples of the cheese extract solution until you obtain concordant results .



# Volhard's Method





- Figure 2 Left flask: before the titration endpoint, addition of  $\text{Ag}^+$  ions leads to formation of silver chloride precipitate, making the solution cloudy. The chromate indicator gives a faint lemon-yellow colour. Centre flask: at the endpoint, all the  $\text{Cl}^-$  ions have precipitated. The slightest excess of  $\text{Ag}^+$  precipitates with the chromate indicator giving a slight red-brown colouration. Right flask: If addition of  $\text{Ag}^+$  is continued past the endpoint, further silver chromate precipitate is formed and a stronger red-brown colour results. NB: The titration should be stopped when the first trace of red-brown colour is observed. Using an incompletely titrated reference flask for comparison is a helpful way to identify the first appearance of red-brown colouration.



### 3. Modified Volhard's Method:

- It is used for determination of Sodium Chloride or Potassium Chloride. In this method, organic liquid like nitrobenzene or dibutyl phthalate is added to coat silver chloride precipitates so that they do not interfere in the titration of excess of silver chloride.
- With bromides, titration error is small, with iodides, the titration error is even less due to low solubility of silver iodide and bromide than silver thiocyanate.



- Volhard titration must be carried out in acidic condition to prevent precipitation of ferric ion of indicator as the hydrated oxide and to prevent precipitation of silver ion as hydroxide.
- The concentration of ferric ammonium sulphate indicator about 0.01 M is employed because at higher concentration yellow colour of ferric ion interferes in end point detection

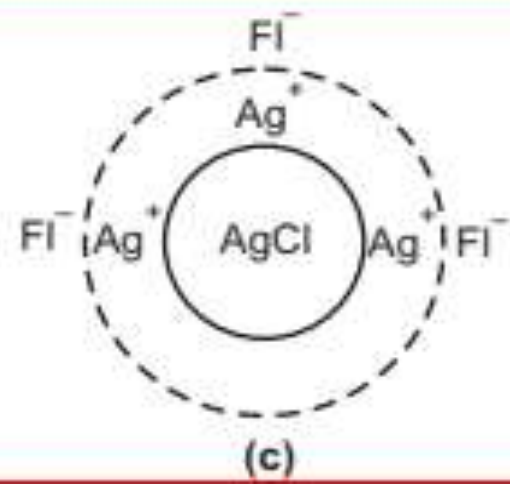
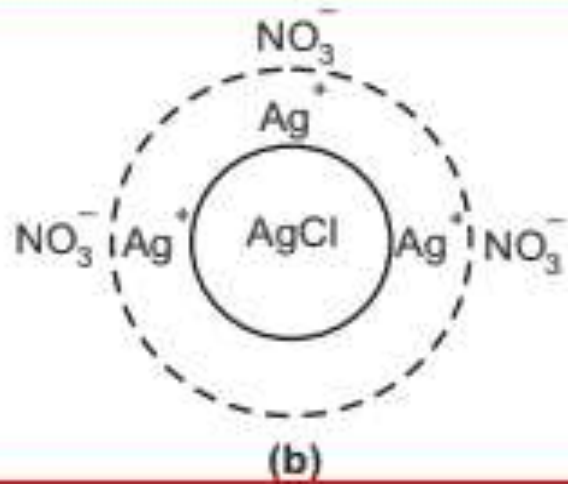
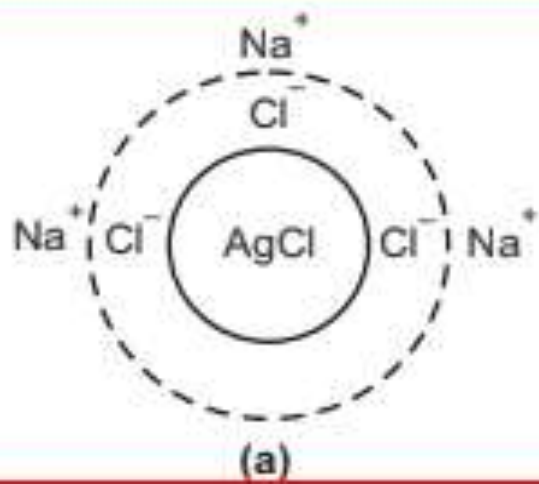


## 4. Fajans method

- It is also called as indicator adsorption method. It was discovered by Kazimierz Fajan.
- This method involves the use of adsorption indicators.
- Such indicators are adsorbed on the surface of precipitate at equivalence point and this adsorption is accompanied by a colour change.
- For example:  
Acidic dyes : Fluorescein, eosin, Diiodomethyl fluorescein, Dichloro-fluorescein.  
Basic dyes : Rhodamine series.



- When a sodium chloride precipitate is titrated with silver nitrate, silver chloride precipitate will adsorb chloride ions which are initially in excess.
- This layer will in turn hold the secondary adsorbed layer of sodium ions.
- After equivalence point, silver ions are in excess, hence silver chloride ions now adsorb silver ions which in turn will adsorb nitrate ions.
- But if sodium salt of fluorescein is present, fluorescein ions would be adsorbed instead of nitrate ions as secondary adsorbed layer and this adsorption leads to formation of **pink** colour as structure of fluorescein gets modified on adsorption of silver ions.





## Conditions which govern choice of adsorption indicators in Fajan's method:

- Indicator ion should have charge opposite to that of precipitating agent.
- Solution should be concentrated enough to give a sharp colour change.
- Indicator should be adsorbed only after equivalence point.
- Precipitate particles should be of colloidal dimension to maximize the quantity of indicator adsorbed.
- Silver halides are sensitized to the action of light by the layer of adsorbed indicator like fluorescein, hence precipitation titrations of halides using argentometry and adsorption indicators should be carried out with minimum exposure to sunlight.



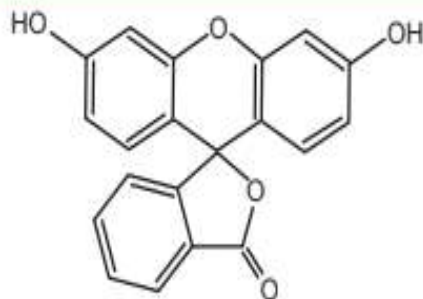


## Limitations of Fajan's method:

- If concentration of species is very low, there will not be enough precipitates to allow colour change to be observed.
- Method is pH dependent, as indicator must be ionized.

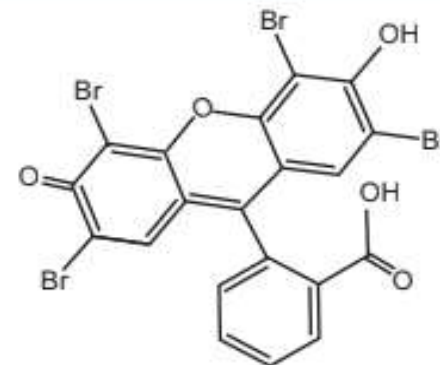
## Some Adsorption Indicators:

### Fluorescein:



0.2 % solution of sodium salt of fluorescein in water/alcohol is used.

### Eosin:



It is orange coloured powder dye, sparingly soluble in alcohol.



# CLASSIFICATION OF METHODS IN PRECIPITATION TITRATION

1. Argentometry
2. Thiocyanometry
3. Mercurometry
4. Sulphatometry
5. Hexacyanoferratometry



## Argentometry:

- Argentometry is a type of titration involving the silver (I) ion.
- Typically, it is used to determine the amount of chloride present in a sample.
- The sample solution is titrated against a solution of silver nitrate of known concentration.
- Chloride ions react with silver (I) ions to give the insoluble silver chloride.
- Preparation of 0.1 M silver nitrate: Finely powder silver nitrate AR. Dry at  $120^{\circ}\text{C}$  and allow to cool it in a desiccator.
- From this, weigh accurately 17 gm and dissolve in distilled water to make volume 1000 ml in volumetric flask.



- If silver nitrate used is not of AR grade, then solution of silver nitrate is standardized against standard solution of sodium chloride.
- **Standardization of silver nitrate:** Weigh accurately 0.1 gm of sodium chloride AR previously dried at  $110^{\circ}\text{C}$  for 2 hours and dissolve it in 5 ml of water. Add 5 ml of acetic acid, 50 ml of methanol and 0.15 ml eosin solution.
- Titrate it against solution of silver nitrate using potassium chromate as indicator till appearance of reddish-brown precipitates.



## Thiocyanometry:

- When ammonium thiocyanate is used as titrant, it is known as thiocyanometry.
- It is used for estimation of halides.
- **Preparation of 0.1 M ammonium thiocyanate:** Dissolve 7.612 gm of ammonium thiocyanate in sufficient water to produce 1000 ml.
- **Standardization of ammonium thiocyanate:** Pipette out 30 ml of 0.1 M silver nitrate into a glass stoppered flask, dilute with 50 ml water. Add 2 ml concentrated nitric acid and 2 ml ferric ammonium sulphate solution.
- Titrate with ammonium thiocyanate solution to first appearance of a red-brown colour.



# APPLICATIONS OF PRECIPITATION TITRATIONS

- Determination of anions: Halides (Bromide, chloride, fluoride).
- Determination of divalent anions ( $S^{2-}$ ).
- Determination of mercaptans ( $CH_3SH$ ).
- Determination of fatty acids.
- Determination of presence of metals in some pharmaceutical dosage forms.
- In plating bath industry.
- In gravimetric analysis.
- Assay of various pharmaceutical dosage forms.



# Keywords

Argenometry (Mohr's Method)

Thiocyanometry (Volhard's Method)



## Question Bank

### Short Answer Question:

1. What are precipitation titrations?
2. Which indicators are used in Fajan's method?
3. What is concentration of potassium chromate indicator required for Mohr's method?
4. Which primary standard is used for standardization of ammonium thiocyanate?
5. Name some adsorption indicators.
6. How will you prepare 0.1 M  $\text{AgNO}_3$  solution?
7. Write a note on various methods to detect end point in precipitation titrations. 8
8. Describe in detail factors affecting solubility.
9. Write a note on thiocyanometry. 10. Write a note on argentometry.





## **Long Answer Questions:**

- 1. Write a note on Mohr's method.**
- 2. What is Volhard's method and modified Volhard's method?**
- 3. What is Fajan's method of precipitation titration? Give its limitations.**
- 4. Give applications of precipitation titration.**
- 5. Give conditions which govern the choice of adsorption indicators.**
- 6. Write a note on estimation of sodium chloride.**
- 7. Differentiate between Mohr's method and Volhard's method.**



***Thank You...!***