

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



B.PHARM

(SEMESTER -I)

SUBJECT NAME: PHARMACEUTICAL ANALYSIS -I

SUBJECT CODE: BP102TP

UNIT 3(a): PRECIPITATION TITRATION

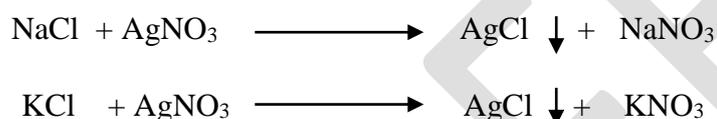
Content

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:

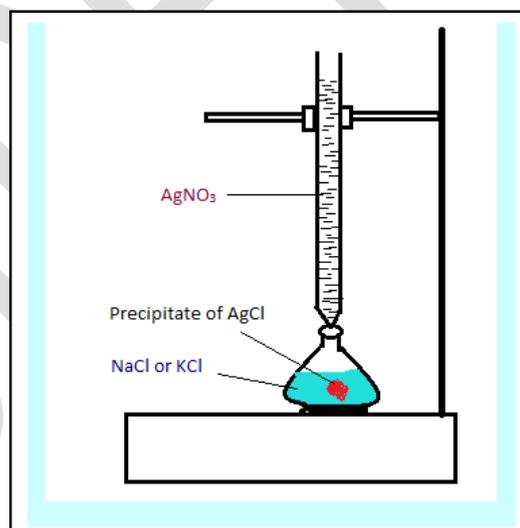


In the above reactions,

Ag^+ is precipitating agent

Cl^- is analyte

AgCl is precipitate.



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 co-precipitation.

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

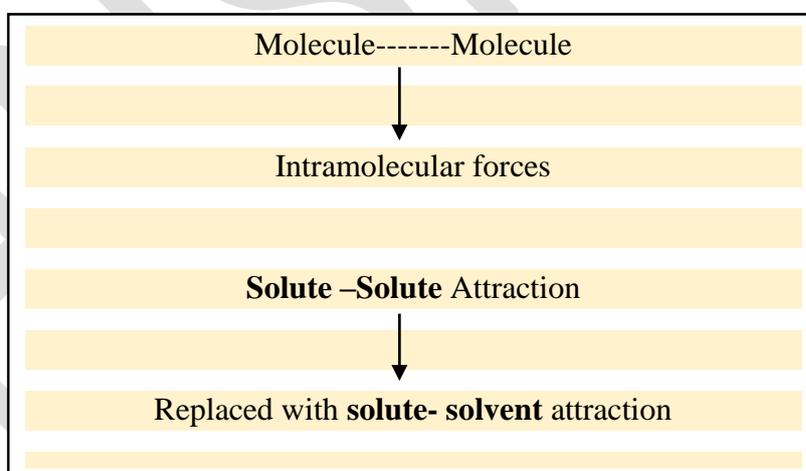
The main precipitation titrations are argentometric titrations in which standard solution of AgNO_3 is used to determine the anions.

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 repeating 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).

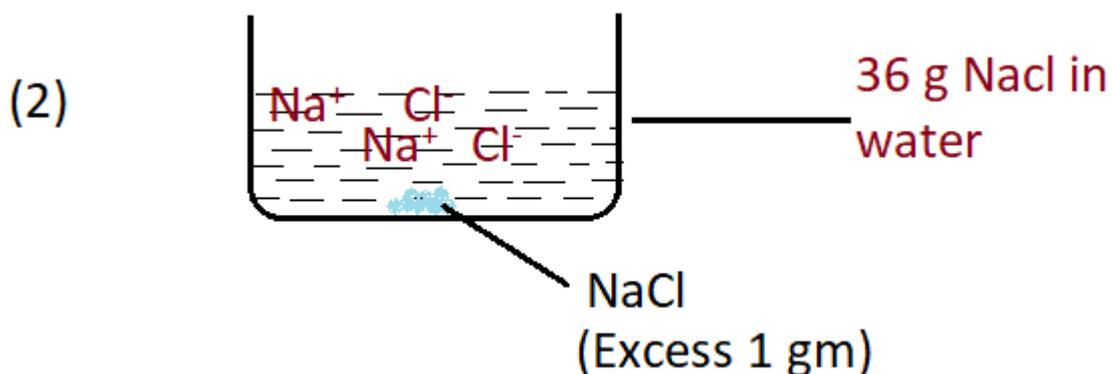
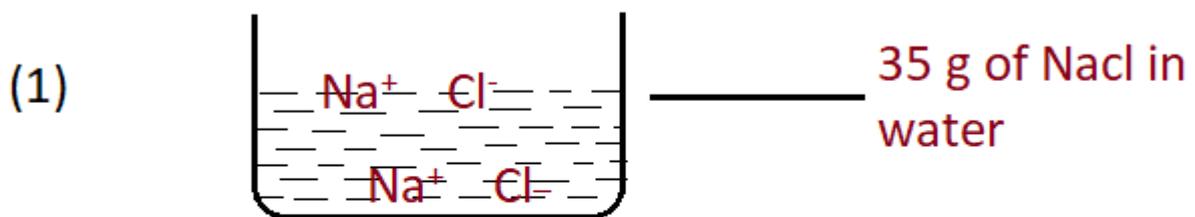
During the precipitation, opposite condition occurs, where the intramolecular forces between the molecules of product are high and solute-solvent forces are replaced by solute-solute forces.

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/100 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 as unionized form. This solution is known as saturated solution.



$$K = \frac{[\text{Na}^+][\text{Cl}^-]}{[\text{NaCl}]} \dots\dots\dots (2)$$

$$K [\text{NaCl}] = [\text{Na}^+][\text{Cl}^-] \dots\dots\dots (3)$$

Here, excess amount NaCl cannot interfere in the concentration of NaCl in the solution. Therefore, concentration of NaCl $[\text{NaCl}]$ is constant in saturated solution.

$$\text{So, } K [\text{NaCl}] = K_{sp} \dots\dots\dots (4)$$

$$K_{sp} = [Na^+] [Cl^-] \dots \dots \dots (5)$$

If $K_{sp} > [Na^+] [Cl^-]$ \longrightarrow No precipitation

If $K_{sp} = [Na^+] [Cl^-]$ \longrightarrow Saturated solution

If $K_{sp} < [Na^+] [Cl^-]$ \longrightarrow Precipitation occurs

Relationship between solubility and solubility product



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

$$K_{sp} = [Na^+] [Cl^-]$$

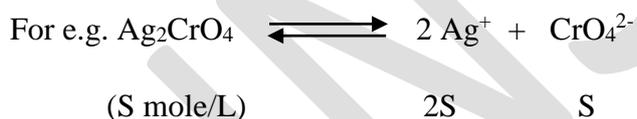
$$K_{sp} = S \times S$$

$$K_{sp} = S^2 \quad \text{OR} \quad S = \sqrt{K_{sp}}$$

Unit of $K_{sp} = (S \text{ mole/L})^2$ where $K_{sp} = \text{Solubility product}$

S = Solubility

When, in the Case of (Complex case),



$$K_{sp} = [2S]^2 [S]$$

$$K_{sp} = 4S^2 \times S$$

$K_{sp} = 4S^3 \longrightarrow$ Product of ionic concentration exceeds the K_{sp} value. Substance will precipitate out. Thus precipitation occurs.

Calculation of solubility & Solubility product

Ex:1 Calculate the solubility product of MgCO_3 if 1 litre of its saturated solution contains 0.533 g of MgCO_3 at 20°C .



$$K_{\text{sp}} (\text{MgCO}_3) = [\text{Mg}^{+2}] [\text{CO}_3^{2-}]$$

$$\text{Molecular weight} (\text{MgCO}_3) = 84.32$$

$$\text{Solubility of } \text{MgCO}_3 = 6.32 \times 10^{-3}$$

$$\begin{aligned} \text{Molar solubility} &= \frac{\text{Solubility}}{\text{Molecular weight}} \\ &= \frac{0.533}{84.32} \\ &= 0.00632 \end{aligned}$$

$$\text{Molar solubility (X)} = 6.32 \times 10^{-3} \text{ mole/litre}$$

Each mole of MgCO_3 , on dissociation forms 1 gram ion of Mg^{+2} and 1 gram ion of CO_3^{2-} . Hence Mg^{+2} and CO_3^{2-} ions in the solution have the same concentration equal to the molar solubility.

$$\begin{aligned} \text{Now,} \quad K_{\text{sp}} (\text{MgCO}_3) &= [\text{Mg}^{+2}] [\text{CO}_3^{2-}] \\ K_{\text{sp}} &= X^2 \\ K_{\text{sp}} &= (6.32 \times 10^{-3})^2 \\ K_{\text{sp}} &= 4 \times 10^{-5} \end{aligned}$$

The solubility product of MgCO_3 is equal to 4×10^{-5}

Calculation of solubility of an electrolyte

Ex:2 Calculate the solubility of $\text{Mg}(\text{OH})_2$ in mg/litre if $K_{\text{sp}} (\text{Mg}(\text{OH})_2)$ is 6×10^{-10} .
Molecular weight of $\text{Mg}(\text{OH})_2$ is 58.33.



If molar solubility of $\text{Mg}(\text{OH})_2$ is x . Then concentration of Mg^{+2} and OH^- ions will be x .

$$K_{sp}(\text{Mg}(\text{OH})_2) = [\text{Mg}^{+2}] [2\text{OH}^-]^2$$

$$K_{sp}(\text{Mg}(\text{OH})_2) = [X] [2X]^2$$

$$K_{sp}(\text{Mg}(\text{OH})_2) = 4X^3$$

$$6 \times 10^{-10} = 4X^3$$

$$X = \frac{6 \times 10^{-10}}{4}$$

$$X^3 = 1.5 \times 10^{-10}$$

$$X = \sqrt[3]{1.5 \times 10^{-10}}$$

$$X = \sqrt[3]{150 \times 10^{-12}}$$

$$X = 5.31 \times 10^{-4}$$

Solubility = Molar solubility x Molecular weight

$$= 5.31 \times 10^{-4} \times 58.33$$

$$S = 309.73 \times 10^{-4} \text{ g/litre}$$

$$S = 0.03097 \text{ g/litre} = 30.97 \times 10^{-3}$$

Solubility of $\text{Mg}(\text{OH})_2$ is $30.97 \times 10^{-3} \text{ g/litre}$

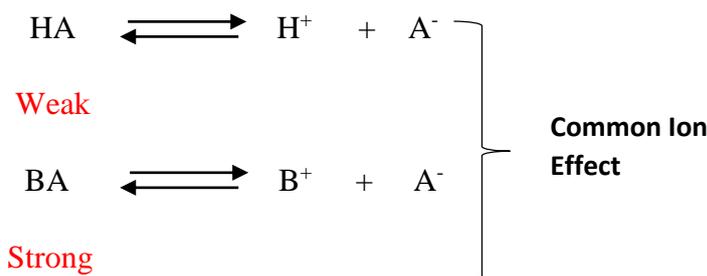
▪ Factors affecting solubility of precipitates

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

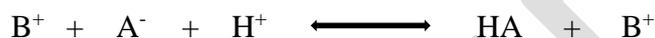
1) Effect of Acid (pH):

- If we add precipitating agent (AgNO_3) 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)



Equilibrium reaction



- Here concentration of A⁻ ion will be increased upon addition of Acid (HA).
- Due to common ion effect, reaction of weak electrolyte ($\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$) 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 K_{sp} value is characteristic for a particular compound at a specific temperature.
- So, as the temperature increases K_{sp} value will also increases and molar concentration of ions will be less than its K_{sp} value.
- To maintain equilibrium more amount of ionization occurs. More solid will get dissolved so that molar concentration of ions is equal to K_{sp}. Solubility increases in this way.
- For e.g. Solubility of BaSO₄ at 10 °C = 2.2 mg/l

Solubility of BaSO₄ at 100 °C = 3.9 mg/l

Solubility of AgCl at 10 °C = 1.72 mg/l

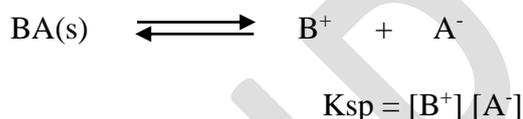
Solubility of AgCl at 100 °C = 21.1 mg/l

3) Effect of Solvent:

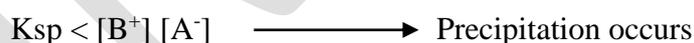
- Most of inorganic compounds are soluble in water but when we add organic solvent like (methyl, ethyl & n-propyl alcohols), solubility of most of inorganic compounds can be reduced.
- For e.g. addition of 20 % alcohol (organic solvent) by volume permits quantitative separation of lead sulphate precipitates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



- This is the equilibrium condition. If however, an excess of either B⁺ or A⁻ are added in the form of another salt (whose 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 (K_{sp}).



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

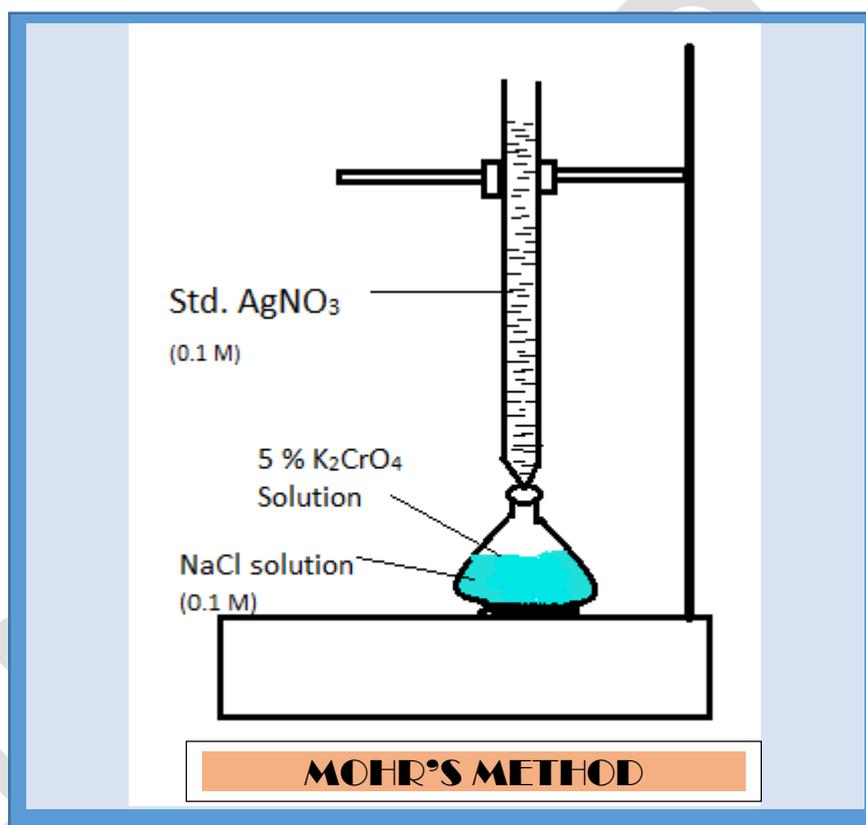
METHODS FOR END POINT DETECTION

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)

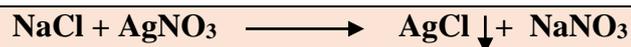
1) MOHR'S METHOD

- 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. (AgNO₃).
- It is one of the oldest titration methods.
- In this method AgNO₃ is used as a titrant and 5 % solution of potassium chromate (K₂CrO₄) is used as an indicator.



- Titration of 0.1 M NaCl by using 0.1 M AgNO₃ in the presence of K₂CrO₄ (5 % solution).
- This reaction is carried out in neutral media for determination of Cl⁻ ions.

Reaction:



$$\text{Here, } K_{sp} (\text{AgCl}) = 1.77 \times 10^{-10}$$

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

PRINCIPLE:

- Titration of 0.1 M NaCl by using 0.1 M AgNO₃ in the presence of K₂CrO₄ (5 % solution).
- AgNO₃ (0.1 M standard) will be added from the burette in to the solution containing NaCl and indicator (K₂CrO₄).
- As per the K_{sp} value **Ag₂CrO₄** should precipitate out first, but this will not be happen because of concentration of Cl⁻ ion is much much higher than CrO₄²⁻.
- Therefore, AgNO₃ first reacts with NaCl and gives white precipitates of **AgCl** when NaCl is completely used in reaction with AgNO₃ it will form saturated solution of AgCl.
- After the completion of NaCl in the solution, excess one drop of AgNO₃ from burette leads to formation of reddish brown precipitates of **Ag₂CrO₄** because now AgNO₃ reacts with K₂CrO₄ solution (CrO₄²⁻ 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⁺ ion precipitated as Silver hydroxide (Ag(OH)₂) & Ag₂O in basic media (alkaline media).
- In highly acidic media chromate ion reacts with H⁺ ions with the formation of HCrO₄⁻ (which is only slightly ionized) thus, decreasing the concentration of chromate ion. It will disturb in detection of end point.



- This method is only applicable to Cl⁻ & Br⁻ ions but not applicable to iodide (I⁻) and thiocyanate (SCN⁻) 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 CrO₄²⁻ will be reduce to Cr³⁺.
- It cannot be done in the presence of anions like PO₄³⁻, S²⁻ etc. because it will give painted precipitates.

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^- , I^- & Br^-) except fluoride ion.
- It is also used for pseudo halides (OCN^- , SCN^- & CN^-) from insoluble precipitates with Ag^+ .

Determination of Halides:

There are two steps for determination of halides (Cl^-) by Volhard's method.

- 1) **Standardization of AgNO_3**
- 2) **Titration of reaction mixture with potassium thiocyanate (KSCN) or ammonium thiocyanate (NH_4SCN)- (Determination of analyte)**

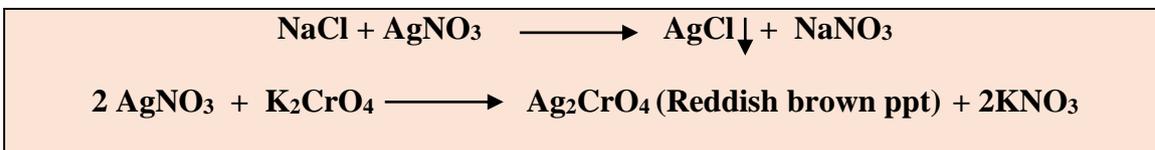
Indicators used in the reactions are:

- Ferric ammonium sulphate ($\text{NH}_4 \text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) or Iron alum

1) Preparation and Standardization of AgNO_3

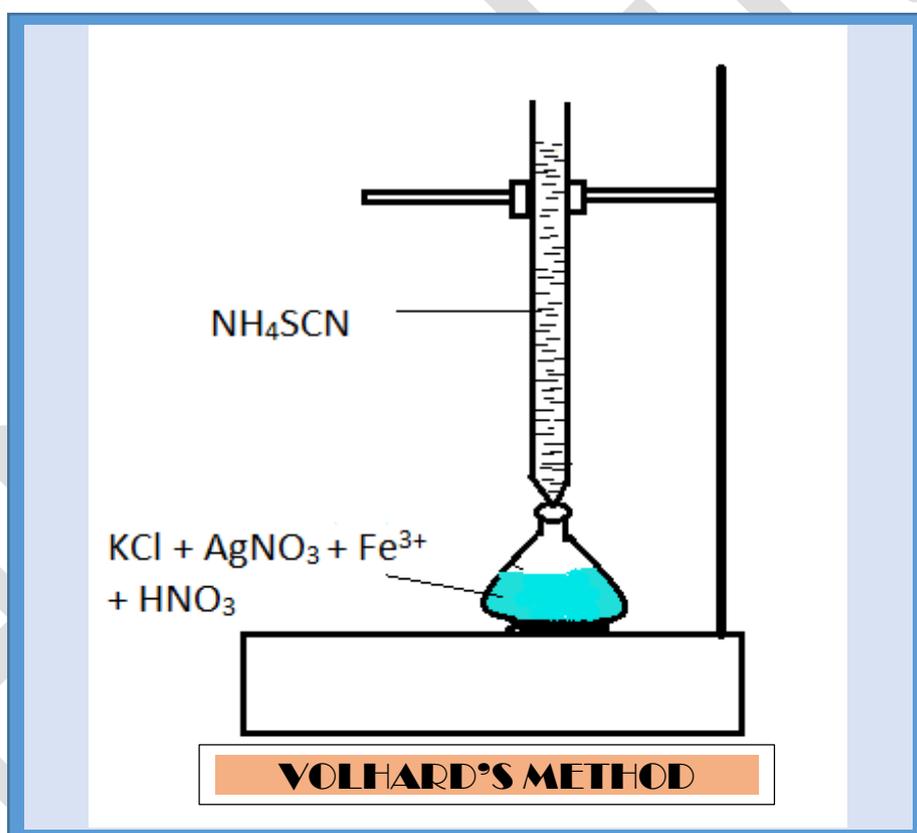
- Here we use AgNO_3 as a reagent. AgNO_3 (silver nitrate) when exposed to atmospheric air gets darkened due to reduction to metallic silver. Hence, AgNO_3 should be standardized.
- Standardization of AgNO_3 is carried out by its titration with primary standard compound NaCl which forms a precipitate of AgCl .

- When all the chloride ion has been titrated the very next drop of silver nitrate (AgNO_3) reacts with potassium chromate (K_2CrO_4). Upon reaction of AgNO_3 with K_2CrO_4 , reddish brown precipitates of Ag_2CrO_4 (silver chromate) forms.
- Formation of reddish brown precipitates of silver chromate indicates the end point.



- The actual molarity of AgNO_3 will be found from above titration.

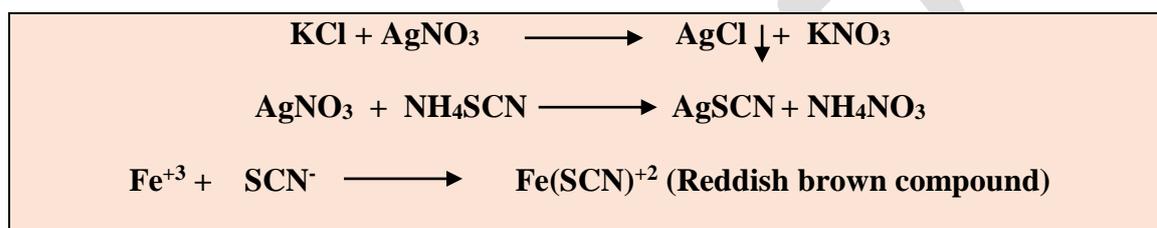
2) Determination of analyte:



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^+ is present, the excess of thiocyanate added reacts with Fe^{3+} to give **reddish brown ferric thiocyanate ($\text{Fe}(\text{SCN})^{+2}$)** compound.

- Volhard's method is carried out in acidic condition provided by nitric acid (0.5-1.5 M). Because HNO_3 prevents hydrolysis of Fe^{+3} to insoluble basic salts and it also prevents colour of Fe^{+3} in the indicator solution.
- In Volhard's method, first sample KCl is reacted with AgNO_3 . Once the sample consumed, excess of AgNO_3 will react ammonium thiocyanate (NH_4SCN) and all excess AgNO_3 is consumed, then NH_4SCN will react with indicator ion (Fe^{+3}). This reaction with indicator gives the **reddish brown $\text{Fe}(\text{SCN})^{+2}$** compound which indicates the end point.

REACTION:**METHODOLOGY:**

- 0.1 N AgNO_3 solution is taken and standardize first. Excess amount of this standardized AgNO_3 solution is taken as a reagent with sample (KCl) in conical flask.
- Add few drops of Fe^{+3} alum indicator.
- Add HNO_3 (nitric acid) for creating acidic media.
- This mixture is being titrated with NH_4SCN .
- When all AgNO_3 is reacted, NH_4SCN is react with Fe^{+3} 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_3 used to react with our sample (KCl). For that substrate volume of AgNO_3 obtained in normal determination from volume of AgNO_3 obtained in determination without sample (Blank determination).
- This volume of AgNO_3 is a volume required to react with sample.

Problems to overcome during Volhard's method:

1. During back titration Ag^+ 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^+ ions.

Alternatively, the mixture is boiled for few minutes and potassium nitrate (KNO_3) is used to prevent reabsorption of Ag^+ .

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

$$\frac{[\text{Cl}^-]}{[\text{SCN}^-]} = \frac{K_{sp}(\text{AgCl})}{K_{sp}(\text{AgSCN})}$$

$$= \frac{1.2 \times 10^{-10}}{7.1 \times 10^{-13}} = 169$$

When all the excess of Ag^+ has reached, the thiocyanate may react with AgCl precipitate.

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

Comment: Why nitrobenzene is used in Volhard's method of nitrogen.

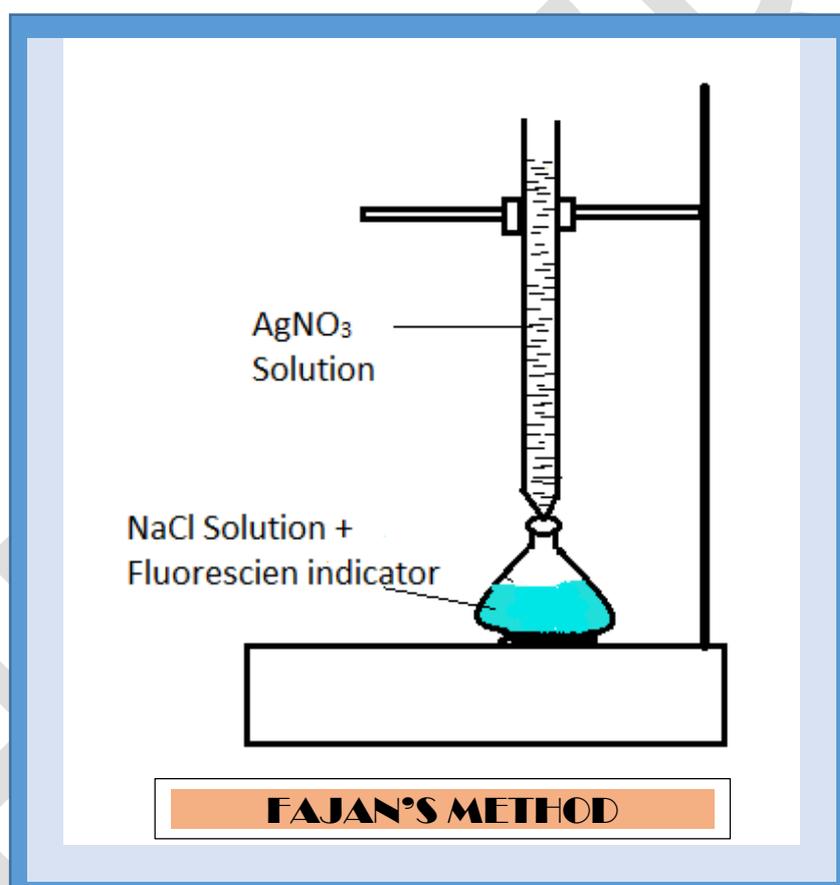
- During titration ammonium thiocyanate may react with Ag^+ ion from AgCl precipitates and error may be introduced in the titration.



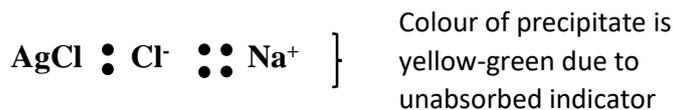
- To avoid this problem AgCl precipitates may be filtered off before titration. The other method to avoid this problem is addition of small volume of a heavy organic liquid that is not miscible with water.
(Like nitrobenzene, dibutyl phthalate, chloroform or carbon tetrachloride)
- These liquid are better 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_3 stays in the aqueous layer and is titrated with standard thiocyanate.

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

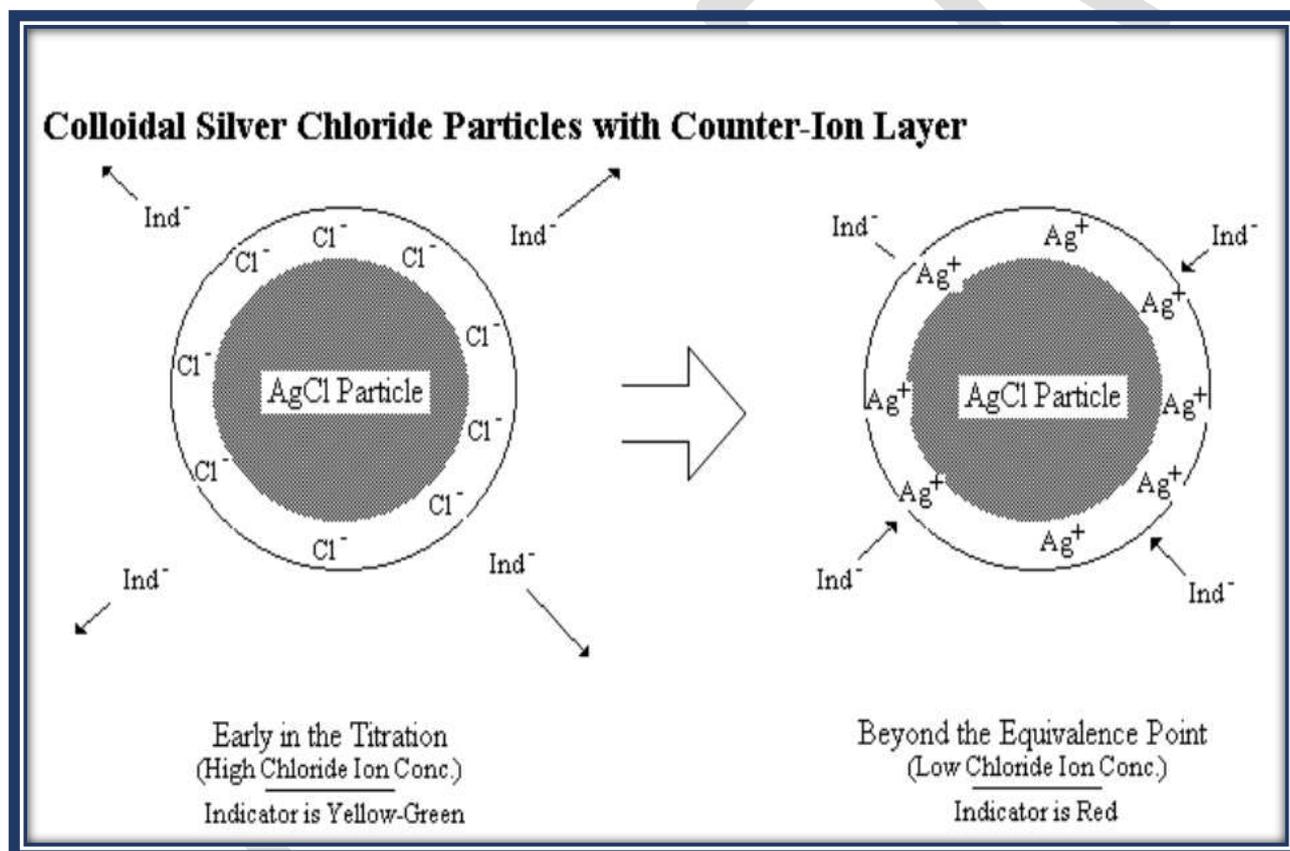
- This method is used to determine chloride, bromides and iodides.
- In Fajan's method, end point is observed by colour change of precipitates by adsorption of indicator on the surface of precipitates.
- K. Fajan through his study, introduced a useful type of indicator for precipitation titrations. For e.g. fluorescein, eosin, dichloro-fluorescein 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 sodium chloride (NaCl) is titrated with silver nitrate (AgNO₃) standard solution by using fluorescein as an indicator.
- In this reaction silver chloride (AgCl) precipitates will be formed and these precipitates will adsorb chloride ions (**Cl⁻, its own ion**) which are initially in excess before equivalence point. (Initially, NaCl is in excess before addition of AgNO₃ and till equivalence point)
- Thus, chloride ions form the primary adsorbed layer. Chloride ions are anions and thus repulses the indicator anion (In⁻) and more loosely held secondary (counter) layer of adsorbed ions is of cations, such as Na⁺.



- After the equivalence point Ag^+ will be in excess and thus surface of the precipitates adsorb positively charge Ag^+ (**its own ion**) from the AgNO_3 and this will form primary adsorbed layer and NO_3^- forms secondary layer. Now if the Na^+ salt of fluorescein is also present in the solution then the negatively charge fluorescein ions (In^-) would be adsorbed instead of NO_3^- as secondary adsorbed layer.



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

The factors which must be considered during selection or choice of an adsorption indicator.

- The indicator ion should have a charge (In^-) 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.

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 dichlorofluorescein 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:

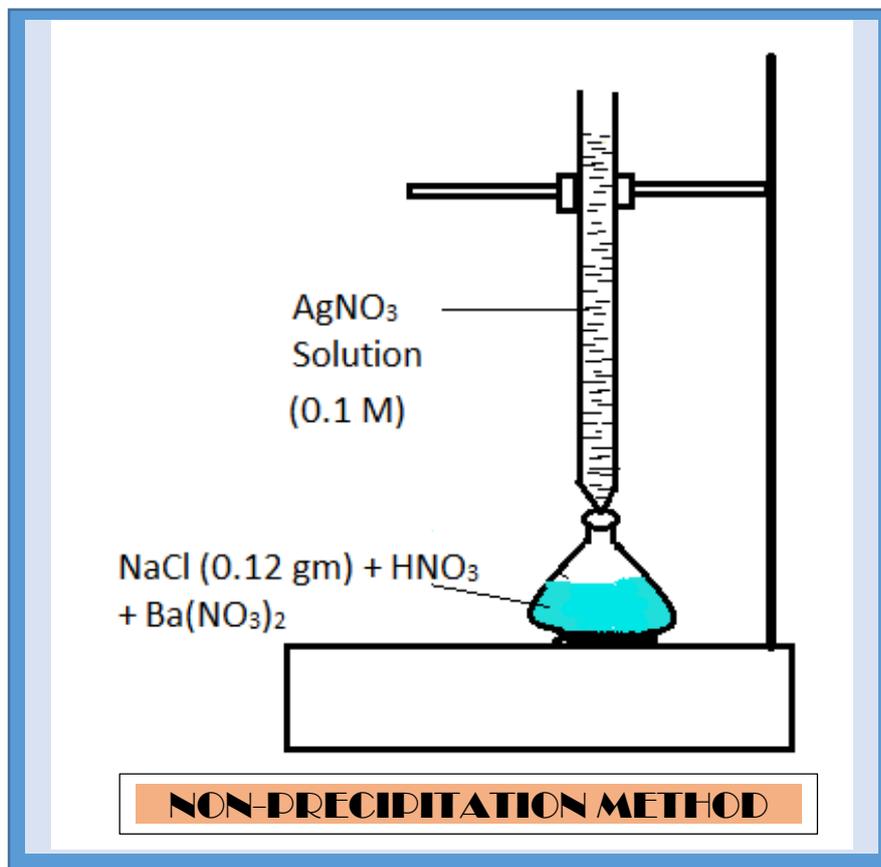
- Low background levels of non-reacting ions to ensure that coagulation does not occur.
[If non-reacting ion level is high coagulation occurs, which is not desired.]
- It cannot work with very low levels as there will not be enough precipitate to allow the colour change to be observed.
[If very low levels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

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.

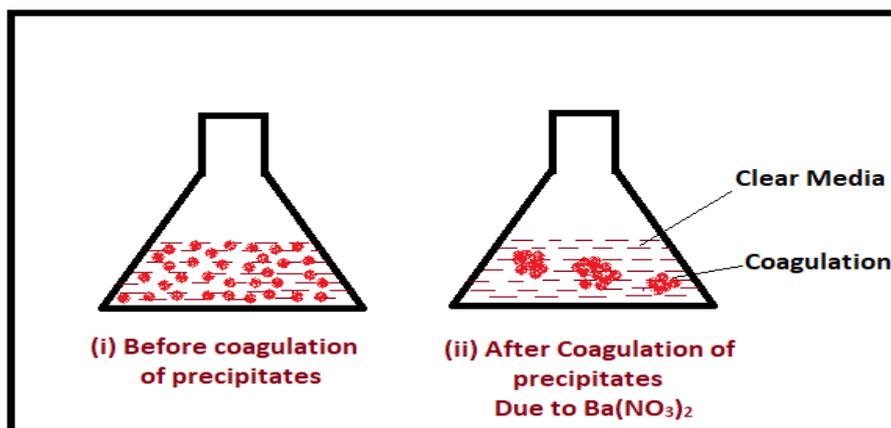
4) Non-Precipitation Method (Turbidity Method or Gay Lussac's method)

- 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 HNO₃ to provide an acidic media. (reaction better takes place in acidic media)
- Add Ba(NO₃)₂ 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_3 which start reaction of NaCl and AgNO_3 .
- First add 20 ml of 0.1 M AgNO_3 (at once) from burette to the mixture present in the conical flask.
- Reaction between NaCl and AgNO_3 takes place.



- AgCl precipitate will be coagulated by the effect of barium nitrate ($\text{Ba}(\text{NO}_3)_2$).
- After coagulation of AgCl precipitate, supernatant liquid will be clear.
- Add 1 ml of AgNO_3 , if chloride ion (Cl^-) will be present then again AgCl will be formed and coagulated.
- Again add 1 ml of AgNO_3 – 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_3 . Add $\text{Ba}(\text{NO}_3)_2$.
- Add 20 ml of 0.1 M AgNO_3 at once.
- AgCl will be coagulated.
- Add AgNO_3 dropwise, again precipitation will take place.
- After 21 ml, if we add 21.1 ml- precipitation occurs

21.2 ml- precipitation occurs

21.3 ml- turbidity observed.

- 21.2 ml is a reading which is end point. Above this result NaCl is no more in solution. All NaCl will be consumed and therefore precipitates will not be formed after 21.2 ml.

- Above this addition of 0.1 ml cause turbidity & therefore this method is known as turbidity method.

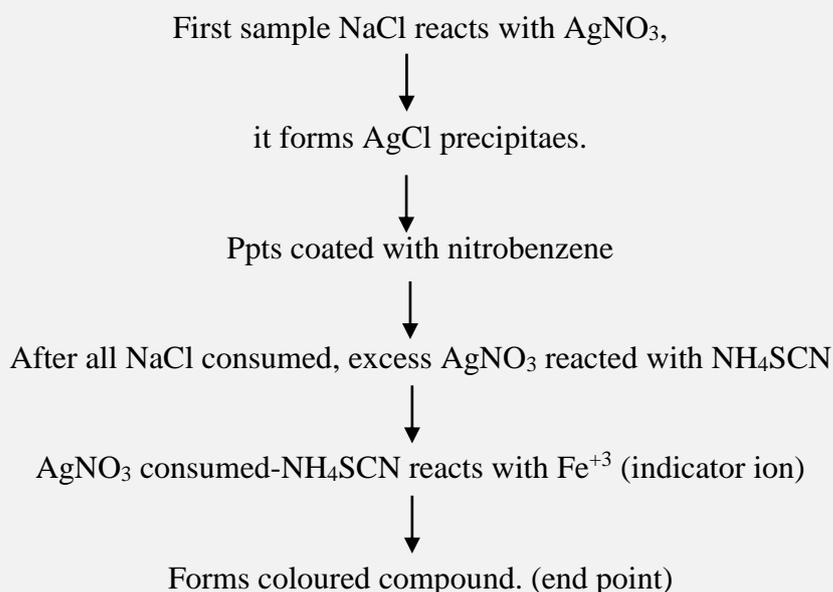
Estimation of Sodium Chloride

PRINCIPLE: (By Volhard's Method)

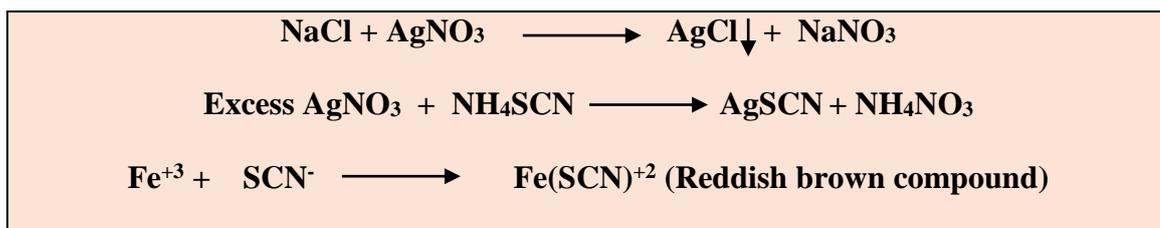
- Volhard's precipitation titration method (argentometric back titration) is used for the estimation of sodium chloride.
- NaCl, sodium chloride (sample) is reacted with excess quantity of AgNO₃ (precipitating agent).
- Precipitates of AgCl formed.
- The interference of AgCl precipitates are removed by coagulating the precipitates by adding nitrobenzene or dibutylphthalate.

Short Explanation:

- If coating by nitrobenzene is not done, AgCl precipitates interfere in the next step.(reaction of excess AgNO₃ with NH₄SCN)



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



- When all excess AgNO_3 is reacted with NH_4SCN , after that NH_4SCN reacts with indicator ion Fe^{+3} which gives the coloured amount of $(\text{Fe}(\text{SCN})^{+2})$.
- End point is detected by formation of reddish brown coloured compound ferric thiocyanate $(\text{Fe}(\text{SCN})^{+2})$.
- This determination gives the volume of AgNO_3 used.
- Take blank determination. Blank determination gives the volume of AgNO_3 reacts with NH_4SCN .
- Now substrate result of normal determination from the result of blank determination.

<u>Blank Determination</u>	<u>Normal Determination</u>
Whole AgNO_3 reacts with NH_4SCN due to absence of sample. (A)	AgNO_3 first reacts with NaCl (sample) After sample consumed remaining AgNO_3 reacts with NH_4SCN . (B)
<u>A-B</u> = gives the volume of AgNO_3 required to react with our sample (NaCl).	

- Thus, this reaction is known as Argentometric Back Titration. 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 2 M Nitric acid (HNO_3), 2 ml of dibutyl phthalate and 50 ml of 0.1 M AgNO_3 .
- Shake vigorously for 2 minutes.
- Add 2 ml of ferric ammonium sulphate (indicator) titrate with 0.1 M NH_4SCN until reddish brown colour appears.

- Perform blank titration.

Factor: Each ml of 0.1 M AgNO_3 is equivalent to 0.00584 gm of NaCl.

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