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MOHRS METHOD & VOLHARDS METHOD

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MOHRS METHOD

- **Karl Friedrich Mohr (1806-1879)** This method utilizes chromate as an indicator.
- Chromate forms a precipitate with Ag^+ but this precipitate has a greater solubility than that of AgCl , for example. Therefore, AgCl is formed first and after all Cl^- is consumed, the first drop of Ag^+ in excess will react with the chromate indicator giving a reddish precipitate.





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- **In this method, neutral medium should be used since, in alkaline solutions, silver will react with the hydroxide ions forming AgOH .**
- **In acidic solutions, chromate will be converted to dichromate. Therefore, the pH of solution should be kept at about 7.**
- **There is always some error in this method because a dilute chromate solution is used due to the intense color of the indicator.**
- **This will require additional amount of Ag^+ for the Ag_2CrO_4 to form.**



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PRECAUTION:

- 1) The titration must be carried out in ph range of 6.5-9 (i.e neutral or slightly in alkaline)**
- 2) In more alkaline medium silver hydroxide may be precipitated out**
- 3) In acidic solution ,concentration of chromate ion decreases greatly as In acidic medium due to the decrease in concentration of brick red color can not seen at the end point of titration**
- 4) In actual practice ,the concentration of chromate produces an intense yellow color to such and extent that the end point is masked . -therefore ,normally 0.003 -0.005M concentration should be employed in analytical procedures**



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VOLHARDS METHOD

- **Jacob Volhard (1834-1910)** This is an indirect method for chloride determination where an excess amount of standard Ag^+ is added to the chloride solution containing Fe^{3+} as an indicator.
- The excess Ag^+ is then titrated with standard SCN^- solution until a red color is obtained which results from the reaction:





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- The indicator system is very sensitive and usually good results are obtained.**
- The medium should be acidic to avoid the formation of $\text{Fe}(\text{OH})_3$.**
 - However, the use of acidic medium together with added SCN^- titrant increase the solubility of the precipitate leading to significant errors. This problem had been overcome by two main procedures.**
 - At end point, initially thiocyanate react with silver ions and forms precipitate. At end point, excess of thiocyanate (SCN^-) react with $\text{Fe}(\text{III})$ and forms reddish brown complex which indicate the end point of reaction.**



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➤ **This volhard method is used to determine the concentration of Ag^+ ions or concentration of halide ions (i.e. Cl^- , Br^- , I^-) indirectly i.e. by back titration.**

PRECAUTIONS:

- **During the titration in resulting solution ,concentration of nitric acid should be 0.5M- 1M.Here ,strong nitric acid is not used because it prevents the formation of thiocyanate iron(III) complex .Here ,acidic medium prevents the hydrolysis of Fe(III) as Fe(OH)_3 .**



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➤ **The solution must be free from nitrous acid otherwise it gives the instant red colouration forming the thiocynic acid.**

- **Temperature of the solution must be maintained below 250C since at an elevated temperature the red colour of the ferric thiocyanate complex fades away rapidly.**
- **When the excess of silver has reacted ,the thiocyanate may react with the silver chloride ,since thiocyanate is less soluble than silver chloride . i.e $\text{AgCl} + \text{SCN}^- \rightarrow \text{AgSCN} + \text{Cl}^-$ this will take place before reaction occurs with the iron (III) ions in the solution ,so there will be considerable titration error .**



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