

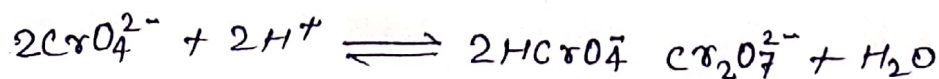
Ans (a) Precipitation indicator:

K_2CrO_4 is used as precipitation indicator in the titration of chlorides by $AgNO_3$ solution in neutral solutions. At the end-point, almost all chloride ions are precipitated as $AgCl$.



After that when a drop of $AgNO_3$ solution is added in excess, the Ag^+ ions combine with CrO_4^{2-} ions to form a brick red ppt of Ag_2CrO_4 . Since $AgCl$ is less soluble than Ag_2CrO_4 and also because the critical concentration of Cl^- ion is high, solubility product of $AgCl$ is first exceeded. After that when $AgNO_3$ solution is added, the solubility product of Ag_2CrO_4 is exceeded and Ag_2CrO_4 is also precipitated as brick red precipitate. This shows the end point. However a drop of $AgNO_3$ has to be added in excess.

The titration cannot be carried out in acid solution due to occurrence of the following reaction.



Since $HCrO_4^-$ is very weakly dissociated, the $[CrO_4^{2-}]$ is decreased very much and the solubility product of Ag_2CrO_4 is not exceeded at the end point and so Ag_2CrO_4 is not precipitated.

A large excess of Ag^+ will have to be added making the analysis wrong. When the solution is alkaline, AgOH may be precipitated and the solubility product of Ag_2CrO_4 is not exceeded and so the brick red ppt of Ag_2CrO_4 is not obtained at the end point.