********** 2ND SECTION (PART I) **********

Volhard's Method

It is a type of precipitation titration that depends on the formation of colored complex ions (colored solution) at the end point.

Main features of Volhard's method:

• **Sample:**	Cl^- , Br^-, I^- & SCN^-.
• **Type of titration:**	Back (Residual) titration.
• **Standard Solutions:**	⇒ 1st standard (25 ml): $AgNO_3$. ⇒ 2nd standard (titrant): NH_4SCN or KSCN.
• **pH:**	Acidic medium (HNO_3).
• **Indicator:**	Ferric salts such as: 1) Ferric alum = Ferric ammonium Sulfate { $FeNH_4(SO_4)_2.12H_2O$ }. OR 2) Ferric nitrate { $Fe(NO_3)_3$ }.
• **Color at E.P.:**	Faint orange or faint red color.

Introduction on Solubility Product (K_{sp}) :

- **K_{sp}** is calculated only for sparingly soluble salts (ex.: AgCl) and it is constant for a certain salt at a specified temperature.
- **Meaning of K_{sp}:**

  For AgCl (for example): $K_{sp} = [Ag^+][Cl^-]$......at saturated soln. (or at equilibrium).

- **K_{sp} values** for a certain salt can be known from reference tables.
- **Significance of K_{sp}:**

  ⇒ For the ppt of AgCl *(for example)* to be formed in a solution:

  $[Ag^+][Cl^-]$ must be > K_{sp} of AgCl.

  ⇒ ↑ **Solubility** product (K_{sp}) ≡ ↑ **Solubility** .... & vice versa.

  ⇒ If different precipitates can be formed:

  ↓ K_{sp} ≡ the salt is precipitated first (i.e: the salt is more insoluble or less soluble).

  ≡ more stable ppt.

N.B.: This rule is not always obeyed in case of non-symmetrical salts (i.e. salts in which the valence of the cation radicle ≠ the valence of the anion radicle) such as Ag_2CrO_4 , PbI_2 ......etc.

{although K_{sp} of Ag_2CrO_4 is less than K_{sp} of AgCl but Ag_2CrO_4 is more soluble than AgCl............*refer to Mohr's method*}.

Important example:

K_{sp} of $AgI < AgBr < AgSCN < AgCl$

So:

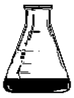
⇒ If a mix. of $\underbrace{I^-, Br^-, SCN^-, Cl^-}$ (of near concentrations) is treated with Ag^+:

$$\xrightarrow{+ Ag^+}$$

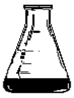
The order of precipitation will be:

1- AgI
2- AgBr
3- AgSCN
4- AgCl

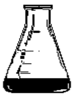
⇒ If we have:



AgCl ppt $\xrightarrow{+ SCN^-}$ AgSCN ppt + Cl^-



AgBr ppt $\xrightarrow{+ SCN^-}$ No reaction

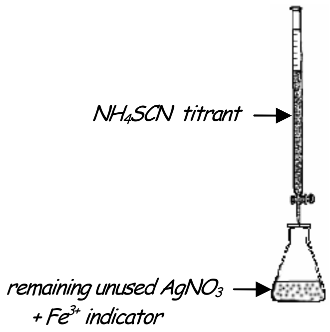


AgI ppt $\xrightarrow{+ SCN^-}$ No reaction

Exp.(5): Determination of NaCl by Volhard's method

Principle : {Back (Residual) titration}

It depends upon the precipitation of Cl^- as AgCl by the addition of a known excess of standard $AgNO_3$ THEN the remaining unreacted $AgNO_3$ is back titrated against standard NH_4SCN using ferric alum indicator.



$\boxed{1}$

$$\underset{\text{(sample)}}{Cl^-} + \underset{\text{(25 ml st. } AgNO_3)}{Ag^+} \longrightarrow \underset{\text{white ppt}}{AgCl\downarrow}$$

$\boxed{2}$ **Titration reaction**:

$$\underset{\text{(remaining unused excess)}}{Ag^+} + \underset{(NH_4SCN\text{ titrant})}{SCN^-} \longrightarrow \underset{\text{white ppt}}{AgSCN\downarrow}$$

$\boxed{3}$ **End point reaction**:

$$\underset{\substack{\text{(1st dr. excess after complete}\\ \text{reactn with the unused } Ag^+)}}{SCN^-} + \underset{\text{(indicator)}}{Fe^{3+}} \longrightarrow \underset{\substack{\text{faint orange}\\ \text{or faint red color}}}{[Fe(SCN)]^{2+}}$$

Notes:

1) Since K_{sp} of AgSCN < AgCl so AgSCN is more stable (more insoluble) than AgCl so after complete reaction between NH_4SCN titrant & the excess unused $AgNO_3$, the SCN^- ions will attack AgCl ppt and replace Cl^-:

$$AgCl_{(solid)} + SCN^- \longrightarrow AgSCN_{(solid)} + Cl^-$$

To overcome this problem: The ppted AgCl must be removed or coated before titrating the excess unused Ag^+ with NH_4SCN & that can be achieved by:

1- Filtration of AgCl ppt before titration.

OR 2- Coating AgCl ppt by the addition of an organic solvent as *nitrobenzene* or *amyl alcohol* which forms a water-proof layer around AgCl ppt protecting it from reaction with NH_4SCN.

***Question**: (Complete the following)*

In the detn. of NaCl by Volhard's method, if AgCl is not removed, the observed E.P. will be higher than the true and the calculated Cl^- content (concn.) will be lower than the true... because it's a back titration.

2) **Strong shaking** near the E.P. is required to prevent adsorption of Ag^+ ions on the freshly ppted AgSCN which leads to occurrence of early E.P.

***Question**: (Complete the following)*

In the detn. of NaCl by Volhard's method, if the titration is done without vigorous shaking at the E.P., the observed E.P. will be lower than the true and the calculated concn. will be higher than the true.

3) The titration is performed only in **acidic medium (HNO_3)** because:

a. In alkaline medium, Ag^+ & Fe^{3+} ions will be ppted as AgOH & $Fe(OH)_3$.

b. HNO_3 prevent precipitation of other Ag^+ salts like carbonate and sulfide because these salts are soluble in HNO_3.

c. HNO_3 helps the coagulation of AgCl ppt & that facilitates its filtration or coating.

BUT too high concentration of HNO_3 should be avoided because that destroys the colored ferric thiocyanate complex formed at the E.P.

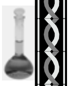
Required Glassware (الأدوات المطلوبة):

- **100-ml measuring (volumetric) flask**  . → *well-closed*
- **Stoppered flask.** → *well-closed*
- **Conical flask.**
- **Burette & burette holder.**
- **10-ml bulb pipette.**
- **25-ml bulb pipette.**
- **10-ml graduated pipette.**
- **10-ml measuring cylinder.**
- **Filter papers (Whatmann no.1).**
- **Funnel.**
- **Beaker.**
- **Dropper.**
- **Calculator.**

Procedure :

!!! BEFORE STARTING THE DETERMINATION, WASH ALL THE GLASSWARE WITH DISTILLED WATER.

(because tap water contains Cl^-).

1 Transfer accurately 10 ml of the sample into a 100-ml measuring flask. 

2 Add 2 ml conc. HNO_3.

3 Add 25 ml of **0.05** N $AgNO_3$.

4 Shake well for few minutes to coagulate the precipitated AgCl.

5 Complete to the mark with **distilled** water.

6 Mix well.

7 Filter through a dry filter paper, rejecting the first few milliliters of the filtrate.

8 Transfer 25 ml of the filtrate into a clean glass **stoppered** flask.

✍

9 Add 1 ml ferric alum indicator.

✍

10 Titrate with **0.01** N NH_4SCN with strong shaking.

Color at E.P.: Faint Orange Color not disappear on strong shaking.

✍

Calculations :

أنظر ورق الحسابات: (القوانين الأساسية) + (من صفحة ١١ إلى صفحة ١٤)

In this exp., the equivalence factor (F) can be calculated on **0.05 N $AgNO_3$ (1^{st} standard "25 ml")** OR on 0.01 N **NH_4SCN (2^{nd} standard "titrant")** but it is preferred to be calculated on the 1^{st} standard.

If (F) is calculated on the 1^{st} standard (0.05 N $AgNO_3$):

Equivalence factor (F):

$$\underset{\textit{standard}}{1\ AgNO_3} \equiv \underset{\textit{sample}}{1\ NaCl}$$

$$\text{each ml of 0.05 N } AgNO_3 \equiv \frac{1 \times \text{M.W. of } NaCl \times 0.05}{1 \times 1000} \equiv \text{..........}\ g\ NaCl$$

Calculation of concentration:

$$\text{Concn.} = \frac{[\overset{\overset{0.05\text{ N}}{\uparrow}}{25} - \underset{\underset{\text{Dilution factor}}{\downarrow}}{4}\ \overset{\overset{0.01\text{ N}}{\uparrow}}{E.P.}\ (\frac{0.01}{0.05})] \times \overset{\overset{\mathbf{0.05\ N}}{\uparrow}}{F} \times 1000}{10} = \text{..........}\ g/L$$

If (F) is calculated on the 2^{nd} standard (0.01 N NH_4SCN):

Equivalence factor (F):

$$\underset{\textit{standard}}{1\ NH_4SCN} \equiv \underset{\textit{sample}}{1\ NaCl}$$

$$\text{each ml of 0.01 N } NH_4SCN \equiv \frac{1 \times \text{M.W. of } NaCl \times 0.01}{1 \times 1000} \equiv \text{..........}\ g\ NaCl$$

Calculation of concentration:

$$\text{Concn.} = \frac{[\overset{\overset{0.05\text{ N}}{\uparrow}}{25}\ (\frac{0.05}{0.01}) - \underset{\underset{\text{Dilution factor}}{\downarrow}}{4}\ \overset{\overset{0.01\text{ N}}{\uparrow}}{E.P.}] \times \overset{\overset{\mathbf{0.01\ N}}{\uparrow}}{F} \times 1000}{10} = \text{..........}\ g/L$$

[Molecular weight of NaCl = 58.5]

Determination of (Cl^-) by Volhard's method

Calculate the concentration of the mentioned chloride sample:

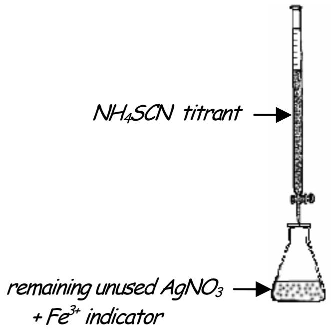
⬇ **Data** ⬇	**1st Problem**	**2nd Problem**	**3rd Problem**	**4th Problem**	**5th Problem**	**6th Problem**
➡ **Sample :**	10 ml NaCl sample (M.W.= 58.5)	10 ml $BaCl_2$ sample (M.W.= 208)	10 ml NaCl sample (M.W.= 58.5)	25 ml NaCl sample (M.W.= 58.5)	10 ml $AlCl_3$ sample (M.W.= 133.3)	20 ml $CaCl_2$ sample (M.W.= 111)
➡ **1st Standard :**	50 ml 0.03 N $AgNO_3$	25 ml 0.4 N $AgNO_3$	25 ml 0.5 N $AgNO_3$	50 ml 0.05 N $AgNO_3$	25 ml 0.6 N $AgNO_3$	50 ml 0.04 N $AgNO_3$
➡ **Volume titrated:** *{ after dilution to 100 ml & then filtration }*	25 ml of the filtrate	25 ml of the filtrate	20 ml of the filtrate	10 ml of the filtrate	25 ml of the filtrate	25 ml of the filtrate
➡ **2nd Standard (Titrant) :**	0.01 N NH_4SCN	0.1 N NH_4SCN	0.1 N NH_4SCN	0.01 N NH_4SCN	0.3 N NH_4SCN	0.02 N NH_4SCN
➡ **End point :**	15 ml	15 ml	15 ml	5 ml	8 ml	12 ml
Answers						
Equivalence factor if calculated on $AgNO_3$:	1.76×10^{-3} *gm NaCl*	0.0416 *gm $BaCl_2$*	0.02925 *gm NaCl*	2.925×10^{-3} *gm NaCl*	0.02666 *gm $AlCl_3$*	2.22×10^{-3} *gm $CaCl_2$*
Equivalence factor if calculated on NH_4SCN	5.85×10^{-4} *gm NaCl*	0.0104 *gm $BaCl_2$*	5.85×10^{-3} *gm NaCl*	5.85×10^{-4} *gm NaCl*	0.01333 *gm $AlCl_3$*	1.11×10^{-3} *gm $CaCl_2$*
⇒ **Concentration :**	**5.265** gm/L	**41.6** gm/L	**29.25** gm/L	**4.68** gm/L	**23.99** gm/L	**2.886** gm/L

Exp.(6): Determination of KBr by Volhard's method

Principle : {Back (Residual) titration}

It depends upon the precipitation of Br^- as AgBr by the addition of a known excess of standard $AgNO_3$ THEN the remaining unreacted $AgNO_3$ is back titrated against standard NH_4SCN using ferric alum indicator.

$$\boxed{1}\quad \underset{\text{(sample)}}{Br^-} + \underset{\text{(25 ml st. } AgNO_3\text{)}}{Ag^+} \longrightarrow \underset{\text{yellowish white ppt}}{AgBr\downarrow}$$



$\boxed{2}$ **Titration reaction**:

$$\underset{\text{(remaining unused excess)}}{Ag^+} + \underset{\text{(}NH_4SCN\text{ titrant)}}{SCN^-} \longrightarrow \underset{\text{white ppt}}{AgSCN\downarrow}$$

$\boxed{3}$ **End point reaction**:

$$\underset{\text{(1st dr. excess after complete reactn with the unused } Ag^+\text{)}}{SCN^-} + \underset{\text{(indicator)}}{Fe^{3+}} \longrightarrow \underset{\text{faint orange or faint red color}}{[Fe(SCN)]^{2+}}$$

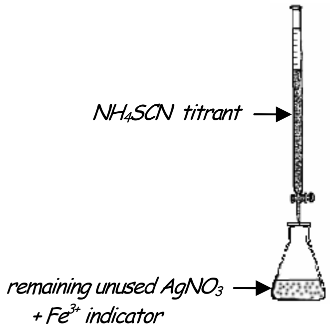
Bromide is determined by Volhard's method in the same way as chloride but without removing the ppted AgBr because it is more insoluble (lower K_{sp}) than AgSCN so SCN^- ion will not attack AgBr ppt after complete reaction with the unused Ag^+.

Exp.(7): Determination of NaI by Volhard's method

Principle: **{Back (Residual) titration}**

It depends upon the precipitation of I^- as AgI by the addition of a known excess of standard $AgNO_3$ THEN the remaining unreacted $AgNO_3$ is back titrated against standard NH_4SCN using ferric alum indicator.

1 $$\underset{\text{(sample)}}{I^-} + \underset{\text{(25 ml st. }AgNO_3\text{)}}{Ag^+} \longrightarrow \underset{\text{yellow ppt}}{AgI\downarrow}$$



2 **Titration reaction**:

$$\underset{\text{(remaining unused excess)}}{Ag^+} + \underset{\text{(}NH_4SCN\text{ titrant)}}{SCN^-} \longrightarrow \underset{\text{white ppt}}{AgSCN\downarrow}$$

3 **End point reaction**:

$$\underset{\text{(1st dr. excess after complete reactn with the unused }Ag^+\text{)}}{SCN^-} + \underset{\text{(indicator)}}{Fe^{3+}} \longrightarrow \underset{\text{faint orange or faint red color}}{[Fe(SCN)]^{2+}}$$

Iodide is determined by Volhard's method in the same way as chloride but differs from chloride in the following:

1. **No need to remove the ppted AgI because it is more insoluble (lower K_{sp}) than AgSCN so SCN^- ion will not attack AgI ppt after complete reaction with the unused Ag^+.**
2. **The iodide solution must be diluted suitably to minimize the adsorptive effect on the ppt.**
3. **HNO_3 must be added after adding $AgNO_3$ (not after adding the sample as in case of chloride) to prevent any oxidation of the iodide (I^-) sample into iodine (I_2).**

Question: (Complete the following)

In the determination of NaI by Volhard's method, if HNO_3 is added directly after the sample, the observed E.P. will be higher than the true.

{because HNO3 will cause oxidation of I sample ≡ ↓ reacted part ≡ ↑ remaining part ≡ ↑ E.P.}.

***** >>Best wishes>> *****