# Precipitimetry II

# End point Detection

## No Indicator methods

1. **Appearance of ppt.**
   - Liebeg's method
   - Denige's method
2. **Disappearance of ppt.**

e.g. titration of $Ag^+$ by $CN^-$

## Indicator methods

1. **Formation of colored ppt.**
   - Mohr's method
2. **Formation of colored complex**
   - Volhard's method
3. **Adsorption indicator method**
   - Fajan's method

# Determination of Chloride/Cyanide Mixture

# Principle

**$CN^-$ Only**

**By Liebeg's method**

**Ksp of AgCN < ksp of AgCl**

**Total $CN^-/Cl^-$**

**Volhard's method**

**Formation of colored complex**

**Remaining unreacted $AgNO_3$**

**$CN^-$ / $Cl^-$**

**Known excess standard $AgNO_3$**

**pH 1-3**

**Titrated against standard $NH_4SCN$**

| AgCN | AgCl |
|---|---|

**Must be <u>filtered</u> .. Why?**

**$Ag^+ + SCN^- \longrightarrow AgSCN$**

**Indicator: ferric alum**

**$Fe^{3+} + 2SCN^- \longrightarrow [Fe(SCN)_2]^+$**

**Red color**

**End point: first faint red color**

**AgCN & AgCl must be <u>filtered</u> .. Why?**

**Ksp of AgSCN < Ksp of AgCl (AgCl is more soluble than AgSCN)**

↓

**$SCN^-$ can replace $Cl^-$ in its ppt of AgCl so, over consumption of $SCN^-$**

# Volhard's method is used in acidic medium (pH 1-3) .. Why?

## In Acidic medium

- ✓ Red color (at end point) is stable in acidic medium
- ✓ $Fe^{3+}$ in indicator is colorless in acid medium, easier to detect end point

## In alkaline medium

- × $Ag^{+}$ is precipitated as $Ag_2O$ (Black ppt.)
- × $Fe^{3+}$ is precipitated as $Fe(OH)_3$ (Red ppt.)

**Acidity of the medium is adjusted using $HNO_3$ .. Why ?**

**Because all $NO_3$ salts are soluble**

**But ..**

**HCl is NOT used ⟶ to prevent pptn of AgCl**

**$H_2SO_4$ is NOT used ⟶ to prevent pptn of $Ag_2SO_4$**

**$CH_3COOH$ is NOT used ⟶ to prevent formation of ferric acetate (red color)**

# Procedure

## $CN^-$ Only

In Conical Flask

10 ml Sample (Taken by burette)+Titrate against $\frac{N}{40}$ $AgNO_3$

End point: First turbidity

mls A

## Total $CN^-/Cl^-$

In 100 ml measuring flask

10 ml Sample (Taken by burette)

+ 25 ml $\frac{N}{40}$ $AgNO_3$

+ 1 ml Conc. $HNO_3$

+ complete to the mark with distilled water & Mix well

+ Filter ⟶ wash the flask with 1st 10 ml of filtrate then discard

In Conical Flask

25 ml of the filtrate (bulb or burette) + 1ml ferric alum

Titrate against $\frac{N}{40}$ $NH_4SCN$

End Point: first faint red color

mls B

| Liebeg's method | Volhard's method |
| --- | --- |
| $2\ CN^- + AgNO_3$ ↓ $[Ag(CN)_2]^- + NO_3^-$ | $CN^- + AgNO_3$ ↓ $AgCN + NO_3^-$ |
| $1\ Ag^+ \approx 2\ CN^-$ | $1\ Ag^+ \approx 1\ CN^-$ |
| $½\ Ag^+ \approx 1\ CN^-$ | |

**Liebeg's gives ½ reading of volhard's**

# 3- Calculation

$F_{KCN}=0.00325g$

$$\text{Concn. of } CN^- = \frac{mls \times F \times 1000}{10\ (sample\ volume)} = \quad g/L$$

Only titration of 25 mls of 100 mls

mls of total= (25) – (mlsB×4×f)

Total reading of volhard's

Reading of CN (Liebeg's)

$$\text{Concn. of } Cl^- = \frac{[(25 - mlsB \times 4 \times f) - mlsA \times 2] \times F \times 1000}{10\ (sample\ volume)} = \quad g/L$$

# Determination of Iodide / chloride sample

# 1- Principle Fajan's Method

## Adsorption indicator

**It is organic dye adsorbed at end point on ppt and change its color**

| Has color when non adsorbed | ⟵ Organic dye ⟶ | Has Another color when adsorbed on ppt |
|---|---|---|

### Types

| | |
|---|---|
| **Weak acid** e.g. Eosin & Fluorscein<br>For example titration of halide sample by $Ag^+$ titrant | **Weak base** e.g. Rhodamine-6-G<br>For example titration of $Ag^+$ sample by halide as titrant |

**N.B**

**Fluorescein is used for all halides at pH 7- 9**

**Eosin (Tetra bromo Fluorescein) being stronger acid than fluorescein used at pH 2 for determination of iodide and bromide**

# For Successful use of adsorption indicator

## PPt. must be ..

1) Colloidal → surface area increase → Adsorption increase
2) ppt strongly adsorb its own ion

## Indicator must be ..

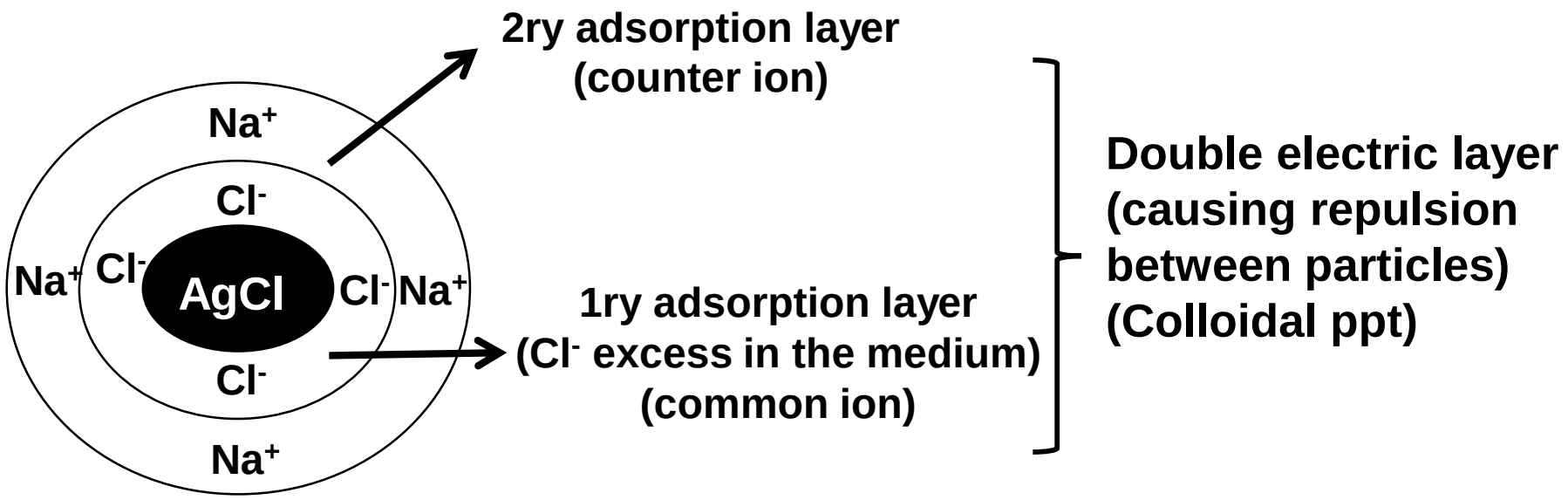
1) Opposite in charge to titrant
2) Adsorption power not higher than the ion to be determined so adsorbed after complete pptn
3) Suitable concn of indicator to ppt after complete pptn of ions (not exceeding the ksp of its silver salt during the titration )

## Medium must be ..

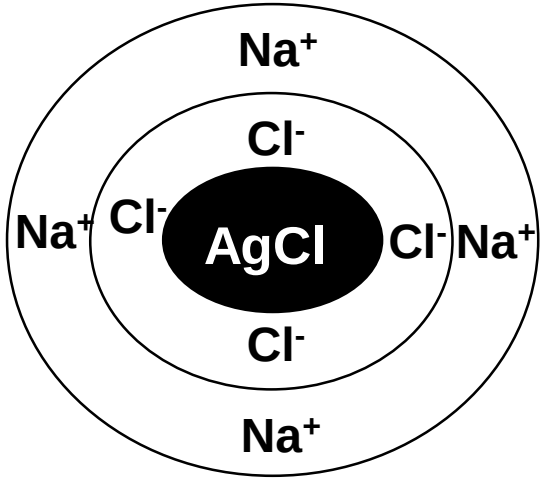
Suitable for ionization of indicator

- Acid indicator acts in alkaline media
- Basic indicator acts in acid media

**For example:**
**Titration of NaCl sample with Std. $AgNO_3$ using adsorption indicator**

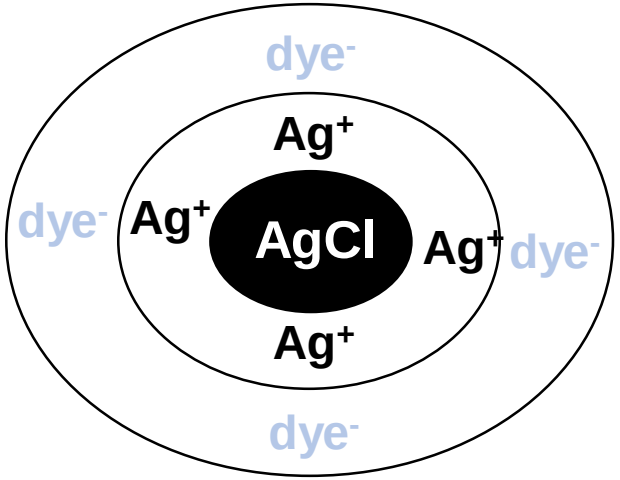


**Before end point**




**At end point**


**1st drop xss after end point**




**AgCl ppt & excess $Cl^-$ is adsorbed to form 1ry Adsorption layer**

↓ promotes

**2ry adsorption of oppositely charged ion**

↓ form

**Double electric layer causing repulsion between particles as colloidal ppt**

**$AgNO_3$ precipitate $Cl^-$ in primary adsorption layer**

↓

**destruction of double electric layer**

↓

**Flocculation starts**

**$Ag^+$ is Adsorbed on the ppt which promote 2ry adsorption either of $NO_3^-$ or Acidic dye**

**Depending on the more electronegative & which form more stable insoluble salt**

## Eosin can NOT be used in determination of chloride .. Why?

**Eosin is more electronegative than chloride and have high adsorption power, so eosin will be adsorbed at 1ry adsorption layer before end point**

# Determination of Chloride/Iodide sample

## Fajan's Method

This method involves the use of <u>adsorption indicator</u>.

At the end point first excess of $AgNO_3$ causes adsorption of indicator on the precipitate (colloidal) → change in color of the indicator

# 2- Procedure

**$I^-$** In Conical Flask

10 ml Sample + 5 dps Eosin + Titrate against $\frac{N}{40}$ $AgNO_3$

End point: Orange ⟶ Pink ppt

mls A

**Total** In Conical Flask

10 ml Sample + 10 dps Fluorescein + Titrate against $\frac{N}{40}$ $AgNO_3$

End point: Pink Flocculates with relatively clear supernatant

mls B

Gentle shaking (rotation) during titration so as not to break double electric layer

To determine the color, look from above on white background

Avoid direct exposure of the flask to the light

# 3- Calculation

$$\text{Concn. of } I^- = \frac{\text{mls}A \times F \times 1000}{10\ (sample\ volume)} = \quad \text{g/L}$$

$1\text{ml}\ \frac{N}{40}\ AgNO_3 = 0.00415\text{g}$

$$\text{Concn. of } Cl^- = \frac{(\text{mls}B - mlsA) \times F \times 1000}{10\ (sample\ volume)} = \quad \text{g/L}$$

$1\text{ml}\ \frac{N}{40}\ AgNO_3 = 0.00146\text{g}$

# Thank You