

# End point Detection in Precipitometry

## No Indicator methods

1 Appearance of ppt.

Liebeg's method

Denige's method

2 Disappearance of  
ppt.

e.g. titration of  $\text{Ag}^+$  by  $\text{CN}^-$

## 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



# • Volhard's method

Direct

□  $\text{Ag}^+$  ions titrated by thiocyanate using ferric alum as indicator

□ End point: First faint red color

Indirect

Known excess standard  $\text{AgNO}_3$  precipitate by halides, cyanide, phosphate then back titrate excess unreacted  $\text{AgNO}_3$  by thiocyanate using ferric alum as indicator

End point: First faint red color

# Determination of Silver sample

**Volhard's method**

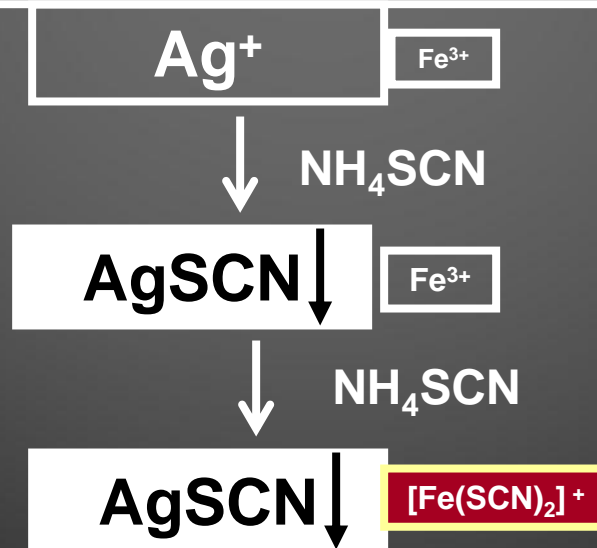


# Principle

- In Acidic medium (pH 1-3)
- Ag ions titrated by thiocyanate using ferric alum as indicator
- $\text{Ag}^+ + \text{NH}_4\text{SCN} \rightarrow \text{AgSCN ppt}$
- First drop excess of  $\text{NH}_4\text{SCN}$  will react with the Ferric alum indicator



- End point: First faint red color



## 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
- ✓  $\text{Fe}^{3+}$  in indicator is colorless, easier to detect end point

### In alkaline medium

- ×  $\text{Ag}^+$  is precipitated as  $\text{Ag}_2\text{O}$  (Black ppt.)
- ×  $\text{Fe}^{3+}$  is precipitated as  $\text{Fe}(\text{OH})_3$  (Red ppt.)

Acidity of the medium is adjusted using  $\text{HNO}_3$  .. Why ?

Because all  $\text{NO}_3^-$  salts are soluble

But ..

$\text{H}_2\text{SO}_4$  is NOT used  $\longrightarrow$  to prevent pptn of  $\text{Ag}_2\text{SO}_4$

$\text{CH}_3\text{COOH}$  is NOT used  $\longrightarrow$  to prevent formation of ferric acetate  
(red color)  $\text{Fe}(\text{CH}_3\text{COO})_3$



## 2- Procedure

### In Conical Flask



10 ml Sample  
+ 1ml ferric Alum (indicator)  
+ 1ml Conc.  $\text{HNO}_3$   
Titrate against N/40  $\text{NH}_4\text{SCN}$   
End point: **1<sup>st</sup> change in colour (red)**

# 3- Calculation

$$\text{Concn. of } \text{Ag}^+ = \frac{\text{mlsA} \times f \times F \times 1000}{10} = \text{g/L}$$

$$\text{M.wt of AgNO}_3 = 169$$



# Determination of Chloride sample

**Volhard's method**



## Volhard's method

Formation of colored complex

Indirect Argentometry

In Acidic medium (pH 1-3)

Known excess standard  $\text{AgNO}_3$  precipitate chloride, then back titrate excess unreacted  $\text{AgNO}_3$  by thiocyanate using ferric alum as indicator

End point: First faint red color



Red color

Remaining unreacted  $\text{AgNO}_3$



$\text{AgCl}$

Must be filtered .. Why?

$K_{sp}$  of  $\text{AgSCN} < K_{sp}$  of  $\text{AgCl}$  ( $\text{AgCl}$  is more soluble than  $\text{AgSCN}$ )



$\text{SCN}^-$  can replace  $\text{Cl}^-$  in its ppt of  $\text{AgCl}$  so, over consumption of  $\text{SCN}^-$

↓ pH 1-3  
Titrated against standard  $\text{NH}_4\text{SCN}$

Indicator: ferric alum

End point: first faint red color



# Procedure

In 100 ml measuring flask



10 ml Sample  
+ 25 ml  $\frac{N}{40}$  AgNO<sub>3</sub>  
+ 1 ml Conc. HNO<sub>3</sub>  
+ complete to the mark with distilled water & Mix well  
+ Filter → wash the flask with 1<sup>st</sup> 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<sub>4</sub>SCN  
End Point: first faint red color

mls B



### 3- Calculation

Only titration of 25 mls of 100  
mls

$$\text{Concn. of Cl}^- = \frac{[25 - (\text{mls} \times 4 \times f)] \times F \times 1000}{10 \text{ (sample volume)}}$$

10 (sample volume)

$$F_{\text{NaCl}} = 0.001463\text{g}$$

**Thank You**

