Precipitimetry

Precipitimetry

Volumetric method involves formation of practically insoluble salt using precipitating agent

Conditions of precipitimetric reaction:

- ✓ **The ppt. must be practically insoluble**
- ✓ **Rapid precipitation**
- ✓ **Easy detection of end point**

The rule that controls formation of precipitate is Solubility product

If a sparingly soluble salt is dispersed in water (or other solvent) ⟶ very small amount of solid phase is converted to soluble molecules ⟶ which will be ionized spontaneously

$$AB \leftrightarrow AB \leftrightarrow A^- + B^+$$

Solid Soluble

$$Ksp = [A^-][B^+]$$

Solubility Product (ksp)

It is the product of molar conc. of ions each raised to a power equal the no. of ions

$$\text{Ksp of } A_nB_m = [A]^n\,[B]^m$$

For example

$$\text{Ksp of } AgCl = [Ag^+][Cl^-]$$

$$\text{Ksp of } Ag_2S = [Ag^+]^2\,[S^{2-}]$$

Substance with lower ksp precipitates first

During precipitation of mixture of I^-, Br^-, Cl^- with $AgNO_3$

AgI precipitate first then AgBr then AgCl

because Ksp AgI < Ksp AgBr < ksp AgCl

Gradual pptn. is due to difference in ksp called
Fractional precipitation

End point Detection

No Indicator method

1. Appearance of ppt.
   - Liebeg's method
   - Denige's method (modified Liebeg's method)
2. Disappearance of ppt.

Indicator method

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 sample

Mohr's method

1- Principle Mohr's Method

Direct Argentometry

In neutral or slightly alkaline medium (pH 7- 9)

Chloride sample is titrated with Std. $AgNO_3$ forming AgCl ppt. using n-chromate as indicator

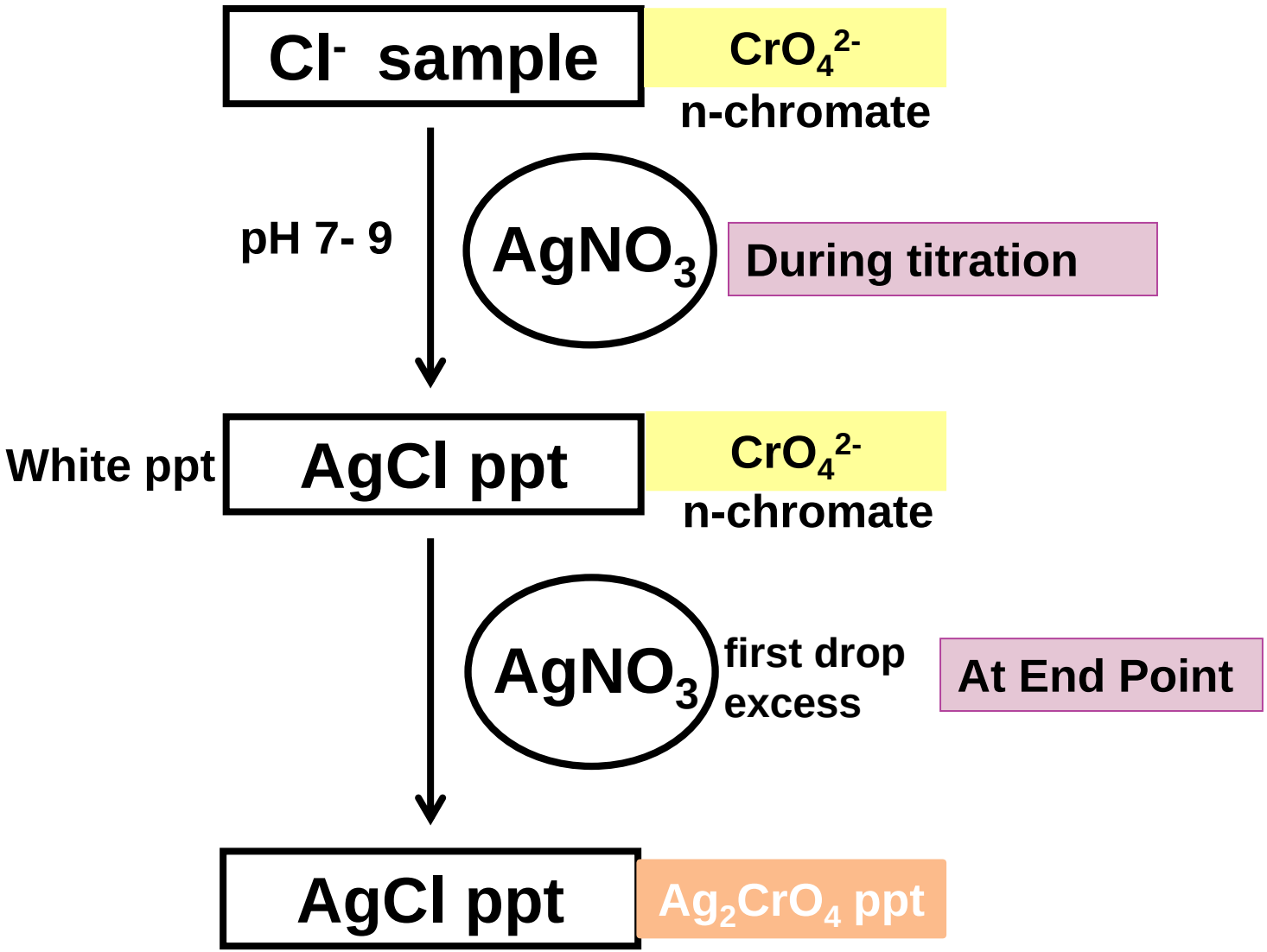
$$NaCl + AgNO_3 \longrightarrow AgCl + NaNO_3$$

After precipitation of all Cl^-

first drop excess of St. $AgNO_3$ react with n- chromate

$\longrightarrow$ **Ag_2CrO_4 brick red ppt.**

Mohr's Method



n-chromate

The yellow color of n-chromate masks the end point → so used in very diluted solution (0.002- 0.005 M)

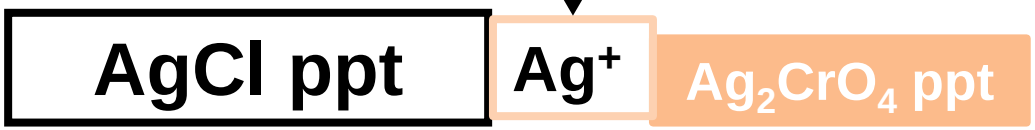
Saturated with $AgNO_3$ BUT still needs Ag^+ to exceed ksp of Ag_2CrO_4

Blank … How ?

10 ml distilled H_2O + talc or $CaCO_3$ (free of Cl^-) + 1ml n-chromate ⟶
titrate against N/40 $AgNO_3$ till <u>first faint brick red</u>

Blank … Why ?

Error



To cancel the amount of $AgNO_3$ needed to produce detectable quantity of Ag_2CrO_4 ppt to <u>human eye</u> especially when using dilute solution of chromate indicator

<u>Blank is</u> <u>subtracted from</u> <u>mls of experiment</u> as <u>correction factor</u>
to cancel error resulting from late detection of end point in medium

2- Procedure

In Conical Flask

10 ml Sample + 1 ml n-chromate
≠

N/40 $AgNO_3$

End Point : Buff color

N.B.
In precipitimetry, <u>GENTLE shaking</u> is required .. To prevent coagulation of ppt.

3- Calculation

1ml standard ≡ ? ? g sample

F

$$1AgNO_3 + 1NaCl \longrightarrow AgCl + NaNO_3$$

Std (left) ≡ Sample(right)

1 mole $AgNO_3$ ≡ 1 mole NaCl

1L 1M $AgNO_3$ ≡M.wt NaCl

$$1L\ 1N\ AgNO_3 \equiv \frac{M.wt\ \ NaCl}{1}$$

$$1ml\ \frac{1}{40}\ AgNO_3 = \frac{M.wt\ \ NaCl\ (58g/mole)}{1\times40\times1000} = \ 0.00145\ \ g\ NaCl$$

$$\text{Conc of } Cl^- = \frac{(mls - Blank)\times F\times1000}{10}$$

$AgNO_3$ is a primary standard

Determination of Cyanide sample

1. Liebeg's method
2. Denige's method

Every Student Must ..

- ✓ Never pipette the sample by mouth .. Use the burette for taking the sample
- ✓ Make the titration carefully
- ✓ Wash his hands thoroughly after the end of experiments

1- Principle

Liebeg's method

No indicator method

Cyanide ion titrated by $AgNO_3$ forming AgCN ppt,

↓

Due to excess of CN^- in the medium the ppt. will dissolve forming argento-cyanide soluble complex .

↓

When all CN^- consumed the first drop of Ag^+ form insoluble silver argentocyanide (White ppt.)

End Point: First turbidity

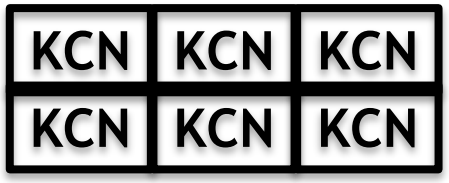
$$KCN + AgNO_3 \longrightarrow AgCN \xrightarrow{KCN} [Ag(CN)_2]^-$$

white ppt. — Sol. Argento-cyanide complex

$$[Ag(CN)_2]^- + AgNO_3 \longrightarrow Ag[Ag(CN)_2]$$

Silver argentocyanide (white ppt.)

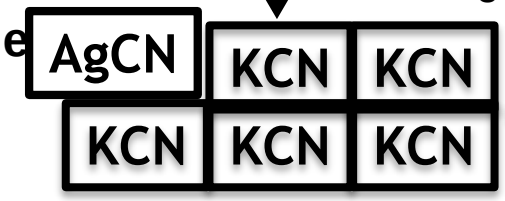
Liebeg's method



Cyanide Sample

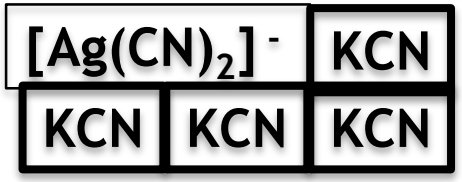
↓ $AgNO_3$ (Titrant)

Silver cyanide (white ppt.)

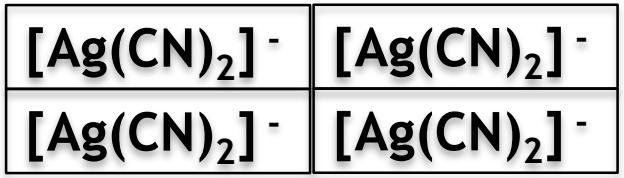


Due to excess of CN^- in the medium the ppt. will dissolve

Argento cyanide <u>soluble</u> complex

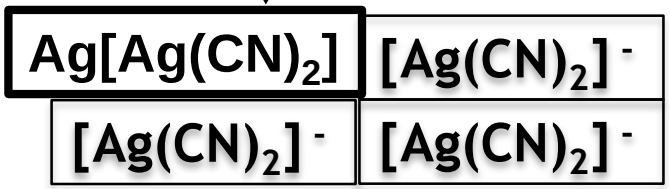


↓ $AgNO_3$



↓ 1^{st} drop excess $AgNO_3$

Silver Argento cyanide (white ppt.)



In Argento Cyanide complex

$1\ Ag^+ \approx 2\ CN^-$

$½\ Ag^+ \approx 1\ CN^-$

End Point: First turbidity

2- Procedure

In Conical Flask

10 ml Sample ≠ N/40 $AgNO_3$

End Point : First Turbidity

N.B.

Titration is done against dark background

3- Calculation

$$1\text{ml}\ \frac{1}{40}\ AgNO_3 = \frac{2\times \text{M.wt KCN(65g/mole)}}{1\times 40\times 1000} = \quad 0.00325 \ \text{g KCN}$$

$$\text{Conc of } CN^- = \frac{mls \times F \times 1000}{10} = \qquad g/L$$

$AgNO_3$ is a primary standard

2 Denige's Method

Modification of liebeg's method to render the end point more clear

1- Principle

Using KI in ammonical medium to detect the end point

The end point will be yellow turbidity of AgI as it has lower solubility product.

$$Ag[Ag(CN)_2] + 2NH_3 \longrightarrow [Ag(NH_3)_2]^+ + [Ag(CN)_2]^-$$

Silver Argento cyanide (white ppt.)

Silver ammine complex

$\downarrow I^-$

$$AgI + 2NH_3$$

Yellow ppt

Denige's method

At End Point

As leibeg's method

Silver Argento cyanide (white ppt.)

$Ag[Ag(CN)_2]$ $[Ag(CN)_2]^-$ $[Ag(CN)_2]^-$ $[Ag(CN)_2]^-$

NH_3

Silver ammine complex (Soluble)

$[Ag(NH_3)_2]^+$ $[Ag(CN)_2]^-$ $[Ag(CN)_2]^-$ $[Ag(CN)_2]^-$

I^-

Silver Iodide (yellow ppt.)

End Point

AgI $[Ag(CN)_2]^-$ $[Ag(CN)_2]^-$ $[Ag(CN)_2]^-$

Silver ammine complex is of low stability constant, easily dissociated to give free Ag^+

2- Procedure

In Conical Flask

10 ml Sample + 2 ml dil NH_3 + 1ml KI

≠

N/40 $AgNO_3$

End Point : First YELLOW Turbidity

3- Calculation

Same as leibeg's method

$$1\text{ml}\ \frac{1}{40}\ AgNO_3 = \frac{2\times \text{M.wt KCN(65g/mole)}}{1\times 40\times 1000} = \quad 0.00325\ \text{g KCN}$$

$$\text{Conc of } CN^- = \frac{mls \times F \times 1000}{10} = \qquad g/L$$

$AgNO_3$ is a primary standard

Week	Date	Subject
1	21/2/2016	Glass ware Preparation and standardization of 0.1 N NaOH
2	28/2/2016	HCl sample, acetic acid sample
3	6/3/2016	HCl/acetic acid mixture
4	13/3/2016	Na_2CO_3 sample, $CaCO_3$ sample
5	20/3/2016	1^{st} Exam + 1^{st} Qz
6	27/3/2016	Determination of Cl^- (mohr's method) Determination of CN^-
7	3/4/2016	Volhard (direct - back)
8	10/4/2016	Determination of I^-/ Cl^- mixture
9	17/4/2016	2^{nd} Exam + 2^{nd} Qz
10	24/4/2016	Gravimetry and Presentation

Thank You