Precipitation Titration

Precipitation Reactions

- **Precipitation** is the formation of a solid in a solution
- solid formed is called the **precipitate**
- A ***precipitation reaction*** occurs when water solutions of two different ionic compounds are mixed and an insoluble solid separates out of solution.

$$KCl + AgNO_3 \longleftrightarrow AgCl + KNO_3$$

Cl^- solution *Precipitating agent* *White precipitate*

- The precipitate is itself ionic; the cation comes from one solution and the anion from another.

Precipitation Titrations

- ***Precipitation titration*** is a titration method based on the formation of precipitate, which is slightly soluble
- **The basic requirements are:**
- The reaction must be sufficiently rapid and complete,
- lead to a product of reproducible composition and of low solubility.
- And a method must exist to locate the end point.

- **Precipitation titrations are not so popular in present–day routine analysis. Why????**

Some difficulties in meeting these requirements must be noted. (Precipitation reactions are generally)

- *Slow*
- *Involving periods of digestion, cooling, filtration etc.*
- *This tends to limit the reactions that are available for titration.*

Argentometric titration:

- Titrations involving **silver** are termed argentometric, from the Latin name for silver, ***argentum***.
- **The major precipitation reaction used is that of silver with a range of anions. These anions include:**

✓Halides (Cl^-, Br^-, I^-)

✓ Pseudo halides (S^{2-}, HS^-, CN^-, SCN^-)

- The reaction rates for the silver salt precipitation is **rapid**.
- The reaction ratio is **1:1** and silver salts formed are generally quite **insoluble**.
- Argentometric methods involving precipitation **titrimetry**:

➢*Mohr's Method*

➢*Fajan's Method*

➢*Volhard's Method*

Mohr's Method:

- This **direct method** uses potassium chromate (**chromate ions (CrO_4^{2-}) as an indicator** in the titration of (**Cl^-, Br^-, and CN^-)ions (analyte)** with a **silver nitrate standard solution (titrant)**.
- After all the chloride has been precipitated as white silver chloride, the first excess of titrant results in the formation of a **silver chromate precipitate**,
- which signals the end point . The reactions are:

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s) \qquad K_{sp} = 1.8 \times 10^{-10}$$

white precipitate

- End point determination by brick red color precipitate, $Ag_2CrO_{4(s)}$:

$$2\,Ag^+(aq) + CrO_4^{2-}(aq) \rightarrow Ag_2CrO_4(s) \qquad K_{sp} = 1.2 \times 10^{-12}$$

- AgCl is less soluble than Ag_2CrO_4 so it will precipitate first

Conditions for Mohr’s method:

- The titrations are performed only in neutral or slightly basic medium to prevent silver hydroxide formation (at pH > 10).

$$2Ag+ + 2OH^- \longrightarrow 2AgOH(s) \longrightarrow Ag_2O(s) + H_2O$$

black precipitate

- Or the formation of chromic acid at pH < 7.

$$CrO4^{2-} + H_3O^+ \longrightarrow HCrO4^- + H_2O$$

$$2\ CrO4^{2-} + 2\ H_3O^+ \longrightarrow Cr_2O_7^{2-} + H_2O$$

bright-orange

- Reducing $[CrO4^{2-}]$ will delay the formation of the precipitate although more Ag^+ to be added to reach end point, which cause error.

Volhard method:

- This method uses a **back titration** with potassium thiocyanate and is suitable for the determination of (Cl^-, Br^-, and I^-) in ***acidic solutions***.
  - First, Cl^- is precipitated by excess $AgNO_3$

$$\mathrm{Ag}^{+}(aq) + \mathrm{Cl}^{-}(aq) \rightarrow \mathrm{AgCl}(s)$$

  - Removing AgCl(s) by filtration / washing
  - Excess Ag^+ is titrated with KSCN in the presence of Fe^{3+}

$$\mathrm{Ag}^{+}(aq) + \mathrm{SCN}^{-}(aq) \rightarrow \mathrm{AgSCN}(s)$$

  - When Ag^+ has been consumed, a *red complex* forms as a result of:

$$\mathrm{Fe}^{3+}(aq) + \mathrm{SCN}^{-}(aq) \rightarrow \mathrm{FeSCN}^{2+}(aq)$$

Red complex

The Volhard titration can be used for any anion that forms an insoluble salt with silver

Conditions for Volhard's method:

- The solution must be ***acidic***, with a concentration of about 1 M in nitric acid to ensure the ***complex formed is stable***, and to prevent the precipitation of Iron(III) as hydrated oxide.

- The **indicator concentration** should not be *more than 0.2M*.
- In case of **I^-,** indicator should not be added until all the I^- is precipitated with Ag^+, since it would be **oxidized by the Fe(III).**

$$2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$$

The AgX ↓precipitate *must be* filtered off, before titrating with SCN^- to prevent any error, for example in the case of chloride ion, AgCl will react with the titrant (SCN^-) and cause a diffuse end point.

$$AgCl + SCN^- \longrightarrow AgSCN + Cl^-$$

OR

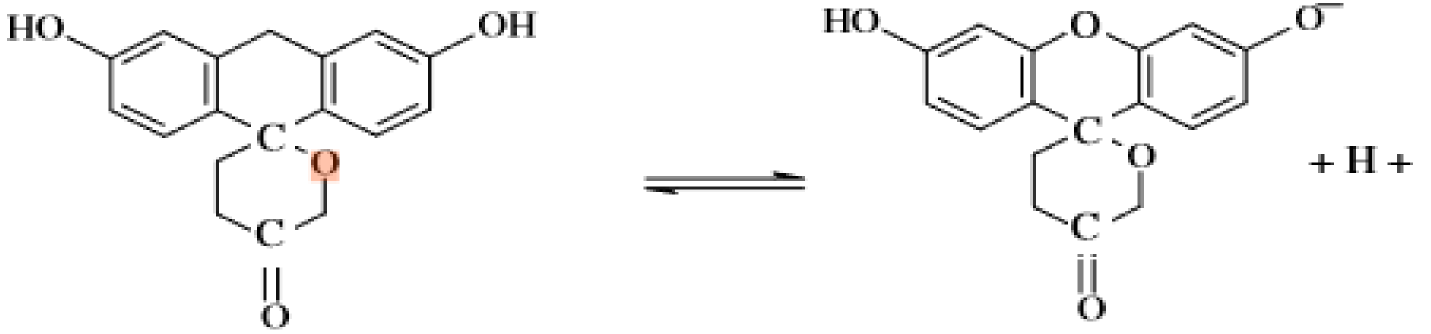
Use tartrazine as indicator instead of Iron(III) .

Fajan’s Method

- This method uses an **adsorption indicator** such of **Fluorescein (Dichlorofluorescein)** and **Eosin.**
- The indicator **adsorb onto the surface of the silver salt precipitate** at the **endpoint**.
- The adsorption process causes a **change in the color** of the **indicator**.
- Common Fajans adsorption **indicators** are **weakly acidic organic compounds** and in **alkaline conditions** will exist as the **conjugate base,(or Ind$^-$).**
- This form of the indicator which interacts with the precipitate.

The mechanism of indicators action:

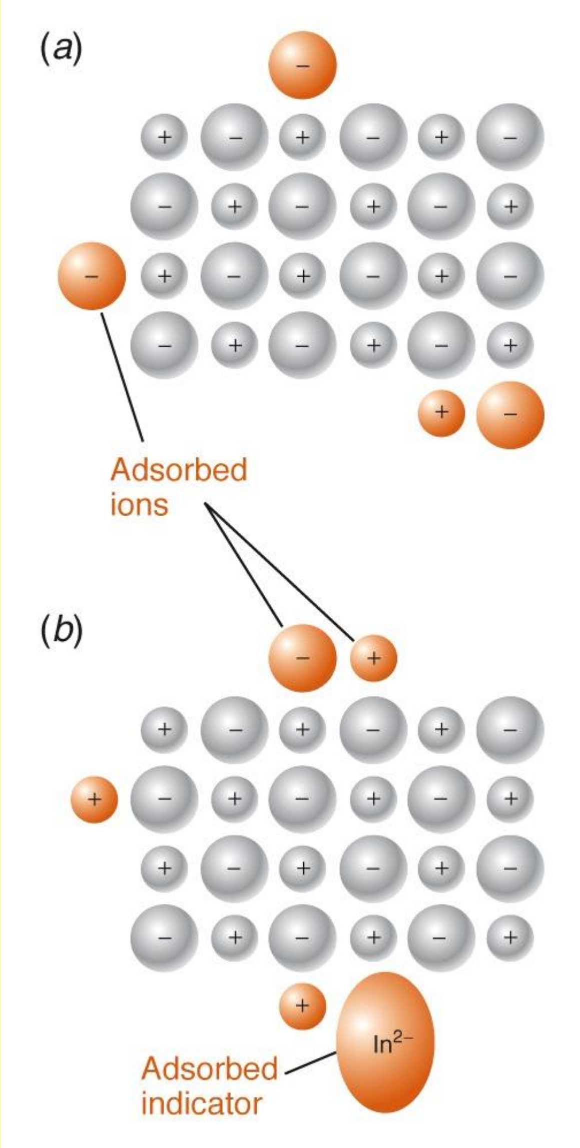
- The best–known adsorption indicator is ***fluorescein***, which is used to indicate the **equivalence point** in the titration of **Cl^- with Ag^+ .** Fluorescein is a weak acid, which partially dissociates in water to form fluoresceinate anion.



Fluorescein

Fluoresceinate anion(Yellow green)

- The fluoresceinate anion has a *yellow–green colour* in solution.



- When Cl^- is titrated with Ag^+ in the presence of fluorescein, the **negatively charged** **fluoresceinate anions** are **initially repelled** by the **negatively charged AgCl colloidal** particles, with their primary **adsorption layer of Cl^- ions**.
- Thus the **fluorescein** remains in a ***yellow–green colour*** prior to the equivalence point.
- ***At the equivalence point***, the colloidal AgCl particles undergo an abrupt change from a **negative charge** to a **positive charge** by **virtue of Ag^+ ions adsorbed in the primary adsorption layer**.
- The **fluoresceinate ions** are strongly **adsorbed** in the counter–ion layer of the AgCl colloids, giving these particles a **red colour** and providing an **end point colour change** from **yellow–green** to **red** or **pink**.

- Adsorption indicator whose color when adsorbed to the precipitate is different from that when it is in solution

Indicator	Solution	Surface of precipitate	Ions
Fluoroscein	greenish yellow	pink	Cl^-
Eosine	**yellowish-red**	**redish - violet**	Br^-, I^-

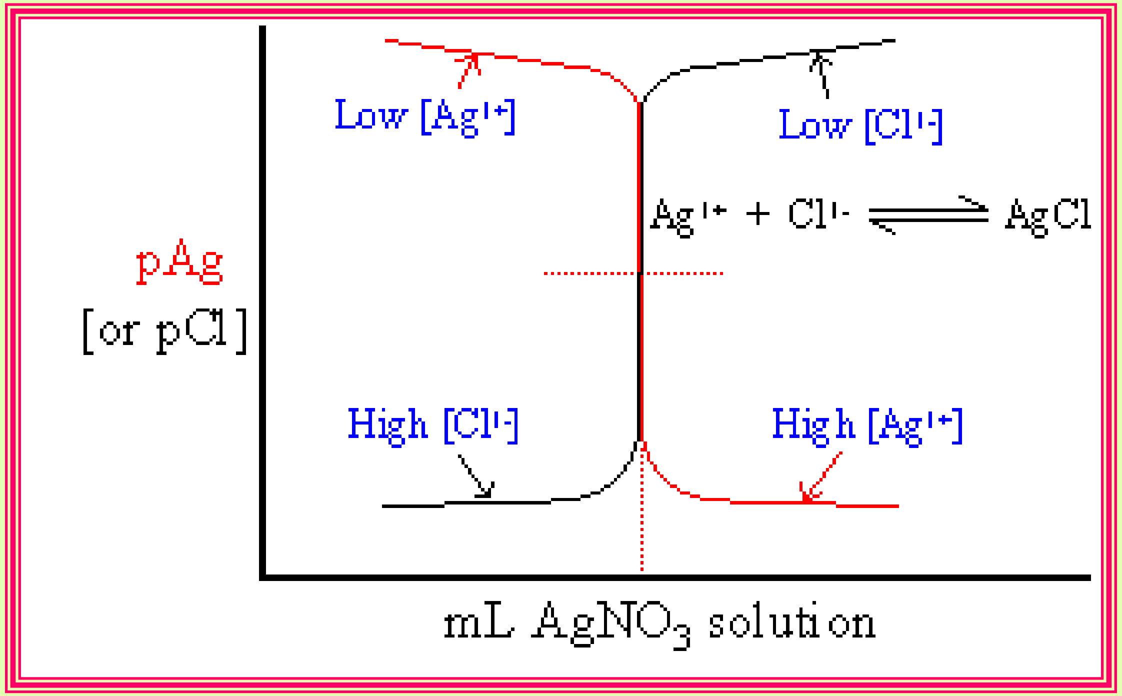
Comparison of argentometric titration methods

Method	Advantages	Disadvantages
Mohr	Simple	• Alkaline solution only • Not suitable for I^- • Requires a blank
Volhard	• Capable for direct Ag^+ and indirect halide analyses • Very clear colour change	• Must use 1M of nitric acid solution • Some problems with some ions
Fajans	• Capability for different pH ranges and selectivity with different indicators	• Difficult with dilute solutions • Should not be a high background ionic level

Titration Curves for Argentometric Methods

Plots of titration curves are normally sigmoidal curves consisting of pAg (or pAnalyte) versus volume of $AgNO_3$ solution added.

Example: Titration of chloride with silver.



A useful relationship can be derived by taking the negative logarithm of both sides of a solubility-product expression. Thus, for silver chloride,

$$K_{sp} = [Ag^{+}][Cl^{-}]$$
$$logK_{sp} = -\log([Ag^{+}][Cl^{-}])$$
$$logK_{sp} = -\log[Ag^{+}] - log[Cl^{-}]$$
$$pK_{sp} = pAg^{+} + pCl^{-}$$

The points on the curve can be calculated, given the analyte concentration, $AgNO_3$ concentration and the appropriate K_{sp}.

Plotting precipitation titration curves

- Consider titration of Cl^- with a standard solution of $AgNO_3$.
- Titration curve prepared by plotting pCl ($-\log[Cl^-]$) against the volume of $AgNO_3$ in a manner similar to acid-base titration.
- **Before titration started** – only have Cl^-.

$$pCl = -\log[Cl^-]$$

- **Titration proceed** – part of Cl^- is removed from solution by precipitation as AgCl.

$$pCl = -\log\,[\text{remaining } Cl^-]$$

- **At equivalence point** - we have solution a saturated solution of AgCl.

$$[Cl^-] = \sqrt{K_{sp}}$$

- **Excess $AgNO_3$ added** – excess Ag^+. $[Cl^-]$ is determine from the concentration of Ag^+ and K_{sp}.

$$[Cl^-] = K_{sp}/[Ag^+]$$

Example

Calculate pCl for the titration of 100.0 ml 0.100 M NaCl with 0.100 M $AgNO_3$ for the addition of 0.0, 20.0, 99.0, 99.5, 100.0 and 110.0 ml $AgNO_3$. K_{sp} AgCl is 1.0×10^{-10}

Solution

a) Addition of 0.0 ml Ag^+

$[Cl^-] = 0.100$ M

pCl = $-\log [Cl^-]$

$= -\log 0.100$

$= 1$

b) Addition of 20.0 ml Ag^+

Initial mmol Cl^- **= 100.0 ml x 0.100 M = 10.0 mmol**
mmol added Ag^+ **= 20.0 ml x 0.100 M = 2.0 mmol**
mmol Cl^- left **= 8.0 mmol**

$$[Cl^-] \text{ left} = \frac{8.0}{(100+20) \text{ ml}} = 0.0667 \text{ M}$$

pCl = $-\log [Cl^-]$
$= -\log 0.0667$
$= 1.18$

c) Addition of 99.0 ml Ag

Initial mmol Cl^- = 100.0 ml x 0.100 M = 10.0 mmol

mmol added Ag^+ = 99.0 ml x 0.100 M = 9.9 mmol

mmol Cl^- left = **0.1** mmol

$$[Cl^-] \text{ left} = \frac{0.1}{(100+99)\text{ml}} = 5.01 \times 10^{-4}\text{ M}$$

pCl = -log $[Cl^-]$

= -log 5.01×10^{-4}

= **3.3**

d) Addition of 100.0 ml

Initial mmol Cl^- = 100.0 ml x 0.100 M = 10.0 mmol

mmol added Ag^+ = 100.0 ml x 0.100 M= 10.0 mmol

Equivalence point is reached. The solution contain saturated AgCl solution

$K_{sp} = [Ag^+][Cl^-] = 1.0 \times 10^{-10}$

$[Cl^-] = \sqrt{K_{sp}} = \sqrt{1.0 \times 10^{-10}}$

$= 1.0 \times 10^{-5}$

pCl = -log 1.0×10^{-5}

= **5**

e) Addition of 100.5 ml Ag^+

Initial mmol Cl = 100.0 ml x 0.100 M = 10.0 mmol

mmol added Ag^+= 100.5 ml x 0.100 M =10.05 mmol

mmol Ag^+ excess = = **0.05** mmol

$[Ag^+]$ excess = **0.05**/200.5 ml = 2.5×10^{-4} M

$K_{sp} = [Ag^+][Cl^-] = 1.0 \times 10^{-10}$

$$[Cl^-] = \frac{K_{sp}}{[Ag^+]} = \frac{1.0 \times 10^{-10}}{2.5 \times 10^{-4}\ M} = 4.0 \times 10^{-7}$$

$pCl = -\log 4.0 \times 10^{-7}$

= **6.4**