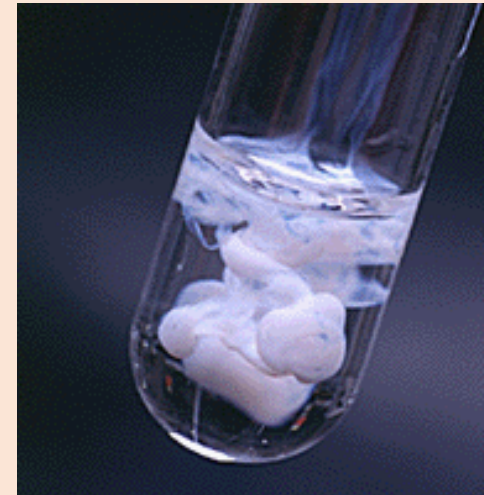
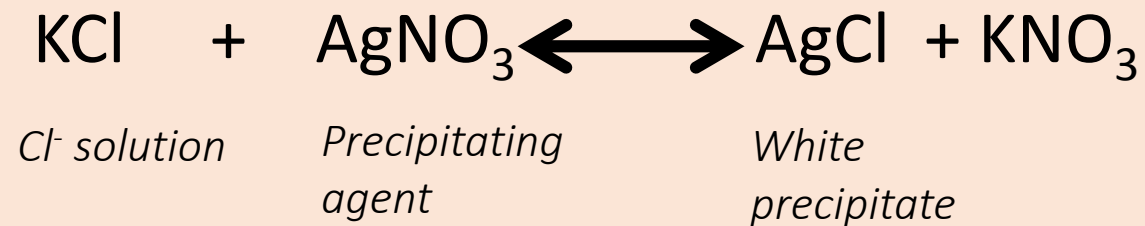




Precipitation Titration

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.



- ❖ 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.*

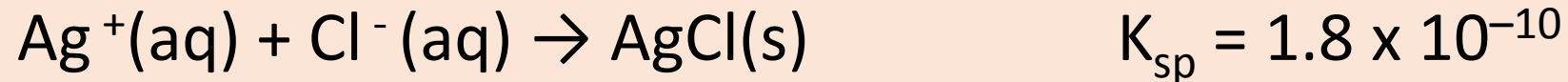


Argentometric titration:

- 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^-)
 - Pseudohalides (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***

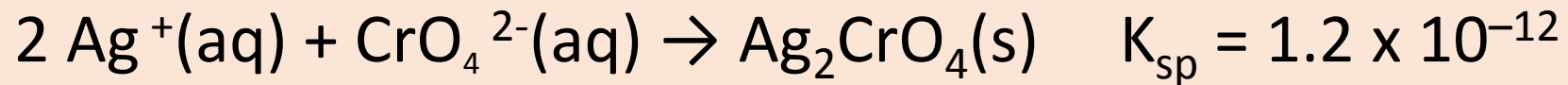
Mohr's Method:

- 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 (1). The reactions are:



white precipitate

- End point determination by **brick red color precipitate**, $\text{Ag}_2\text{CrO}_4(\text{s})$:



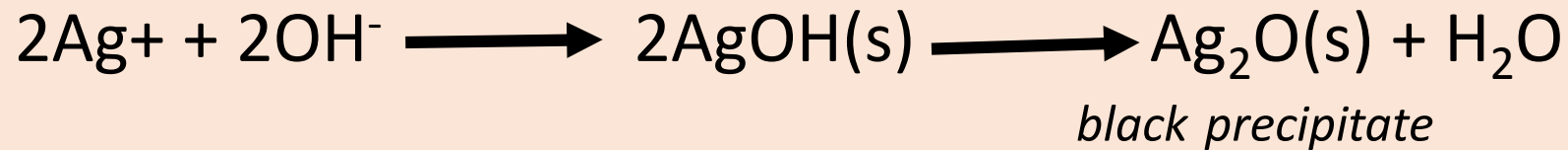
- AgCl is less soluble than Ag_2CrO_4 so it will precipitate first



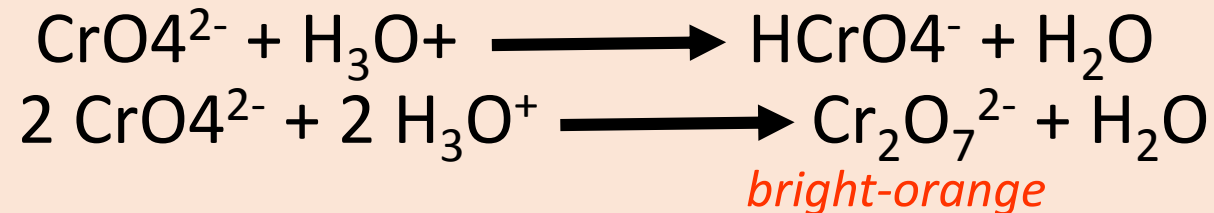


Conditions for Mohr's method:

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



- Or the formation of chromic acid at $\text{pH} < 7$.



- Reducing $[\text{CrO}_4^{2-}]$ 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 chlorides, bromides and iodides in **acidic solutions**.

- First, Cl^- is precipitated by excess AgNO_3



- Removing $\text{AgCl}(s)$ by filtration / washing

- Excess Ag^+ is titrated with KSCN in the presence of Fe^{3+}



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



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)**.



The $AgX \downarrow$ 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.



OR

Use tartrazine as indicator instead of Iron(III) .

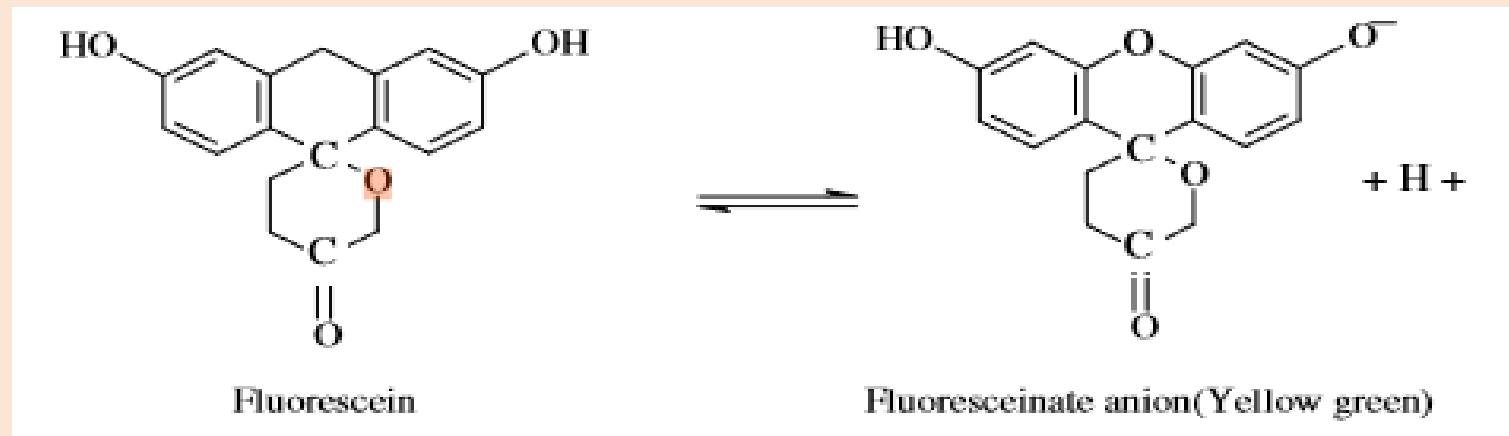


Fajan's Method

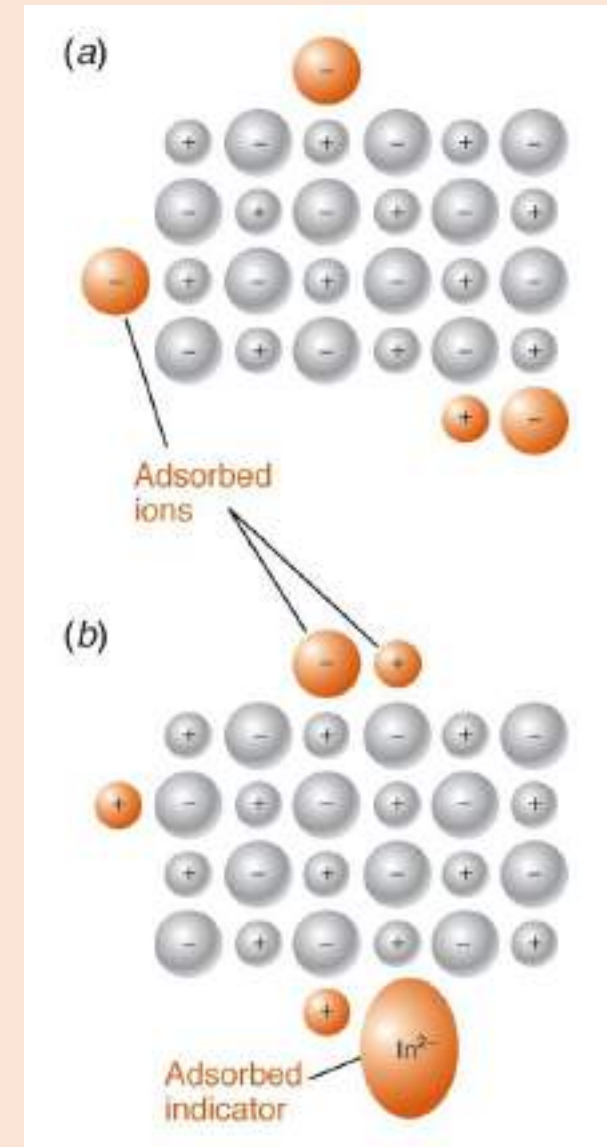
- This method uses an **adsorption indicator** such of **Fluorescein (Dichlorofluorescein)** and **Eosin**.
- The indicator **adsorb onto the surface of the silver salt precipitate** at the **endpoint**.
- The adsorption process causes a **change in the color of the indicator**.
- Common Fajans adsorption **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.



- 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	<ul style="list-style-type: none">Alkaline solution onlyNot suitable for I^-Requires a blank
Volhard	<ul style="list-style-type: none">Capable for direct Ag^+ and indirect halide analysesVery clear colour change	<ul style="list-style-type: none">Must use 1M of nitric acid solutionSome problems with some ions
Fajans	<ul style="list-style-type: none">Capability for different pH ranges and selectivity with different indicators	<ul style="list-style-type: none">Difficult with dilute solutionsShould not be a high background ionic level



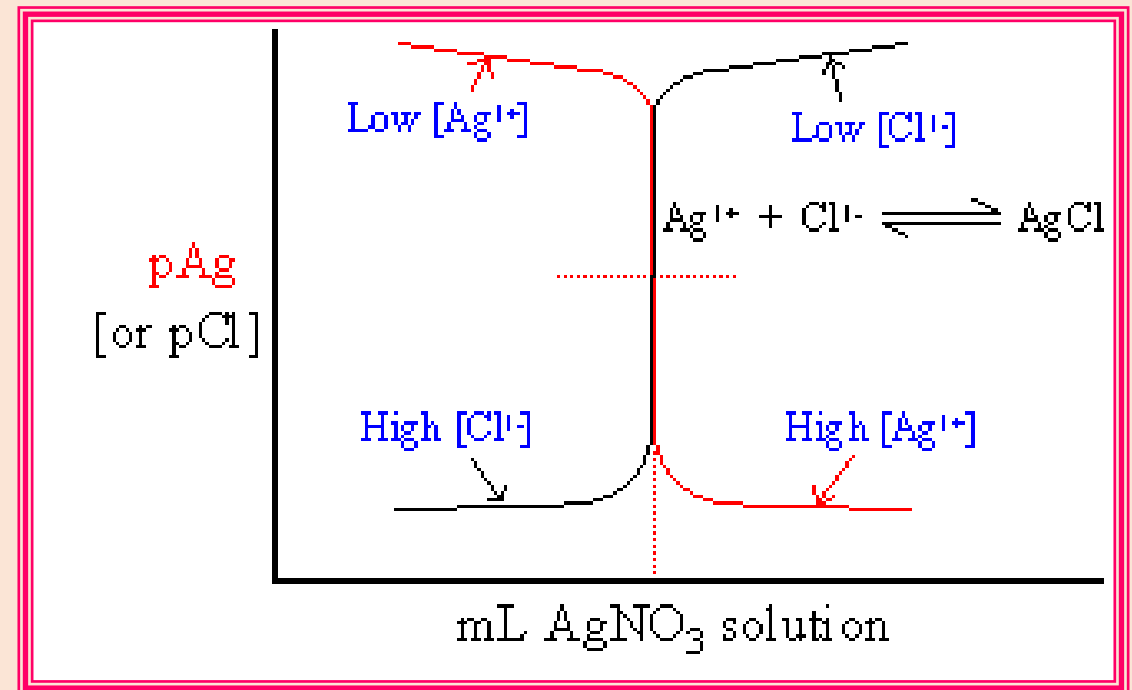
Titration Curves for Argentometric Methods

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,

$$\begin{aligned}K_{sp} &= [\text{Ag}^+][\text{Cl}^-] \\ \log K_{sp} &= -\log([\text{Ag}^+][\text{Cl}^-]) \\ \log K_{sp} &= -\log[\text{Ag}^+] - \log[\text{Cl}^-] \\ pK_{sp} &= p\text{Ag}^+ + p\text{Cl}^-\end{aligned}$$



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 ($-\log[\text{Cl}^-]$) against the volume of AgNO_3 in a manner similar to acid-base titration.
- **Before titration started** – only have Cl^- .

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

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

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

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

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

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

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



Example

Calculate pCl for the titration of 100.0 ml 0.100 M NaCl with 0.100 M AgNO₃ for the addition of 0.0, 20.0, 99.0, 99.5, 100.0 and 110.0 ml AgNO₃.
K_{sp} AgCl is 1.0 x10⁻¹⁰

Solution

a) Addition of 0.0 ml Ag⁺

$$[\text{Cl}^-] = 0.100 \text{ M}$$

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

$$= -\log 0.100$$

$$= \mathbf{1}$$

b) Addition of 20.0 ml Ag⁺

$$\text{Initial mmol Cl}^- = 100.0 \text{ ml} \times 0.100 \text{ M} = 10.0 \text{ mmol}$$

$$\text{mmol added Ag}^+ = 20.0 \text{ ml} \times 0.100 \text{ M} = 2.0 \text{ mmol}$$

$$\text{mmol Cl}^- \text{ left} = \mathbf{8.0 \text{ mmol}}$$

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

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

$$= -\log 0.0667$$

$$= \mathbf{1.18}$$



c) Addition of 99.0 ml Ag

$$\text{Initial mmol Cl}^- = 100.0 \text{ ml} \times 0.100 \text{ M} = 10.0 \text{ mmol}$$

$$\text{mmol added Ag}^+ = 99.0 \text{ ml} \times 0.100 \text{ M} = 9.9 \text{ mmol}$$

$$\text{mmol Cl}^- \text{ left} = \mathbf{0.1} \text{ mmol}$$

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

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

$$= -\log 5.01 \times 10^{-4}$$

$$= \mathbf{3.3}$$

d) Addition of 100.0 ml

$$\text{Initial mmol Cl}^- = 100.0 \text{ ml} \times 0.100 \text{ M} = 10.0 \text{ mmol}$$

$$\text{mmol added Ag}^+ = 100.0 \text{ ml} \times 0.100 \text{ M} = 10.0 \text{ mmol}$$

Equivalence point is reached. The solution contains saturated AgCl solution

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

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

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

$$\text{pCl} = -\log 1.0 \times 10^{-5}$$

$$= \mathbf{5}$$



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 x 10⁻⁴ M

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

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

pCl = - log 4.0 x 10⁻⁷

= **6.4**