Fajan's Method

It is a type of precipitation titration that depends on the formation of a colored adsorption compound at the end point. IN OTHER WORDS, It depends on the use of an adsorption indicator which is adsorbed on the surface of the ppt at the E.P. leading to change in the ppt color.

Main features of Fajan's method:

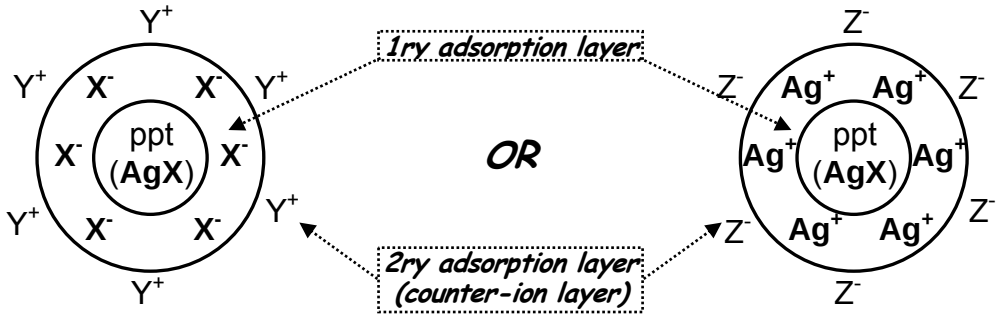
• **Sample:**	Generally, it can be used for $\underline{Cl^-}$, $\underline{Br^-}$, $\underline{I^-}$ & $\underline{SCN^-}$. [Fluorescein ind. is used for $\underline{Cl^-}$, $\underline{Br^-}$, $\underline{I^-}$ & $\underline{SCN^-}$ **but** Eosin ind. is used for $\underline{Br^-}$, $\underline{I^-}$ & $\underline{SCN^-}$ (Not for Cl^-)]	
• **Type of titration:**	Direct titration.	
• **Standard Solution:**	Standard $AgNO_3$.	
• **Indicator:**	Different adsorption indicators can be used but the most common indicators are:	
	Fluorescein	Eosin
• **pH:**	neutral or slightly alkaline (pH = 7 - 10)	at pH down to 2 (<u>i.e.</u> pH ≥ 2)
• **Color at E.P.:**	Pink ppt	Reddish violet ppt

Introduction :

♦ The action of adsorption indicators depends on the electrical phenomena associated with the formation of colloidal precipitates.

⇒ ***Remember*** **:**

- **Colloidal ppt** tends to form an electrical double layer around its particles when it is in contact with a solution. This electrical double layer consists of:
  - a) 1ry adsorption layer: in this layer, the ppt tends to adsorb one of its own ions (the ion present in excess).
  - b) 2ry adsorption layer: a layer of opposite charge (counter-ion layer) containing oppositely charged ions from the surrounding solution.
- *Examples of colloidal precipitates:* AgCl, AgBr, AgI, AgSCN,……etc.



♦ Types of Adsorption indicators:

1. **Acid dyes:** such as **Fluorescein** & **Eosin** which are Na^+-salts of weak acids.
2. **Basic dyes:** such as **Rhodamine 6G** & **Phenosafranine** which are Cl^--salts of weak bases.

♦ **Fluorescein** & **Eosin** can be represented in equations as $\mathbf{In^-Na^+}$.

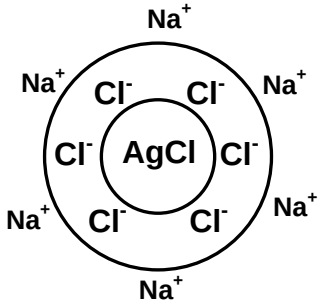
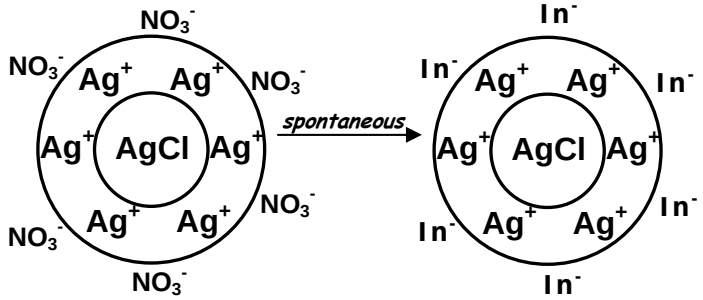
Exp.(3): Determination of NaCl by Fajan's method using Fluorescein indicator *(demonstration)*

Principle (Theory or Mechanism of action of adsorption indicators):

It depends on the titration of NaCl sample with standard $AgNO_3$ using fluorescein indicator. At the E.P., the formed $AgCl\downarrow$ ppt becomes pink.

Titration reaction: $\underset{\textit{sample}}{NaCl} + \underset{\textit{titrant}}{AgNO_3} \xrightarrow{\text{fluorescein ind.}} AgCl\downarrow + NaNO_3$

Before starting titration: *the ions present in the soln. are Na^+, Cl^- & In^-.*

Stage of titration:	**A During titration (before E.P.)**	**B 1st drop excess of $AgNO_3$ immediately after the E.P.**
Ions present in the soln.:	Cl^- + Na^+ + In^- + NO_3^- *sample* *from sample & ind.* *ind.* *titrant* *(Ag^+ is precipitated as AgCl)*	Ag^+ + NO_3^- + Na^+ + In^- *titrant* *titrant* *from sample & ind.* *ind.* *1st drop xss after E.P.*
Diagram:		
Color of the ppt:	White ppt in green fluorescence	Pink ppt in faint colored solution
Explanation:	At start of tit., (Cl^-) ions present in excess so the 1ry adsorption layer will be (Cl^-) ions [own ions of ppt] and the 2ry adsorption layer will be the oppositely charged (Na^+) ions [counter-ions].	Immediately after the E.P., $AgNO_3$ is present in excess so (Ag^+) ions form the 1ry ads. Layer [own ions of ppt] {*Note that all (Cl^-) ions from sample are already precipitated*}. The 2ry adsorption layer of the opposite charge will be (NO_3^-) BUT since fluorescein ions carry (-ve) charge also & it is more strongly adsorbed than (NO_3^-), so fluorescein replaces (NO_3^-) and the 2ry layer becomes (In^-) & the ppt becomes pink due to deformation of the electronic system of the indicator anion.

Notes:

1) Eosin indicator can **not** be used for the determination of (Cl^-) because eosin is too strongly adsorbed to the surface of the ppt and may replace (Cl^-) ions in the 1ry adsorption layer before the E.P. giving **early** E.P. [*stage A in the diagram*]
2) **Effect of pH**: In Fajan's method, the pH should be adjusted to keep the indicator dissociated.

For fluorescein indicator:

Fluorescein (In^-Na^+) is a sod. salt of a very weak acid and it's hydrolyzed in water to give the parent acid (InH) which is very weak and so its dissociation is suppressed in acidic medium due to common ion effect.

$$InH \longleftarrow H^+ + In^-$$
$$H^+$$

So fluorescein is used in neutral or slightly alkaline medium (pH=7-10).

[Note that strong alkaline pH is prohibited in argentometric tit. because Ag^+ will be precipitated as $AgOH\downarrow$ (brown to black ppt) leading to Consumption of the titrant & Masking of the E.P. color].

For eosin indicator:

Eosin (In^-Na^+) is a sod. salt of a more stronger acid and so its dissociation is not affected in acidic medium. Therefore, eosin can be used at pH down to 2 (i.e. $pH \geq 2$).

Procedure: (Demonstration)

10 ml sample → dilute to 50 ml with dist. water → add 15 drops fluorescein indicator → Titrate ≠ 0.05 N $AgNO_3$.

At the E.P., the formed $AgCl\downarrow$ ppt becomes pink

Exp.(4): Determination of NaI by Fajan's method using Eosin indicator *(demonstration)*

Principle (Theory or Mechanism of action of adsorption indicators):

The principle is in the same manner as the determination of NaCl using fluorescein indicator BUT the formed ppt during titration will be **AgI (yellow ppt)** and the color of the ppt at the E.P. will be **Reddish Violet**. Also, the procedure involves the addition of acetic acid to decrease the pH of the medium because the color change is more sharp in acidic pH.

*****>>*Best wishes*>>*****