

# Analytical Chemistry

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# Precipitation titration

- ❖ Precipitation formation
- ❖ Precipitation condition and precipitation purity
- ❖ **Methods in Precipitation titration**
- ❖ Mohr method
- ❖ Volhard method
- ❖ Fajans method

# Precipitation titration

- ❖ Titrations with precipitating agents are useful for determining certain analytes e.g.  $\text{Cl}^-$  can be determined when titrated with  $\text{AgNO}_3$ .

# Methods in Precipitation Titration

## Detection of end point:

### Chemical

- Precipitation Type - Mohr's method
- Adsorption – Fajan's method
- For silver analyses –Volhard method

### Sensors –Potentiometric or amperometric

## **The chemical types are also classified into:**

1. Indicators reacting with titrant forming specific color.
2. Adsorption indicators.

# Mohr Method

- ❖ Direct titration
- ❖ Basis of endpoint: formation of a colored secondary precipitate
- ❖ Indicator: soluble chromate salt ( $\text{Na}_2\text{CrO}_4$ ,  $\text{K}_2\text{CrO}_4$ )

# Endpoints for Argentometric Titrations

*Precipitation Type - Mohr's method*

***$Ag_2CrO_4$  precipitation in neutral pH  
solution..***

***Product is coloured***

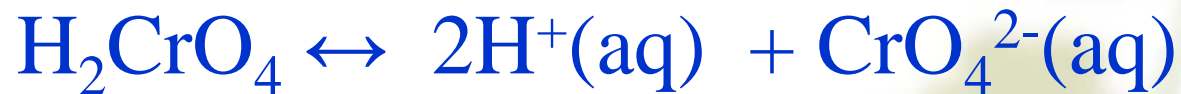
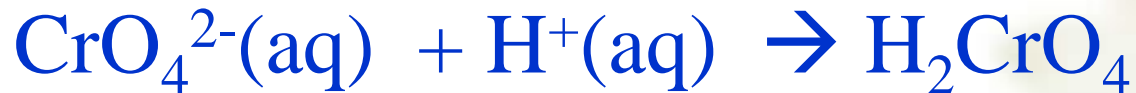
*Colour forms just after  $AgCl$  or  $AgI$  forms .*

*Small error involved.*

# Mohr Method

❖ Has to be performed at a neutral or weak basic solution of pH 7-9 (or 6-10)

❖ In a lower pH (acid solution)



❖ In a higher pH (basic solution)



# Mohr Method for Cl<sup>-</sup> determination

- ❖ Relies on K<sub>sp</sub> differences for two insoluble silver salts



- ❖ AgCl is less soluble than Ag<sub>2</sub>CrO<sub>4</sub> so it will precipitate first
- ❖ Ag<sub>2</sub>CrO<sub>4</sub> is brick red in color so a color change is observed at the endpoint



## Commonly used silver measurement:

- \* Mohr method                      Indictor :                       $K_2CrO_4$
- \* Volhard method                      indictor :                       $(NH_4)_2 Fe (SO_4)_2$
- \* Fajans method                      indictor :                      adsorption indicator

The problem should be pay attention to:

★The consumption of the indicator :  $5 \times 10^{-3}$  mol/L .If the concentration of the  $K_2CrO_4$  is too high, the end point is advance, result is low; if the concentration of the  $K_2CrO_4$  is too low ,the end point is delay ,result is high . $K_2CrO_4$  exert titration produce positive error, the measured concentration is low, it need a blank test.

# Volhard Method

❖ Used as a procedure for titrating  $\text{Ag}^+$ ; determination of  $\text{Cl}^-$  requires a back-titration

↪ First,  $\text{Cl}^-$  is precipitated by excess  $\text{AgNO}_3$



↪ Excess  $\text{Ag}^+$  is titrated with  $\text{KSCN}$  in the presence of  $\text{Fe}^{3+}$



↪ When  $\text{Ag}^+$  has been consumed, a red complex forms



# Endpoints for Argentometric Titrations

Chemical method for silver analyses

Volhard's method using thiocyanate,  $\text{CNS}^-$ , as titrant.

Iron (III) is the indicator as it forms a red complex ion with thiocyanate,  $\text{CNS}^-$ ,  $\text{Fe}(\text{CNS})^{2+}$

The method can be adapted to Chloride analyses.

**$\text{AgNO}_3$  is added in excess. The  $\text{AgCl}$  precipitate is often filtered off. Then the excess  $\text{Ag}^+$  backtitrated with thiocyanate,  $\text{CNS}^-$ .**

Iron (III) acts as the indicator as above.

# Endpoints for Argentometric Titrations

## Chemical

### Adsorption – Fajan's method

A red dye attaches to the silver salt, on the surface of the analyte precipitate particle.

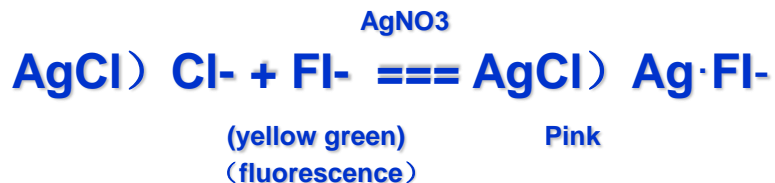
**This happens only when the silver ion  $\text{Ag}^+$  is in excess, ie just after the equivalence point.**

# Fajans Titration

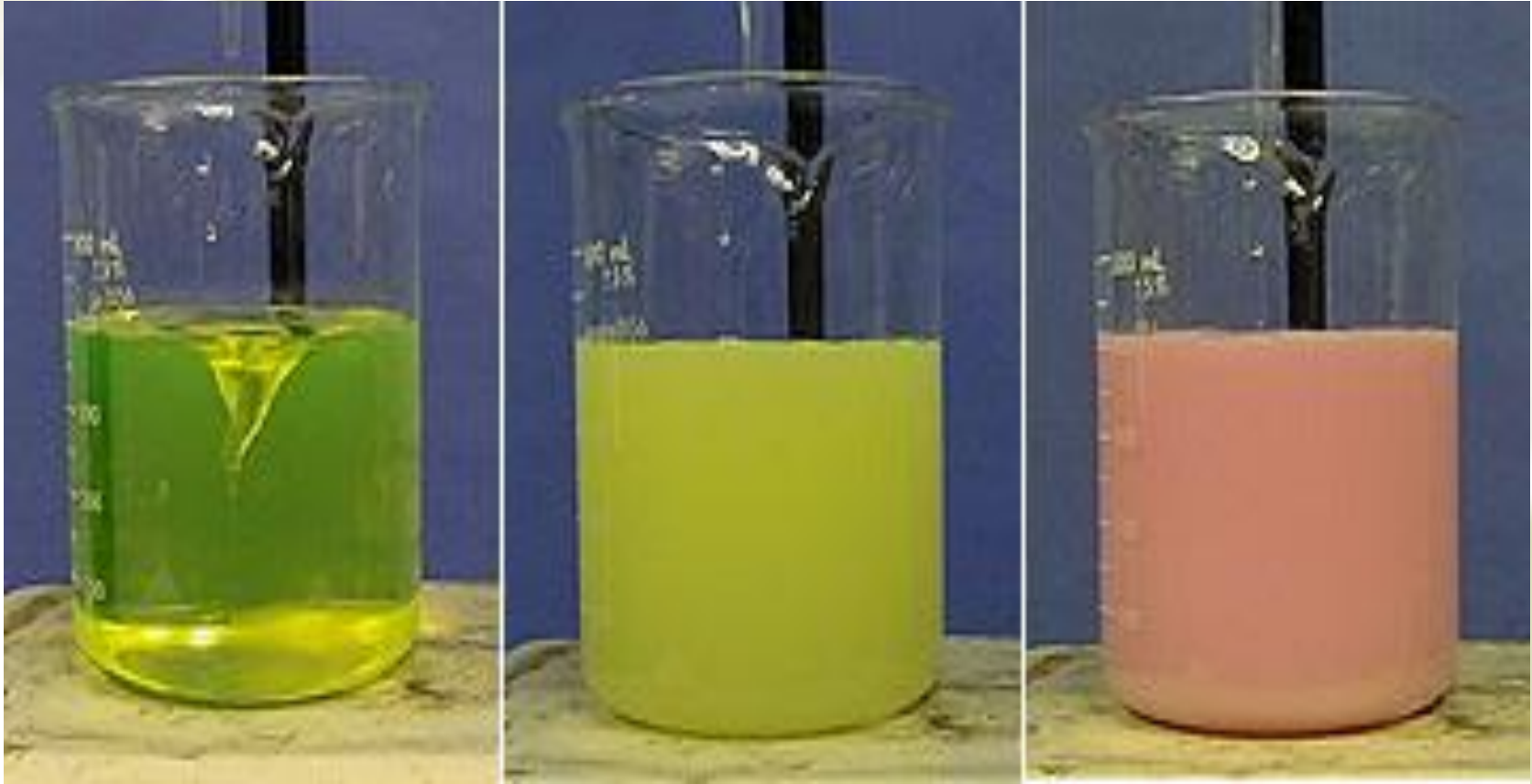
## ❖ Fajans- adsorption indicator

→ adsorption indicator

One kind is the acid dyes, for example fluorescence yellow and its derivative, they are the organic weak acid, dissociates the indicator anion; Another is the alkalinity dye, like the gentian violet, Luo Danming 6G and so on, dissociates the indicator positive ion.

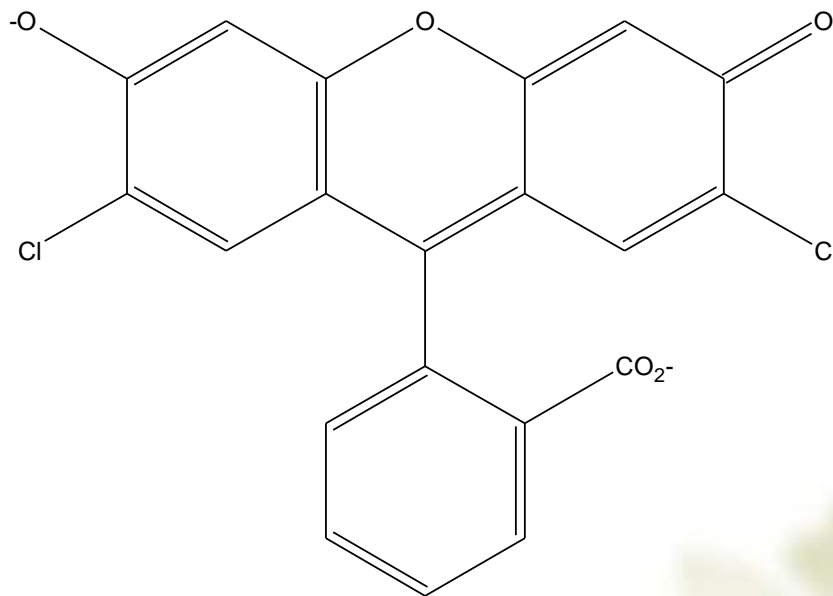


# Fajans Titration



# Fajans Titration

- ❖ Uses adsorption indicator



Dichlorofluorescein is green in solution but pink when adsorbed on AgCl



## →Measurement

(1) by adding protective colloid dextrin to prevent sedimentation AgCl excessive pool.

(2)  $\text{Cl}^-$  above  $0.005\text{mol/L}$  ; when the concentration of the  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{SCN}^-$  as low as  $0.001\text{ mol/L}$ , also can titrate accurately .

(3) avoid titrate under strong sunlight .

(4) acid scope is different ,see the table.

(5) The adsorption ability of colloidal particles to the indicator is slightly less than the measured ions .Too big the end is early, too small the end is delay.

the adsorption capacity of AgX :  $\text{I}^- > \text{SCN}^- > \text{Br}^- > \text{Eosin} > \text{Cl}^- > \text{fluorescence yellow}$

## Applications

→ The precipitation titration of mixed ion

In precipitation titration, whether the two ions were able to accurate titration or not, it depends on the size of the solubility product ratio.

$$\frac{[I^-]}{[Cl^-]} = \frac{K_{sp}(AgI)}{K_{sp}(AgCl)} \approx 5 \times 10^{-7}$$

Can titrate respectively but I<sup>-</sup> is adsorbed by AgI has errors.

$$\frac{[Br^-]}{[Cl^-]} = \frac{K_{sp}(AgBr)}{K_{sp}(AgCl)} \approx 3 \times 10^{-3}$$

can not titrate respectively  
can titrate the volume

→The determination of the chlorine contained in natural water  
Mohr and Volhard Method

→The determination of Silver contained in silver alloy: Volhard method

→The determination of halogen contained in organic compounds such as food, organochlorine pesticides, used Volhard method.



→The determination of sodium chloride

contained in MSG :Mohr method ,no more than 20%

glutamate more than 95% grade level

glutamate more than 80% second level

# The uses of Precipitation titration

- ❖ mostly used for neutralization reactions when the salt is occurred the precipitation can be observed we use indicators to see the pH range
- ❖ Ppt titration is used for such reaction when the titration is not recognised by changing the colours. during the reaction a salt is precipitated as the titration is completed.
- ❖ Precipitation titration is an Amperometric titration in which the potential of a suitable indicator electrode is measured during the titration.
- ❖ It is used for determination of chloride by Mohr's Method using Silver nitrate.



طالبات المجموعه :

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منيرة الدوسري