GRAVIMETRIC ANALYSIS

DR. KHAWLA SALMAN

ARGENTOMETRIC TITRATIONS

Titrations with Ag+ are called argentometric titrations.

For argentometric titrations , three classical methods based on color indicators can be used for endpoint detection:

- **Mohrs titration**

Formation of colored precipitated at the end point.

- **Volhards titration**

Formation of a soluble , colored complex at the end point.

- **Fajans titration**

Adsorption of a colored indicator on the precipitate at the endpoint

MOHR METHOD

- The Mohr method was first published for chloride analysis.

1-) Direct method for determination halides

2−) In the precipitation of chloride by silver ion, chromate ion CrO_4 is used as an indicator.

3-) At end point formation Ag_2CrO_4, a reddish-brown precipitate formed .

-At first titration.

$$Ag^+ + Cl^- \longrightarrow AgCl(s)$$

titrant analyte white precipitate

•Mohr indicator reaction (end point),

$$2Ag^+ + CrO_4 \longrightarrow Ag_2CrO_4(s)$$

titrant indicator reddish-brown precipitate

MOHR METHOD

4-)The titrations are performed only in neutral or slightly basic medium(PH 7-10) to prevent silver hydroxide formation

*at pH > 10.

$$2Ag^{+} + 2OH^{-} \rightleftharpoons 2AgOH \rightleftharpoons Ag_2O_{(s)} + H_2O$$

↓

black precipitate

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

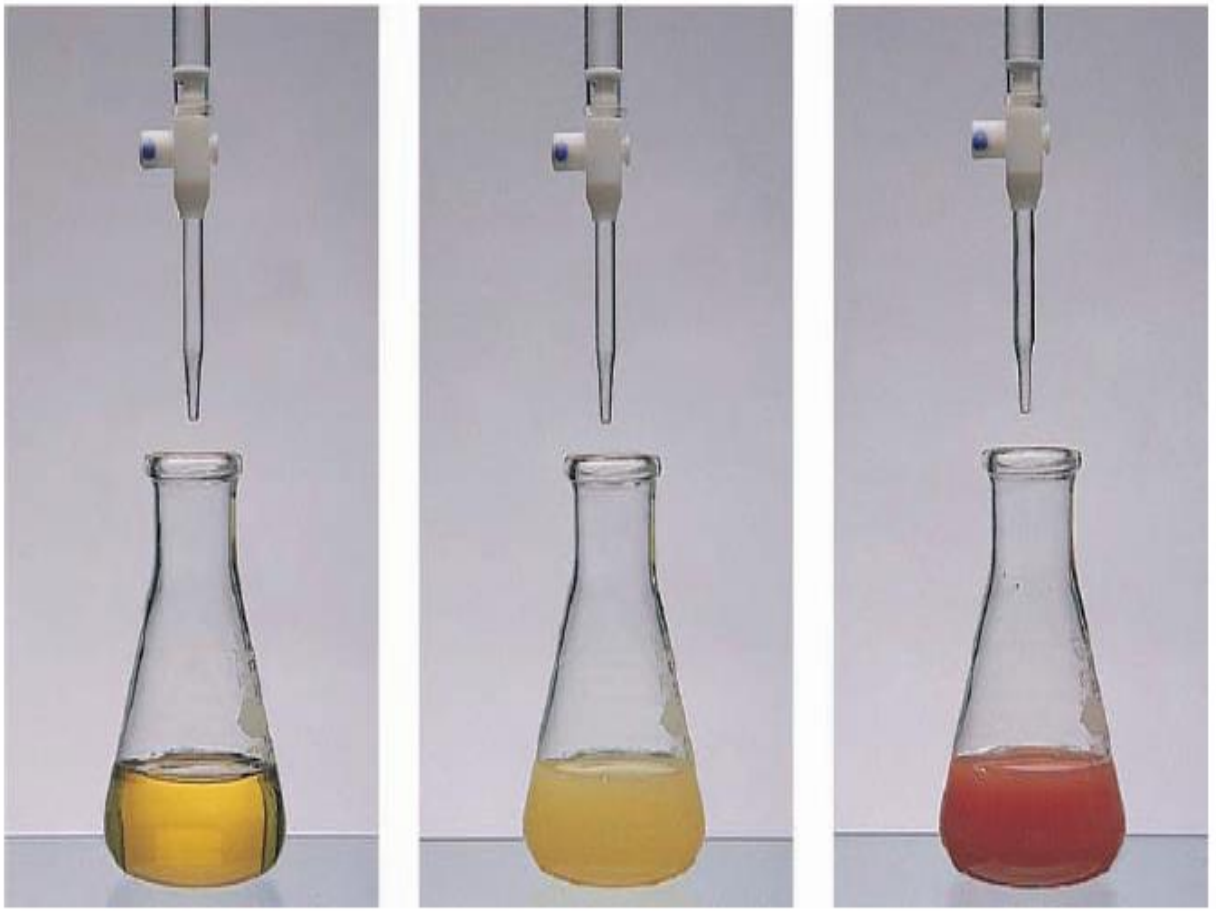
$$2CrO_4^{-2} + 2H^{+} \rightleftharpoons 2HCrO_4^{-2} \rightleftharpoons Cr_2O_7^{-2} + H_2O$$

[$CrO_4$2−]become lower , more Ag+ to be added to reach endpoint, which cause error.

MOHR METHOD

FIGURE 17.5

Titration of chloride ion by silver nitrate using potassium chromate as an indicator
Left: A small amount of K_2CrO_4 (yellow) has been added to a solution containing an unknown amount of Cl^- ion. *Center:* The solution is titrated by $AgNO_3$ solution, giving a white precipitate of AgCl. *Right:* When nearly all of the Cl^- ion has precipitated as AgCl, silver chromate begins to precipitate. Silver chromate, Ag_2CrO_4, has a red-brown color, and the appearance of this color signals the end of the titration. An excess of Ag^+ was added to show the color of Ag_2CrO_4 more clearly.



VOLHARD METHOD

- Indirect method for determination of halides
- Determination of Cl- For titration of silver ion with thiocyanate (SCN^-)
- Used back titration for standered solution(KSCN)
- At end point red solution appear from Fe(SCN)+2 complex.
- Iron(III) used as an indicator .
- The titration is usually done in acidic medium(HNO_3) to prevent precipitation of iron hydroxides, $Fe(OH)_3$.
- Reactions:
- titrant -1-
- $Ag^+ + Cl^- \rightarrow AgCl$
- excess white precipitate
- titrant -2-
- $Ag^+ + SCN^- \rightarrow AgSCN$ ⌈(s)
- white precipitate
- $SCN^- + Fe^{3+} \rightarrow [FeSCN]^{2+}$
- Indicator red solution

VOLHARD METHOD

- The endpoint is routinely used for halide determinations where a known excess of silver ion is added to precipitate the halide ion , and the excess silver ion is back titrated using the thiocyanate /iron(III) as the indicator.
- The silver chloride precipitate is filtered, and the excess silver ion is titrated with thiocyanate producing a white precipitate of AgSCN.
- •Once the silver is consumed , the excess thiocyante reacts with the iron(III) ion producing a red $FeSCN^{2+}$ complex. Thus , the appearance of the red color at the endpoint.

VOLHARD METHOD

- The titration must be done in acidic medium to prevent the precipitate of Iron(III) as hydrated oxide (iron hydroxide) . also , most of ions in neutral or weak acid medium are gives a precipitate with Ag+ . It found from the experimental ,
- volhared method can be applicated for the indirect determination of halides by measured the excess of standard silver nitrate sol. that added to the sample (halides) , and the excess of silver ion determine by back-titration with a standard thiocyanate sol.

$$Ag^+ + Cl^- \rightleftharpoons AgCl + Ag_{\text{excess}}$$

$$Ag_{\text{excess}} + SCN^- \rightleftharpoons AgSCN$$

VOLHARD METHOD

- To found the weight of Cl ion in sample
- 1-find the ml of AgNO3 equil volume SCN(back titration)
- $N_{SCN} \times V_{SCN} = N_{AgNO3} \times (V \text{ ml } _{AgNO3}?)$
- 2-find the volume of AgNO3 reacted with Cl
- $V_{AgNO3 \text{ reacted with Cl}} = 20ml - V_{AgNO3}?$
- Not. 20 ml the excess volume of AgNO3 was added at begging
- $N_{AgNO3} \times N_{AgNO3} = Wt \text{ of CL-/eq.wt CL-}$
- Wt of CL- =(----)

Fajans Method (Adsorption Indicators)

- **Adsorption indicators** are organic compounds that tend to be adsorbed on to the surface of the solid precipitate in a precipitation titration.

Fluoresceinate adsorbs to silver ions on the surface of a precipitate when excess silver ion is present, producing a reddish-colored surface

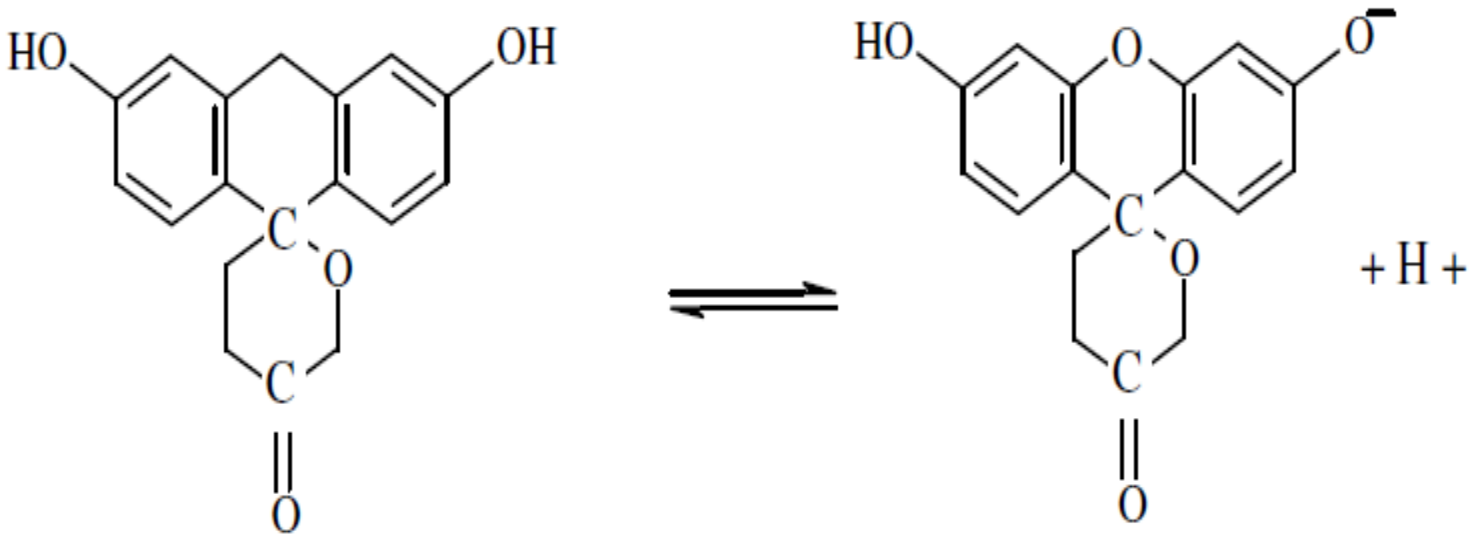
Fajans Method

Titration of NaCl with AgNO3

- $Ag^+ + Cl^- \longrightarrow AgCl(s)$
- titrant analyte white precipitate

- During the titration, colloids are formed.
- Before the equivalence point, the surface of the precipitant particles will be negatively charged due to the adsorption of excess Cl^- on the surface of the particles. A diffuse positive counter-ion layer will surround the particles.
- The primary adsorption layer is negatively charged and the anionic indicator is repelled

Fajans Method



Fluorescein

Fluoresceinate anion(Yellow green)