



Faculty of science

Precipitation Titrations

3rd Year Students, General- Science

Course Code: 317 Chem.

Lecture# 8

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Quiz on Complexometric titrations

Part I: Fill in the blank(s) with the most appropriate word(s). (1 pt. each)

- 1) Coordination compound is defined as-----
- 2) A ligand is defined as-----
- 3) The chelates of trivalent cations with EDTA are stable in strong -----solution.

Part II: Indicate the most appropriate answer in the blank provided (1 pt. each)

1. Indicators used in the titration of EDTA respond to-----
 - a) the change in the metal ion concentration
 - b) the change in the EDTA concentration
 - c) The change in the pH of buffer solution
 - d) a, b, c

2. Calcium can be determined in the presence of Magnesium by titration with EDTA in the presence of -----
 - a) Eriochrome black T in Ammonia buffer pH 12
 - b) Murexide
 - c) Ammonia buffer pH 10
 - d) Murexide in alkaline buffer pH=12

3. To increase the selectivity of EDTA reactions, we use
 - a) masking agent
 - b) demasking agent
 - c) control pH of solution
 - d) a, b, c

Classification of Quantitative analysis



Quantitative
analysis

Volumetric

Gravimetric

Acid base
titration

Oxidation
reduction

Complexometric

**Precipitation
Titration**



Analytical Problem

You are provided with a water sample contaminated with chloride ion, how can you estimate the sample purity?

Precipitation Reactions

- The reaction that forms a sparingly soluble compound (precipitate).
- For sparingly soluble compound, there is an equilibrium between ppt and its ions:



Solid

saturated soln.

$$K = \frac{[Ag^+][Cl^-]}{[AgCl]} \Rightarrow [Ag^+][Cl^-]$$

The product of ionic concentrations is constant at a given temperature. This constant is called “solubility product” “ K_{sp} ”

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

K_{sp}: Product of the molar concentrations of ions involved, raised to power of number of the ions in molecules:

$$[A]^x [B]^y = S_{AxBy}$$

K_{sp} is used to calculate the solubility

If the solubility of AgCl in water is 0.0015 g/L

So, the Molarity = $0.00015/143.5 = 1.05 \times 10^{-5}$ M

Since salts freely ionize, the concentration of the salt equals the concentration of its ions $[AgCl] = [Ag^+][Cl^-]$

In a saturated solution, the concentration of Ag⁺ ions =
concentration of Cl⁻ ions = concentration of the salt AgCl = 1.05×10^{-5} M

$$[Ag^+][Cl^-] = (1.05 \times 10^{-5}) \times (1.05 \times 10^{-5}) = 1.1 \times 10^{-10} = K_{sp}$$

How does the precipitate form?

A precipitate is formed in a solution of sparingly soluble salts, when the product of its ions concentrations **exceed** its solubility product.

$$\text{Ionic product} \gg K_{sp}$$

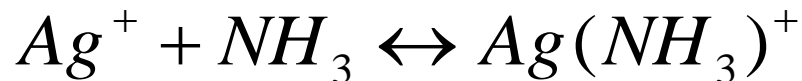
Factors affecting the solubility of formed precipitate

- 1. Complexation ion**
- 2. Solvent effect**
- 3. Common ion effect**

1. Complexation ion

If a ppt. is placed in a solution of a ligand, a complex will be formed with the metal ion of the ppt. and the solubility of the ppt. will be increased.

Example: By adding NH_3 to AgCl ppt. the following equilibria will take place:



The solubility of AgCl increases and equals $[\text{Cl}^-]$.

However, $C_{\text{Ag}} = [\text{Cl}^-] = s$

$$C_{\text{Ag}} = [\text{Ag}^+] + [\text{Ag}(\text{NH}_3)^+] + [\text{Ag}(\text{NH}_3)_2^+]$$

2- Effect of solvent:

- The solubility of most inorganic compounds is reduced by the addition of organic solvents (methanol, ethanol, acetone).
- 20% ethanol renders the solubility of lead sulphate & calcium sulphate.

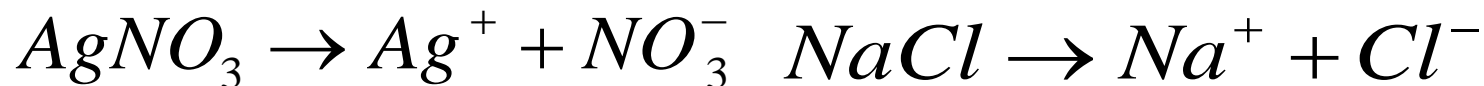
3. Common Ion Effect (C.I.):

A common ion is one of the ions of sparingly soluble salt in its saturated solution such as AgCl is dissolved in NaCl or KCl.

- The Cl^- is a common ion with chloride ion ionized from AgCl.
- The common ion usually reduce the solubility.

When Ag^+ is added (from AgNO_3) to AgCl ppt, K_{sp} of AgCl = $[\text{Ag}^+][\text{Cl}^-]$

Excess Ag^+ disturbs the equilibrium and combines with Cl^- to form AgCl ppt. till equilibrium is reached ($[\text{Ag}^+][\text{Cl}^-] = K_{sp}$), the solubility decreases.



Precipitation (Argentometric) Titration

- Formation of insoluble compound (precipitate) as a result of titration of analyte and titrant
- Titrations of precipitates formation.
- Argentometric titration: titrimetric reaction that use AgNO_3 as titrant
- Used for determining halides e.g. Cl^- by titration with AgNO_3 .
- According to the indicator used, three methods can be described.

Precipitation Titrations

Direct

1. **Mohr's method**: use Chromate as indicator (colored ppt)
2. **Fajans method** :Use adsorption indicators.

Indirect

3. **Volhard method** (colored solution)

An excess of silver ion is added to unknown chloride sample, and the remaining silver ion is back-titrated with a standard SCN^- solution using Fe(III) as an indicator.

Method	Indicator
Mohr	Na_2CrO_4 or K_2CrO_4
Fajans	Fluorescein (adsorption indicator)
Volhard	$(\text{NH}_4)_2\text{FeSO}_4$

Titration curves in precipitometry

A titration curve for a precipitation titration can be constructed by plotting volume of Ag^+ versus pX (X: Cl^- , Br^- , I^- , or SCN^-).

The sharpness of the end point is directly proportional to:

- a) K_{sp} of the silver salt.
- b) The concentration of reactants.

This is true when a suitable indicator concentration is used.

Plot the titration curve for the following reaction:

0.1 N AgNO_3 solution with 100 mL of 0.1 N NaCl solution?

We will calculate the ionic concentration of chloride ion at various stages of titration with the knowledge of the solubility product.

A) At the Beginning, Before Adding AgNO₃

Cl⁻ concentration = 0.1 , pCl=1

B) Upon adding 50 ml AgNO₃

The concentration of NaCl is 50 ml of 0.1 N solution in a dilution of 150 ml, the concentration of Cl will be

$$\frac{50 \times 0.1}{150} = 1/30 = 3.3 \times 10^{-2} \quad \text{pCl} = -\log(3.3 \times 10^{-2}) = 1.48$$

C) Upon adding 90 ml of AgNO₃ solution:

The concentration is 10 ml of 0.1 N in a solution of 190 ml, and the concentration will be

$$\frac{10 \times 0.1}{190} = 1/190 = 5.3 \times 10^{-3} \quad \text{pCl} = -\log(5.3 \times 10^{-2})$$

D) At the Equivalent Point:

There is no excess of Cl^- or Ag^+ , but a concentrated of AgCl

$$[\text{Ag}^+] \times [\text{Cl}^-] = S = 1.1 \times 10^{-10}$$

$$[\text{Ag}^+] = [\text{Cl}^-] = \sqrt{S_{\text{AgCl}}} = \sqrt{1.1 \times 10^{-10}} = \dots$$

$$\text{pCl} = -\log(1.05 \times 10^{-5}) = 4.98$$

The concentration of Ag^+ in all the previous calculations and its pC is easily obtained from the following equations

$$K_{sp} = [Ag^+] \times [Cl^-] = 1.1 \times 10^{-10}$$

$$p[Ag^+] + p[Cl^-] = -\log(1.1 \times 10^{-10}) = 9.96$$

This value is constant .i.e. if $p[Ag^+]$ increases, $p[Cl^-]$ decreases.

So that the sum of both exponents remains 9.96 and hence:

$$\text{If } pCl^- = 1.48, \text{ then for } pAg^+ = 9.96 - 1.48 = 8.48$$

$$\text{If } pCl^- = 2.28, \text{ then for } pAg^+ = 9.96 - 2.28 = 7.68$$

At equivalence points, $pCl^- = 4.98$

$$\text{So, } pAg^+ = 9.96 - 4.98 = 4.98$$

F) Beyond the equivalence point

When 101 ml of 0.1 M AgNO_3 is added, so 1 ml excess pAg^+ will be

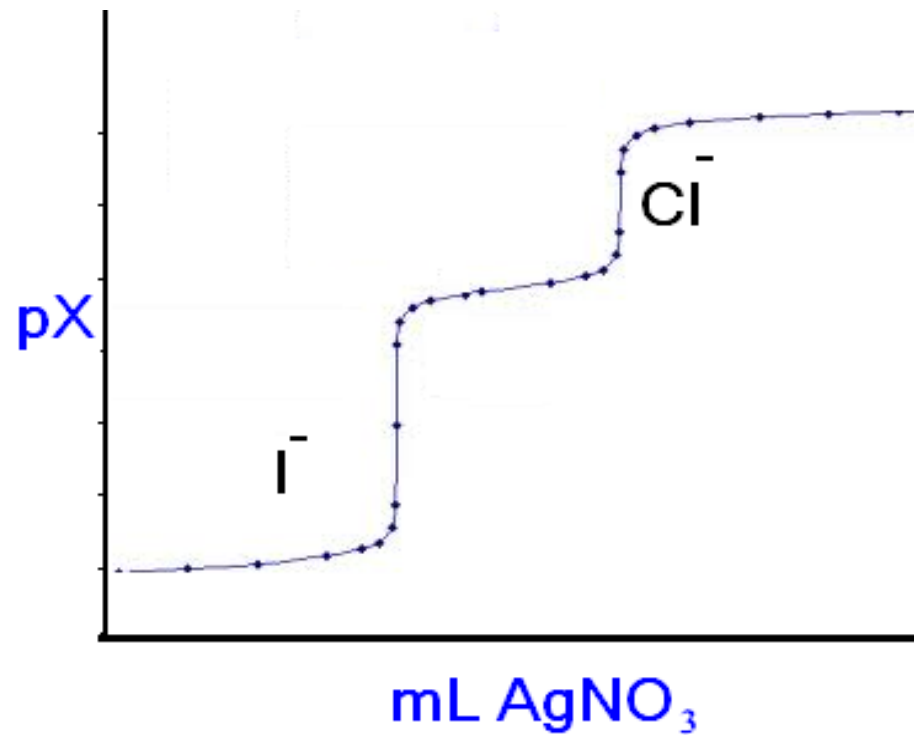
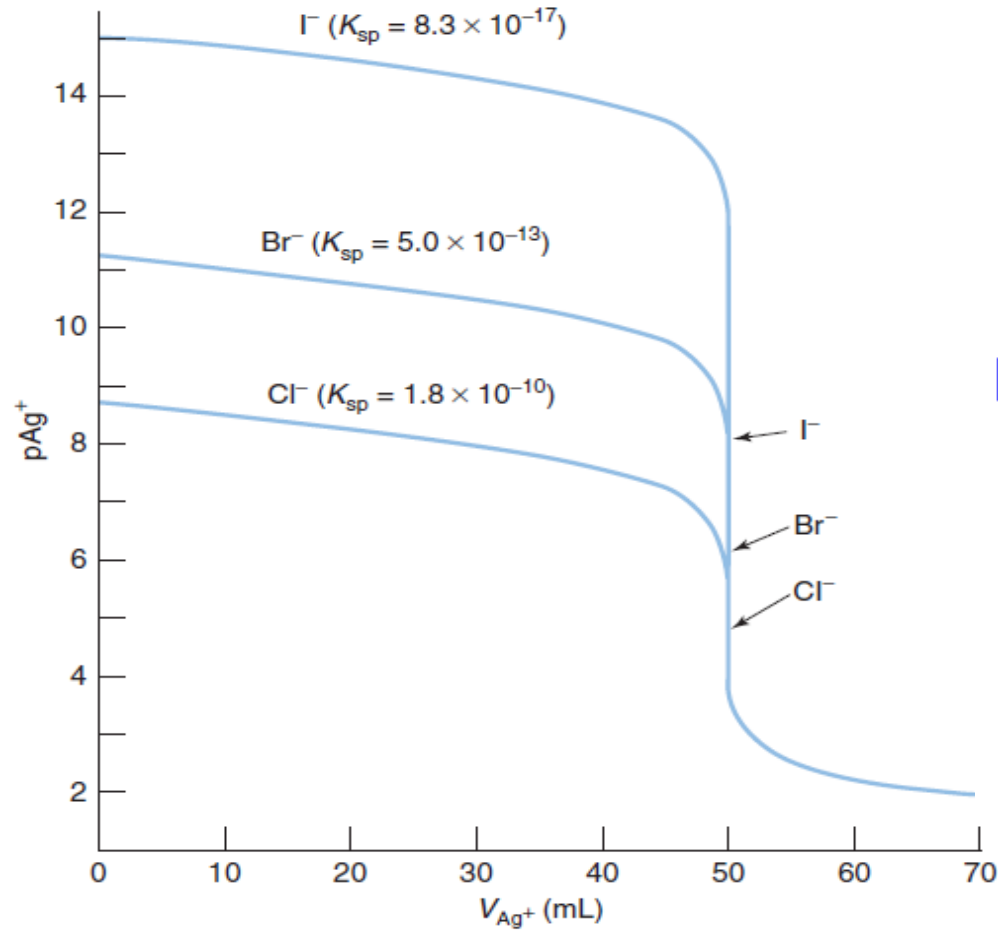
$$[\text{Ag}^+] = \frac{1 \times 0.1}{100 + 101} = \frac{0.1}{201} = 5 \times 10^{-4}$$

$$\text{pAg}^+ = 4 - (\log 5) = 3.3$$

$$\text{So, pCl}^- = 9.96 - 3.3 = 6.66$$

Volume of AgNO ₃	pCl ⁻

Complete this table and plot the titration curves by considering the 0.01, 0.001 M AgNO₃ against 0.01, 0.001 M Cl⁻, respectively?



Effect of K_{sp} on the shape of titration curve.

Mixtures can be titrated at enough difference in the solubilities of the two silver salts exists (at least 10^3).

Formation of Colored Precipitate (Mohr's method)

- **Direct titration**
- **Indicator:** soluble chromate salt (Na_2CrO_4 , K_2CrO_4)
- **Endpoint:** formation of colored secondary precipitate
- Relies on K_{sp} differences for two insoluble silver salts
- Ag_2CrO_4 (red) precipitated in neutral pH solution
- Colour forms just after AgCl or AgI formation.



- Chromate forms a ppt with Ag^+ of larger solubility than of AgCl .
- Thus AgCl is formed first and after all Cl^- is consumed, the first drop of Ag^+ will react with the chromate indicator giving a reddish ppt.

Factors affecting Mohr's titration method

1. The amount of indicator used

Ag_2CrO_4 is precipitated when the K_{sp} is exceeded.

Because CrO_4^{2-} forms yellow color solution, it might mask the end point

So, only small amount of K_2CrO_4 is added.

Thus, the end point is always later than the equivalence point.

To compensate for this positive error

1. An analyte-free reagent blank is analyzed to determine the volume of titrant needed to change in the indicator's color.
2. Subtracting the end point for the reagent blank from the titrand's end point gives the titration's end point.

2. Hydrogen ion concentration, pH

For the successful use of the chromate ion as indicator, the medium must be neutral or slightly alkaline with a pH between 6.5-9.0

In strong alkaline media (pH>9) AgOH might be precipitated.



In acidic media, the chromate ion changes into acid chromate then bi-chromate



Acid chromate and dichromate form with Ag⁺ more soluble salts and do not give the reddish brown ppt.

Cl⁻ ion free solution of CaCO₃, NaHCO₃, MgO or borax will be used. Na₂CO₃ can not be used as it will precipitate Ag₂CO₃.

Alkaline solution must be made slightly acidic with acetic acid.

3. Effect of salts

• Ions of SO_4^{2-} , HCO_3^- , tartrate or acetate, do not affect the sensitivity of CrO_4^{2-} indicator, but PO_4^{3-} , AsO_3^{3-} , SO_3^- , S^{2-} , F^- interfere strongly.

4. Effect of temperature

Silver chromate is more soluble in hot H_2O so the titration must be carried out at room temperature

5. Adsorption error

AgI and AgSCN adsorb the CrO_4^{2-} and form adsorption complex of Ag_2CrO_4 and AgI or AgSCN at the end point which is less colored & less sharp end point is obtained.

So, Mohr's method is not suitable for I^- & SCN^-

Adsorption Indicator (Fajans Method)

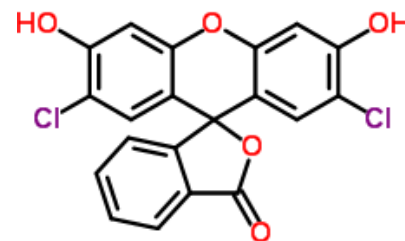
- Direct titration, uses certain dyes as internal adsorption indicators.
- These indicators are adsorbed by the ppt. and at the end point, a color changes.
- Upon adding of AgNO_3 to Cl^- , the colloidal AgCl ppt. adsorb ions from solution (even if its own ions).
- These ions form the primarily adsorbed layer and could hold a secondarily layer of oppositely charged ion from the solution.

Types of indicators:

- (1) Acid dyes such as the **Fluorescein series** e.g. **Fluorescein** and **Eosin** as sodium salts.
- (2) Basic dyes such as **Rhodamine 6G** or **phenosafranine** as halogen salts.

Adsorption Indicator (Fajans Method)

Fluorescein is adsorbed onto the surface of colloidal AgCl. After all chloride is used, the first drop of Ag⁺ will react with fluorescein (Fl⁻) forming a reddish color.

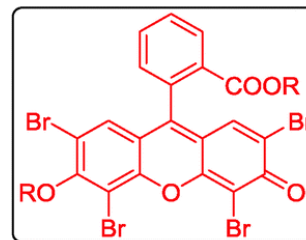


Dichlorofluorescein

Fluorescein & its derivatives are weak acids, the pH should be slightly alkaline to keep its anion form

but, not alkaline enough to convert Ag⁺ into AgOH.

Eosin is strong acid and used at acidic pH without problems.



Eosin



End point

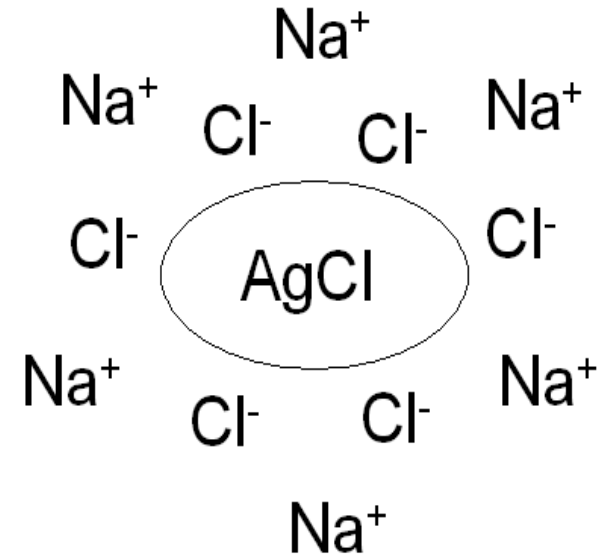
Principle of Adsorption

In the titration of Cl^- with Ag^+

• Before the Equivalence Point

Cl^- is in excess and forms the primary layer.

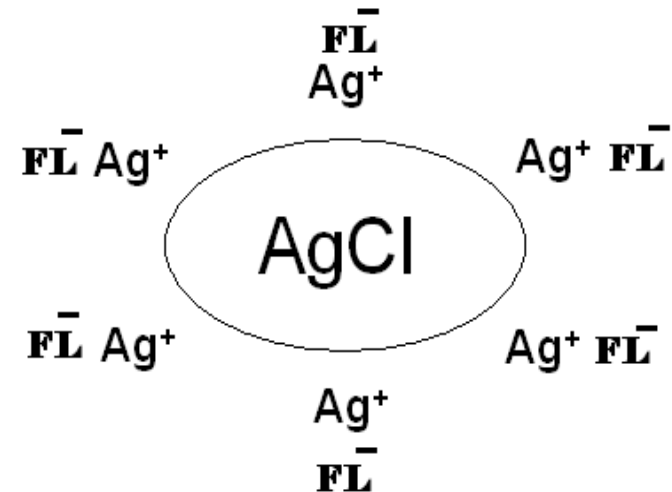
This repulses the indicator anions; and the more loosely held secondary (counter) layer of adsorbed ions.



• Beyond the Equivalence Point

Ag^+ is in excess, and the surface of the ppt. becomes positively charged (1^o layer being Ag^+).

This will now attract the indicator anion and adsorb it in the 2^o (counter) layer.



Factors affecting the adsorption of indicator

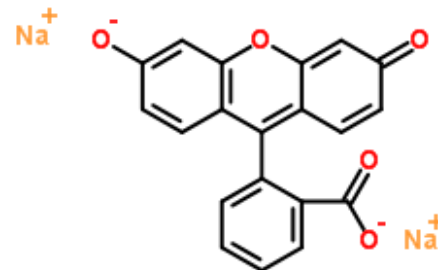
1. H⁺ ion concentration

Fluorescein is a very weak acid

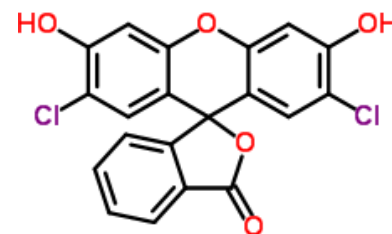
The color change depends on adsorption of the **fluoresceinate ions**. The optimum conditions of pH is 7-10

Dichlorofluorescein is stronger acidic and can be used down to pH 4.

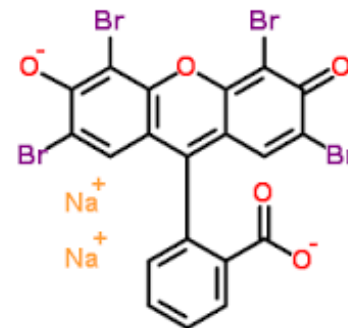
Eosin is strong acid, used down to pH 1, the color change is sharp at pH 3 (acetic acid medium)



Fluorescein



Dichlorofluoresceins



Eosin
(Cl⁻ Br⁻, I⁻, SCN⁻)

2. Effect of salts

The ppt. should be separated as far as possible in the colloidal state.

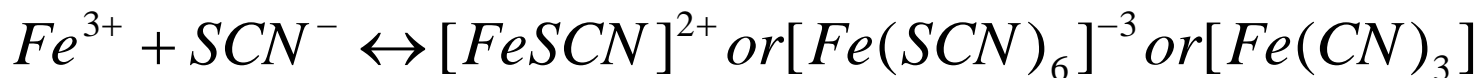
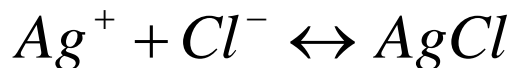
Because large quantities of salts may cause coagulation of the ppt. and hence a poor end point.

List of adsorption indicators and their uses

Ion determined	Titrant	Indicator
Cl ⁻ , Br ⁻ , I ⁻ , SCN ⁻	AgNO ₃	Fluores, Dichloro- Flu
Br ⁻ , I ⁻ , SCN ⁻	AgNO ₃	Eosin, Flu
I ⁻	AgNO ₃	Diiodo, flu

Formation of colored complex (Volhard's method)

- Indirect titration for **halides** with **AgNO₃** in nitric acid, and the excess **AgNO₃** is determined by titration with **KSCN** using ferric alum as indicator.
- Used for the direct titration of **Ag⁺** against **SCN⁻** using the same indicator.
- The reaction of Fe(III) with SCN⁻ is very sensitive, very small amount of SCN⁻ is needed to give color at the end point
- After complete precipitation of AgSCN, SCN⁻ reacts with ferric alum indicator to give highly colored ferrithiocyanate complex.



At higher concentration of SCN⁻

Factors affecting Volhard method

1. Amount of indicator

The color of the Fe^{3+} indicator is intense yellow, which prevents observation of the $\text{Fe}(\text{SCN})^{2+}$ red color.

A dilute Fe^{3+} indicator solution should be used.

2. H^+ concentration

- The procedure is performed in HNO_3 (0.2-1.6 M) .
- Too high acid conc. retards the formation of ferri thiocyanate complex.
- Too low acid conc. allows anions (PO_4^{3-} , ASO_4^{3-}) to interfere, so, acid conc. must be raised to 2 N.
- HNO_3 is important to prevent hydrolysis of ferric indicator.

3. Temperature

By increasing the temperature higher than 25 °C, HNO₃ will bleach the color of ferrithiocyanate complex.

So, this procedure must be applied at temperature lower than 25 °C.

4. Effect of salts

- Hg(II) and Cu(I) interfere by reaction with SCN⁻.
- Cu(I) interference could be eliminated by oxidation with HNO₃ to Cu(II) and Hg(II) ppted with H₂S.

SO₄⁻ and colored ions interfere (mask the endpoint).

- Volhard method could be used to determine CN⁻, oxalate, S⁻, CrO₄²⁻, CO₃²⁻ and SCN⁻

Advantages of Volhard's Method

- More accurate than Mohr or Fajans methods
- Does not require much care in adjusting the pH and the other conditions.
- Widely used for the direct estimation of Ag^+ and SCN^- and indirectly for the estimation of many ions which react with either ion.
- The titration is performed **only in acidic medium** since both ferric and silver ions are precipitated as hydroxides in alkaline medium.

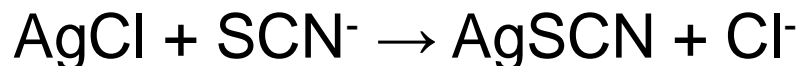
Estimation of Chloride by Volhard

In titration of chloride with excess Ag^+ solution, the ppt AgCl is formed

Back- titrating of the excess Ag^+ against SCN^- using ferric alum.

- At the end of the titration, we have both ppts AgSCN and AgCl .
- K_{sp} of $\text{AgCl} = 1 \times 10^{-10}$ is greater than that of AgSCN ($K_{sp} = 1 \times 10^{-12}$).

The following reaction takes place when all Cl^- is over:



This is an important reason for error, if not taken care of.

How could we overcome this problem?

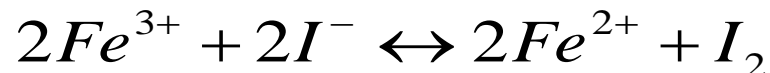
- Addition of some nitrobenzene, which surrounds the AgCl ppt. and shields it from the aqueous medium.
- The filtration of the ppt. directly after precipitation, which protects the ppt. from coming in contact with the added SCN⁻ solution.

For the case of AgI and AgBr

Both are less soluble than AgSCN, so, no reaction occur between AgI or AgBr and SCN⁻.

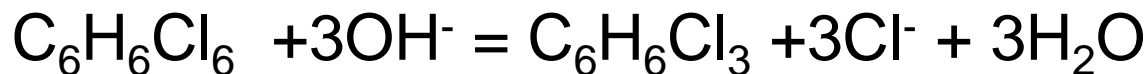
So, no need for filtration or addition of organic solvents.

But, when I⁻ is titrated, the indicator should be added only after adding the excess AgNO₃, because Fe³⁺ may oxidize I⁻ into I₂



Applications

- Determination of the chloride in natural water: Mohr and Volhard
- Determination of Silver content in silver alloy: Volhard method
- Determination of halogen content in organic compounds such as food, organochlorine pesticides: **Volhard method.**



Limitation of Argentometric Titrations

- Reducing agents e.g. formalin, sulphur dioxide and others interfere by reducing Ag^+ and must be removed.
- Colored compounds obscure the end point.
- Titration must be carried out in indirect light as AgX is photosensitive and undergo photodecomposition
- Fe^{3+} forms colored hydroxides in neutral or slightly basic solution.
- Hg^{2+} forms solution complex with I^- e.g. $(\text{HgI}_4)^{2-}$.

Examples of Precipitation Titrations

Titrand	Titrant ^a	End Point ^b
AsO_4^{3-}	AgNO_3 , KSCN	Volhard
Br^-	AgNO_3 AgNO_3 , KSCN	Mohr or Fajans Volhard
Cl^-	AgNO_3 AgNO_3 , KSCN	Mohr or Fajans Volhard*
CO_3^{2-}	AgNO_3 , KSCN	Volhard*
$\text{C}_2\text{O}_4^{2-}$	AgNO_3 , KSCN	Volhard*
CrO_4^{2-}	AgNO_3 , KSCN	Volhard*
I^-	AgNO_3 AgNO_3 , KSCN	Fajans Volhard
PO_4^{3-}	AgNO_3 , KSCN	Volhard*
S^{2-}	AgNO_3 , KSCN	Volhard*
SCN^-	AgNO_3 , KSCN	Volhard*

Problems

1. Describe how to analyze a solution of NaI by using the Volhard titration?
2. A 30 mL solution of I^- was treated with 50 mL of 0.365 M $AgNO_3$. $AgI(s)$ was filtered off, and the filtrate (plus Fe^{3+}) was titrated with 0.287 M KSCN. When 37.6 mL had been added, the solution turned red. How many milligrams of I^- were in the original solution?
3. A 0.238 g sample contained only NaCl and KBr. It was dissolved in water and required 48.40 mL of 0.048 M $AgNO_3$ for complete titration of both halides [giving $AgCl(s)$ and $AgBr(s)$]. Calculate the weight percent of Br in the solid sample.
4. A 10 mL of a chloride sample was treated with 15 mL of 0.1182 M $AgNO_3$. The excess silver was titrated with 0.101 M SCN^- requiring 2.38 mL to reach the red $Fe(SCN)^{2+}$ end point. Find the concentration of chloride (AtWt = 35.5) in g/L.

5. Find the concentration of chloride in a 25 mL solution to which few drops of K_2CrO_4 were added, if the end point required 20 mL of 0.10 M $AgNO_3$.

6 Find the pCl in a 20 mL of a 0.10 M Cl^- solution after addition of 0, 10, 20, and 30 mL of 0.10 M $AgNO_3$. $K_{sp} = 1.0 \times 10^{-10}$.

7. A solution is prepared by mixing 0.10 L of 0.12 M sodium chloride with 0.23 L of a 0.18 M $MgCl_2$ solution. What volume of a 0.20 M $AgNO_3$ solution is required to precipitate all of the chloride ion as silver chloride?

Reference

Daniel Harris,(2007), “Quantitative Chemical Analysis” 7th Edition, New York.