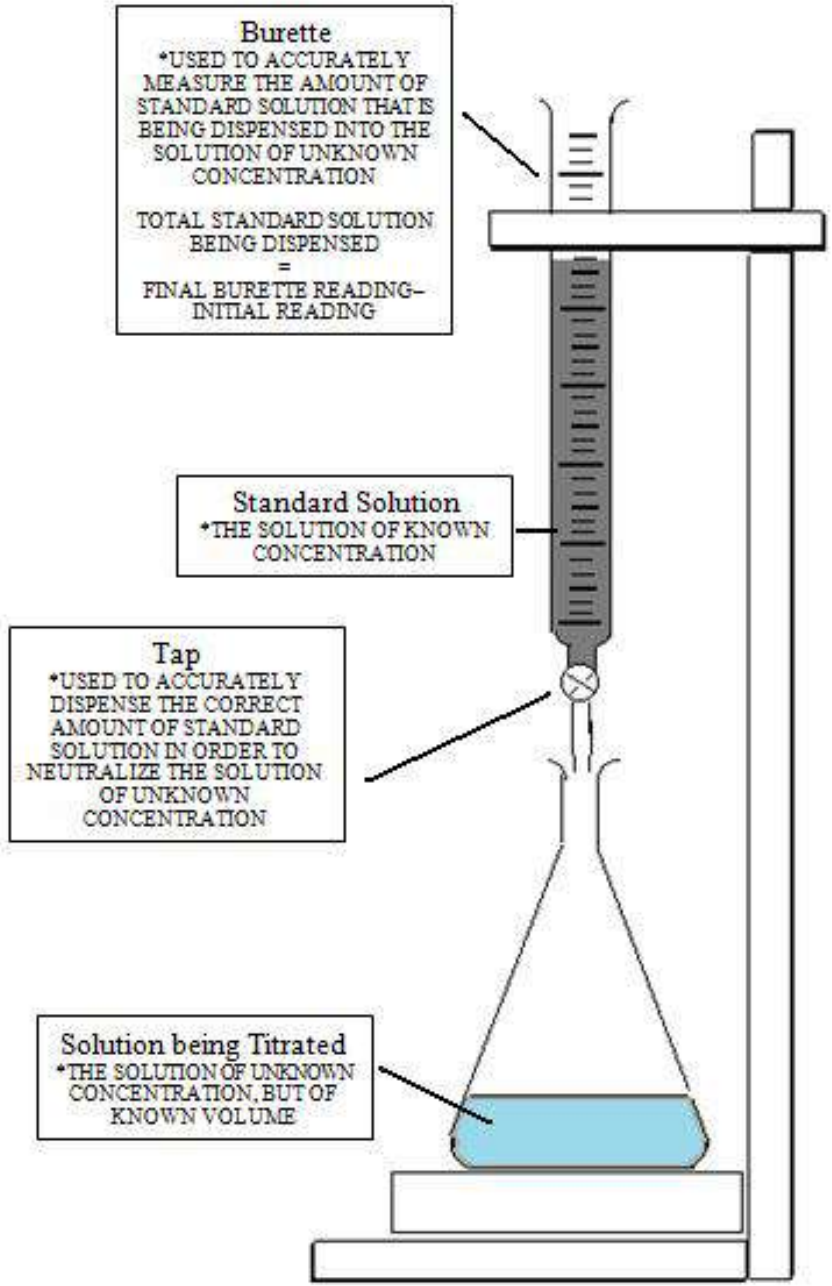
Lecture № 20

Analytical chemistry

Precipitation titration



Precipitation titration is a special type of titrimetric procedure, which involves the formation of precipitates during the course of titration.

The titrant react with the analyte forming an insoluble material and the titration continues till the very last amount of analyte is consumed. The first drop of titrant in excess will react with an indicator resulting in a colour change and announcing the termination of the titration.

PRECIPITATION TITRATION CAN BE CLASSIFIED ACCORDING TO THE TITRANTS:

- **Argentometry – titrant $AgNO_3$,**
- **Thiocyanatometry – titrant NH_4SCN, or (KSCN, NaSCN),**
- **MercurOmetry – titrant $Hg_2(NO_3)_2$,**
- **Sulfatometry – titrant H_2SO_4, (or Na_2SO_4)**
- **Hexacyanoferatometry – titrant $K_4[Fe(CN)_6]$ or** Kolthoff titration

Requirements to chemical reaction used in a precipitation titration:

1. Reaction should be fast and the stoichiometry should be known and reproducible. No secondary reactions of interference.
2. The reaction should be complete. In general a precipitation titration is considered complete when the precipitate is hard soluble with $K_{sp} < 10^{-8}$
3. It should not be formed a supersaturated solution.
4. It should be an indicator to find the equivalence point which, for this type of titration, corresponds to when precipitation of the analyte is complete.
5. Phenomenon of co-precipitation should be avoided.

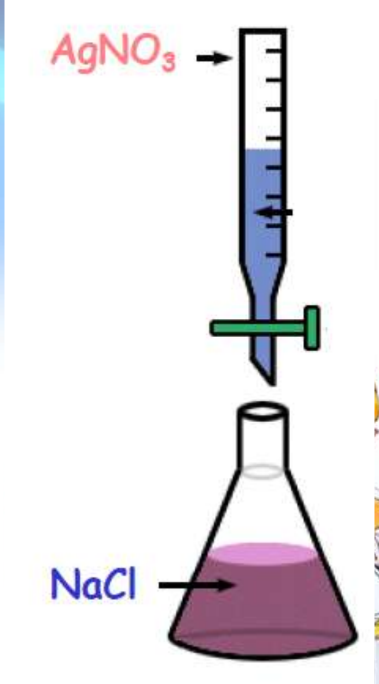
TITRATION CURVE

Titration curves for precipitation reactions are derived in a completely analogous way to the methods described for titrations involving strong acids and strong bases.

P-functions are derived for the preequivalence-point region, the postequivalence point region, and the equivalence point for a typical precipitation titraton.

When calculating a precipitation titration curve, we can choose to follow the change in the titrant’s concentration or the change in the analyte’s concentration.

Let’s calculate the titration curve for the titration of 100.0 mL of 0.1000 M NaCl with 0.100 M $AgNO_3$. The reaction in this case is.



$$AgNO_3 + NaCl \rightarrow AgCl \downarrow + NaNO_3$$

Most indicators for argentometric titrations respond to changes in the concentration of silver or chloride ions. As a consequence, titraton curves for precipitation reactions usually consist of a plot of pAg (or pCl) versus volume of $AgNO_3$.

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

$$pK_{sp} = pAg + pCl$$

- **Before the titration**

$$c(Cl^-) = 1 \cdot 10^{-1}\ mol/l$$

$$pCl = -\lg c(Cl^-) = -\lg 1 \cdot 10^{-1} = 1$$

- **Before the equivalence point** the analyte, NaCl, is in excess. We will calculate pCl before the equivalence point by determining the concentration of unreacted NaCl. The concentration of unreacted Cl⁻ after adding 90.0 mL of Ag⁺, for example,

$$c(Cl^-) = \frac{c_0(Cl^-) \cdot V_{rest}(NaCl)}{V(total)} = \frac{0{,}1 \cdot 10}{190} = 5 \cdot 10^{-3}\ mol/l$$

$$pCl = -\lg c(Cl^-) = -\lg 5 \cdot 10^{-3} = 2{,}3$$

The concentration of unreacted Cl⁻ after adding 99.0 mL of Ag+,

$$c(Cl^-) = \frac{c_0(Cl^-) \cdot V_{rest}(NaCl)}{V(total)} = \frac{0{,}1 \cdot 1}{199} = 5 \cdot 10^{-4}\ mol/l$$

$$pCl = -\lg c(Cl^-) = -\lg 5 \cdot 10^{-4} = 3{,}3$$

The concentration of unreacted Cl⁻ after adding 99.9 mL of Ag⁺,

$$c(Cl^-) = \frac{c_0(Cl^-) \cdot V_{rest}(NaCl)}{V(total)} = \frac{0{,}1 \cdot 0{,}1}{199{,}9} = 5 \cdot 10^{-5}\ mol/l$$

$$pCl = -\lg c(Cl^-) = -\lg 5 \cdot 10^{-5} = 4{,}3$$

- **At the titration’s equivalence point**

we know that the concentrations of Ag^+ and $Cl^–$ are equal. To calculate the concentration of $Cl^–$ we use the K_{sp} expression for AgCl; thus

$$c(Cl^-) = c(Ag^+) = \sqrt{K_{SP}} = \sqrt{10^{-10}} = 10^{-5}\ mol/l$$

$$pCl = pAg = -\lg 10^{-5} = 5$$

- **After the equivalence point**, the titrant is in excess. We first calculate the concentration of excess Ag^+ and then use the Ksp expression to calculate the concentration of $Cl^–$.

For example, after adding 100,10 mL of titrant:

$$c(Ag^+) = \frac{c_0(Ag^+)\cdot V_{rest}(AgNO_3)}{V(total)} = \frac{0,1\cdot 0,1}{200,1} = 5\cdot 10^{-5}\ mol/l$$

$$pAg = -\lg c(Ag^+) = -\lg 5\cdot 10^{-5} = 4,3$$

$$pCl = 10 - pAg = 10 - 4,3 = 5,7$$

After adding 101 mL of titrant:

$$c(Ag^+) = \frac{c_0(Ag^+)\cdot V_{rest}(AgNO_3)}{V(total)} = \frac{0{,}1\cdot 1}{201} = 5\cdot 10^{-4} \quad mol/l$$

$$pAg = -\lg c(Ag^+) = -\lg 5\cdot 10^{-4} = 3{,}3$$

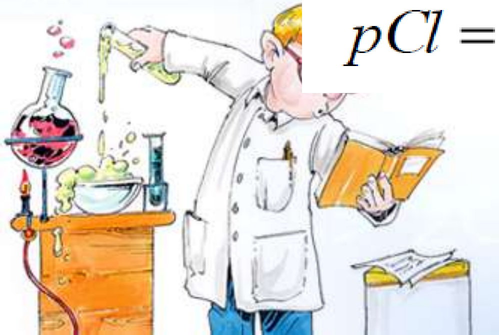
$$pCl = 10 - pAg = 10 - 3{,}3 = 6{,}7$$

After adding 110 mL of titrant:

$$c(Ag^+) = \frac{c_0(Ag^+)\cdot V_{rest}(AgNO_3)}{V(total)} = \frac{0{,}1\cdot 10}{210} = 5\cdot 10^{-3}\ mol/l$$

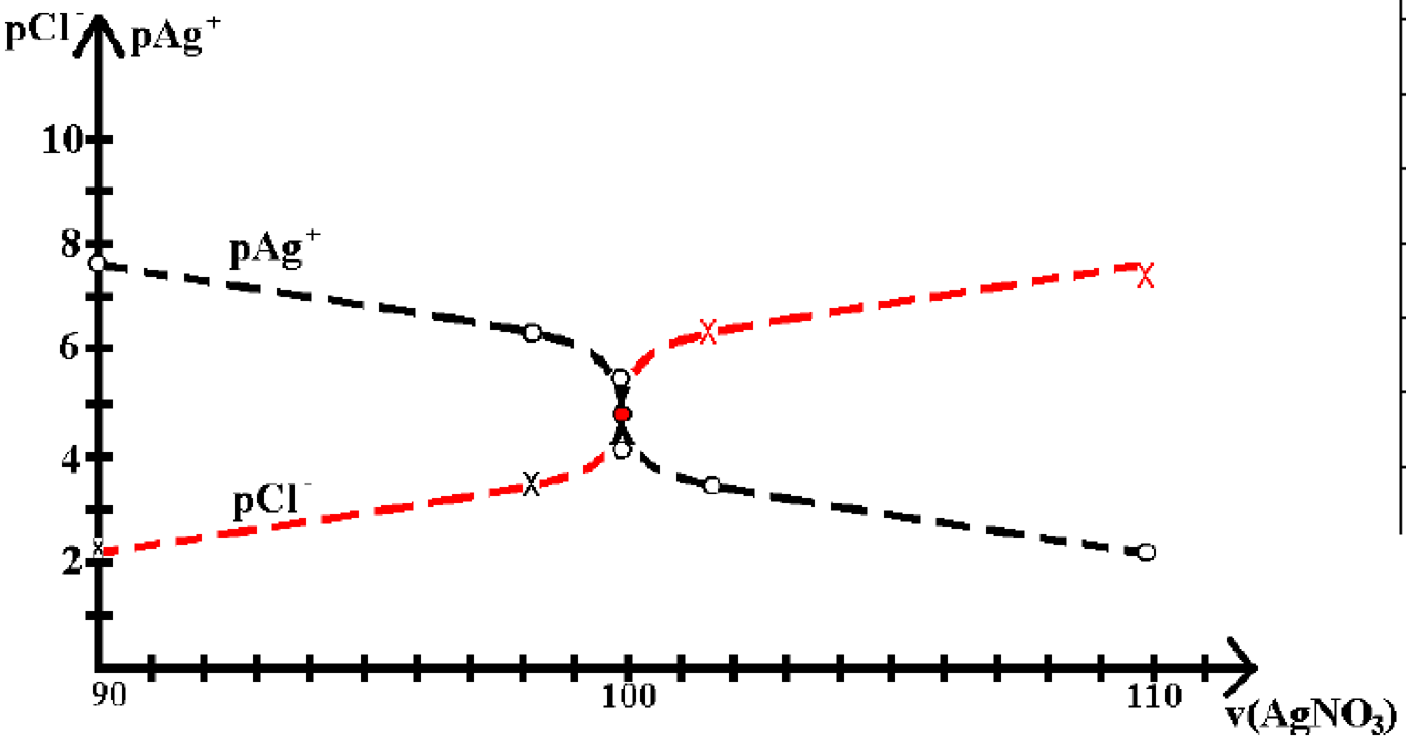
$$pAg = -\lg c(Ag^+) = -\lg 5\cdot 10^{-3} = 2{,}3$$

$$pCl = 10 - pAg = 10 - 2{,}3 = 7{,}7$$

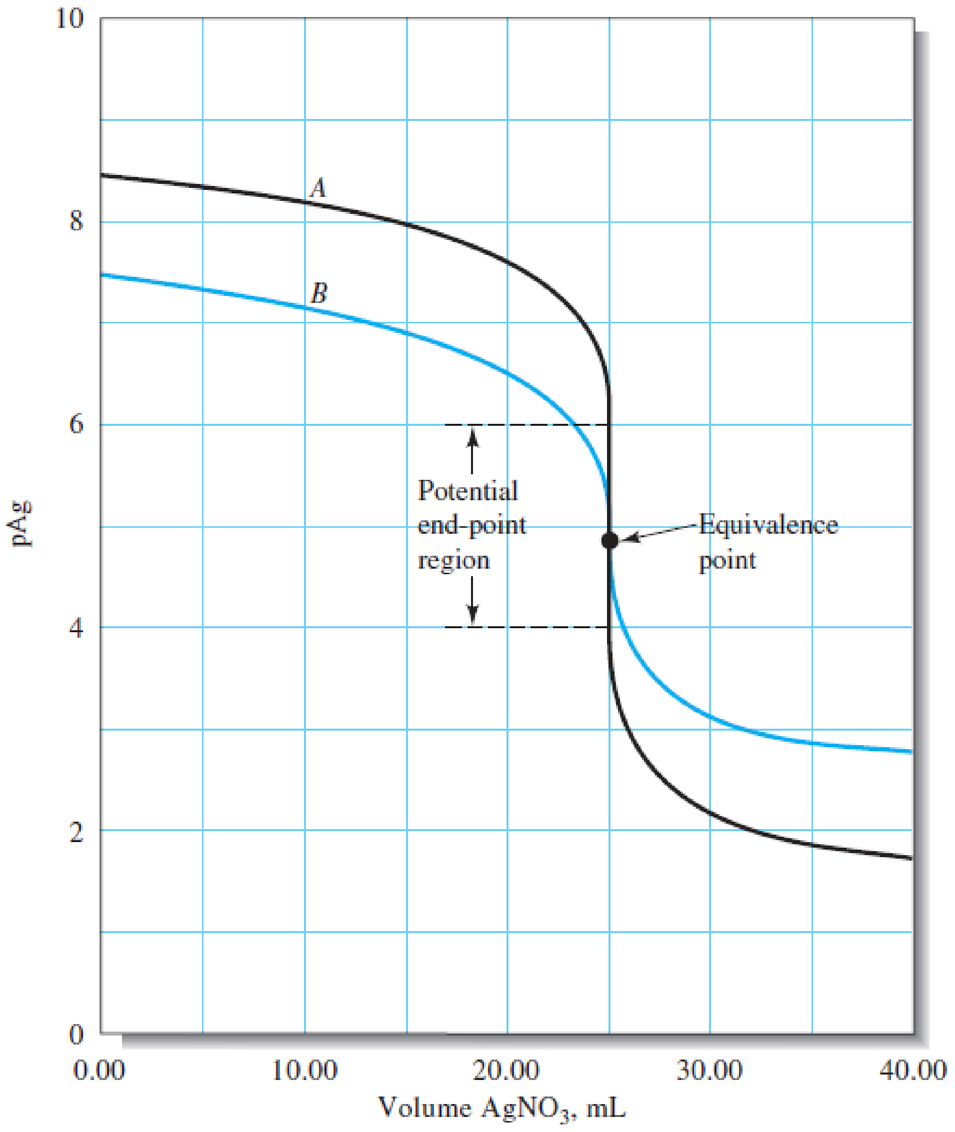


Titration curve for the titration of 100.0 mL of 0.1000 M NaCl with 0.1000 M $AgNO_3$. Black line – a precipitation titration curve, calculated by the change in the $AgNO_3$ concentration; Red line - a precipitation titration curve, calculated by the change in the NaCl concentration.

№	$V(AgNO_3)$	pCl	pAg
1	90	2.3	7.7
2	99	3.3	6.7
3	99,9	4.3	5.7
4	100	5	5
5	100,1	5.7	4.3
6	101	6.7	3.3
7	110	7.7	2.3



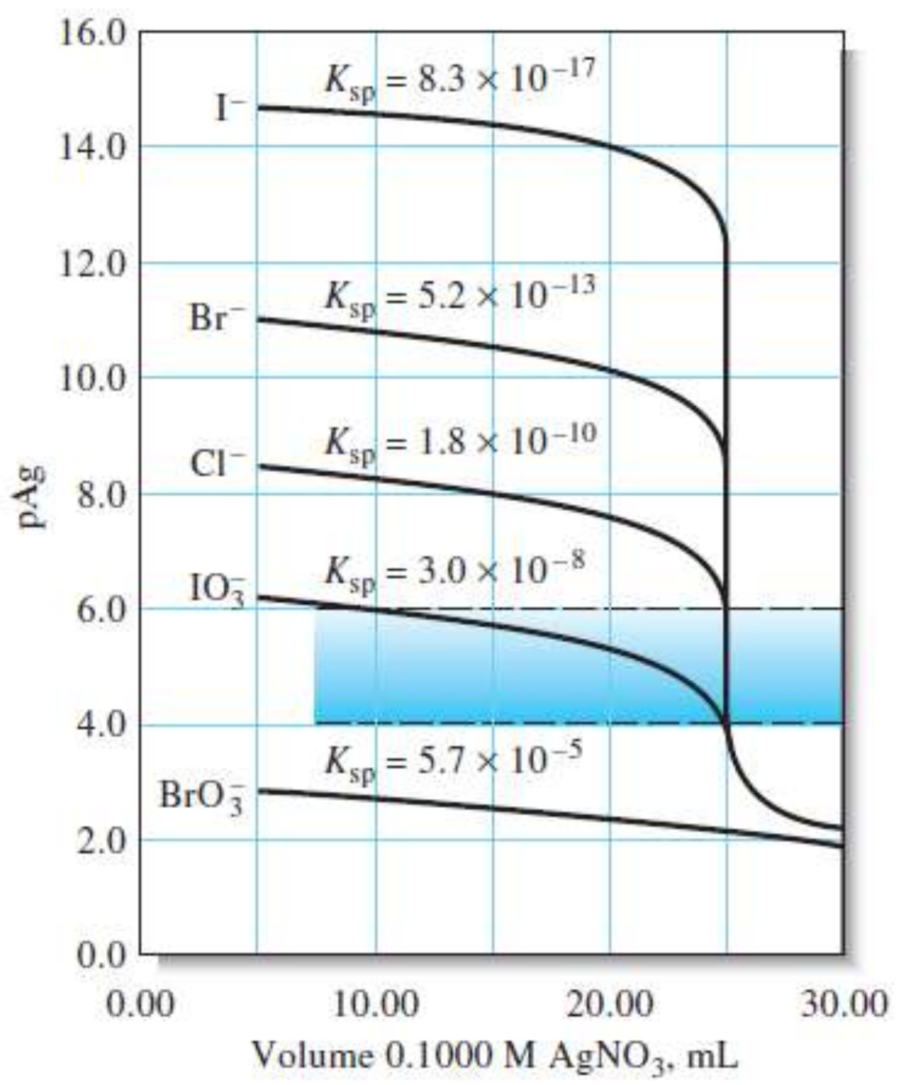
The Effect of Concentration on Titration Curves



Titration curve for
A 50.00 mL of **0.05000** M NaCl titrated with **0.1000** M $AgNO_3$, and
B 50.00 mL of **0.00500** M NaCl titrated with **0.01000** M $AgNO_3$.

Note the increased sharpness of the break at the end point with the more concentrated solution.

The Effect of Reaction Completeness on Titration Curves



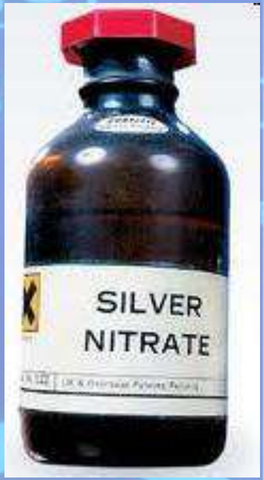
For each curve, 50.00 mL of a 0.0500 M solution of the anion was titrated with 0.1000 M $AgNO_3$.

Note that smaller values of K_{sp} *give much* sharper breaks at the end point.

Conclusions

1. As the concentrations of analyte and titrant decrease, the end point break decreases
2. The titration curve brake depends on K_{sp} of the precipitate. As K_{sp} becomes larger, the inflection near the equivalence point decreases, until the equivalence point becomes too shallow to detect. It is not practical to titrate an analyte when it forms too soluble precipitate ($K_{sp} > 10^{-10}$)
3. The titration curve brake depends on temperature also, and increases with the temperature decreasing.

ARENTOMETRY titrant $AgNO_3$



Precipitation titrimetry, which is based on reactions that yield ionic compounds of limited solubility, is one of the oldest analytical techniques. The slow rate of formation of most precipitates, however, limits the number of precipitating agents that can be used in titrations to a handful. The most widely used and important precipitating reagent, *silver nitrate*, which is used for the determination of the halogens, the halogen-like anions. Titrations with silver nitrate are sometimes called argentometric titrations.

Argentometry is the most usefull method of precipitatometric titration, as it caused of very low solubility product of halide (or pseudohalide) salts,i.e.

Ksp AgCl = 1,82 . 10^{-10}
Ksp AgCNS = 1,1 . 10^{-12}
Ksp AgBr = 5,0 . 10^{-13}

Ksp AgCN = 2,2 . 10^{-16}
Ksp AgI = 8,3 . 10^{-17}

There are 3 techniques of end point determination

- method of **Mohr** **(indicator: chromic potassium)**
- method of **Volhard** **(indicator: ferric salt)**
- method of **Fajans** **(indicator: fluorosceince)**

Preparation of titrant $AgNO_3$

Silver nitrate is available in pure form, but it is hygroscopic and therefore unable to be used as a primary standard. It can be standardized against dried sodium chloride.

$$AgNO_3 + NaCl = AgCl\downarrow + NaNO_3$$

$$n(AgNO_3) = n(NaCl)$$

$$c(AgNO_3)\cdot V(AgNO_3) = c(NaCl)\cdot V(NaCl)$$

Solution of silver nitrate should be protected from unnecessary exposure to light: a dark coloured bottle is recommended. Concentration of silver nitrate solution changes over time.

The Mohr method

Joseph L. Gay-Lussac (1778–1850) performed silver assay by turbidimetric titration to <*0.05%* relative accuracy and precision in 1829.

Karl F. Mohr (1808–1879) improved the end-point method by using K_2CrO_4 indicator.

Potassium chromate (K_2CrO_4) can serve as an indicator for the direct argentometric determination of chloride, bromide, cyanide and thiocyanide ions by reacting with silver ion to form a reddish-brown silver chromate (Ag_2CrO_4) precipitate in the equivalence-point region. Mohr method is not feasible for I^- as of the salt precipitate adsorption.

Chromate is yellow in neutral and alkaline conditions and at endpoint is more soluble than silver halide. It will only form after all the analyte has been precipitated.

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The Mohr titration. The solution is initially yellow, the color of chromate ion, as the white AgCl forms. Near the endpoint, the red silver chromate forms but it dissipates with swirling. The endpoint is the first permanent red color.

- **Left flask:** before the titration endpoint, addition of Ag+ ions leads to formation of silver chloride precipitate, making **the solution cloudy**. The chromate indicator gives a **faint lemon-yellow colour.**
- **Centre flask:** **at the endpoint**, all the Cl− ions have precipitated. The slightest excess of Ag+ precipitates with the chromate indicator giving a **slight red-brown colouration.**
- **Right flask:** If addition of Ag+ is continued past the endpoint, further silver chromate precipitate is formed.

The reactions involved in the direct argentometric determination of chloride, bromide, thiocyanide (X^-) are

$$Ag^+ + X^- \rightarrow AgX \downarrow$$

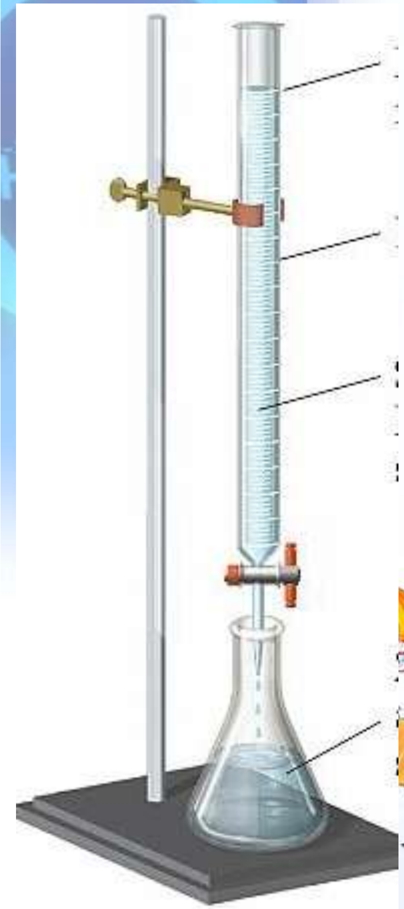
white precipitate

, where X = Cl^-, Br^-, CN-, SCN^-

indicator K_2CrO_4 (or Na_2CrO_4),

$$2Ag^+ + CrO_4^{2-} \rightarrow Ag_2CrO_4 \downarrow$$

reddish–brown precipitate



The change of precipitate colour occurs at the end point!!!!!

Conditions of argentometric titration (to overcome errors)

1. It is very important the order of the titration. Always to an analyzed solution (NaCl, KCl, KBr etc) titrant $AgNO_3$ should be added, and not vice versa. Mohr's method cannot be used to titrate silver with a standard chloride solution. This is not possible in since chromate added to a silver solution would immediately cause a reddish-brown precipitate.

2. Mohr titration has to be performed at a neutral or weak basic solution of pH 7-8. Above this pH, silver will form a precipitate with hydroxide. Below this pH chromate converts to dichromate, a bright orange colour thereby obscuring the endpoint.

3. Cations which also can be precipitated with CrO_4^{2-} (Ba^{2+}, Pb^{2+}, Bi^{3+}, Hg^{2+}) and anions precipitated by Ag^+ (PO_4^{3-}, AsO_4^{3-}, $C_2O_4^{2-}$ etc.) must be absent in the analyzed solution.

- **Volhards Method or THIOCYANATOMETRY titrant NH_4SCN**

Thiocyanatometric method uses a direct titration with ammonium thiocyanate for the determination of silver and mercury(I) salts. The titration uses iron alum $NH_4Fe(SO_4)_2 \times 12H_2O$ as the indicator.

$$AgNO_3 + NH_4SCN = \underset{white}{AgSCN}\downarrow + NH_4NO_3$$

$$Fe^{3+} + nSCN^- \rightarrow \underset{red\ solution}{[Fe(SCN)_n]^{3-n}}$$

$$n(AgNO_3) = n(NH_4SCN)$$

At the equivalent point

The iron alum indicator works by forming the coloured complex when an excess of thiocyanate occurs. The solution must be acidic, with a concentration of about 1 M nitric acid to ensure the complex formed is stable.

$$Hg_2(NO_3)_2 + 2NH_4SCN = Hg_2(SCN)_2\downarrow + 2NH_4NO_3$$

$$Fe^{3+} + nSCN^- = [Fe(SCN)_n]^{3-n}$$

This method also uses a ***back titration*** with ammonium thiocyanate for the determination of chlorides, bromides and iodides in acidic solutions. A known excess of silver nitrate solution is added to the sample and the excess is back titrated with standard thiocyanate solution.

Determination of KBr

$$KBr + AgNO_3(excess) = AgBr\downarrow + KNO_3 + AgNO_3(leftover)$$

$$AgNO_3(leftover) + NH_4SCN = AgSCN\downarrow + NH_4NO_3$$

$$Fe^{3+} + nSCN^- = [Fe(SCN)_n]^{3-n}$$

$$n(KBr) = n(AgNO_3) - n(NH_4SCN)$$

Determination of $BaCl_2$

$$BaCl_2 + 2AgNO_3(excess) = 2AgCl\downarrow + Ba(NO_3)_2 + AgNO_3(leftover)$$

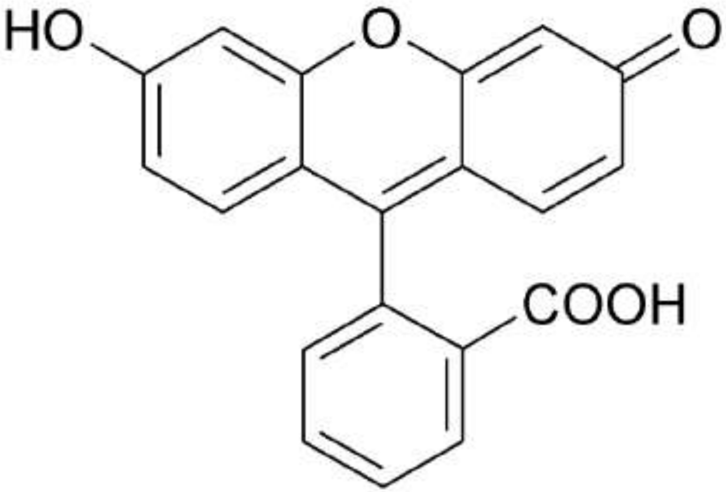
$$AgNO_3(leftover) + NH_4SCN = AgSCN\downarrow + NH_4NO_3$$

$$Fe^{3+} + nSCN^- = [Fe(SCN)]^{3-n}$$

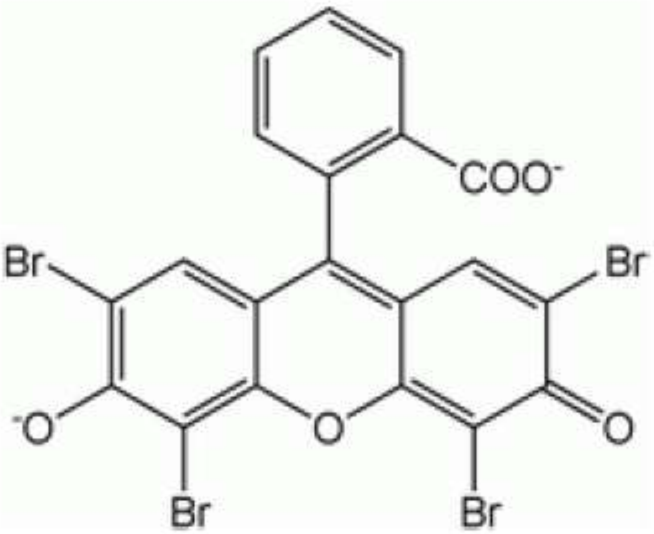
In a similar way KI and NaI can be determined

• Fajans' method

Fajans titration use adsorption indicators, i.e. organic compounds which is adsorbed into colloidal precipitate surface during the titration processes.



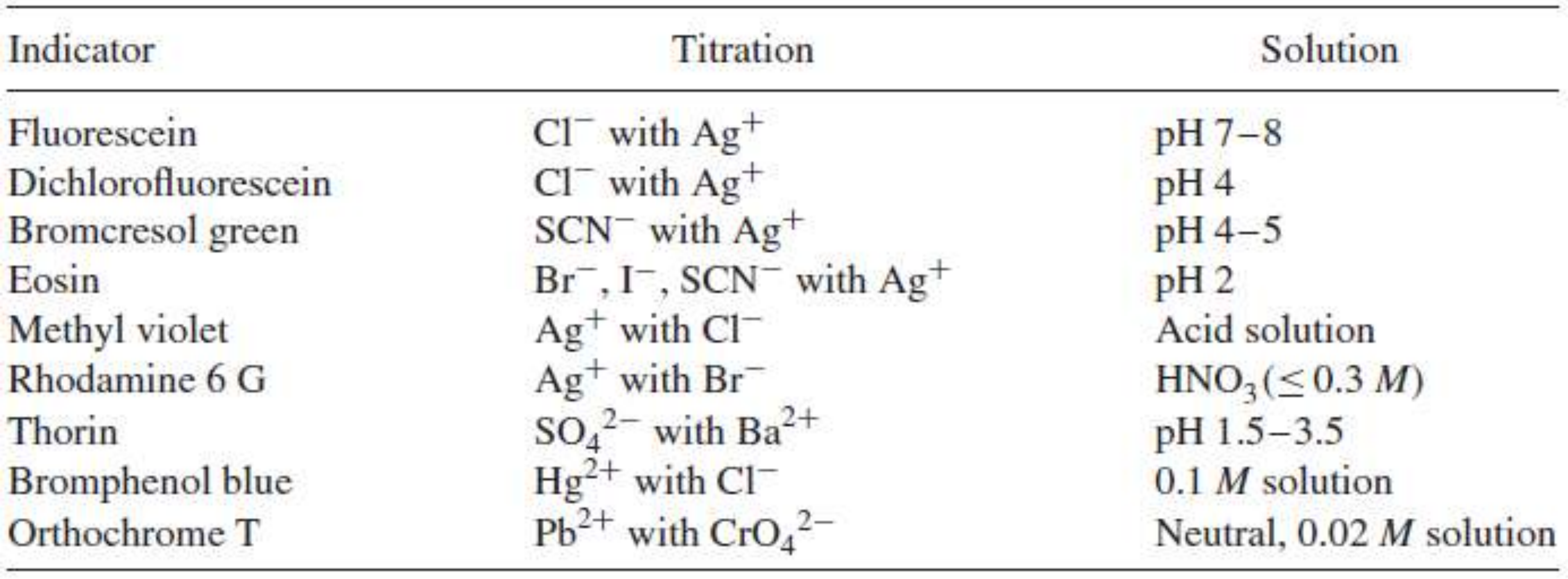
Fluorescein



Eosin

An adsorption indicator is an organic compound that tends to be adsorbed onto the surface of the solid in a precipitation titration. Ideally, the adsorption occurs near the equivalence point and causes a change in the colour of the indicator.

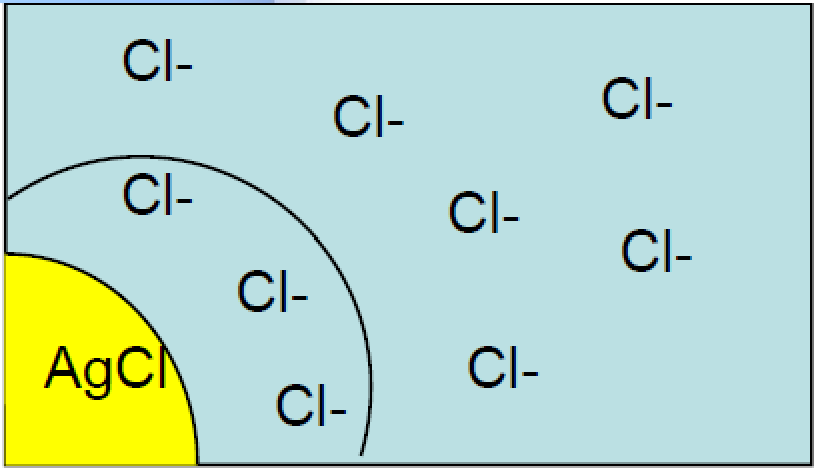
Adsorption Indicators



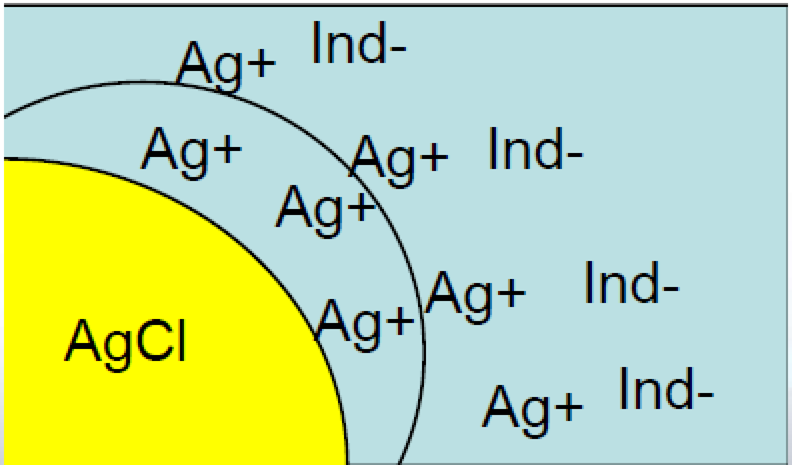
Indicator	Titration	Solution
Fluorescein	Cl^- with Ag^+	pH 7–8
Dichlorofluorescein	Cl^- with Ag^+	pH 4
Bromcresol green	SCN^- with Ag^+	pH 4–5
Eosin	Br^-, I^-, SCN^- with Ag^+	pH 2
Methyl violet	Ag^+ with Cl^-	Acid solution
Rhodamine 6 G	Ag^+ with Br^-	HNO_3 (≤ 0.3 *M*)
Thorin	SO_4^{2-} with Ba^{2+}	pH 1.5–3.5
Bromphenol blue	Hg^{2+} with Cl^-	0.1 *M* solution
Orthochrome T	Pb^{2+} with CrO_4^{2-}	Neutral, 0.02 *M* solution

Example: Fluoresence in form of its fluorescenate (yellowish green) anion react with Ag^+ to form an intensive red precipitate which is adsorbed to AgCl precipitate surface caused by ionic pair interaction.

First step of titration



Final step of titration: **Ag^+Ind^-**

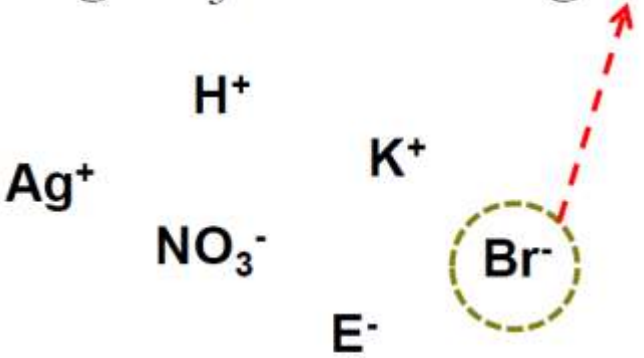


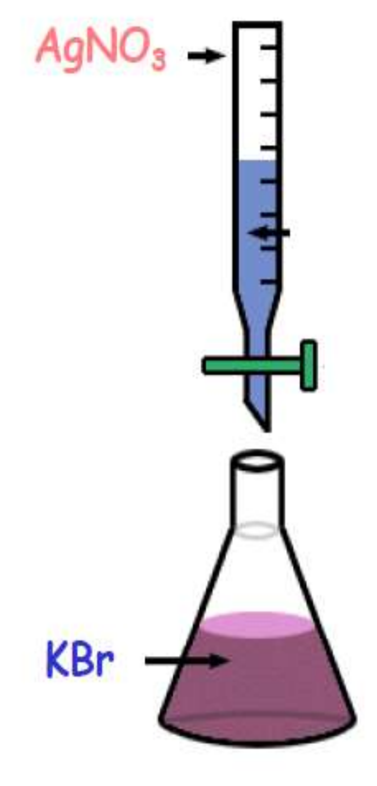
Example:

Consider a titration of KBr with $AgNO_3$ titrant in the presence of eosin (HE).

Before the end point $AgNO_3$ added to a dilute solution of KBr, the solution becomes turbid and if other electrolytes are absent, coagulation does not occur immediately.

$$AgNO_3 + KBr \rightarrow AgBr \downarrow + KNO_3$$





The colloidal sized AgBr particles adsorb Br^- (because KBr in excess before the end point) and these attract silver ions. Colloidal particles are electrically charged and repel each other preventing coagulation. As titration continues, the amount of bromide decreases but there is still some surface charge which acts to repel the negatively charged indicator ion (E^-).

$$AgBr \xrightarrow{Br^-, Ag^+} AgBr \bullet Br^- | Ag^+$$

$$\left\{\begin{array}{l} AgBr \xrightarrow{NO_3^-,\,Ag^+} AgBr \bullet Ag^+ \middle| NO_3^- \\ AgBr \bullet Ag^+ | NO_3^- + \underset{\text{eosinium ion}}{E^-} \Leftrightarrow \underset{red-violet\ colour}{AgBr \bullet Ag^+ | E^-} + NO_3^- \end{array}\right.$$

Immediately after endpoint there is an excess of silver ions which will adsorb onto the surface of the precipitate. The charged surface has now changed polarity and attracts the negative indicator ion. A colour change will be observed.

Limitations of Fajan’s method

1. Fluorescein can be used for titration of Cl^-, Br^-, I^-, SCN^-. Eosin only for Br^-, I^-, SCN^-, no chlorides can be alalysed

2. The pH must be well controlled for maintaining indication ionic concentration, in basic or acidic solution. For example, fluorescein ($K_a = 10^{-7}$) in a solution having pH>7 will release small quantity of fluoreseinate ion, hence we can not observe colour change of the indicator. Fluorescein is used feasibly in a solution of pH 7-10, eosin ($K_a = 10^{-4}$) is at pH 3-7.

3. Titration should be performed at steering of the solution.

List of Precipitation Titrations

ANALYTE	TITRANT	INDICATOR	METHOD
Cl^-, Br^-	$AgNO_3$	K_2CrO_4	Mohr
Cl^-,Br^-,I^-,SCN^-	$AgNO_3$	Adsorption	Fajans
Br^-,I^-,SCN^-,AsO_4^{3-}	$AgNO_3$ + KSCN	Fe(III)	Volhard (not filtered)
Cl^-,CN^-,CO_3^{2-},S^{2-} $C_2O_4^{2-}$,CrO_4^{2-}	$AgNO_3$ + KSCN	Fe(III)	Volhard (filtered)
F^-	Th(IV)	Alizarin	Fajans
SO_4^{2-}	$BaCl_2$	Tetrahydroxyquinoline	Fajans
PO_4^{3-}	$PbAc_2$	Dibromofluorescein	Fajans
CrO_4^{2-}	$PbAc_2$	Fluorescein	Fajans
Ag^+	KSCN	Fe(III)	Volhard
Zn^{2+}	$K_4Fe(CN)_6$	Diphenylamine	Fajans
Hg_2^{2+}	NaCl	Bromphenol blue	Fajans

MERCUROMETRY titrant $Hg_2(NO_3)_2$

When halide ions are titrated with mercury(I) nitrate solution, precipitation of Hg_2X_2 occurs during the titration process. After equivalent point, excess of Hg_2^{2+}, react with indicator.

$$Hg_2^{2+} + 2X^- \Leftrightarrow Hg_2X_2 \downarrow$$

whrer X = Cl^-, Br^-.

There are 2 indicators for end point determination:

- $[Fe(SCN)]Cl_2$
- diphenylcarbazone

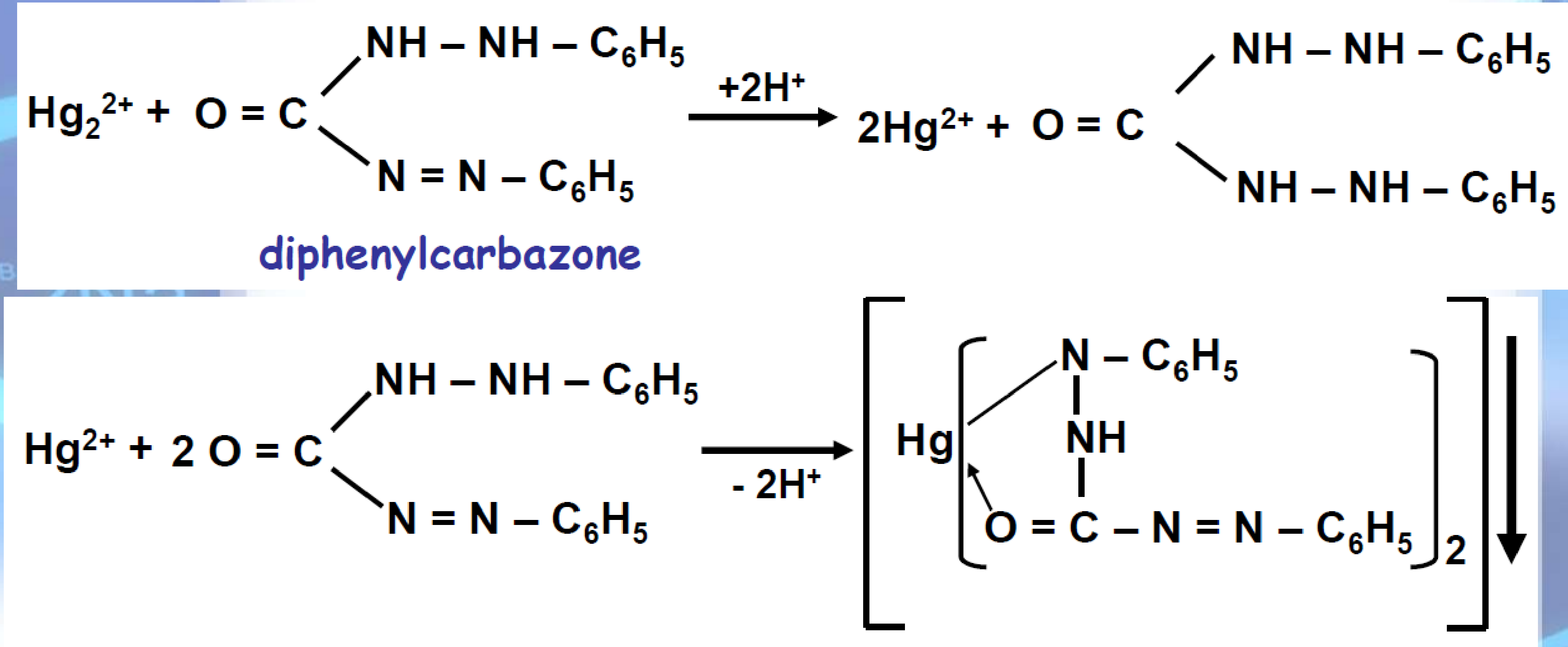
Application of $[Fe(SCN)]Cl_2$ as indicator.

In this case excess of titrant leads to decomposition of $[Fe(SCN)]Cl_2$ and red colour of the solution turns yellow.

$$Hg_2^{2+} + 2[Fe(SCN)]^{2-} = Hg_2(SCN)_2 \downarrow + 2Fe^{3+}$$

Application of diphenylcarbazone as indicator.

In this case excess of Hg_2^{2+} reacts with diphenylcarbazone, oxidizes to Hg^{2+} , and forms complex compound of blue violet colour.



Blue violet colour

pH = 0 (HNO_3)

Preparation of titrant $Hg_2(NO_3)_2$

Mercury (I) nitrate is not a primary standard. It should be standardized against dried sodium chloride.

$$Hg_2(NO_3)_2 + 2NaCl = Hg_2Cl_2 \downarrow + 2NaNO_3$$

Advantages of mercurometry:

1. Not required expensive silver salts.
2. Mercury(I) precipitates are less soluble than analogous silver salts. Therefore, equivalence point is clearly marked.
3. Mercurometric determination are carried out with direct titration in acidic solution.
4. Chloride ion can be determined with reducing agents (S^{2-}, SO_3^{2-}) and oxidising agents (MnO_4^-, $Cr_2O_7^{2-}$) presence.
5. Titration can be carried out in turbid and coloured solutions.

SULPHATOMETRY titrant H_2SO_4 (Na_2SO_4)

Determination of $BaCl_2$

Sulfate can be determined by titrating with barium ion, to precipitate $BaSO_4$.

$$\underset{}{Ba^{2+}} + \underset{\text{free indicator colour}}{HInd^{2-}} \Leftrightarrow \underset{\text{colour of complex}}{BaInd^{-}} + H^{+}$$ **Before end point**

$$BaInd^{-} + SO_4^{2-} + H^{+} \Leftrightarrow BaSO_4 + HInd^{2-}$$ **After end point**

The titration is carried out in an aqueous–organic solvent mixture. The organic solvent decreases the dissociation of the indicator and thereby hinders formation of a barium–indicator complex. It also results in a more flocculant precipitate (formed when colloids come out of suspension in the form of flocs or flakes) with better adsorption properties for the indicator.

HEXACYANOFERATOMETRY titrant $K_4[Fe(CN)_6]$

Zinc sulfate solution is titrated directly with potassium ferrocyanide, using mixture of diphenylamine and $K_3[Fe(CN)_6]$ as an indicator, equivalent point can entirely be found owing to the appearance of blue colour.

$$3Zn^{2+} + 2[Fe(CN)_6]^{4-} + 2K^+ = \underset{green}{Zn_3K_2[Fe(CN)_6]_2} \downarrow$$

Redox Indicator

$K_3[Fe(CN)_6]$ + $(C_6H_5)_2NH$
diphenylamine

Titration end point is detected by using external indicator such as uranylnitrate, ammonium molybdate, $FeCl_3$, etc, which needs a special technical skill. So it is better to use internal indicators such as diphenylamine, diphenylbenzidine, diphenylamine sulfonate, etc.

Acidic solution of ferro-ferric cyanide has much lower reduction potential compared to those required to oxydize the indicator, forms intensive coloured of oxidized form. When Zn^{2+} is added to this solution then a Zn-ferrocyanide will be formed, followed with increasing reduction potential for $Fe(CN)_6^{4-}$ removed from the solution. After completely reaction, a sharp increase of reductionpotential which is followed by appearing blue colour of oxidized form of indicator, caused by excess of Zn^{2+} in the solution.

This method can be attributed to the precipitation as well as redox titration

Compared to acid-base or reduction-oxidation titrations the precipitatometric titration has no much more methods

- Difficult to select a suitable indicator

- Difficult to obtain an accurate precipitate composition,
the coprecipitation effect is oftenly occured.