Unit-3

Precipitation titrations: Mohr's method, Volhard's, Modified Volhard's, Fajans method, *estimation of sodium chloride.

-Complexometric titration: Classification, metal ion indicators, masking and demasking reagents, estimation of Magnesium sulphate, and calcium gluconate.

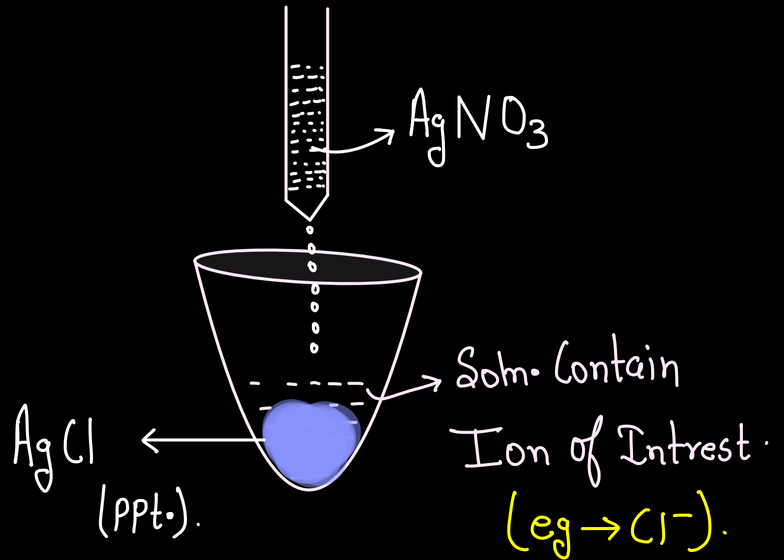
-Gravimetry: Principle and steps involved in gravimetric analysis. Purity of the precipitate: co-precipitation and post precipitation, Estimation of barium sulphate.

-Basic Principles,methods and application of diazotisation titration.

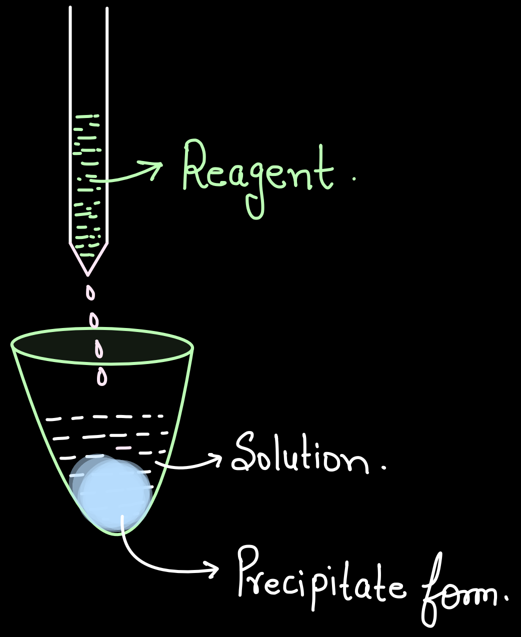
Precipitation Titration

Precipitation titration is a type of chemical analysis where a reagent is gradually added to a solution until a precipitate (solid) forms. This method is used to determine the concentration of a specific substance in a solution by measuring the amount of reagent required to react completely with the substance.

In this type of titration, a solution containing an ion of interest is treated with a reagent that reacts with the ion to form an insoluble compound (precipitate).



This Method is Used to determine the Concentration of Substance in Solution. by Calculating the Reagent Used.



Here's a step-by-step explanation of how precipitation titration works:

Preparation of the Sample: A sample containing the ion to be analyzed is dissolved in a suitable solvent, usually water.

Addition of Titrant: A reagent (titrant) is slowly added to the sample. The titrant contains ions that will react with the ions in the sample, forming an insoluble precipitate.

Formation of Precipitate: As the titrant is added, the reaction between the ions causes the formation of a solid precipitate. The precipitate continues to form as long as the reaction proceeds.

End Point Detection: The endpoint of the titration is reached when no more precipitate forms, indicating that all the ions from the sample have reacted with the titrant. This can be detected visually or using an indicator that changes color at the endpoint.

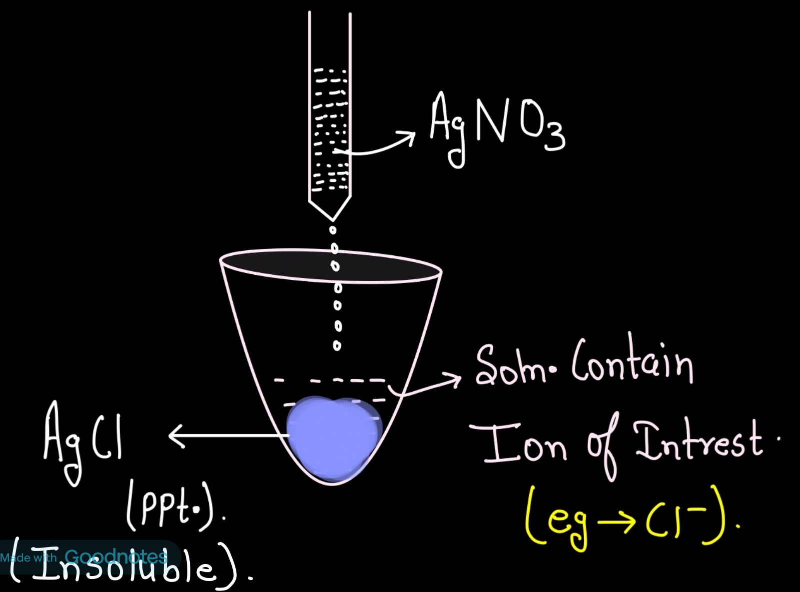
Calculation: The volume of titrant used to reach the endpoint is measured. By knowing the concentration of the titrant and the volume used, the amount of the substance in the sample can be calculated.

1. Mohr's method-

The Mohr method is a type of precipitation titration used to determine the concentration of chloride ions (Cl^-) in a solution.

It relies on the reaction of chloride ions with silver nitrate ($AgNO_3$) to form an insoluble precipitate of silver chloride ($AgCl$).

This method is named after the German chemist Karl Mohr, who developed it.

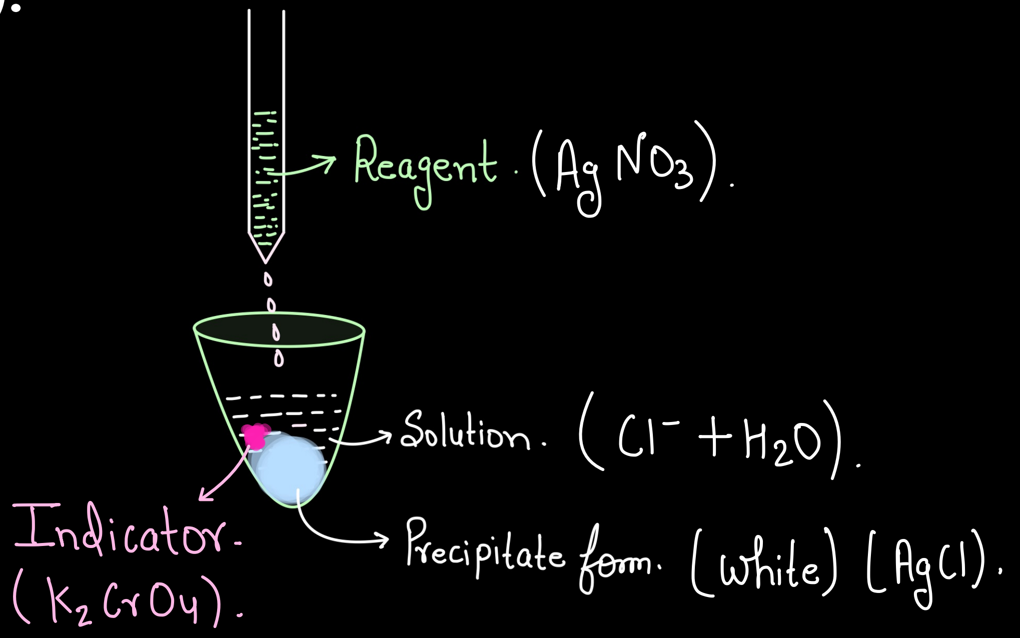


Steps Involved in the Mohr Method:

1.Preparation of the Sample: The sample containing chloride ions is dissolved in water, and a few drops of potassium chromate (K_2CrO_4) are added as an indicator. Potassium chromate forms a yellow color in the presence of chromate ions (CrO_4^{2-}).

2.Titration with Silver Nitrate: A solution of silver nitrate ($AgNO_3$) is gradually added to the sample. Silver ions (Ag^+) from the $AgNO_3$ react with chloride ions (Cl^-) in the solution to form a white precipitate of silver chloride (AgCl).

$$\left[Ag^+ + Cl^- \longrightarrow AgCl_{(s)} \right]$$



$$\left[K_2CrO_4 \xrightarrow{H_2O} 2K^+ \; CrO_4^{-2} \right]$$

3. End Point Detection: As more silver nitrate is added, the chloride ions are consumed, and eventually, the solution reaches a point where all the chloride has reacted. The endpoint is detected when a small excess of silver ions begins to react with the chromate ions (CrO_4^{2-}), forming a reddish-brown precipitate of silver chromate (Ag_2CrO_4). This signals the end of the titration.

$$\left[2Ag^+ + CrO_4^{-2} \longrightarrow Ag_2CrO_4\,(s). \right]$$

Reddish Brown
ppt. of Silver Chromate.

4. Calculation: The volume of silver nitrate solution required to reach the endpoint is recorded. Using the concentration of the silver nitrate solution and the volume used, the amount of chloride ions in the sample can be calculated.

Key Points:

Indicator: Potassium chromate (K_2CrO_4) is used as an indicator in the Mohr method.

End Point: The end point is marked by the appearance of a reddish-brown precipitate of silver chromate (Ag_2CrO_4).

Applications: The Mohr method is commonly used for determining the concentration of chloride ions in solutions, such as water or salts.

This method works best in neutral or slightly alkaline conditions because silver chloride is soluble in very acidic solutions.

The Mohr method is primarily used for the determination of chloride ions (Cl^-) in a sample. This precipitation titration method is widely applied in various fields due to its accuracy and simplicity. Here are some of the main applications:

1. Analysis of Chloride Content in Water

Drinking Water: The Mohr method is often used to measure the chloride concentration in drinking water, helping ensure that water quality standards are met.

Wastewater: It is used in environmental testing to measure chloride levels in wastewater and effluents, which is important for environmental monitoring and pollution control.

2. Food Industry

Food Products: It is sometimes used to measure the chloride content in food products, especially in products like salt, to ensure they meet regulations or desired specifications.

5. Determining Chloride in Sea Water

The Mohr method is used for marine water analysis to monitor the concentration of chloride in seawater, which is important for understanding oceanic chemistry and environmental studies.

6. Soil Testing

The method can be applied to measure chloride levels in soil samples, which helps in assessing soil salinity and its effects on agriculture.

Advantages of the Mohr Method:

Cost-effective: It uses inexpensive chemicals and is relatively simple to perform.

Accurate: When carried out correctly, it provides accurate results for chloride determination.

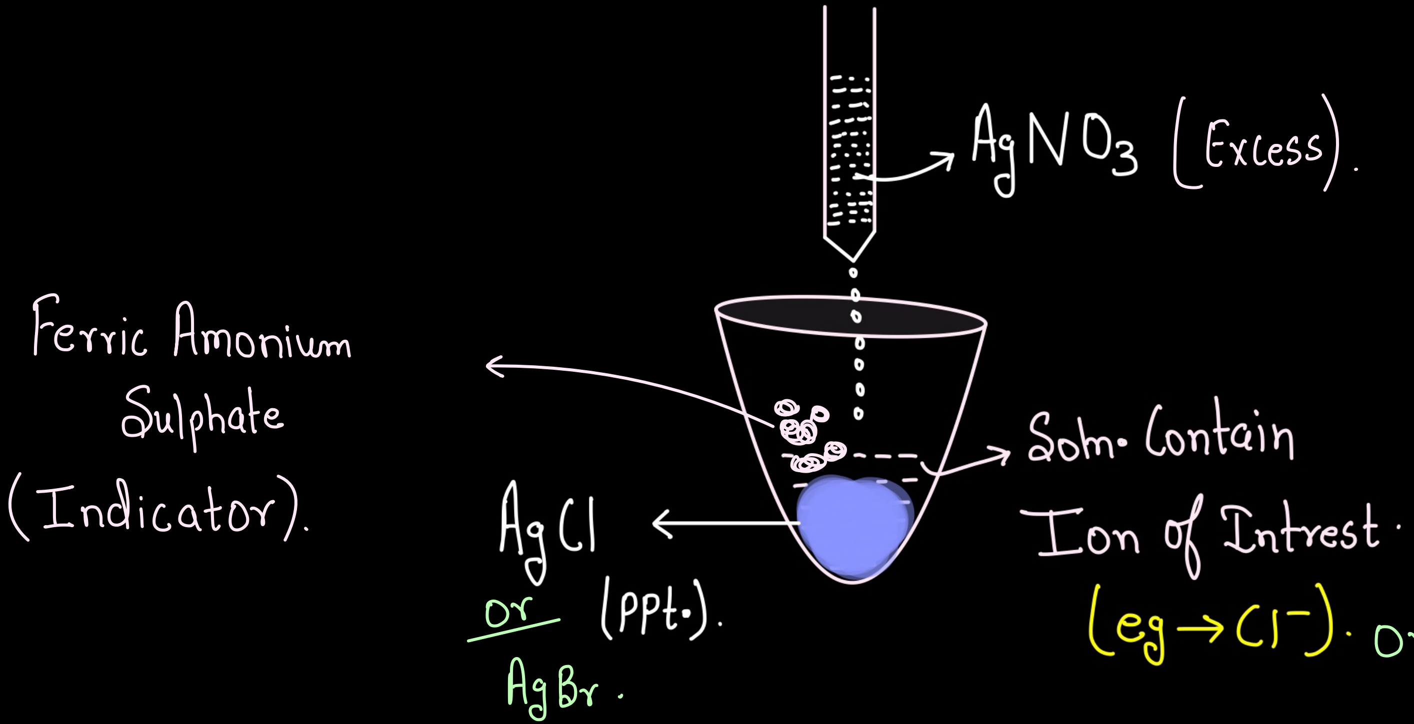
No Need for Special Equipment: It does not require complex instruments like spectrophotometers, making it practical for many laboratory setups.

Because Here Back Titration Occur. ← (Indirect Method)

Volhard's, & Modified Volhard's method (Occurs in Acidic Condition).

Volhard's method is a classic analytical technique used to determine the halide content (such as chloride or bromide) in a sample through a process known as argentometric titration.

This method involves titrating a halide sample with a standard solution of silver nitrate ($AgNO_3$) in the presence of an excess of ammonium thiocyanate (NH_4SCN) and using ferric ammonium sulfate as an indicator.



$$AgNO_3 + X^- \rightarrow AgX\downarrow + NO_3^-$$

Key Steps in Volhard's Method:

Preparation of Sample: The halide solution (such as chloride or bromide) is prepared for titration.

Titration with Silver Nitrate: The sample is first titrated with a known concentration of silver nitrate solution. This forms an insoluble silver halide precipitate (e.g., $AgCl$ or $AgBr$).

Excess Silver Nitrate: After the halide ions in the sample have reacted with the silver nitrate, some excess silver nitrate remains in the solution.

Addition of Ammonium Thiocyanate: Ammonium thiocyanate is added, which reacts with the excess silver ions to form a soluble complex.

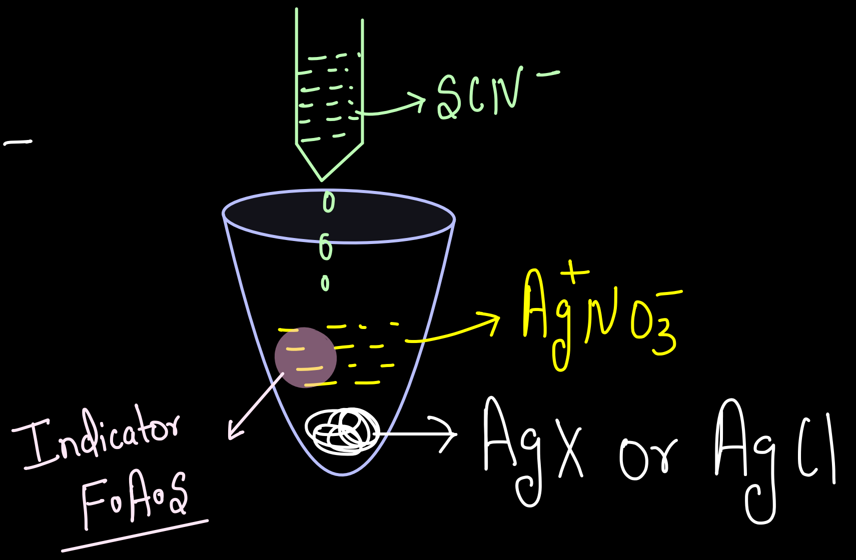
Indicator: Ferric ammonium sulfate ($Fe(NH_4)_2(SO_4)_2$ is added as an indicator. It gives a reddish-brown color when it binds with the excess thiocyanate ions.

Titration: The excess silver ion is then titrated with the thiocyanate solution until the endpoint is reached, indicated by the color change of the ferric ion.

Calculation: The amount of thiocyanate used to react with the excess silver nitrate can be used to calculate the concentration of halides in the original sample.

A Condition where all $AgNO_3$ Convert into $AgSCN$ then SCN^- (Titrant) react with Indicator.

$$Ag^+NO_3^- + SCN^- \longrightarrow AgSCN + NO_3^-$$



$$SCN^- + Fe^{+3} \longrightarrow [Fe(SCN)]^{+2}$$

Reddish Brown Colour.

Made with Goodnotes

Volhard's method is primarily used to determine the concentration of halide ions (such as chloride, bromide, and iodide) in a solution. Here are some key applications of Volhard's method:

1. Determination of Chloride in Water

Volhard's method is commonly used for determining the chloride content in water samples, such as drinking water, industrial water, or seawater. Since chloride ions are abundant in water, this method allows for precise quantification, especially in complex matrices where other methods like direct titration with silver nitrate might face interference.

2. Analysis of Chlorides in Industrial Samples

Volhard's method is applied in industries where chloride content is critical, such as in the chemical industry, food processing (for salt content), and in the production of pharmaceuticals. In such contexts, it's important to control and measure chloride levels for quality assurance and regulatory compliance.

5. Pharmaceutical and Clinical Applications

In the pharmaceutical industry, Volhard's method can be used to measure chloride content in raw materials or finished drug products. Similarly, it can be applied in clinical laboratories to measure chloride levels in bodily fluids, such as blood or urine, for diagnostic purposes.

6. Determining Bromide and Iodide Levels

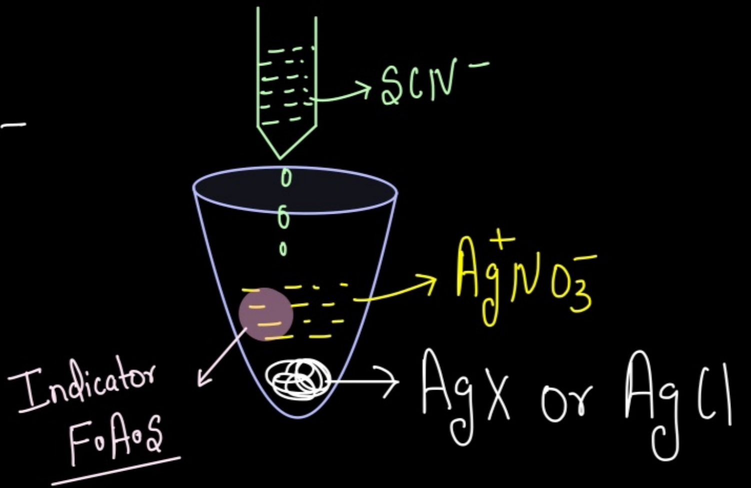
Though it is most commonly used for chloride, Volhard's method can also be adapted to measure bromide and iodide levels in various samples. For example, it is used to determine the bromide content in certain pharmaceuticals or iodide in certain dietary supplements.

Modified Volhard's method

The modified Volhard's method is an adapted version of the traditional Volhard's method for the determination of halide ions (typically chloride, bromide, or iodide) in a sample. The modifications are made to improve the method's sensitivity, speed, accuracy, and ability to handle complex or challenging sample matrices.

A Condition where all $AgNO_3$ Convert into AgSCN then SCN^- (Titrant) react with Indicator.

$$SCN^- + Fe^{+3} \longrightarrow [Fe(SCN)]^{+2}$$



But may be Titrant reacts with AgCl (ppt.) & error Occur

$\Downarrow$

So, we go for Modified Vollhard Method.

Now this error can be overcome by following method-

1. Use Wetting agents like Nitrobenzene which will coat the AgCl ppt hence it is protected from SCN.

Here titration error is small for bromide and iodide (negligible).

Improved Detection Methods: Use of potentiometric, photometric, or instrumental techniques to detect the endpoint more accurately, reducing human error.

Increased Sensitivity: Enhanced sensitivity to detect halides at lower concentrations, often through more precise reagents or detection methods.

Faster Titration: Reductions in reagent consumption and fewer steps to speed up the process.

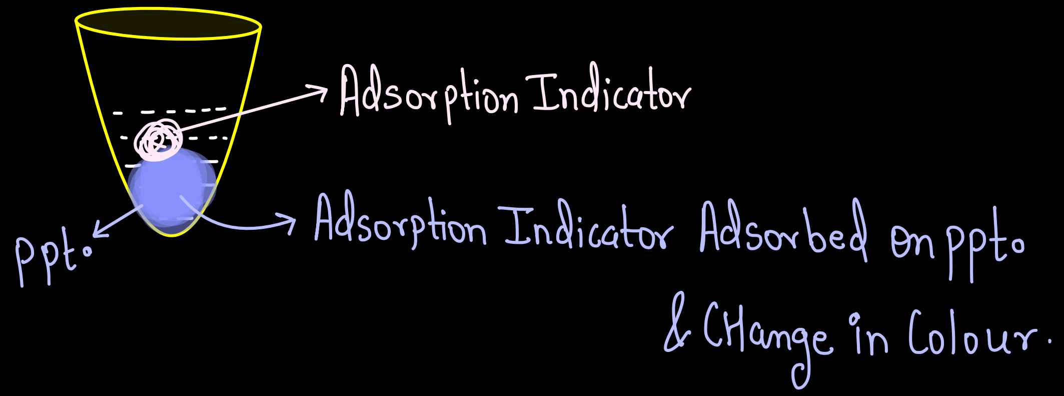
Handling Complex Samples: Modifications to handle samples that might contain interfering ions or are colored or turbid, where endpoint detection can be difficult.

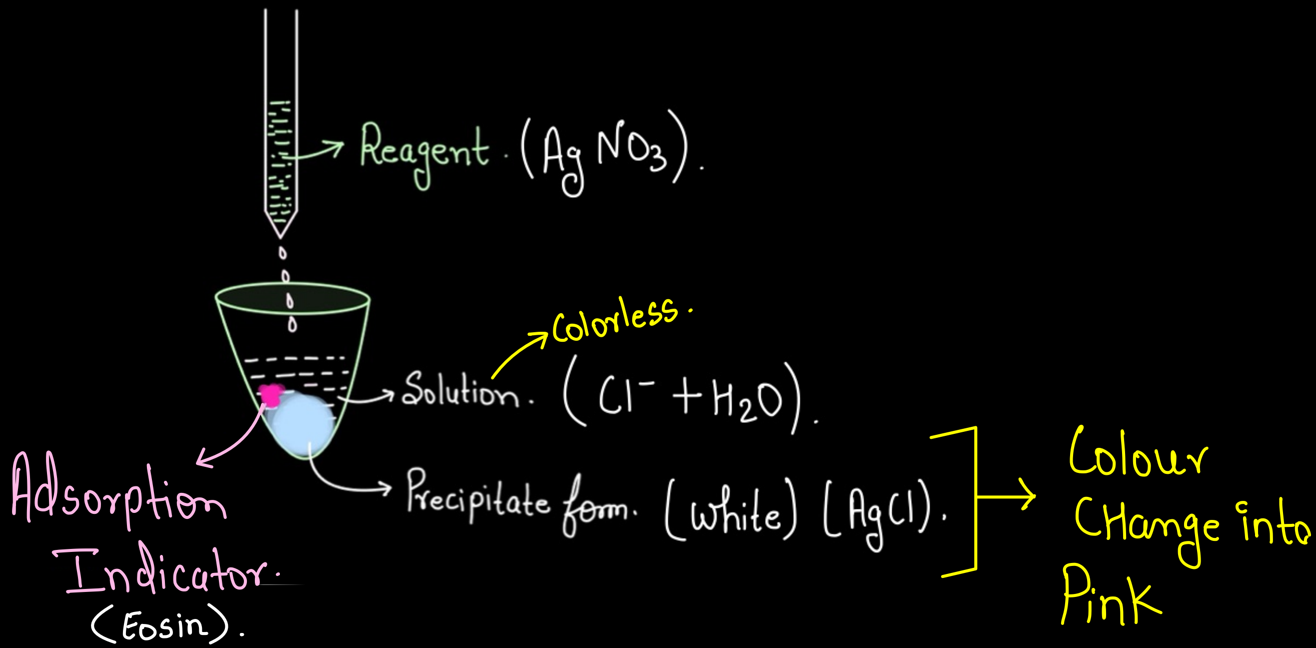
The modified Volhard's method is therefore a more versatile and efficient version of the original, tailored to provide more accurate results in various analytical scenarios.

Fajan's method → Here Adsorption Indicator is Used.

Fajans' method is a type of adsorption indicator method used for the determination of halide ions (such as chloride, bromide, or iodide) in a sample.

This method is a form of argentometric titration, where a solution of a halide is titrated with a standard solution of silver nitrate ($AgNO_3$). The endpoint is detected through the use of an indicator that adsorbs onto the precipitate of silver halide formed during the titration.





Key Features of Fajans' Method:

Titration Process:

Silver nitrate ($AgNO_3$) is added to a solution containing halide ions, and silver halide (e.g., AgCl, AgBr, or AgI) precipitates out.

Indicator:

or dichlorofluorescein.

A special adsorption indicator, such as eosin or fluorescein, is used. These indicators are typically anionic and are adsorbed onto the surface of the silver halide precipitate as it forms. When all halide ions have reacted, the indicator changes color due to its adsorption to the silver halide surface.

$$\underset{\text{(ppt.)}}{AgCl} + Fl^{\ominus} \longrightarrow (AgCl)(AgFl).$$

Coloured.

Endpoint Detection:

The endpoint is detected when there is a color change in the solution. For example, eosin changes from colorless to pink when it adsorbs to the surface of the precipitate after the halide ions are fully precipitated, indicating the end of the titration.

Role of pH:

The pH of the solution is important in Fajans' method. It is typically maintained in the acidic or neutral range to ensure the proper adsorption of the indicator and the formation of a stable silver halide precipitate.

Advantages of Fajans' Method:

No Need for Excess Reagents: Unlike other argentometric methods, Fajans' method does not require an excess of silver nitrate, making it more efficient.

Clear Endpoint: The color change in the solution makes the endpoint detection clear and straightforward.

Can Handle Low Concentrations: It is sensitive enough to detect low concentrations of halides.

Applications:

Fajans' method is commonly used in analytical chemistry for the determination of halide concentrations in various samples, such as water, food, and industrial products.

Estimation of NaCl

Sodium chloride (NaCl) can be estimated using silver nitrate, refractometers, or titration.

Silver nitrate

Weigh a known amount of the sample containing NaCl
Dissolve the sample in distilled water
Add a few drops of potassium chromate indicator
Titrate the sample with a standardized silver nitrate solution using a burette
Record the volume of silver nitrate solution used
Calculate the amount of NaCl in the sample using the formula: