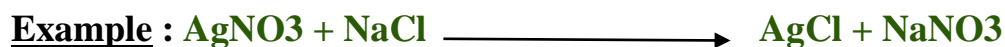


Precipitation Titration

A special type of titrimetric procedure involves the formation of precipitates during the course of titration. The titrant reacts 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 color change and announcing the termination of the titration.



Characteristics of Precipitation Titration

They are fast and the stoichiometry is known and reproducible, (no secondary reactions of interference.) They are complete or can be quantified depending on the amount of solubility product (in general a precipitation titration is considered complete when $K_{ps} < 10^{-8}$)

An indicator can be used to find the equivalence point or titration end point which, for this type of titration, corresponds to when precipitation of the analyte under analysis is complete

Principle of Precipitation Titration

The main principle of the precipitation titrations is that the quantity of the added precipitating reagent or precipitant is equivalent to the substance being precipitated.

Methods of Precipitation Titration

According to end point detection method, three main procedures are widely used depending on the type of application. These are:

- Mohr Method
- Volhard Method
- Fajans Method

Mohr Method :

Karl Friedrich Mohr (1806-1879)

This method utilizes chromate as an indicator. Chromate forms a precipitate with Ag^+ but this precipitate has a greater solubility than that of AgCl , for example.

Therefore, AgCl is formed first and after all Cl^- is consumed, the first drop of Ag^+ in excess will react with the chromate indicator giving a reddish precipitate.



In this method, neutral medium should be used since, in alkaline solutions, silver will react with the hydroxide ions forming AgOH . In acidic solutions, chromate will be converted to dichromate. Therefore, the pH of solution should be kept at about 7. There is always some error in this method because a dilute chromate solution is used due to the intense color of the indicator. This will require additional amount of Ag^+ for the Ag_2CrO_4 to form.

Volhard Method :

Jacob Volhard (1834-1910)

This is an indirect method for chloride determination where an excess amount of standard Ag^+ is added to the chloride solution containing Fe^{3+} as an indicator. The excess Ag^+ is then titrated with standard SCN^- solution until a red color is obtained which results from the reaction:



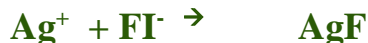
The indicator system is very sensitive and usually good results are obtained. The medium should be acidic to avoid the formation of $\text{Fe}(\text{OH})_3$

However, the use of acidic medium together with added SCN^- titrant increase the solubility of the precipitate leading to significant errors.

Fajans Method :

Kazimierz Fajans (1887-1975)

Fluorescein and its derivatives are adsorbed to the surface of colloidal AgCl . After all chloride is used, the first drop of Ag^+ will react with fluorescein (FI^-) forming a reddish color.



Among these methods, the Volhard Method is widely used because we can detect the end point of precipitation titration very well.

Limitations of Precipitation Titration

A few number of ions such as halide ions (Cl^- , Br^- , I^-) can be titrated by precipitation method.

Co-precipitation may be occurred.

It is very difficult to detect the end point.

How to overcome the problems of precipitation Titration?

In the assay of substances which react with nitrate but which can't be determined by direct titration with silver nitrate solution.

Excess standard silver nitrate solution is added together with concentrated nitric acid and the excess silver nitrate titrated with 0.1N ammonium thiocyanate solution. (This is called Volhard Method)

In the case of chlorides it is usually filtering off the AgCl or to coagulate the precipitate by means of nitrobenzene, which is non-toxic, because AgCl reacts slowly with ammonium thiocyanate.

This makes the end points rather that since involves the production of red iron (III). Thiocyanate complex with the thiocyanate

Indicator of Precipitation Titration

Potassium Chromate (K_2CrO_4)

Silver Chromate (Ag_2CrO_4)