# THEORY OF QUANTITATIVE ANALYSIS

It is used to **determine mass percent** i.e. to determine the mass of every element present. It can also be defined as a method used to determine the number of chemicals in a sample

They are of 2 types: a) volumetric analysis and b)gravimetric analysis

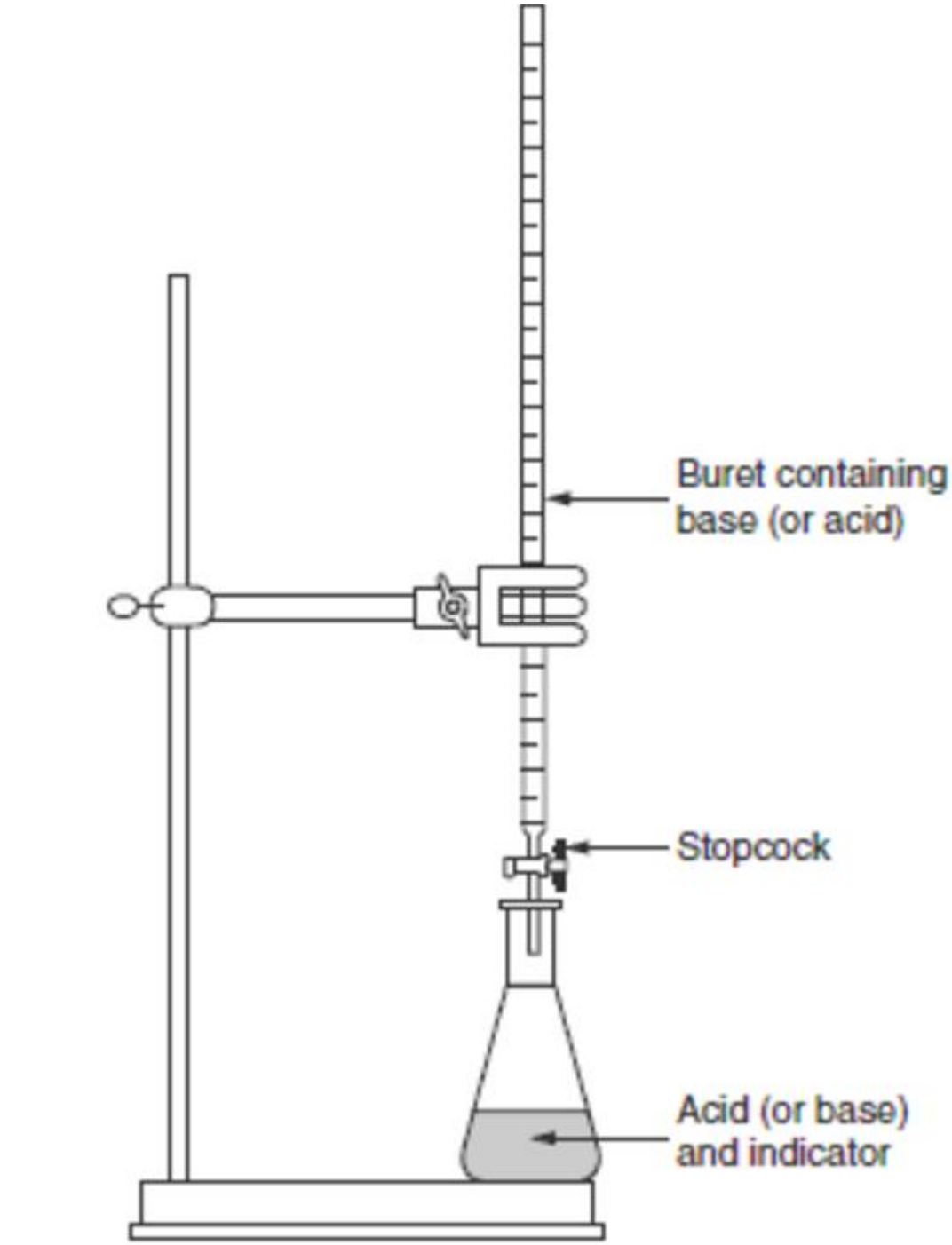
## ☛ VOLUMETRIC ANALYSIS:

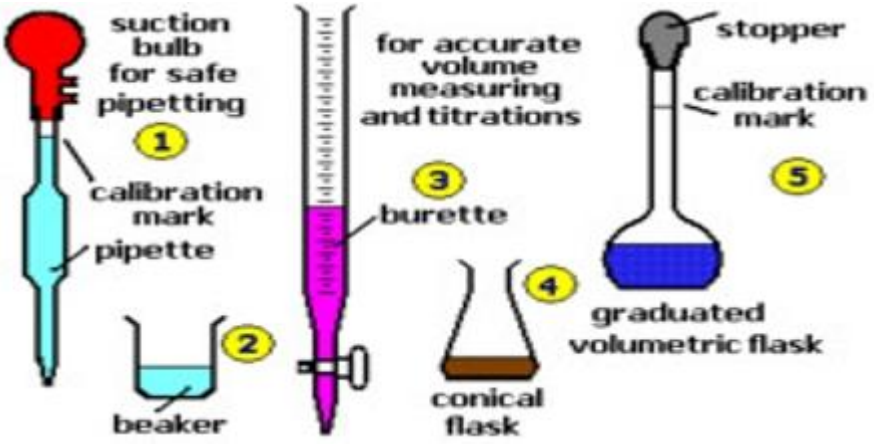
The analytical method wherein the concentration of a substance in a solution is estimated by adding exactly the same number of equivalents of another substance present in a solution of known concentration is called volumetric analysis

- **Titrant** or **Titrator** is a standard solution whose concentration and volume are known.
- **Titrand** is an analyte or sample whose concentration and volume are unknown. It is the solution to which a titrant reacts.
- **Titration volume** is the volume of titrant reacted with titrand.
- An **indicator** is an organic dye that determines the equivalence point by changing the colour of the solution.
- An **equivalence point** or **stoichiometric point** is when the amount of added titrant is equal to the amount of analyte being analyzed.
- The **endpoint** is when the colour changes in a system by indicating that the titration has been completed.

Acid-Base titration depends on the **neutralization reaction** between an acid and a base in a solution. In this, one of the solutions is acid, and the other is a base. It uses **acid-base indicators** that indicate the endpoint of titration by changing colour.

Principle**: The principle of acid-base titration is relatively simple. If you know the stoichiometry of a reaction and the quantity of one species, you can calculate the quantity of the other.**


Buret containing base (or acid)
Stopcock
Acid (or base) and indicator


suction bulb for safe pipetting
1
calibration mark
pipette
2
beaker
for accurate volume measuring and titrations
3
burette
4
conical flask
stopper
calibration mark
5
graduated volumetric flask

## ✓ The Theory of Acid–Base Indicators:

Ostwald, developed a theory of acid base indicators which gives an explanation for the colour change with change in pH. According to this theory, a hydrogen ion indicator is a weak organic acid or base. The undissociated molecule will have one colour and the ion formed by its dissociation will have a different colour.

Let the indicator be a weak organic acid of formulae HIn. It has dissociated into $H^+$ and $In^-$. The unionized molecule has one colour, say colour (1), while the ion, $In^-$ has a different colour, say colour (2). Since HIn and $In^-$ have different colours, the actual colour of the indicator will dependent upon the hydrogen ion concentration $[H^+]$. When the solution is acidic, that is the $H^+$ ions present in excess, the indicator will show predominantly colour (1). On other hand, when the solution is alkaline, that is, when $OH^-$ ions present in excess, the $H^+$ ions furnished by the indicator will be taken out to form undissociated water. Therefore there will be larger concentration of the ions, $In^-$. thus the indicator will show predominantly colour (2).

Some indicators can be used to determine pH because of their colour changes somewhere along the change in pH range. Some common indicators and their respective colour changes are given below.

| Indicator | Colour on Acidic Side | Range of Colour Change | Colour on Basic Side |
|---|---|---|---|
| **Methyl Violet** | Yellow | 0.0 - 1.6 | Violet |
| **Bromophenol Blue** | Yellow | 3.0 - 4.6 | Blue |
| **Methyl Orange** | Red | 3.1 - 4.4 | Yellow |
| **Methyl Red** | Red | 4.4 - 6.2 | Yellow |
| **Litmus** | Red | 5.0 - 8.0 | Blue |
| **Bromothymol Blue** | Yellow | 6.0 - 7.6 | Blue |
| **Phenolphthalein** | Colourless | 8.3 - 10.0 | Pink |
| **Alizarin Yellow** | Yellow | 10.1 - 12.0 | Red |

i.e., at pH value below 5, litmus is red; above 8 it is blue. Between these values, it is a mixture of two colours.

## Indicators Used for Various Titrations:

## 1. Strong Acid against a Strong Base:

Let us consider the titration of HCl and NaOH. The pH values of different stages of titration shows that, at first the pH changes very slowly and rise to only about 4. Further addition of such a small amount as 0.01 mL of the alkali raises the pH value by about 3 units to pH 7. Now the acid is completely neutralized. Further of about 0.01 mL of 0.1 M NaOH will amount to adding hydrogen

ions and the pH value will jump to about 9. Thus, near the end point, there is a rapid increase of pH from about 4 to 9.

An indicator is suitable only if it undergoes a change of colour at the pH near the end point. Thus the indicators like ***methyl orange, methyl red and phenolphthalein*** can show the colour change in the ph range of 4t0 10. Thus, in strong acid- strong base titrations, any one of the above indicators can be used.

## 2. Weak Acid against Strong Base:

Let us consider the titration of acetic acid against NaOH. The titration shows the end point lies between pH 8 and 10. This is due to the hydrolysis of sodium acetate formed. Hence ***phenolphthalein*** is a suitable indicator as its pH range is 8-9.8. However, methyl orange is not suitable as its pH range is 3.1 to 4.5.

## 3. Strong Acid against Weak Base:

Let us consider the titration ammonium hydroxide against HCl. Due to the hydrolysis of the salt, $NH_4Cl$, formed during the reaction, the pH lies in the acid range. Thus, the pH at end point lies in the range of 6 to 4. Thus ***methyl orange*** is a suitable indicator while phenolphthalein is not suitable.

| StrongAcids | StrongBases | WeakAcids | WeakBases |
|---|---|---|---|
| HCl | NaOH | Acetic acid | Ammonia |
| $HNO_3$ | KOH | Hydrocyanic acid | Magnesium hydroxide |
| HBr | etc | HF | Pyridine |
| $H_2SO_4$ | | Oxalic acid | Sodium carbonate |
| HI | | Ethanoic acid | Potassium carbonate |
| $HClO_4$ | | etc | etc |
| | | | |

# Redox titration:

A reaction in which one or more electrons are lost is known as *oxidation* and a reaction in which one or more electrons are gained is known as *reduction*. Accordingly, a substance which can accept one or more electrons is known as *oxidizing agent* and a substance which can donate one or more electrons is called reducing agent. Titrations of this type are called *redox titrations*. Thus, redox titrations are those involving transfer of electrons from the reducing agent to the oxidizing agent.

Potassium permanganate, potassium dichromate, ceric sulphate, etc., are the common oxidizing agents used in redox titrations. Oxalic acid, Mohr's salt and arsenious oxide are reducing agents commonly used in redox titrations.

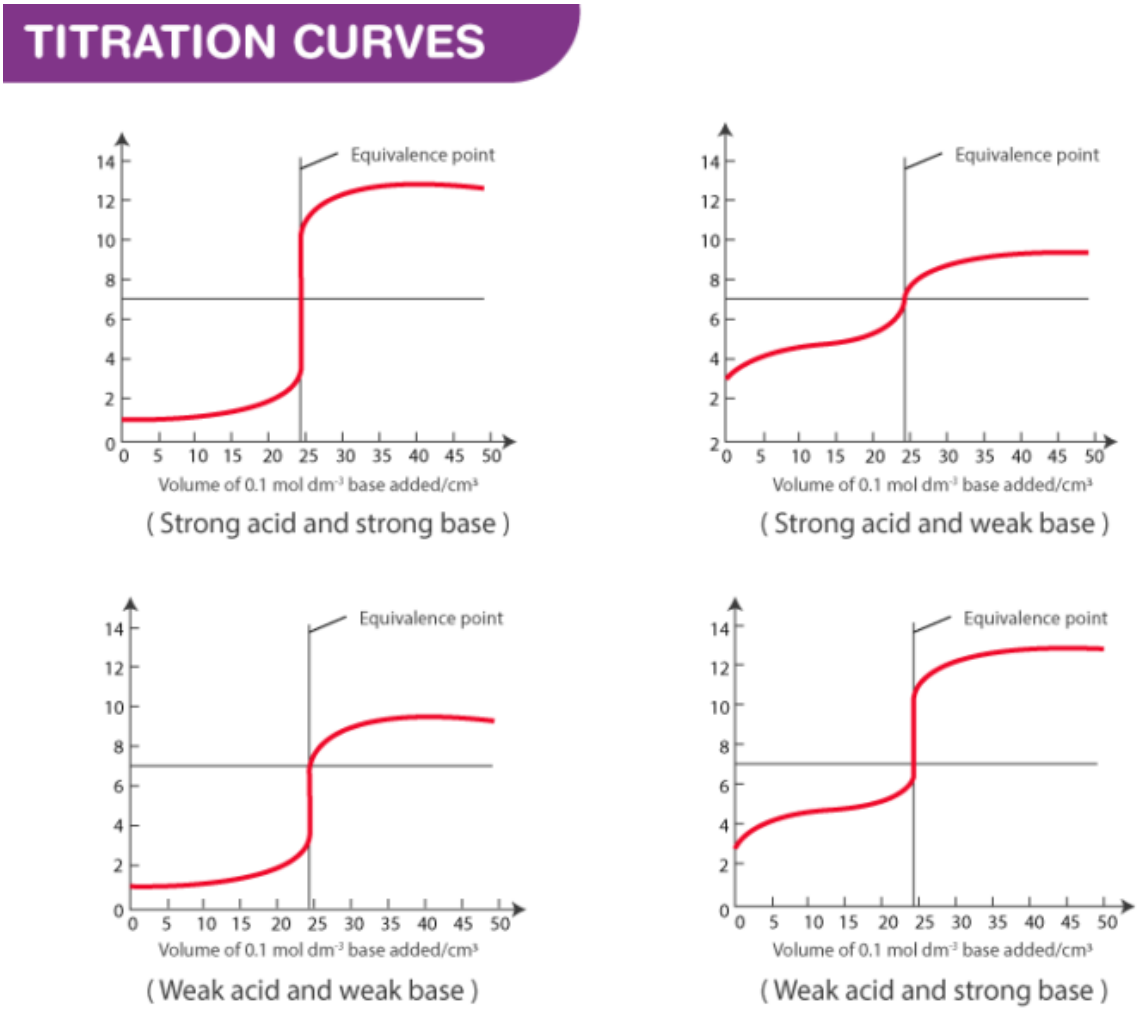
**Iodometry and Iodimetry:**

Iodine is a mild oxidizing agent. In the presence of a suitable reducing agent, it is reduced to iodine ion, $I^-$. In addition to this, all oxidizing agents having electrode potential greater than 0.54 V can oxidize $I^-$ to $I_2$. When iodine solution is directly used for the estimation of reducing agents, the titration is called *iodimetric titration (iodimetry)*. The titrations involving the iodine liberated in a chemical reaction are called *iodometric titration (iodometry)*.

## Titration Curve & Equivalence Point

In a titration, the equivalence point is the point at which exactly the same number of moles of hydroxide ions have been added as there are moles of hydrogen ions. In a titration, if the base is added from the burette and the acid has been accurately measured into a flask. The shape of each titration curve is typical for the type of acid-base titration.

.




## What is Redox Titration?

Redox Titration is a laboratory method of determining the concentration of a given analyte by causing a redox reaction between the titrant and the analyte. These types of titrations sometimes require the use of a potentiometer or a redox indicator.

Redox titration is based on an oxidation-reduction reaction between the titrant and the analyte. It is one of the most common laboratory methods to identify the concentration of unknown analytes.

In order to evaluate redox titrations, the shape of the corresponding titration curve must be obtained. In these types of titration, it proves convenient to monitor the reaction potential instead of monitoring the concentration of a reacting species.

As discussed earlier, redox reactions involve both oxidation and reduction. The key features of reduction and oxidation are discussed below.

## Reduction

A substance can undergo reduction can occur via:

- The addition of hydrogen.
- The removal of oxygen.
- The acceptance of electrons.
- A reduction in the overall oxidation state.

## Oxidation

The following points describe a substance that has undergone oxidation.

- The addition of oxygen.
- Removal of hydrogen which was attached to the species.
- The donation/loss of electrons.
- An increase in the oxidation state exhibited by the substance.

Thus, it can be understood that redox titrations involve a transfer of electrons between the given analyte and the titrant. An example of redox titration is the treatment of an iodine solution with a reducing agent. The endpoint of this titration is detected with the help of a starch indicator.

In the example described above, the diatomic iodine is reduced to iodide ions ($I^-$), and the iodine solution loses its blue colour. This titration is commonly referred to as iodometric titration.

# Redox Titration Example

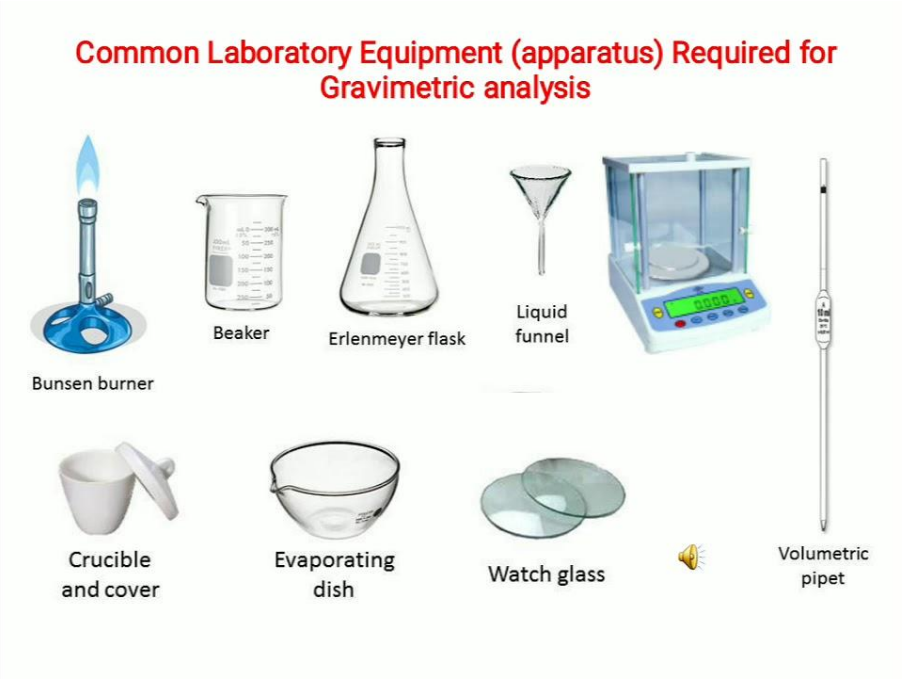
An example of redox titration is the titration of potassium permanganate ($KMnO_4$) against oxalic acid ($C_2H_2O_4$). The procedure and details of this titration are discussed below.

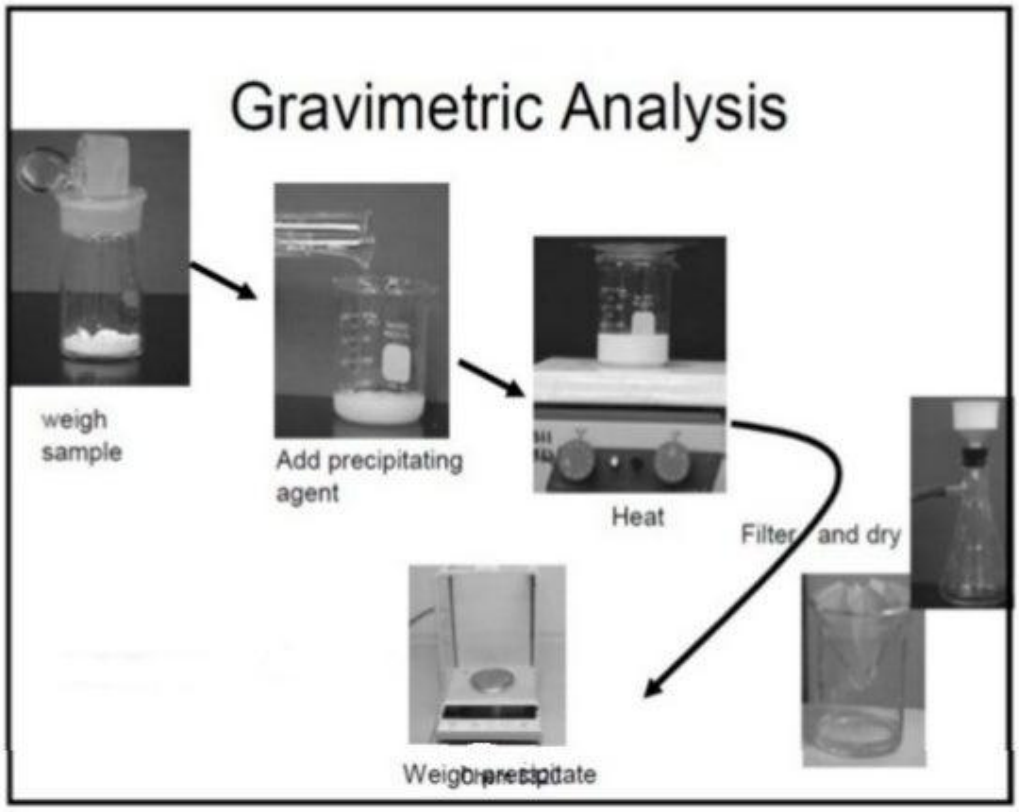
## Titration of Potassium Permanganate against Oxalic Acid

Gravimetric analysis is a method of a quantitative assessment of laboratory techniques based mostly on the dimension of an analyte's mass. One example of a gravimetric evaluation technique may be used to decide the quantity of an ion in an answer by way of dissolving a regarded quantity of a compound containing the ion in a solvent to break up the ion from its compound. The ion is then induced or evaporated out of the answer and weighed. This form of gravimetric evaluation is referred to as precipitation gravimetry. In this technique, compounds in an aggregate are separated by way of heating them to chemically decompose the specimen. unstable compounds are vaporized and misplaced (or gathered), leading to a measurable reduction within the mass of the solid or liquid pattern

## Principle of Gravimetric analysis

The analysis is based on the estimation of the mass percent of an ion in an impure compound of an acknowledged amount via a manner of determining the mass of the equal ion in a natural compound. For you to decide the mass, the ion of the hobby wishes to be absolutely isolated. This isolation of ions is completed with the assistance of precipitation.






**Transferring a filter paper and precipitate from a funnel to a crucible and its subsequent ignition.**

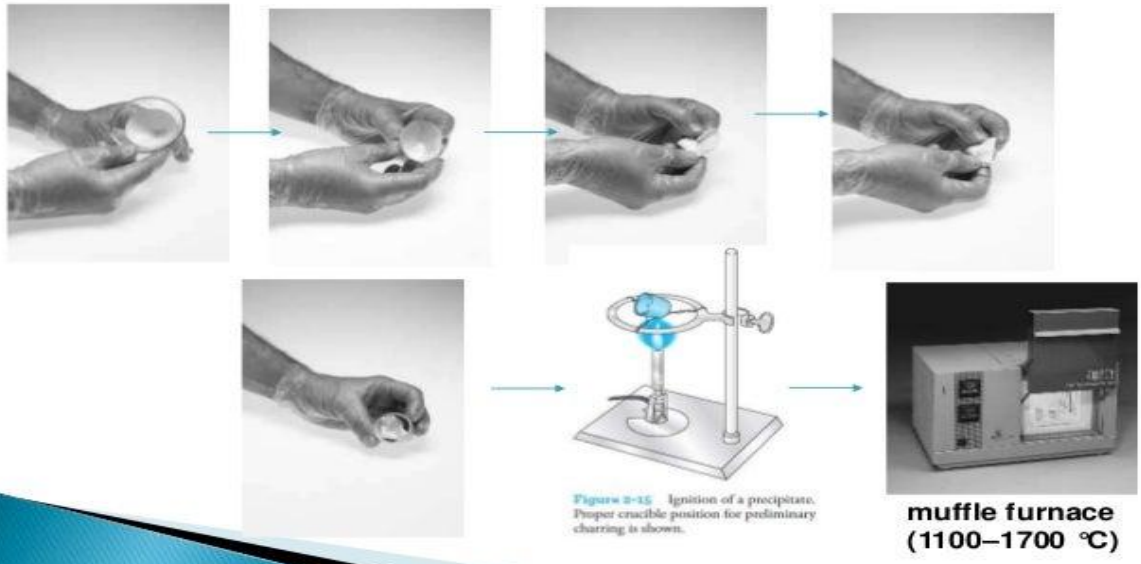



Figure 2-15 Ignition of a precipitate. Proper crucible position for preliminary charring is shown.

## Steps of gravimetric analysis:

## 1.weighing the sample

**2. Preparation of solution**

**3.Precipitation**

**4.digestion**

**5.filteration**

**6.washing**

**7.drying**

**8.incineration**

**9.weighing of the product**

# The Gravimetric Estimation of Nickel:

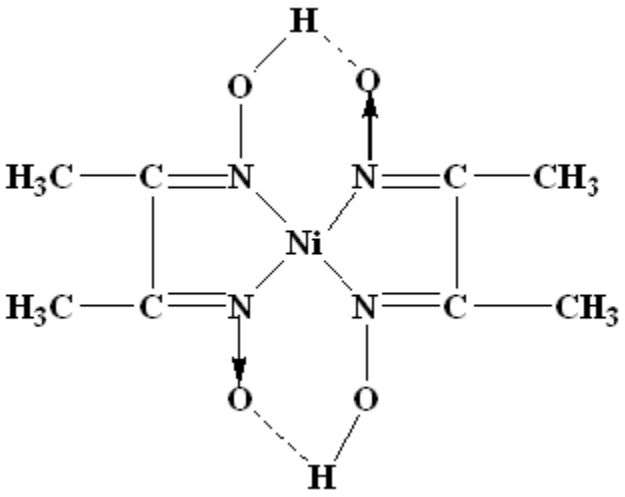
The nickel is precipitated as nickel dimethyl glyoxime by adding alcoholic solution of dimethyl glyoxime $C_4H_6(NOH)_2$ and then adding a slight excess of aqueous ammonia solution.

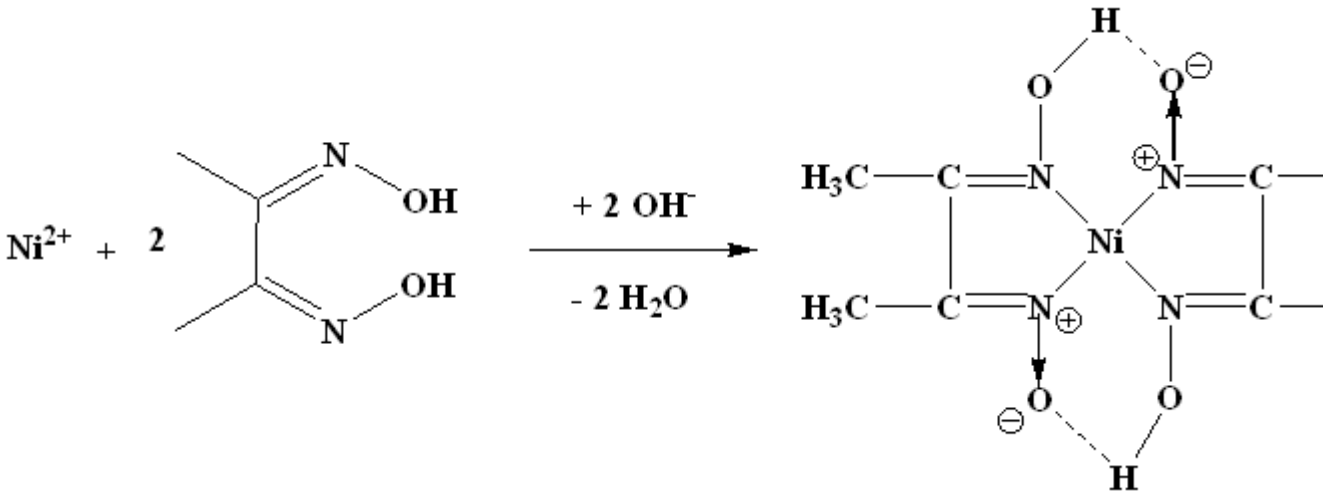
When the pH is buffered in the range of 5 to 9, the formation of the red chelate occurs quantitatively in a solution. The chelation reaction occurs due to donation of the electron pairs on the four nitrogen atoms, not by electrons on the oxygen atoms. The reaction is performed in a solution buffered by either an ammonia or citrate buffer to prevent the pH of the solution from falling below 5. If the pH does become too low the equilibrium of the above reaction favors the formation of the nickel (II) ion, causing the dissolution of Ni $(DMG)_2$ back into the mother liquor.

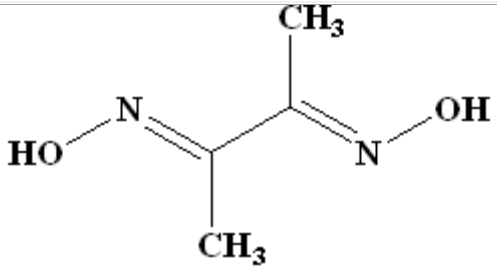
A slight excess of the reagent has no action on the precipitate, but a large excess should be avoided because of the possible precipitation of the reagent itself. The precipitate is soluble in the free mineral acids. It is therefore crucial to avoid the addition of too large and excess of the reagent because it may crystallize out with the chelate. It is also important to know that the complex itself is slightly soluble to some extent in alcoholic solutions. By adding small amount of chelating agents will minimize the errors from these sources. The amount of the reagent added is also governed by the presence of other metals such as cobalt, which form soluble complexes with the reagent. If a high quantity of these ions is present, a greater amount of DMG must be added. The nickel dimethylglyoximate is a very bulky precipitate. Therefore, the sample weight used in the analysis must be carefully controlled to allow more convenient handling of the precipitate during the transfer to the filtering crucible. The compactness of the precipitate is improved by adjusting the pH to 3 or 4, followed by the addition of ammonia solution.

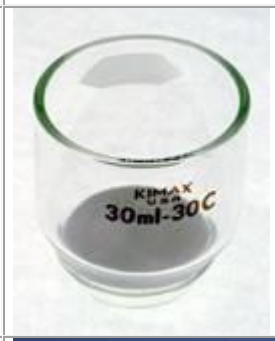
A slow increase in the concentration of ammonia in the solution causes a slight increase in the pH gradually and results in the precipitation of the complex. The result is the formation of a denser precipitate. Once the filtrate has been collected and dried, the nickel content of the solution is calculated stoichiometrically from the weight of the precipitate.

*The structure of DMG & the complex with nickel ions is given below;*






| | |
|---|---|
| DMG |  |

| | |
|---|---|
| Nickel solution |  |
| Ni-DMG Complex |   |
| Crucible |  |
| Desiccator |  |
| | |