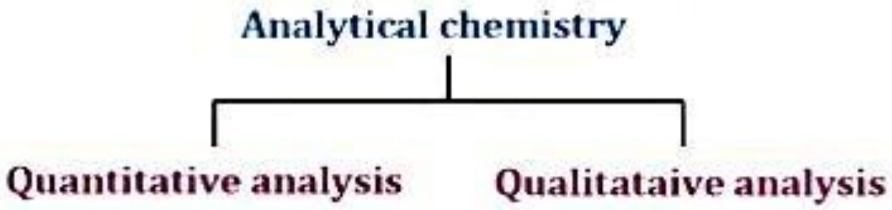
❑ INTRODUCTION TO ANALYTICAL CHEMISTRY

- It is the branch of chemistry which deals with the analysis of substance.
- Analytical chemistry involves the separation, identification, and the quantification of matter.
- It is mainly divided in two parts



❖ Qualitative Analysis

- It is primary concerned with the identification of the constituents present in a chemical substance or a mixture of substance.

❖ Quantitative Analysis

- It is primary concerned with the exact determination of the quantity of constituents present in the chemical substance or a mixture of substance.

❑ FUNDAMENTALS OF VOLUMETRIC ANALYSIS

❖Introduction

- The volumetric analysis is an analytical method of estimating the concentration of a substance in a solution by adding exactly same number of equivalents of another substance present in a solution of known concentration.
- Volumetric analysis deals with quantitative chemical analysis and it is also called as titrimetric analysis, since it involves the process titration.

❖ Important Term's in Volumetric Analysis

- **Titration** - The gradual addition of a solution of accurately known concentration to another solution of unknown concentration until the chemical reaction between the two solutions is complete.

- **Titrate** - The substance to be analyzed is called titrate.
- **Titrant** - The reagent of known concentration which is added to the solution of the substance to be analyzed is called titrant.
- **Equivalence Point** - The point at which just adequate reagent is added to react completely with a substance.
- **Indicator** - A species added to the analyte to give an observable change at (which is the endpoint) or near the end point.
- **End point** - The endpoint is the point where the colour change occurs in a system. It depicts the completion of titration.
- **Primary standard** - Those substances which can easily be obtained in highly pure and crystalline form and used in preparation of standard solution.
- **Secondary standard** - These are substance used for the standardization and whose concentration has been determined by comparison with primary standard.
- **Molarity** - Molarity is defined as the moles of a solute per liters of a solution. It is represented by "M".
- **Normality** - The number of gram or mole of equivalents of solute present in one liter of a solution. It is represented by "N".
- **Molality** - The molality of the solution is defined as the number of moles solute dissolved in 1KG of solvent. It is represented by "m"

❑ BASIC PRINCIPLES OF VOLUMETRIC ANALYSIS

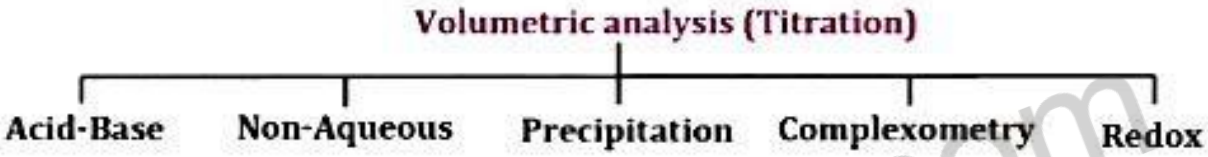
- Volumetric analysis is a quantitative approach used to **determine the concentration of the analyte.**
- An **unknown number of chemical substances** that need to be examined must be present in the solution.
- **Reagents with unknown concentrations** should react with the chemical substance of a **known amount in the presence of an indicator** (phenolphthalein) to show the endpoint.
- The reaction **between the reagent and the solution undergoes titration.**
- The overall amount of reagent is shown by the **volume and concentration of the reagent used in the titration.**
- The **amount of reagent and solution** is indicated by the volume and concentration of the reagent used in the titration.
- The **mole fraction of the equation** tells us how much of the unknown chemical is in the particular volume of solution.

- **Once the reaction reaches its endpoint**, the amount of reactant used is measured and used to calculate the analyte's volumetric analysis using the following formula:

$$C_a = C_t V_t M/V_a$$

Where, Ca is the concentration of the analyte,
C_t is the concentration of titrant,
V_t is the volume of the titrant,
M is the mole ratio of the analyte and the reactant,
V_a is the volume of the analyte.

❑ CLASSIFICATION OF VOLUMETRIC (TITRIMETRIC) ANALYSIS



❑ ACID-BASE TITRATION

❖ Introduction

- An acid base titration is a quantitative analysis method for estimating the **concentration of an acid or base** by precisely neutralizing it with a known **concentration standard solution of base or acid.**
- The titration of acids and bases is also known as neutralization titration.

❖ An acid-base titration can be used to determine the following.

- The **strength of an acid or base**
- The **strength or weakness of an unknown acid or base.**
- The **pKa of an unknown acid or the pKb of an unknown base**, where pKa and pKb are numbers that describe the acidity and basicity respectively of a particular molecule.

$$\text{Acid} + \text{Base} \rightleftharpoons \text{Salt} + \text{Water}$$

$$HCl + NaOH \rightleftharpoons NaCl + H_2O$$

$$CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$$

❖ ACID BASE THEORY

➢ Arrhenius Theory

- It is also known as Arrhenius theory of dissociation.
- Acid is defined as a substance which when **dissolved in water donate hydrogen (proton) ions.**
- Base is defined as a substance which when **dissolved in water donate hydroxyl (hydroxide) ions.**

$$HCl_{(aq)} \rightleftharpoons H^+ + Cl^-$$

$$NaOH_{(aq)} \rightleftharpoons Na^+ + OH^-$$

➢ Bronsted-Lowry Theory

- This theory states that an acid is any substance that **can donate a proton**, and a base is any substance **that can accept a proton**.

$$HF \rightleftharpoons H^+ + F^-$$

$$OH^- + H^+ \rightleftharpoons H_2O$$

➢ Lewis Theory

- An acid is a substance **which accepts an electron pair.**
  Example: HCl
- A base is a substance **which donates an electron pair.**
  Example: NH_3

The following chart will simplify all three theories about acids & bases

COMPOUND	ARRHENIUS	BRONSTED-LOWRY	LEWIS
Acid	Hydrogen ion (H^+) donor	Proton(H^+) donor	Electron pair accepter
Base	Hydroxide(OH^-) donor	Proton(H^+) accepter	Electron pair donor

Table 2.1 - Theories about acids & bases

❖ TYPES OF ACID-BASE TITRATION

S.NO	TYPES	EXAMPLES
1.	Strong acid-strong base	Hydrochloric acid and Sodium hydroxide
2.	Weak acid-strong base	Ethanoic acid and Sodium hydroxide
3.	Strong acid-weak base	Hydrochloric acid and Ammonia
4.	Weak acid-weak base	Ethanoic and Ammonia

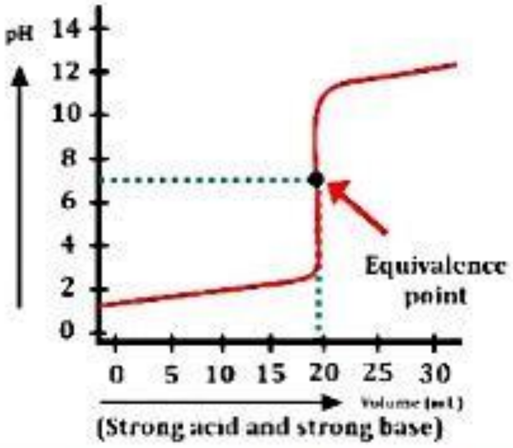
Table 2.2 – Types of acid – base titration

❖ ACID-BASE INDICATORS

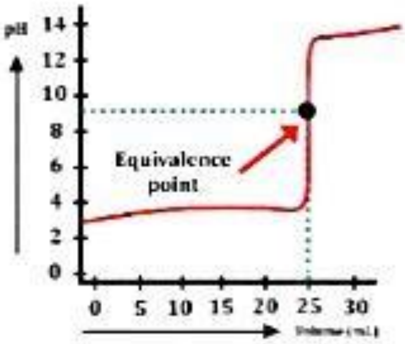
S. NO	INDICATOR	PH RANGE	ACIDIC MEDIUM	BASIC MEDIUM
1.	Thymol blue	1.2 to 2.8	Blue	Yellow
1.	Bromophenol Blue	3.0 to 4.6	Yellow	Blue
1.	Methyl orange	3.1 to 4.4	Red	Yellow
1.	Methyl red	4.4 to 6.2	Red	Yellow
1.	Naphtholphthalein	7.3 to 8.7	Yellow	Blue
1.	Phenolphthalein	8.3 to 10.0	Colorless	Pink

❖ TYPE OF ACID BASE TITRATION & OBTAINED CURVE

1. **Strong acid -strong base -** Phenolphthalein is usually preferred because of its more easily seen colour change.

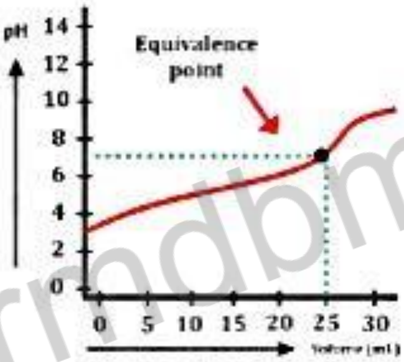


2. Weak acid -strong base - Phenolphthalein is used and changes sharply at the equivalence point and would be a good choice.



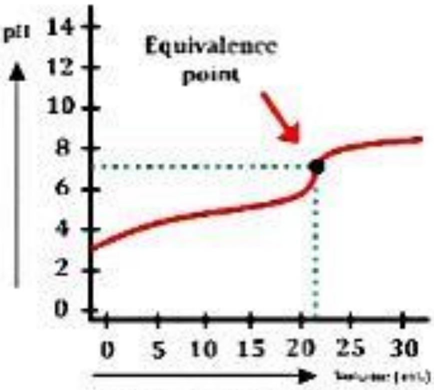
(Weak acid and strong base)

3. Strong acid -weak base - Methyl orange will change sharply at the equivalence point.



(Strong acid and Weak base)

4. Weak acid -weak base - No indicator is suitable because it requires a vertical portion of the curve over two pH units.



(Weak acid and Weak base)

NON – AQUEOUS TITRATION

- Titrations against **acids or bases are performed in a non-aqueous solvent** with **dissolved analytes or samples.**
- Due to the **absence of water molecules** in non-aqueous titrations, it **gives sharp endpoints and accurate results.**

TYPES OF NON – AQUEOUS SOLVENTS

1. Protogenic solvent

- Protogenic solvent are **acidic in nature** and they can **donate the proton.**
- These solvents are typically **more acidic than water.**
- Example – Sulfuric acid, Hydrogen fluoride

2. Protophilic solvent

- Protophilic solvents are those that **have higher basicity than water.**
- These solvents have a strong attraction to positively charged protons.
- Example – Pyridine, Ethylene diamine and Dimethylformamide

3. Amphoteric solvent

- Amphiprotic solvents are those **that have both protophilic and protogenic properties.**
- Amphiprotic solvents are **chemically similar to water molecules** in that they have both acidic and basic properties.
- Example – Acetic acid, Ethanol and methanol.

4. Aprotic solvent

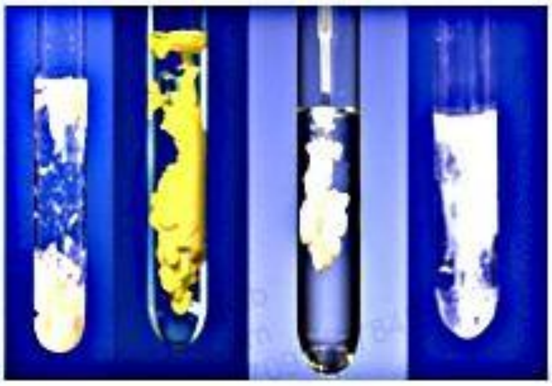
- Aprotic solvents are **chemically inert.**
- These solvents are **non-reactive and do not react with acids or bases.**
- Example – Benzene, Carbon tetrachloride, Toluene

❖ INDICATORS FOR NON-AQUEOUS TITRATION

S.NO	INDICATORS	DESCRIPTION
1.	**Crystal Violet**	It is used as a 0.5% (w/v) solution in Glacial acetic acid. It colour change is from violet through blue, followed by green, then to greenish – yellow.
2.	**Methyl red**	It is used as a 0.2% (w/v) solution in Dioxane with a yellow to red colour change.
3.	**α-Naphthol Benzein**	It is used as a 0.2% (w/v) solution in Acetic acid gives a yellow to green colour. It gives sharp end points in Nitromethane containing Acetic anhydride for titrations of weak bases against Per chloric acid.
4.	**Oracet Blue**	Used as a 0.5% (w/v) solution in Glacial acetic acid. Colour change from blue to purple.
5.	**Thymol Blue**	0.2% (w/v) in Methanol is used for titrations of substances acting as acids in Dimethylformamide solution. The end point change from yellow to blue.
6.	**Methyl Violet**	0.2% (w/v) in Chlorobenzene, violet is blue.

Table 2.4 – Indicators of non aqueous titration

❑ PRECIPITATION TITRATION

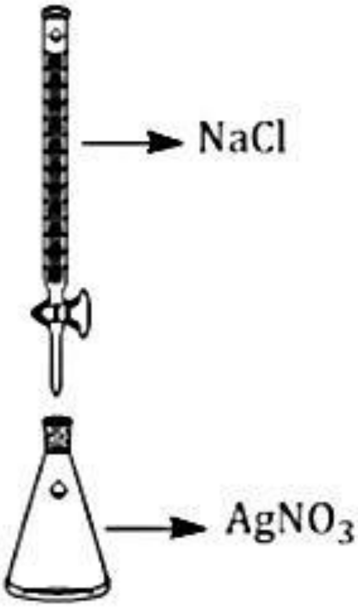


- Precipitation is the process of **conversion of a solution into solid** by converting the substance into insoluble form.
- Precipitation titrations are most common types involve the reactions of metallic halides with silver nitrate.
- Such precipitation titration also known as Argentometric processes.

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

❖TYPES OF PRECIPITATION TITRATION

➢ Mohr Method



- This method falls under the category of determining the end point by **formation of colored precipitate**, and is used for the determination of **chlorides and bromides in a neutral solution**
- Silver nitrate is used as titrant and it is a secondary standard solution, so $AgNO_3$ is standardized by primary standard solution of NaCl

$$AgNO_3 + NaCl \rightarrow AgCl\ (\text{Precipitate}) + NaNO_3$$

Potassium chromate is used as indicator and it forms reddish brown precipitate

$$2AgNO_3 + K_2CrO_4 \rightarrow Ag_2CrO_4 + 2KNO_3$$

➢ Volhards Method

- Volhard method is a titration method that involves the reaction of a compound containing **chromates, phosphates and halides** (chlorine, bromine and iodine) with **excess silver nitrate in a thiocyanate solution.**
- Iron is used as an indicator in these reactions.
- An oxidizing agent such as **silver nitrate is used to titrate** the acidic analyte i.e. the halide ion solution.
- **Titration is carried out with KSCN standard solution** using ferric ion as an indicator. Silver precipitates in the form of white silver thiocyanate.
- Then the **excess of titrant and the ferric ions react** and form a soluble red complex, which indicates completion of reaction i.e. and ferrous thiocyanate complex formed.

$$AgNO_3 + NH_4SCN \rightarrow AgSCN + NH_4NO_3$$
$$AgNO_3 + KSCN \rightarrow AgSCN + KNO_3 \downarrow$$

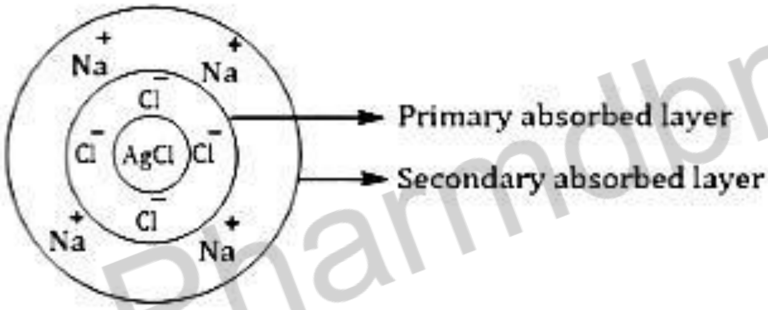
Volhard Method Applications

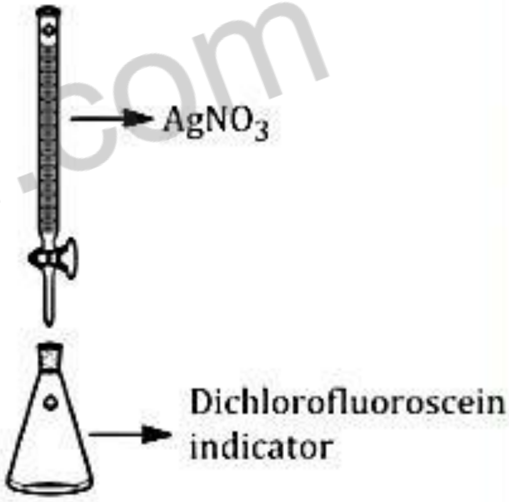
- It is used for the **determination of halides** (chloride, bromide and iodide).
- **Determination of anions** like phosphate, arsenate, chromate, sulphide, oxalate and carbonate.

Fajan's Method

- In this method **chloride ions present in excess** are adsorbed on **silver chloride surface.**
- These indicators are **basically dyes that adsorb or desorb on the surface** of the precipitate at the **equivalence point and produces the colour change.**
- These indicators **are acid dyes, e.g. fluorescein, eosin** etc. or **basic dyes, e.g. rhodamine series.**
- The best indicator known is fluorescein for the titration of chloride ions with silver.

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





COMPLEXOMETRIC TITRATION

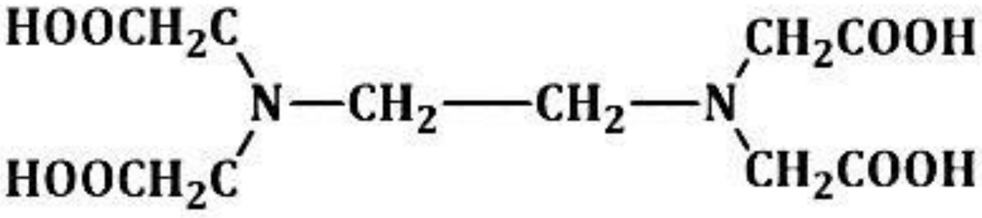
- Complexometric titration is a volumetric analysis where the endpoint of the analysis or titration is identified by the **formation of a coloured complex.**

IMPORTANT TERMINOLOGY

- **Ligand -** A ligand is an ion or molecule, which **donates a pair of electrons** to the central metal atom or ion to form a coordination complex. Example – H_2O, NH_3, Cl, Br.
- **Chelation -** It is **complex formed between the ligand containing two or more donor groups and metal to form ring structure.**
- **Chelating agent -** Organic molecules containing two or more donor groups which combine with metal to form complex having ring structure.

- **Masking agent** - Masking agents are used to prevent the interference of unwanted metal ions, masking agents are typically chelating agents that can form complexes with the interfering metal ions
- **Damasking agent** - Damasking agent is used to break the metal ion complexing agent stable complex.

❖ EDTA



- The complexometric indicator **ethylene diamine tetra acetic acid**, or EDTA, is made up of **two amino groups and four carboxyl groups known as Lewis bases.**
- Because it may signify six pairs of lone electrons through the creation of covalent bonds, **EDTA is a hexadentate ligand.**
- Small metal ions would cause a noticeable shift in color even in their absence.
- A weak complex is created as a result of this.
- The majority of complexing agents are free acids and are less soluble in water.

❖ INDICATORS

- Common indicators for determining metal cation titrations using EDTA are organic dyes such **Eriochrome Red B, Eriochrome Black T, and Fast Sulphone Black.**
- When the **endpoint is achieved**, a change in color indicates that the indicator has been **displaced from the metal cations** in solution, usually by EDTA.

❖ TYPES OF COMPLEXOMETRIC TITRATION

- **Direct titration** - It is the **simplest and the most convenient method** in which the **standard solution of EDTA** is slowly added to **the metal ion solution** till the **end point is achieved**. Example: Calcium gluconate injection is assayed for determining the calcium chloride.

- **Back titration** - In this method, an **excess of a standard solution of EDTA** is added **to the metal solution** being determined so as to complex formation with the metal is back titrated with a standard solution of a second metal ion. Example - Mn determination and ZnO determination.

- **Replacement titration** - The metal to be **analyzed is added to a metal EDTA complex.** The **analyte ion displaces EDTA from the metal** and the metal is subsequently titrated with standard EDTA
- **Indirect titration -** This method is also called Alkalimetric titrations The **anion is first precipitated with a metal cation and the precipitate** is washed and boiled with an excess of disodium EDTA solution to form the metal complex.

❖ APPLICATION OF COMPLEXOMETRIC TITRATION

- Used to determine concentration of metal ion in solution.
- Can be used to determine how much of calcium, magnesium or other minerals is in a food product.
- Used to determine the concentration of certain toxic metals.
- Water hardness can be determined by titrating it with EDTA.

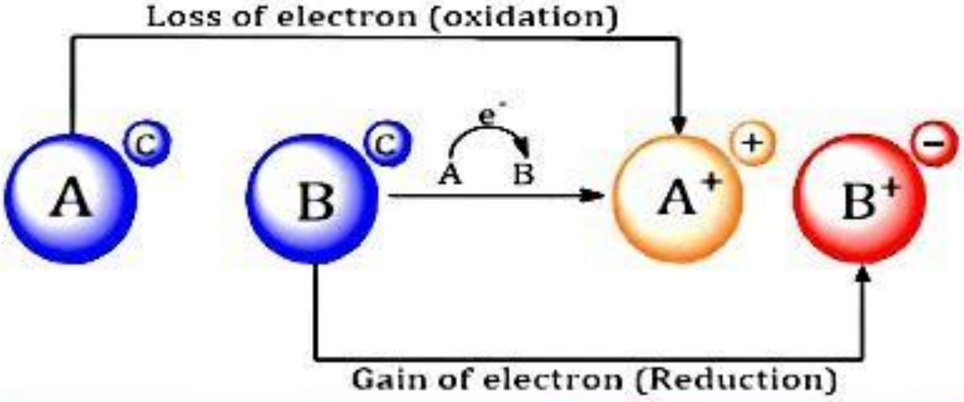
❑ REDOX TITRATION

- Redox titration is a type of titration based on a **redox chemical reaction between analyte and titrant.**
- Redox titration refers to a laboratory method to **determine the analyte concentration** by carrying out a redox reaction between the analyte and the titrant.
- The redox titration often needs a redox indicator or a potentiometer.

Reduction + Oxidation = Redox

❖ PRINCIPLE

- The **loss of electrons** and the corresponding **increase in the oxidation state** of a given reactant is called oxidation.
- The **gain of electrons** and the corresponding decrease in the **oxidation state of a reactant is called reduction.**



❖ OXIDIZING AGENT

- Oxidizing agents are defined as **substance containing an atom or ion, which accept an electron.**
- Example: $KMnO_4$, $K_4Cr_2O_7$, I_2, KIO_3

❖ REDUCING AGENT

- A reducing agents are defined as **substance containing an atom or ion, that loose electrons.**
- Example – $FeCl_2$, H_2S, NaH, LiH, $LiAlH_4$, CaH_2

❖ DETECTION OF END POINT IN REDOX TITRATION

S.NO	INDICATORS	EXAMPLES
1.	Self-indicator	• It is actually a chemical substance which can mark the end point of a titration or any other reaction along with self – participation in the reaction. • Example – I_2 and $KMnO_4$.
2.	External indicator	• External indicators are those which are added from outside that is they do not exist in the reaction. • Example – Phenobarbitone, Methyl orange.
3.	Internal indicator	• Internal Indicators are substances which have different colours in their Oxidized and Reduced form. The reaction is Reversible. Most of the internal indicators are dyes, the reduced forms of which are colourless. • Example- Methyl Blue, Starch.

Table 2.5 – End Point in redox titration

❖ TYPES OF REDOX TITRATION

- **Iodometry** - Iodometry is used to determine the concentration of oxidizing agents through an indirect process involving iodine as the intermediary.
- **Iodimetry** - When an analyte that is a reducing agent is directly titrated with a standard iodine solution, the method is called iodimetry.
- **Bromatometry** - The titration involves use of bromine in place of iodine as an oxidizing agnet in redox titration.
- **Cerimetry** - Titration involving cerci sulfate as an oxidizing agent are called as cerimetry titration.
- **Permanganometry** - The titration method involves the usage of potassium permagnet as oxidizing agent.

- **Dichrometry -** Titration with potassium dichromate in acidic solution.

APPLICATION

- Determination of concentration of an unknown solution that contains an oxidizing or reducing agent.
- It provides pharmacopeial methods for the assay unformulated drugs and excipients and some formulated drugs.
- Used for standardization of raw materials in drug synthesis.
- Oxidation-Reduction reactions also find their application in sanitizing water and bleaching materials.

GRAVIMETRIC ANALYSIS

- Gravimetric analysis is a group of analytical methods in which the **amount of analyte** is determined by the **measurement of the mass of a pure substance containing the analyte.**

STEPS INVOLVED IN GRAVIMETRIC ANALYSIS

Preparation of the solution

- Sample solution is prepared for the analysis; precipitation should be carried out in dilute solution.
- Adjustment of the volume, appropriate pH and getting the desired properties of the solution for the precipitate is taken care in this step.

Precipitation

- This step requires addition of the precipitating agent in the form of solution to the sample solution.
- After addition of the first drop of the precipitating agent, supersaturation occurs and nucleation starts to occur, where molecules of precipitate aggregate together and forms a nucleus.

Digestion

- Let precipitate stand in contact with the solution from precipitated usually at high temperature.
- The small particles tend to dissolve and precipitate on the surfaces of the larger crystals.
- This process is called as digestion.

Digestion

- Let precipitate stand in contact with the solution from precipitated usually at high temperature.
- The small particles tend to dissolve and precipitate on the surfaces of the larger crystals.
- This process is called as digestion.

Filtration and Washing

- It is crucial to wash the precipitate very well in order to remove all adsorbed species which will increase the weight of the precipitate.
- Dilute nitric acid, ammonium nitrate, or dilute acetic acid may be used for washing.
- Usually it is good practice to check for the presence of precipitating agent in the filtrate of the final washing solution.
- Filtration should be done in appropriate sized gooch filter or ignition filter paper.

Drying or Ignition

- To remove solvent and wash electrolytes it is heated at 110 to 120°c for 1 to 2hrs.

Weighing

- After the precipitate is allowed to cool it is weighted
- It is properly calibrated analytical balance instrument.
- Advanced and good weighing technique.

Calculation

- Weight of analyte is calculated from the weight of precipitate. Stoichiometric calculations method is used for gravimetric determination.
- The result of gravimetric determination usually is reported as a percentage of analyte.
- Two value are needed the weight of analyte and the weight of the sample.
- To calculate the weight of analyte from the weight of the precipitate a gravimetric factor (GF) is used.

$$\%A = \frac{\text{Grams of analyte}}{\begin{array}{l}\text{Grams of sample taken}\\ \text{for the analysis}\end{array}} \times 100$$

❖ Types of Gravimetric Analysis

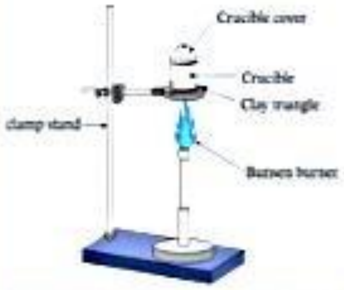
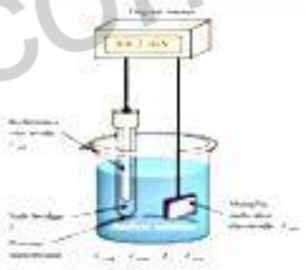
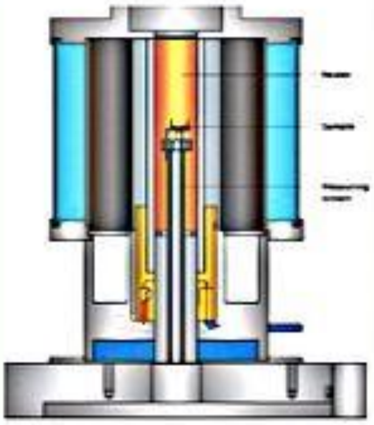
S.NO.	TYPES	DESCRIPTION	FIGURE
1.	**Volatilization Gravimetry**	Volatilization gravimetry includes isolating components of our mixture by means of heating or chemically decomposing the sample.	
2.	**Precipitation Gravimetry**	Precipitation gravimetry uses a precipitation reaction to split one or more parts of a solution by incorporating it right into a strong solution.	
3.	**Electro-Gravimetry**	Electrogravimetry is a method used to split and quantify ions of a substance, commonly a steel.	
4.	**Thermo-Gravimetry**	Thermogravimetric is a technique of thermal analysis in which changes in physical and chemical properties of substances are measured as a function of increasing temperature or as a characteristic of time.	

Table 2.6 – Types of gravimetric analysis

❖ APPLICATION

- Quantification of inorganic and organic compounds.
- Elemental analysis.
- Uses in modern analytical chemistry.
- High Sensitivity and accuracy of gravimetric method.