

## Topic – 1 General Principles of Chemical Analysis

**Syllabus:** General principles of chemical Analysis - Chemical analysis, its types, Advantages and Disadvantages of instrumental and non-instrumental methods, Different ways to express concentration of solution. Numerical problems. Standards and its types. Titrimetric analysis, Definition of terms associated with titrimetry. Classification of titrimetry, Gravimetry and its requirements, applications.

**Chemical analysis:** Chemical analysis is defined as '**The resolution of a substance, material or chemical compound into its proximate or ultimate parts**'. It includes either determination of its elements or presence of any impurities, contaminants, foreign substances present in it.

This definition outlines the scope of analytical chemistry. When a completely unknown sample is presented to an analytical chemist, the first thing is usually to check what substances/elements are present in it. This basic problem may be used to decide what impurities are present in sample under test, or knowing that certain impurities are absent. The solution of such problems comes under scope of qualitative analysis. On examining different constituents in sample the chemist is asked to determine how much of each component, or of specified components, is present. Such determinations come in scope of quantitative analysis, and to get the required information a variety of techniques/ methods are available.

### 1.1 Types of Chemical analysis :( Classification)

Chemical analysis is classified based on different ways i.e. type of information required from it, sample size, amount of constituent present in substance under test etc.

The type of information required may include very detailed data, results of a general character with respect to the information which is essential, different types of chemical analysis may be classified as follows:

**a) Purpose of analysis** – If sample received for analysis is only tested for different elements present in it then it is **Qualitative chemical analysis**, while if it is tested for knowing exact composition of specific or all components/elements then it is **Quantitative chemical analysis**.

#### b) Type of information required-

1. **Proximate analysis**- Here the amount of each element in a sample is determined with no concern as to the actual compounds.
2. **Partial analysis**- It deals with the determination of selected constituents in the sample;
3. **Trace constituent analysis**- Analysis which deals with the determination of specified components present in very minute quantity;
4. **Complete analysis**- Here proportion of each component of the sample is determined.

#### c) Based on sample size - Analytical methods are often classified as:

1. Macro- the analysis of quantities of 0.1 g or more;
2. Meso (semi micro)- dealing with quantities ranging from  $10^{-2}$  g to  $10^{-1}$  g;
3. Micro- for quantities in the range  $10^{-3}$  g to  $10^{-2}$  g;
4. Sub micro- for samples in the range  $10^{-4}$  g to  $10^{-3}$  g;
5. Ultra micro- for quantities below  $10^{-4}$  g.

#### d) Method used for analysis -Based on method used there are three types i) Titrimetric/Volumetric analysis ii) Gravimetric analysis iii) Instrumental chemical analysis.

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| <b>Questions-</b> 1 Define Chemical analysis, Qualitative analysis, Quantitative analysis, Macro, Meso, Micro, Sub micro and Ultra micro analysis, Proximate analysis, Ultimate analysis (1mark each)<br>2. Define term chemical analysis and give an account of its classification. (5 marks)<br>3 Discuss significance of Chemical analysis in modern era of industrialization. (3marks) |
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## **1.2 Applications /Significance of chemical analysis –**

Very accurate determination of substances presents in extremely minute quantities. The development of new products (which may be mixtures rather than pure materials, as for example a polymer composition, or a metallic alloy) also requires the services of the analytical chemist. It will be necessary to ascertain the composition of the mixture which shows the optimum characteristics for the purpose for which the material is being developed.

## **1.3 Titrimetric Analysis/ Volumetric analysis –**

The term 'titrimetric analysis' defined as quantitative chemical analysis involving determining the volume of a solution of accurately known concentration which reacts quantitatively with a measured volume of a solution of the substance to be determined.

The solution of accurately known strength is called the standard solution.

### **1.3.1 Terms associated with titrimetry -**

- i) **Titrant**- It is solution of accurately known concentration used as standard solution. The standard solution is usually added from a long-graduated tube called a **burette**.
- ii) **Titrand** – The substance under determination is titrand (Analyte).
- iii) **Titration** - The process of adding the titrant to titrand till the reaction between them is just completes. (The substance to be determined is titrated.)
- iv) **Equivalence point** -The stage during titration when reaction between titrant and titrand just completes is called the equivalence point or the theoretical (or stoichiometric) end point. The completion of the titration is detected by some physical change, produced by the standard solution itself (e.g. the faint pink colour formed by potassium permanganate) or, more usually, by the addition of an auxiliary reagent, known as an indicator.
- v) **Practical end point** - The stage during titration when reaction between titrant and titrand just completes and is indicated via visible physical change by using an auxiliary substance. (either a colour change or the formation of turbidity)
- vi) **Indicator** – Auxiliary substance employed during titration to indicate completion of reaction between titrant and titrand via visible physical change.
- vii) **Titration error** – Difference between equivalence point and practical end point is titration error.  
(\*\*In the ideal titration, the visible end point will coincide with the stoichiometric or theoretical end point. In practice, however, a very small difference usually occurs; this represents the titration error. The indicator and the experimental conditions should be so selected that the difference between the visible end point and the equivalence point is as small as possible.)

**1.3.2 Types / Classification of titrimetric methods –** The titrimetric methods are classified on the basis of type of chemical reaction taking place between titrant and titrand.

**For use in titrimetric analysis a reaction must fulfil the following conditions.**

1. The reaction must be simple and can be expressed by a chemical equation; the substance to be determined should react completely with the reagent in stoichiometric or equivalent proportions.  $\text{NaOH} + \text{HCl} \longrightarrow \text{NaCl} + \text{H}_2\text{O}$
2. The reaction must be instantaneous or relatively fast. (Most ionic reactions satisfy this condition.) In some cases, the addition of a catalyst may be necessary to increase the speed of a reaction.
3. There must be an alteration in some physical or chemical property of the solution at the equivalence point.
4. An indicator should be available which, by a change in physical properties (colour or formation of a precipitate), should sharply define the end point of the reaction.

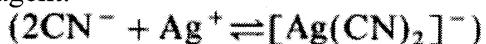
5. If no indicator is available, the detection of the equivalence point can often be possible by following the course of the titration by measuring (a) the potential between an indicator electrode and a reference electrode (potentiometric titration), (b) The change in electrical conductivity of the solution (conductimetric titration) etc.

Based on type of chemical reaction there are four main titrimetric methods.

- 1. Neutralisation Titrations** - These include the titration of free bases, or those formed from salts of weak acids by hydrolysis, with a standard acid (**Acidimetry**), and the titration of free acids, or those formed by the hydrolysis of salts of weak bases, with a standard base (**Alkalimetry**).

The reaction involved is neutralization reaction between acid and base, the combination of hydrogen and hydroxide ions to form water and neutral salt.

- 2. Complexometric titrations** - These depend upon the combination of ions, other than hydrogen or hydroxide ions, to form a soluble, slightly dissociated ion or compound, as in the titration of a solution of a cyanide with silver nitrate. The reaction involved is conversion of metal ions (analyte) in to a complex using standard solution of suitable reagent called complexing agent.



- 3. Precipitation Titrations** - These depend upon the combination of ions to form a simple precipitate as in the titration of silver ion with a solution of a chloride. The reaction involved is precipitation of analyte ion using suitable precipitating agent as standard solution.

- 4. Oxidation-reduction titrations** – Titrations involving oxidation – reduction reactions.  
The standard solutions are either oxidising or reducing agents.

### 1.3.3 Standards in Titrimetry –

In titrimetry certain chemical substances are used frequently to prepare solutions of accurately known concentration. Such substances are called as standard substances. There are two types of standards i) **Primary standards** or ii) **Secondary standards**.

A primary standard is a compound of sufficient purity from which a standard solution can be prepared by direct weighing of a quantity of it, followed by dilution to give a defined volume of solution. The solution produced is then a primary standard solution. A primary standard should satisfy the following requirements.

1. It must be easy to obtain, to purify, to dry (preferably at 110-120 °C), and to preserve in a pure state.
2. The substance should be unaltered in air during weighing; this condition implies that it should not be hygroscopic, oxidised by air, or affected by carbon dioxide. The standard should maintain an unchanged composition during storage.
3. The substance should be capable of being tested for impurities by qualitative and other tests of known sensitivity. (The total amount of impurities should not, in general, exceed 0.01-0.02 per cent.)
4. It should have a high relative molecular mass so that the weighing errors may be negligible. (The precision in weighing is ordinarily 0.1-0.2 mg; for an accuracy of 1 part in 1000, it is necessary to employ samples weighing at least about 0.2 g.)
5. The substance should be readily soluble under the conditions in which it is employed.
6. The reaction with the standard solution should be stoichiometric and practically instantaneous. The titration error should be negligible, or easy to determine accurately by experiment.

The substances not fulfilling above requirements are secondary standard substances and solution prepared out of this is not directly employed in titrimetry but it is first standardized with suitable primary standard to know its exact concentration.

In practice, an ideal primary standard is difficult to obtain, and a compromise between the above ideal requirements is usually necessary. The substances commonly employed as primary standards are indicated below:

- (a) **Acid-base reactions** - Sodium carbonate  $\text{Na}_2\text{CO}_3$ , Sodium tetra borate  $\text{Na}_2\text{B}_4\text{O}_7$ , Potassium hydrogen phthalate  $\text{KH}(\text{C}_8\text{H}_4\text{O}_4)$ , constant boiling point hydrochloric acid, Potassium hydrogen iodate  $\text{KH}(\text{IO}_3)_2$ , benzoic acid ( $\text{C}_6\text{H}_5\text{COOH}$ ).
- (b) **Complex formation reactions** - Silver, Silver nitrate, Sodium chloride, various metals e.g. spectroscopically pure zinc, magnesium, copper, and manganese.
- (c) **Precipitation reactions** - Silver, Silver nitrate, Sodium chloride, Potassium chloride, and Potassium bromide (prepared from potassium bromate).
- (d) **Oxidation-reduction reactions** - Potassium dichromate  $\text{K}_2\text{Cr}_2\text{O}_7$ , Potassium bromate  $\text{KBrO}_3$ , Potassium iodate  $\text{KIO}_3$ , Potassium hydrogen iodate  $\text{KH}(\text{IO}_3)_2$ , Sodium oxalate  $\text{Na}_2\text{C}_2\text{O}_4$ , Arsenic(III) oxide  $\text{As}_2\text{O}_3$ , and pure iron.

Primary standards	Secondary standards
1. Available in extreme pure form	May or may not
2 Can be purified by simple means	May or may not
3 Tested for impurities by easy means	May or may not
4 Preserved in unaltered form for longer time	May or may not
5 Stable in all types of weathering conditions	May or may not
6 Non-hygroscopic, oxidisable, carbonisable and not undergo change in mass.	May or may not
7 Its solution of definite concentration is directly employed in titrimetry	Its solution of definite concentration is not directly employed in titrimetry but on standardisation.

### 1.3.4 Solutions and ways to express concentration of solutions –

**Solution** – Homogeneous mixture of two or more different substances on atomic or molecular level is termed as solution. The solution is composed of two components solvent and solute which may be present in any physical state viz. solid, liquid or gas.

**Solvent** – Component of solution which is present in greater proportion.

**Solute** – Component of solution which is present in lesser proportion.

**Concentration of solution** – Amount of solute per unit volume or mass of solution is called as concentration of solution.

As per concentration solutions are roughly classified as

- i) **Dilute solution** – Solutions containing negligible amount of solute in it.
- ii) **Concentrated solutions** – Solutions containing considerable amount of solute in it.
- iii) **Saturated solutions** – Solutions containing maximum possible amount of solute in it.

### 1.3.5 Ways to express concentration of solution with respect to titrimetry

- a) **Concentration expressed in molar terms** – Here amount of solute is taken as number of moles of solute.

A mole of solute is amount of solute equal to its molecular weight in grams.

If  $w$  is amount of solute in gram then number of moles of solute  $n = w/m$

Where  $m$  is its molecular weight. As per molar terms solution is prepared in two different ways bearing its concentration as

- i) **Molarity** – Number of moles of solute per litre of solution i.e.  $M = n/v = w/m/v$

ii) **Molality** – Number of moles of solute per kilogram of solvent i.e.  $m = n/W$ , where  $W$  is weight of solvent in kilograms.

b) **Concentration expressed in normal terms** - Here amount of solute is taken as number of gram equivalents of solute.

A gram equivalent of solute is amount of solute equal to its equivalent weight in grams.

If  $w$  is amount of solute in gram then number of gram equivalents of solute  $e = w/E$

Where  $E$  is its equivalent weight.

**Equivalent weight** – It is that fraction of molecular weight by means which a substance will tend to combine with or release one part by weight of hydrogen / eight parts by weight of oxygen / thirty-five point five parts by weight of chlorine. But for redox reactions equivalent weight is based on change in oxidation state or loss/gain of number of electrons.

As per normal terms solution is prepared bearing its concentration as

i) **Normality** – Number of gram equivalents of solute per litre of solution i.e.  $N = e/v = w/E/v$

c) **Concentration expressed in percent terms** -Here amount of solute is taken in terms of direct percentage compared to mass/volume of solution. Percent solutions are of three types depending on physical states of solute and solvent i.e. percent by weight to volume (% W/V), percent by volume to volume (% V/V), percent by weight to weight(%W/W)

**Example** – Explain how you would prepare 18% of 300 cc NaCl solution?

**Answer** – 18 gram NaCl per 100 cc solution i.e. 54 gram NaCl for 300 cc solution.

54 grams NaCl is first dissolved in 200cc distilled water, then solution is diluted to final volume of 300cc with distilled water.

### 1.3.6. Comparison of Concentration scales –

**Molar** concentration and **Normality** scales are useful for volumetric experiments, in which the amount of solute in each portion of solution is related to the measured volume of solution. where the normality scale is very convenient for comparing, the relative volumes required for two solutions to react chemically with each other (avoiding a limiting reactant situation). A limitation of the normality scale is that a given solution may have more than one normality, depending on the reaction for which it is used. As an example, different ions in a compound that is not in a 1:1 ratio, such as  $\text{Ag}_2\text{SO}_4$ , will have a different normality

When focusing on silver than when sulfate is the important ion for consideration. On the other hand, the molar concentration of a solution is a fixed number because the molar mass of a substance does not depend on the reaction for which the substance is used.

The molality scale is useful for experiments in which physical measurements (freezing point, boiling point, vapour pressure, osmotic pressure, etc.) are made over a wide range of temperatures. The molality of a given solution, which is determined solely by the masses of solution components, is independent of temperature.

In contrast, the molar concentration (or the normality) of a solution is defined in terms of volume; it may vary appreciably as the temperature is changed, because of the temperature-dependence of the volume. As a point of interest, in dilute aqueous solutions (less than 0.1 M), the molality is very close numerically to the molarity.

### 1.3.7. Solved Problems

1. Explain how you would prepare 60mL of an aqueous solution of  $\text{AgNO}_3$  that is 0.030 g  $\text{AgNO}_3$  per mL.

**Solution-**

Since each mL of solution is to contain 0.030 g  $\text{AgNO}_3$ , the calculation is

$$(0.030 \text{ g/mL}) * (60 \text{ mL}) = 1.8 \text{ g } \text{AgNO}_3$$

The solution can be prepared by dissolving 1.8 g  $\text{AgNO}_3$  in much less than 60mL  $\text{H}_2\text{O}$  (3/4 of the final volume works well). Stir until dissolved, then add water to bring up to 60mL final volume while stirring.

(If you had used 60mL of water, there is no guarantee that the final volume will be 60 mL! The only way to make certain of the final volume of 60mL is to dilute to 60 mL, not add 60mL H<sub>2</sub>O.)

2. What mass of 5.0% by weight NaCl solution is necessary to yield 3.2 g NaCl?

**Solution –**

A 5.0% NaCl solution contains 5.0 g NaCl in 100 g solution. Then, 1 g NaCl is contained in 100/5.00 g solution

and 3.2 g NaCl are contained in  $(3.2) * (100/5.00)$  g solution = 64 g solution

Another setup for the problem takes advantage of the ratio and proportion (w is the mass desired):

$$\frac{5.0 \text{ g NaCl}}{100 \text{ g solution}} = \frac{3.2 \text{ g NaCl}}{w}, \text{ then } w = 64 \text{ g solution}$$

3. How much wet NaOH containing 8% moisture is required to prepare 20 litre of N/4 solution (MW-40)

**Solution -**

1 N 1 litre solution need 40 g NaOH Therefore 1 litre N/4 solution =  $40/4 = 10$  g pure NaOH  
1g NaOH containing 8% moisture is equivalent to  $1 \times 100/92 = 1.087$  g pure NaOH

Now 20 lit N/4 solution need  $20 \times 10 = 200$  g pure NaOH

Therefore, wet NaOH required =  $200 \times 1.087 = 217.4$  g

4. Calculate Normality and Molarity of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solution obtained by dissolving 250mg Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> in distilled water to get 500ml solution. (MW Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> = 342.15)

**Solution –**

$$M = n/V = 0.250/342.15/0.5 = 0.001461 \text{ moles/L} \quad N = M \times 6 = 0.0087 \text{ g equivalent/L}$$

5. Calculate Normality and Molarity of concentrated sulphuric acid having density 1.213 g/cc and containing 55% acid by weight. (MW – 98)

**Solution –**

Amount of H<sub>2</sub>SO<sub>4</sub> in 1 litre concentrated acid =  $1213 \times 0.55 = 667.15$  g

$$M = 667.15/98/1 = 6.807 \text{ moles/L}, N = M \times 2 = 6.807 \times 2 = 13.615 \text{ g equivalents/L}$$

**Questions-** 1 Define Titrimetry, titrant, titrand, equivalence point, titration, indicator, titration error, practical end point, standard, primary standard, secondary standard, solution, normality, molarity, molality, saturated solution (1mark each)

2. Define term titrimetric / volumetric analysis and give an account of its classification. (5 marks)

3 Discuss significance of primary standards in titrimetric analysis. (3marks)

4. Discuss requirements of chemical reaction suitable for titrimetric analysis (3 marks)

5. Compare / distinguish between primary and secondary standards. (4 marks)

6. What are primary standards? Discuss/Explain criteria of deciding primary standard substance (5 marks)

7.Define standard and list advantages of primary standards over secondary standards

8. What do you mean by concentration of solution? Discuss different ways to express concentration of solution. (5 marks)

9. Give reasons -i) Equivalence point and practical end point never coincide ii) A chemical reaction taking place during titrimetry must be instantaneous iii) Solution prepared with secondary standard is used in titrimetry after standardization iv) For preparing solution of accurately known concentration a substance with high molecular weight is preferred v) A substance used for preparing standard solution should not lose or gain weight on storage (1 mark each)

10. Solve the following (3,4,5 marks as per problem)

- i. Compute volume of concentrated HNO<sub>3</sub> having density 1.121g/cc and containing 60%acid required to prepare 35 litre of N/50 solution. (MW-63)
- ii) Explain how you would prepare 2 litre of 16% KI solution.
- iii) 10cc H<sub>2</sub>SO<sub>4</sub> was diluted and excess BaCl<sub>2</sub> solution was added to it. The dried precipitate of BaSO<sub>4</sub> weighed 850 milligrams. Calculate Normality and % concentration of original acid solution. (MW- H<sub>2</sub>SO<sub>4</sub> =98, BaSO<sub>4</sub> = 233.38).
- iv) For given unbalanced equation Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> + Fe<sup>2+</sup> + H<sup>+</sup> → Cr<sup>3+</sup> + Fe<sup>3+</sup> + H<sub>2</sub>O
- What is normality of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution if 35cc solution contain 3.87g K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (MW =294.185)
  - What is normality of FeSO<sub>4</sub> solution if 750cc solution contain 96.3g FeSO<sub>4</sub> (MW =151.908)
- v) What mass of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.5H<sub>2</sub>O is needed to make up 500cc solution of 0.2 N for following reaction  
(MW-248.18)                  2S<sub>2</sub>O<sub>3</sub><sup>2-</sup> + I<sub>2</sub> → S<sub>4</sub>O<sub>6</sub><sup>2-</sup> + 2I<sup>-</sup>

## 1.4 Acid base and Complexometric titration –

**1.4.1. Acid base / Neutralisation titration** -It is based on neutralisation of acidic or basic components from analyte.

It is performed in two ways i) **Acidimetry** – It is titration between standard acid solution with alkaline / basic analyte ii) **Alkalimetry** – Titration between standard base solution and acidic analyte.

It needs standard acid or base solution and suitable indicator.

**Indicators** – Acid - Base titrations use acid base indicators. An acid base indicator is organic weak acid or base undergoing visible colour change within specific pH range. There are several such substances available to be used as acid base indicators but it is essential to choose correct one.

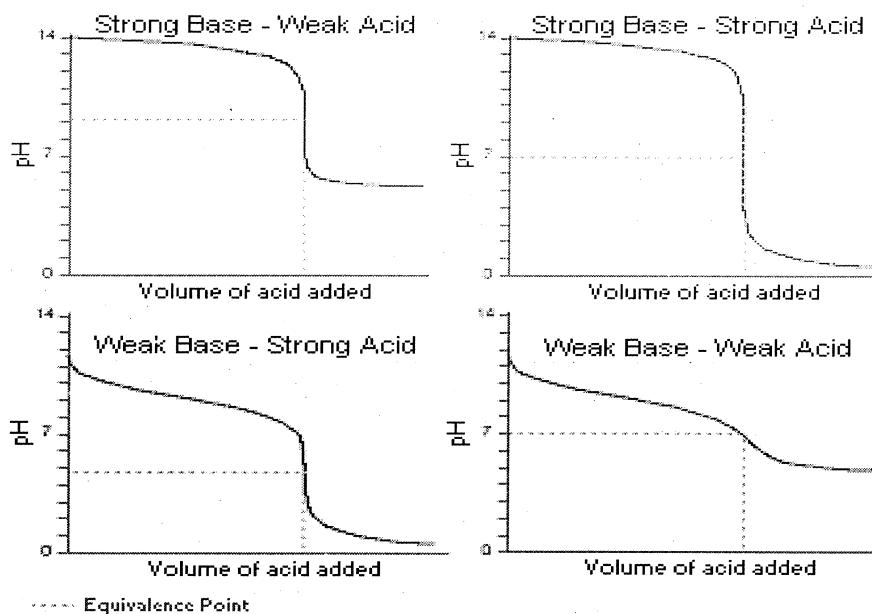
**A suitable indicator to be selected in desired titration depends on**

- Type of titration to be performed – Acidimetric or Alkalimetric
- Type of acid and base involved in titration – Strong or Weak
- pH range at equivalence point of titration
- Colour transition pH range of an indicator

In following table there are some examples of acid base indicators along with pH range for colour transition to occur, initial and final colour.

Name	Acid Color	pH Range of Color Change	Base Color
Methyl violet	Yellow	0.0 - 1.6	Black
Thymol blue	Red	1.2 - 2.8	Yellow
Methyl orange	Red	3.2 - 4.4	Yellow
Bromocresol green	Yellow	3.8 - 5.4	Black
Methyl red	Red	4.8 - 6.0	Yellow
Litmus	Red	5.0 - 8.0	Black
Bromothymol blue	Yellow	6.0 - 7.6	Black
Thymol blue	Yellow	8.0 - 9.6	Black
Phenolphthalein	Colorless	8.2 - 10.0	Red
Thymolphthalein	Colorless	9.4 - 10.6	Red
Alizarin yellow R	Yellow	10.1 - 12.0	Red

The pH range at equivalence point depends on type of acid base involved i.e. strong or weak. The figure shows pH range at equivalence point for different combinations (strong and weak) of acid and base. (All graphs for acidimetric titrations)



From this it is concluded that,

For strong acid vs strong base titrations pH range at end point is sufficiently broad (3 to 10) and almost all acid base indicators work within this, hence they can use any acid base indicator, therefore are preferred.

For strong base verses, weak acid or vice versa pH range at end point is narrow and limited indicators are available.

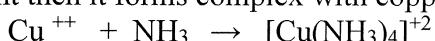
For weak base verses, weak acid pH range at end point is not distinct and it is difficult to choose proper indicator hence are mostly avoided.

The indicators undergo colour change within specific pH range since these organic weak acid or bases are sensitive to  $H^+$  ion conc. The change in concentration of  $H^+$  ions during titration bring structural changes and at certain pH particular structure is stable which possess different colour than another structure stable at different pH.

#### 1.4.2. Complexometric Titration-

It is titrimetric method in which analyte ions convert into stable complex on reaction with standard solution. It one of best method for quantitative determination of metals, alloys, ores, minerals, medicinal drugs, food stuff etc.

In this method, a standard solution is prepared out of suitable complexing/ chelating agent. The complexing agent is any reagent capable of forming stable complex with metal ion. Say  $NH_3$  is complexing agent then it forms complex with copper as shown below.



To choose correct/suitable complexing agent in order to prepare standard solution for titrimetric analysis it is essential to obey following criteria or requirements.

- It must be readily available and economical.
- It must form stable complex with almost all metal ions.
- It must be sensitive to metal ion even at very low concentration.
- It must be selective to specific metal ion under certain condition. (Say pH)
- A masking agent must be available to avoid interference of unwanted ions.
- It must be possible to conduct titration in different manners/ways by using same complexing agent.

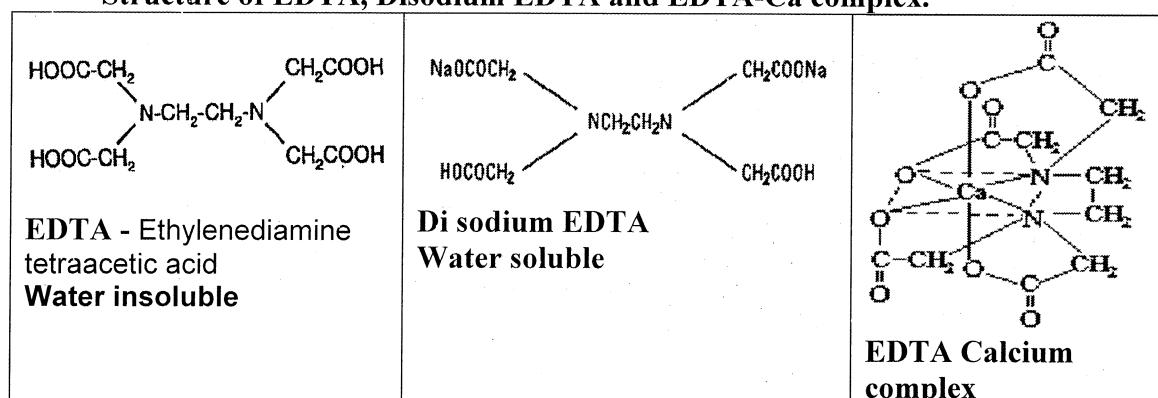
By considering above **EDTA - Ethylenediaminetetraacetic acid** is known as **versatile complexing agent** in complexometry as

- EDTA is readily available and economical.
- EDTA forms stable complex with almost all metal ions.
- EDTA is sensitive to metal ion even at very low concentration.
- EDTA is selective to specific metal ion at particular pH i.e. selective to Ca and Mg ions at pH 9.5 to 10
- Masking agents are available to avoid interference of unwanted ions for EDTA.
- Using EDTA titrations can be conducted in four different manners/ways as discussed below

#### 1.4.3. EDTA titrations-

- Direct EDTA titration** – A known volume of analyte solution is directly titrated with standard EDTA solution.
- EDTA back titration** – To a known volume of analyte solution a known excess of standard EDTA is added and unused EDTA is determined by titrating it with standard solution of suitable metal ion.
- Replacement type EDTA titration** – The original metal ion from known volume of analyte solution is replaced with suitable metal ion and then directly titrated with standard EDTA.
- Alkalimetric EDTA titration**- To a known volume of analyte solution a known excess of standard EDTA is added and unused EDTA is determined by titrating it with standard solution of suitable base (As  $2H^+$  ions are released when it traps one metal ion to form a complex)

#### Structure of EDTA, Disodium EDTA and EDTA-Ca complex.



**1.4.4. Indicator** -Complexometric titrations use metal ion indicator. Metal ion indicator is coloured complexing agent which indicates completion of titration via dissociation of its complex formed with analyte. This is explained with example of **Eriochrome Black T (EBT)** as below.

1 Analyte solution + EBT  $\rightarrow$  EBT analyte complex  $\rightarrow$  Std. EDTA  $\rightarrow$  EDTA analyte complex

Specific colour      added during Titration

2 When all analyte ions convert in to EDTA analyte complex the solution contain two complexes. Now excess drop of EDTA solution dissociates EBT analyte complex and covert release metal ion to EDTA analyte complex thereby releasing free indicator. When all indicator sets free in solution a visible colour transition occurs. (Blue colour of EBT observed).

**Questions –**

- 1 Define acidimetry, alkalimetry, strong acid, weak acid, strong base, weak base, acid base indicator, metal ion indicator, complexing agent, masking agent.
- 2 Discuss how you select an indicator for proposed acid base titration.
- 3 Give an account of characteristics/ requirements/ features of complexing agent considered suitable for preparing standard solution for complexometry.
- 4 Justify that EDTA is versatile complexing agent in complexometric titrations.
- 5 Draw structure of i. EDTA, ii. Di-sodium EDTA iii. EDTA Ca complex/Metal ion complex.
- 6 Give reasons –
  - i. Strong acid and strong base titrations can use any acid base indicator
  - ii. Weak acid weak base titrations are generally avoided
  - iii. Limited acid base indicators are available for weak acid strong base or vice versa type titrations
  - iv. pH range at end point is essential while choosing an indicator for acid base titration
  - v. Complexing agent used for preparing standard solution must be selective to metal ion
  - vi. Indicator metal complex must be always less stable than EDTA analyte complex.
- 7 Discuss different possible ways to conduct EDTA titrations.

**1.5 Gravimetric Analysis -**

**Gravimetric analysis or quantitative analysis by weight is the process of isolating and weighing an element or a definite compound of the element in as pure form as possible.** The element or compound is separated from a weighed portion of the substance being examined.

A large proportion of the determinations in gravimetric analysis is concerned with the transformation of the element or radical to be determined into a pure stable compound which can be readily converted into a form suitable for weighing.

The weight of the element or radical may then be readily calculated from a knowledge of the formula of the compound and the relative atomic masses of the constituent elements.

The separation of the element or of the compound containing it may be effected in different ways, the most important of which are: (a) Precipitation -precipitation gravimetry (b) Volatilisation – volatilisation gravimetry; (c) Electroanalytical methods – electro gravimetry (d) Thermal methods – thermogravimetry and (e) Extraction and chromatographic methods.

It is essential to mention reasons for the continuing use of gravimetric analysis even the disadvantage as more time-consuming.

The advantages offered by gravimetric analysis are:

- (a) It is **accurate and precise** when using modern analytical balances.
- (b) Possible sources of error are **readily checked**, since filtrates can be tested for completeness of precipitation and precipitates may be examined for the presence of impurities.
- (c) It has the important advantage of being an **absolute method**, i.e. one involving direct measurement **without any form of calibration** being required.
- (d) Determinations can be carried out with relatively **inexpensive apparatus**, the most expensive requirements being a muffle furnace and, in some cases, platinum crucibles.

Two general applications of gravimetric analysis are

- (a) the analysis of standards which are to be used for the testing and/or calibration of instrumental techniques;
- (b) analyses requiring high accuracy, although the time-consuming nature of gravimetry.

### 1.5.1 Precipitation gravimetry -

This is the most important technique with which we are concerned in gravimetric analysis. The constituent being determined is precipitated from solution in a form which is so slightly soluble that no appreciable loss occurs when the precipitate is separated by filtration and weighed. Thus, in the determination of silver, a solution of the substance is treated with an excess of sodium chloride or potassium chloride solution, the precipitate is filtered off, well washed to remove soluble salts, dried at 130-150°C, and weighed as silver chloride. Frequently the constituent being determined is weighed in a form other than that in which it was precipitated. Thus, magnesium is precipitated, as ammonium magnesium phosphate  $Mg(NH_4)PO_4 \cdot 6H_2O$ , but is weighed, after ignition, as the pyrophosphate  $Mg_2P_2O_7$ .

#### The following factors determine a successful analysis by precipitation.

1. The precipitate must be so insoluble that no appreciable loss occurs when it is collected by filtration. In practice this usually means that the quantity remaining in solution does not exceed the minimum detectable by the ordinary analytical balance, viz. 0.1 mg.
2. The physical nature of the precipitate must be such that it can be readily separated from the solution by filtration, and can be washed free of soluble impurities. These conditions require that the particles are of such size that they do not pass through the filtering medium, and that the particle size is unaffected (or, at least, not diminished) by the washing process.
3. The precipitate must be convertible into a pure substance of definite chemical composition; this may be effected either by ignition or by a simple chemical operation, such as evaporation, with a suitable liquid.

Factor 1, which is concerned with the completeness of precipitation, has already been dealt with about the solubility-product principle, and the influence upon the solubility of the precipitate of (i) A salt with a common ion, (ii) Salts with no common ion, (iii) Acids and bases, and (iv) Temperature.

#### Supersaturation and precipitate formation

The solubility of a substance at any given temperature in each solvent is the amount of the substance dissolved by a known weight of that solvent when the substance is in equilibrium with the solvent.

The solubility depends upon the particle size, when these are smaller than about 0.01 mm in diameter; the solubility increases greatly the smaller the particles, owing to the increasing role played by surface effects.

A supersaturated solution is one that contains a greater concentration of solute than corresponds to the equilibrium solubility at the temperature under consideration. Super saturation is therefore an unstable state which may be brought to a state of stable equilibrium by the addition of a crystal of the solute ('seeding' the solution) or of some other substance, or by mechanical means such as shaking or stirring. The difficulty of precipitation of ammonium magnesium phosphate will at once come to mind as an example of super saturation.

### 1.5.2 Conditions of precipitation

No universal rules can be given which are applicable to all cases of precipitation, but, by the intelligent application of the principles enumerated in the foregoing paragraphs, a number of fairly general rules may be stated:

1. Precipitation should be carried out in dilute solution, due regard being paid to the solubility of the precipitate, the time required for filtration, and the subsequent operations to be carried out with the filtrate. This will minimise the errors due to co-precipitation.
2. The reagents should be mixed slowly and with constant stirring. This will keep the degree of super saturation small and will assist the growth of large crystals. A slight excess of the reagent is all that is generally required; in exceptional cases a large excess may be

necessary. In some instances, the order of mixing the reagents may be important. Precipitation may be effected under conditions which increase the solubility of the precipitate, thus further reducing the degree of super saturation.

3. Precipitation is effected in hot solutions, provided the solubility and the stability of the precipitate permit. Either one or both solutions should be heated to just below the boiling point or other more favourable temperature. At the higher temperature: (a) the solubility is increased with a consequent reduction in the degree of super saturation, (b) coagulation is assisted and sol formation decreased, and (c) the velocity of crystallisation is increased, thus leading to better-formed crystals.
4. Crystalline precipitates should be digested for as long as practical, preferably overnight, except in those cases where post-precipitation may occur. As a rule, digestion on the steam bath is desirable. This process decreases the effect of co-precipitation and gives more readily filterable precipitates. Digestion has little effect upon amorphous or gelatinous precipitates.
5. The precipitate should be washed with the appropriate dilute solution of an electrolyte. Pure water may tend to cause peptization. (For theory of washing)
6. If the precipitate is still appreciably contaminated because of coprecipitation or other causes, the error may often be reduced by dissolving it in a suitable solvent and then re-precipitating it. The amount of foreign substance present in the second precipitation will be small, and consequently the amount of the entrainment by the precipitate will also be small.

#### Factors affecting precipitation:

1. **Choice of precipitant:** The precipitant should be such that it produces a precipitate which is completely insoluble i.e. solubility product should not exceed  $10^{-6}$  mol. The structure of the precipitate formed should be such to allow rapid filtration and washing.

Organic reagents have a special place in inorganic analysis (generally termed as organic precipitants) because of the following advantages offered by them

- i. Many of the chelate compounds are very insoluble in water, so that metal ions may be quantitatively precipitated.
- ii. The organic precipitant often has a high molecular weight. Thus a small amount of metal may yield a large weight of precipitate, minimizing weighing errors.
- iii. Some of the organic reagents are fairly selective, yielding precipitates with only a limited number of cations. By controlling factors such as pH and the concentration of masking agents, the selectivity of an organic reagent can often be greatly enhanced.
- iv. The precipitates obtained with organic reagents are often coarse and bulky and hence can be easily handled.
- v. Further, metal chelates are mostly anhydrous. Hence, the precipitates dry quickly. This can be accelerated by washing the precipitate with alcohol.

2. **Amount of precipitant:** The amount of precipitant added is also of great importance.

If a large excess of precipitant is added, the precipitate formed redissolves as it raises the solubility of the precipitate and

If just enough amount is added then complete precipitation might not take place as some amount is required to reach the solubility product value. Hence, in precipitating a substance, a reasonable, excess of precipitant is invariably added to ensure completeness of precipitation. The excess precipitant provides excess of common ions and the solubility of precipitate is decreased. For analogous reasons, the precipitate is washed with a solution containing common ions.

- 3. Effect of temperature:** The solubility product of a substance is constant only when its temperature is unaltered. Usually the solubility increases with the increase in temperature. When the precipitation is carried out at higher temperature, the precipitate formed is of high purity due to better crystal structure. Hence, wherever possible, precipitation which is carried out at higher temperature is most advantageous but then it should be cooled before filtration.
- 4. Effect of pH:** The solubility of the precipitate with the change in pH of the solution is inevitable. The effect depends on the type of precipitate. Generally, the precipitate of metal hydroxides and those of sparingly soluble salts of weak acids are precipitated only in alkaline or neutral pH ranges. Smaller the dissolution constant for the acid, higher is the pH required for practically complete precipitation of its salt. The selectivity of organic reagents can always be improved by the control of pH.
- 5. Effect of complex formation:** In the presence of certain ions, the desired component is likely to form complex ions having higher dissociation constants and this will lead to incomplete re precipitation. So the unwanted ions should be prevented from getting precipitated out by masking them. Masking is the procedure of forming soluble complexes with the unwanted ions and thus keeping them in solution.

### Types of precipitate

Precipitates are classified into crystalline, curdy and gelatinous precipitates. Crystalline precipitates are relatively pure and consist of easily filterable particles. Curdy precipitates are agglomerates of colloidal particles and are of filterable size. However, they are more easily contaminated than crystalline precipitates and hence must be washed with an electrolyte solution. Gelatinous precipitates are flocculated colloids. The particle size is smaller than that of curdy precipitates and hence is difficult to filter. They must also be washed with an electrolyte solution to prevent peptization.

### Purity of the analytical precipitate

When a precipitate separate from a solution, it is not always perfectly pure. It may contain varying amounts of impurities due to:

- 1. Co-precipitation:** If a precipitate is contaminated by substances which are normally soluble in the solution under the condition of precipitation, then co-precipitation is said to have taken place. Co-precipitation (12) occurs by the adsorption or occlusion.
- 2. Post-precipitation:** The process by which an impurity is deposited after precipitation of the desired substance is termed as post-precipitation. When there is a possibility that post-precipitation may occur, directions call for filtration to be made shortly after the desired precipitate is formed.

### Digestion or Ageing

Generally, the primary precipitate obtained from a hot dilute solution is in the form of crystals of nearly perfect lattice structure. However, those obtained from concentrated solutions are generally very small crystals of imperfect structure. There is considerable variation in particle size for any given primary precipitate. Such a primary precipitate is subjected to digestion or ageing. This is done by allowing the primary precipitate to remain in contact with the solution from which it is formed, normally at higher temperature. The smaller particles exhibit higher solubility and dissolve. As a result, the solution becomes supersaturated with respect to the larger particles. This results in the deposition of the dissolved particles on the larger particles and increase in the average particle size. This is known as digestion, ageing or Ostwald ripening of the precipitate. Under suitable conditions, the process of ageing also improves the perfection of the crystal lattice structure to some extent. For various reasons, most of the precipitates carry with them impurities from the

solution. During digestion, these impurities, to some extent, return to the solution when smaller particles dissolve.

### Filtration

Filtration is the separation of the precipitate from the mother liquor. The systems employed are filter papers, Gooch crucibles and sintered-glass crucibles. The choice of the filtering medium will be controlled by the nature of the precipitate and the cost.

### Washing of precipitate

The wash liquid is normally water, sometimes containing an electrolyte. The choice of the wash liquid depends on the following aspects

- 1) Higher solubility for the impurities and lower solubility for the precipitate.
- 2) If the precipitate is a flocculated colloid; a suitable electrolyte is added to wash the liquid to prevent peptization of the precipitate.
- 3) If the ions of the adsorbed impurities are of non-volatile nature, an electrolyte which can exchange its ions with the impurities to form a volatile adsorbate is added. These volatile ions may be removed during drying and ignition.

In addition to the choice of the suitable wash liquid, the mode of washing is also equally important. The precipitate on the filter paper should be thoroughly stirred using a jet of wash liquid. This should be followed by washing the edges of the filter paper with the jet of wash liquid since the precipitate might spread out during washing. A large number of washes with small volume of wash liquid is more efficient to remove the impurities than a small number of washes with large volume of wash liquid.

### Drying and Ignition of precipitates

The precipitate which has been collected by filtration and washing is dried and/or ignited to a compound of known composition. This is then cooled under proper condition to be weighed accurately. Use of ash-free filter papers has greatly simplified the ignition step. The drying and/or ignition, and finally the weighing are repeated till constant weight of the residue is obtained to ensure the completion of these two processes.

The temperature at which the precipitate should be ignited depends on the following factors: The precipitate should be ignited at such a temperature range at which it is converted into a new compound of known and definite composition. Ignition at higher than the optimum temperature should be avoided, as it may cause loss of the precipitate due to volatilization, sublimation or decomposition. Most of the precipitates are dried in an oven at about 373-423 K to remove water if it is only loosely held, and not strongly adsorbed or occluded. Drying should be done at a temperature at which anti peptization electrolyte associated with the precipitate is completely volatilized. In such cases the precipitate will have a known and definite composition and can be weighed. Ignited residue must be cooled inside a desiccator containing a dehydrating agent to remove moisture that might have been adsorbed by the residue when exposed to the atmosphere during initial cooling. Sometimes, a carbon dioxide free atmosphere might have to be maintained inside the desiccator if the residue is capable of absorbing carbon dioxide.

### Weighing

Modern balances can readily weigh samples directly and masses from several grams to a few micrograms can be used accurately and quickly. It is essential that the conditions are the same for the initial weighing as for the final weighing. Temperature is especially important and hot samples should never be placed directly onto a balance.

### Calculations

In the usual gravimetric procedure, a precipitate is weighed, and from this value, the weight of the analyte in the sample is calculated with the aid of a gravimetric factor (GF). The GF is the ratio of the formula weight of the substance sought to that of the substance weighed.

$$\text{Gravimetric factor (GF)} = \frac{\text{Formula weight (substance sought)}}{\text{Formula weight (substance weighed)}}$$

Usually, the purpose of a quantitative analysis is to determine the percentage of a certain element or ion (A) in a sample, which can be calculated as:

$$\% A = \frac{\text{Weight of precipitate} \times GF \times 100}{\text{Weight of sample}}$$

### Solved Problems –

1. Purity of soda ash was determined by gravimetric analysis. 0.75g soda ash was dissolved in distilled water to get 100cc solution. By adding lime solution precipitate of  $\text{CaCO}_3$  was obtained. Which on isolation, ignition gave 0.3829 g  $\text{CaO}$ . Calculate purity of soda ash( $\text{Na}_2\text{CO}_3$ ) (MW –  $\text{CaO}$  -56,  $\text{Na}_2\text{CO}_3$  -106)

$$\text{Solution - GF} = \frac{106}{56} = 1.892, \% \text{ Na}_2\text{CO}_3 = \frac{0.3829 \times 1.892 \times 100}{0.75} = 96.59\% \text{ pure}$$

2. Ni in nichrome was determined by gravimetric analysis. 0.55g of an alloy was dissolved in nitric acid and diluted with distilled water to get 100cc solution. Ni from solution was precipitated as  $\text{Ni}(\text{C}_4\text{H}_7\text{O}_2\text{N}_2)_2$  weighing 0.660 g. Calculate %w/w Ni in alloy. (MW – Ni- 58.7,  $\text{Ni}(\text{C}_4\text{H}_7\text{O}_2\text{N}_2)_2$  -288.03)

$$\text{Solution - GF} = \frac{58.7}{288.03} = 0.2037, \% \text{ Ni} = \frac{0.660 \times 0.2037 \times 100}{0.55} = 24.44\% \text{ w/w Ni}$$

### Questions-

1. Define gravimetric analysis and discuss its advantages.
2. What is gravimetric analysis? Discuss different ways of performing gravimetric analysis.
3. Discuss factors that assure successful analysis by precipitation gravimetry.
4. Explain in detail conditions for precipitation.
5. Discuss different factors that affect precipitation during gravimetric analysis,
6. Compare co-precipitation with post precipitation
7. Explain advantages of organic precipitants in gravimetric analysis.
8. Write notes on i) Digestion and aging of precipitate
  - ii) Co-precipitation
  - iii) Post precipitation
  - iv) Washing of precipitate
  - v) Ignition and drying of precipitate.
9. Give reasons
  - i) Gravimetric analysis do not need calibration
  - ii) Analytical balance is always preferred in gravimetric analysis
  - iii) Precipitate obtained must be convertible into pure substance of definite composition by different ways like ignition
  - iv) Precipitation should be carried out from dilute solutions
  - v) If solubility/stability of precipitate permits, it is better to carry out precipitation from hot solutions
  - vi) Digestion of precipitate must be avoided if chances for post precipitation are there
  - vii) Dilute solution of suitable electrolyte is generally used to wash precipitate than distilled water.
10. Define – Gravimetry, Co-precipitation, Post precipitation, Digestion of precipitate,
11. Solve the following –
  - i) Purity of common salt was tested by gravimetric analysis. 0.85g  $\text{NaCl}$  was dissolved in distilled water to get 100cc solution. The solution on treatment with  $\text{AgNO}_3$  gives 1.98 g

AgCl. Calculate purity of salt. (MW – AgCl -143.32, NaCl -58.5)

- ii) Calcium tablets were tested for its calcium content by gravimetric analysis. 30 tablets were randomly picked and crushed to fine powder weighing 12 g. 4 g of this powder was dissolved in acid and solution is diluted to 100ml with distilled water. Calcium from solution was isolated as CaC<sub>2</sub>O<sub>4</sub> which on ignition gave 1.41g CaO, Calculate amount of calcium per tablet as CaCO<sub>3</sub>. (MW – CaCO<sub>3</sub> -100, CaO -56)
- iii) The concentration of Arsenic in an insecticide was determined by gravimetric analysis. As was precipitated as MgNH<sub>4</sub>AsO<sub>4</sub> and weighed as Mg<sub>2</sub>As<sub>2</sub>O<sub>7</sub> to 106.5mg from 1.630g sample. Determine %w/w of As as As<sub>2</sub>O<sub>3</sub>. (MW- Mg<sub>2</sub>As<sub>2</sub>O<sub>7</sub> - 310.45, As<sub>2</sub>O<sub>3</sub> -197.84) iv) A sample of iron ore containing approximately 55% w/w Fe. The amount of Fe was determined gravimetrically by isolating it as Fe<sub>2</sub>O<sub>3</sub>. What mass of sample do you need to isolate at least 1g Fe<sub>2</sub>O<sub>3</sub>. (MW – Fe -55.84, Fe<sub>2</sub>O<sub>3</sub> – 159.7)
- v) To determine amount of magnetite in pure iron ore a 1.55g sample was dissolved in HCl giving mixture of Fe<sup>++</sup> and Fe<sup>+++</sup>. Adding HNO<sub>3</sub> Fe<sup>++</sup> oxidised to Fe<sup>+++</sup> and then diluted with distilled water. Fe<sup>+++</sup> was isolated as Fe(OH)<sub>3</sub> and on filtration and ignition 0.87g pure Fe<sub>2</sub>O<sub>3</sub> was obtained. Calculate %w/w Fe<sub>3</sub>O<sub>4</sub> in sample. (Fe<sub>3</sub>O<sub>4</sub>-231.54,Fe<sub>2</sub>O<sub>3</sub>-159.69)