MODULE-5

Water Chemistry and Method of Chemical Analysis

WATER CHEMISTRY

Water is abundant in earth. It covers nearly three fourth of earth's surface. Water is nature's most wonderful, abundant and useful compound of the many essential elements for the existence of human beings, animals and plants and other living creatures around the world. Water is needed for domestic and industrial purposes.

Sources of water are classified as

1. *Surface water:* These are water are rain water, river water, lake water and sea water.
2. *Underground water:* These are spring & well water.

Impurities in water may be broadly classified into four categories:

1. *Dissolved gases:* Water contains dissolved gases such as Carbon dioxide, Oxygen, Sulphur dioxide, Ammonia and oxides of Nitrogen all of them which are derived from atmosphere.

2. *Suspended Impurities:* Suspended impurities are the dispersion of solid particles, which can be removed by filtration or settling. There are two types Inorganic: Includes sand, clay, silica, oxides of Fe & Mn etc. Organic: Includes wood pieces, disintegrated particles of dead animals, leaf, fishes, Bacteria, Algae etc**.** The suspended impurities impart turbidity and colour to water.

3.**Dissolved impurities:** The dissolved impurities present in water include bicarbonates, chlorides and sulphates of calcium, magnesium and sodium. In addition, small amounts of nitrates, nitrites, silicates, ammonium and ferrous salts are also present.

4.**Microscopic matter:** These contain bacteria and other microorganisms (algae and Fungi). Generally responsible for water borne disease.

Potable Water

Potable water is water that is safe to be used as drinking water. It is the water that is suitable for human consumption. Potable water is also known as drinking water and comes from surface water and groundwater sources. This water is treated to levels that meet state and federal standards for consumption. Drinkable water means it is free of unpleasant odors, tastes and colors, and is within reasonable limits of temperature.

CHARACTERISTICS OF WATER

As per the suggestion given by World Health Organisation (WHO) and by Indian Council of Medical Research (ICMR), the following are the important characteristics of potable water.

1. It should be clear, colourless and odourless.
2. It should be cool and pleasant to taste.
3. It should be free from harmful bacteria and suspended impurities.
4. It should be free from dissolved gases like CO_2, H_2S, NH_3, etc., and poisonous minerals like lead, arsenic, manganese, etc.
5. pH should be between 6.5 -8.5.
6. TDS should be maximum of 500.
7. Hardness should be less than 500 ppm.
8. Chloride ion content should be less than 250 ppm.
9. Fluoride ion content should be less than 1.5 ppm.

Hardness of water

Hardness of water is due to presence of Calcium and Magnesium salts in water. Hard water does not produce lather easily with soap but produces a scum or precipitate with soap or detergent. Hardness in water is of two types namely

(i) Temporary hardness and (ii) Permanent hardness.

Temporary hardness is caused due to the presence of bicarbonates of calcium and magnesium. Temporary hardness can be removed by boiling of water as bicarbonates are converted to insoluble carbonates.

Permanent hardness is caused by the presence of chlorides and sulphates of calcium and magnesium. Permanent hardness requires chemical processes for softening. The sum of temporary and permanent hardness is referred as Total hardness. Hardness is normally expressed in terms of parts per million of $CaCO_3$.

Determination of Hardness using EDTA

Principle:

The total hardness of water sample is determined by titrating against ethylenediamine tetraacetic acid [EDTA].
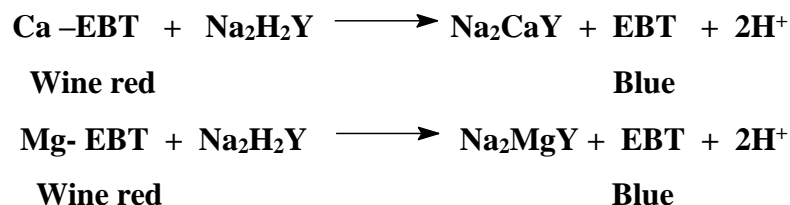
The structure of EDTA is

$$HOOCH_2C \diagdown N-CH_2-CH_2-N \diagup CH_2COOH$$
$$HOOCH_2C \diagup \qquad\qquad\qquad \diagdown CH_2COOH$$
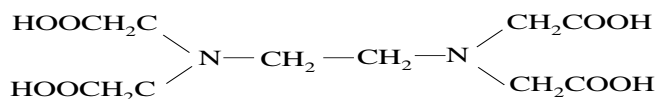
EDTA is insoluble in water so its disodium salt Na_2H_2Y is readily soluble in water is used in preparation of reagent. The disodium salt of EDTA has two replaceable hydrogen ions.

Hardness of water is determined by titrating a known volume of water sample with EDTA, using Eriochrome black –T (EBT) as indicator, in the presence of ammonium hydroxide– ammonium chloride buffer (pH 10).

When EBT is added to the hard water at pH 10, it forms wine red complex with Ca^{+2} and Mg^{+2} ions of hard water. When EDTA is added to this solution it forms complexes with the free Ca^{+2} and Mg^{+2} ions. Near the end point when all metal ions are exhausted, EDTA dissociates the metal – EBT complex consumes the metal ion and releases the blue-coloured free indicator. Therefore, at the end point colour changes from wine red to blue.

$$Ca-EBT \ + \ Na_2H_2Y \ \longrightarrow \ Na_2CaY \ + \ EBT \ + \ 2H^+$$
$$\text{Wine red} \qquad\qquad\qquad\qquad\qquad \text{Blue}$$
$$Mg-EBT \ + \ Na_2H_2Y \ \longrightarrow \ Na_2MgY \ + \ EBT \ + \ 2H^+$$
$$\text{Wine red} \qquad\qquad\qquad\qquad\qquad \text{Blue}$$

Procedure:

Determination of total hardness:

50 ml of water sample is pipetted out into a clean conical flask. 2 ml of $NH_4OH – NH_4Cl$ buffer solution and 3 - 4 ml drops of eriochrome black – T indicator are added to it. Then it is titrated with 0.01M EDTA solution till the colour changes from wine red to clear blue.

Let the volume of EDTA consumed be **V₁ml.**

Determination of permanent hardness:

Exactly 50 ml of water sample is transferred into a clean 500 ml beaker and boiled gently for 20 – 30 minutes. It is cooled and filtered directly into a 250 ml conical flask. 2ml of buffer solution and 3 – 4 drops of eriochrome black –T indicator are added to it. It is then titrated against 0.01M EDTA till the colour changes from wine red to clear blue. Let the volume of EDTA consumed be **V₂ ml**.

Calculation:

1000 ml of 1M EDTA = 100g of $CaCO_3$ (Molecular weight of $CaCO_3$ = 100g)

V_1 ml of 0.01 M EDTA $\quad = \quad \dfrac{V_1 \times 0.01 \times 100}{1000}$ g of $CaCO_3$

50 ml of water sample contains $= \dfrac{V_1 \times 0.01 \times 100}{1000 \times 50}$ g of $CaCO_3$

10^6 ml of water sample contains $= \dfrac{V_1 \times 0.01 \times 100 \times 10^6}{1000 \times 50}$ g of $CaCO_3$

$= 20 \times V_1$ g of $CaCO_3$

Total hardness of water sample $= 20 \times V_1$ ppm $CaCO_3$ equivalent

Similarly,

Permanent hardness $= \dfrac{V_2 \times 0.01 \times 100 \times 10^6}{1000 \times 50}$

Permanent hardness $= 20 \times V_2$ ppm of $CaCO_3$

Temporary hardness $= 20 (V_1 - V_2)$ ppm $CaCO_3$ equivalent

Biological oxygen demand (BOD)

It is defined as the amount of oxygen required for biological oxidation of organic matter present in one litre of waste water at 20ºC over a period of 5 days. The unit of BOD is mg/dm³ or ppm.

Chemical oxygen demand (COD):

COD is defined as the amount of oxygen required to oxidize the total oxidizable impurities present in one litre of sewage water using strong oxidizing agent like acidified $K_2Cr_2O_7$.

It is represented in mg/dm³ or ppm. COD value is always greater than BOD, since COD includes both biologically oxidizable & non oxidizable impurities.

Determination of COD

Principle:

A known volume of sewage sample is refluxed with a known excess of potassium dichromate in H_2SO_4 medium and in the presence of Ag_2SO_4 and $HgSO_4$. Potassium dichromate oxidizes all the chemically Oxidizable impurities. Silver sulphate (Ag_2SO_4) catalyses the oxidation of organic matter. Mercuric sulphate ($HgSO_4$) avoids the interference of chloride ions by forming soluble complex with them.

The amount of unconsumed potassium dichromate is determined by titration with standard ferrous ammonium sulphate solution. The amount of potassium dichromate consumed corresponds to the COD of the sample.

Procedure:

A known volume of sewage water is taken in a conical flask. 1g of $HgSO_4$ followed by 2 test tubes of silver sulphate / sulphuric acid solution to it. Also pipette out 25ml of given potassium dichromate solution into it. Add a porcelain piece, attach the flask with a reflux condenser and reflux the mixture for half an hour. Cool the flask to room temperature; wash the inner side of the condenser with distilled water into the same flask. The contents are cooled and 1 test tube of 1:1 sulphuric acid and 1-2 drops of ferroin indicator was added. Titrate the mixture with standard Mohr's salt solution till the colour changes from bluish green to dark red.

Blank titration: The above procedure is repeated by taking same volume of distilled water in place of sewage water.

Calculation:

Volume of waste water sample = V ml

Volume of standard FAS consumed in sample titration = A ml

Volume of standard FAS consumed in blank titration = B ml

Normality of FAS solution = N

Hence amount of $K_2Cr_2O_7$ consumed for the oxidation in terms of FAS solution = (B – A) ml

$$\text{Therefore Normality of water sample} = \frac{N \times (B-A)}{V}$$

$$= \frac{N \times (B-A) \times 8}{V} \ g/dm^3$$

$$\text{i.e, COD of the sample} = \frac{N \times (B-A) \times 8 \times 1000}{V} \ mg/dm^3$$

METHODS OF CHEMICAL ANALYSIS

Introduction:

Analytical Chemistry deals with methods for determining the chemical composition and quantity of matter. A qualitative method yields information about the identity of atomic or molecular species or the functional groups in the sample. Whereas a quantitative method, in contrast provides information about amount of element or substance present in the sample. Quantitative analysis involves

✓ **Volumetric analysis** where the substance to be analyzed is made to react with a standard solution of appropriate reagent.

✓ **Gravimetry**, where the substance to be analyzed is precipitated by the addition of reagent, the precipitate is collected and weighed.

✓ **Instrumental analysis**, uses classical or advanced instrument to measure physical quantities of the analyte be relating the concentration with light absorption,fluorescence, conductivity or potential.

Instrumental analysis can be classified into two types.

Electrical method: It involves measurement of current, voltage or resistance in order to find the concentration of a certain species in a solution.eg Potentiometry, conductometry etc.

Optical method: These are based on how the sample acts towards electromagnetic radiation in order to find the concentration of a certain species in a solution.eg Flame photometry, AAS, Colorimetry etc.

Volumetric Analysis

Volumetric analysis is a quantitative analytical method that determine the quantity of a substance in terms of volume, thus the name volumetric analysis. For this type of analysis, a solution of a substance that is to be calculated is taken and a known quantity of another substance of known concentration is to be taken. When the chemical reaction is completed, the volume of the solution is measured. The endpoint of this reaction is specifying by a change in colour or precipitation etc. So, in this measurement process, the estimated volume of two analytes is taken and the concentration of one of them is known then conveniently the concentration of the other can be calculated.

Principle of Volumetric (Titrimetric) analysis

✓ The sample solution to be analyzed contains an unknown amount of the substance.

✓ The solution or reagent that is of known concentration reacts with sample solution containing unknown amount of substance in the presence of an indicator to indicate the endpoint of the reaction during titration

✓ The Volume is measured by titration which completes the reaction between the sample solution and standard solution.

✓ The volume and concentration of reagent used in the titration gives the amount in moles.

✓ The quantity of unknown substances in the measured volume of solution is calculated by the mole fraction equation.

Requirements of Volumetric (Titrimetric) analysis

It is a simple and accurate method of analysis. This method can determine amount of substance in terms of volume accurately, hence the name volumetric analysis and the method followed is called Titration. It requires,

✓ _Titrant:_ the standard solution of known concentration.

✓ _Titrate:_ a solution of a substance whose concentration is to be calculated

✓ _Location of Equivalence point:_ The theoretical point at which the chemical reaction is completed.

✓ _End point:_ a point at which a physical change (change in color or precipitation etc) isobserved near the equivalence point

✓ _Indicator:_ the substance used for visual detection (change in color) when the chemical reaction is completed.

✓ _Apparatus:_ The apparatus such as burette, pipette, standard flasks, beakers, test tubes etc

Standard Solution: A solution whose concentration is known is called standard solution. Any substance, which is stable at room temperature and does not react with solvent in which it is dissolved, can be directly weighed to prepare its standard solution.

There are two types of standard solutions: Primary and secondary standards

Primary standard: It is a compound of sufficient purity in which total amount of impurities does not exceed 0.01-0.02%. The standard solution can be prepared by direct weighing of a sample followed by its dissolution in water (or solvent) to obtain a definite volume of solution. The concentration of the primary standard is calculated in terms of normality, molarity or molality.

The substance to be used as a primary standard should also satisfy the following requirements:

1. It must be easily available in pure form.

2. It should be less hygroscopic.

3. Highly stable.

4. Anhydrous in nature.

5. Weighed easily

6. Nontoxic

7. Should not be expensive.

8. It should have high relative molecular mass so that weighing errors are neglible.

9. The substance should be readily soluble in water.

Secondary standard: A secondary standard is a standard that is prepared in laboratory for a specific analysis, whose concentration varies with time. They provide a reference to determine the unknown concentration. It is standardized using primary standard solution. Secondary standards are used in preparation of reagents or in laboratories. These have less purity and less stability then primary standard but more reactive than primary standard. Sodium hydroxide and potassium permanganate are examples of secondary standards.

Normality: It is the number of gram equivalents of the solute dissolved in one litre of solution.

Normality = mass per dm^3 / equivalent weight. It is denoted by N

Molarity: It is the number of gram molecular weight (moles) of the solute dissolved in one litre of Solution. It represented by the symbol 'M'.

Molarity = mass per dm^3 / molecular weight

Molality: It is the number of moles of the solute dissolved in 1 kg of the solvent. It is represented by symbol 'm'. Molality = Moles of solute / Weight of solvent in kg.

Mole fraction: It is the number of moles of a specific substance in the solution divided by the total number of moles in the given solution (Molecular weight). It is represented by symbol 'X

PPM: This is an abbreviation for "parts per million". The number of parts (by weight or volume) of solute per million parts of solution. The very low concentration of the solute in solution can be expressed in ppm. It can be expressed as milligrams per liter (mg/L) or ppm.

INSTRUMENTAL METHOD OF ANALYSIS:

COLORIMETRY

Theory / Principle:

It is an analytical technique used to determine the concentration of substance in a solution which are colored or which give a colour when mixed with suitable reagent by measurement of relative absorption of light radiations in visible region with respect to the known concentration of the same substance.

When a monochromatic radiation of intensity Io is passed through a solution of sample under investigation, taken in a cell of thickness **t**, a portion of the radiation is absorbed **(Ia)**, a portion is reflected, **(Ir)**, remaining is transmitted **(It)** through the medium.

Then, **Io = Ia + Ir + It**

For glass cells, **Ir** is negligible, Therefore, **Io = Ia + It**

$$It / Io = T, \text{ where } T \text{ is the Transmittance}$$

log 1/T = log Io/It, which is called Absorbance(A) or Optical density(OD)

$$A = \textbf{log Io/It}$$

Colorimetry follows *Beer Lambert's law.*

LAMBERT'S LAW:

It states that, "When a monochromatic light passes through a transparent medium, the intensity of the transmitted light decreases exponentially as the thickness of the absorbing medium increases arithmetically."

Mathematically, it can be represented as,

$$\textbf{It = Io e}^{\textbf{-kt}} \quad \text{-------------(1)}$$

If **Io** is the intensity of incident light and **It** is intensity of transmitted light

Thus, Lambert's law can be expressed as,

$$\textbf{A = log Io/It = Kt} \text{ -------------- (2)}$$

Where **K** is constant and **t** is thickness of the medium.

This equation shows that, absorbance (A) is directly proportional to thickness (t) of medium.

BEER'S LAW:

It states that "When a monochromatic light passes through a transparent medium, the intensity of the transmitted light decreases exponentially as the concentration of the medium increases arithmetically."

Then,

$$\textbf{It = Io e}^{\textbf{-k'c}}, \text{ ---------- (3) where, c = molar concentration of sample solution.}$$

$$\textbf{A = log Io/It = K'c} \text{ -------------- (4)}$$

This equation shows that, absorbance is directly proportional to concentration of medium

Combining equations (2) and (4) for Beer' law and Lambert's law, equation for Beer-Lambert's law is obtained and is written as,

log   **Io/It**   =

εct

Where ε is molar absorption coefficient, a constant for a given substance at a given wavelength.

If path length **(t)** or thickness of the cell is kept constant, then absorbance A is proportional to concentration **c** ie   **A α c**

Therefore, absorbance **A** is directly proportional to concentration of the substance when thickness of the medium is kept constant is called Beer Lambert's law.

INSTRUMENTATION

The instrument used to measure absorbance of the solution is known as photoelectric colorimeter. The essential parts of a colorimeter are

- Tungsten lamp as light source.
- A filter which provides the desired wavelength range where solution gives maximum absorbance. The function of the filter is to isolate any desired spectral region by filtering off the undesired radiation.
- A sample cell ie a cuvette to take the solution.
- A detector or photocell to measure the transmitted light and a meter to display the output from the detector.
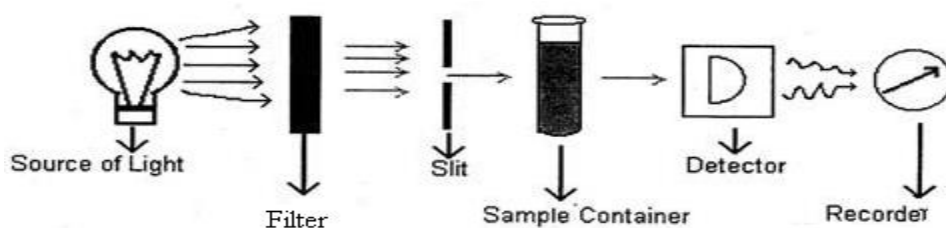
ESTIMATION:

When Cu^{2+} ions are treated with ammonia solution, a deep blue colored cuprammonium complex is obtained. The absorbance is measured at 620nm (λmax) since the complex shows maximum absorbance at this wavelength. When absorbance of known solutions is plotted against concentration, a straight line is obtained. From this, unknown solution concentration can be obtained by measuring the absorbance of that solution.

$$Cu^{2+} + 4NH_3 \longrightarrow \left[Cu(NH_3)_4 \right]^{2+}$$
<div align="center">Deep blue</div>
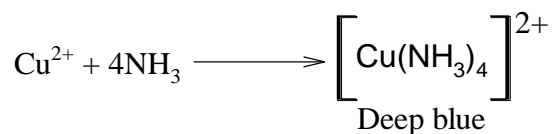
PROCEDURE:

5, 10, 15, 20 and 25ml of standard Copper sulphate solution is taken in separate standard flasks. 5ml of ammonia is added to each of these flasks and made up to the mark using distilled water. The flasks are stoppered and shaken well for uniform concentration. To the given test solution, 5ml of ammonia is added and made up to the mark with distilled water, stoppered and shaken well. A blank solution is also prepared taking 5ml of ammonia, making up to the mark using distilled water and shaken well. The absorbance of solutions against blank is measured at 620nm using colorimeter. A calibration curve is drawn by plotting concentration of Cu against absorbance. From this, concentration of Cu in test solution can be determined.

APPLICATIONS:

✓ The method is used to estimate Copper in brass, Mn in steel, glucose in fluids etc.
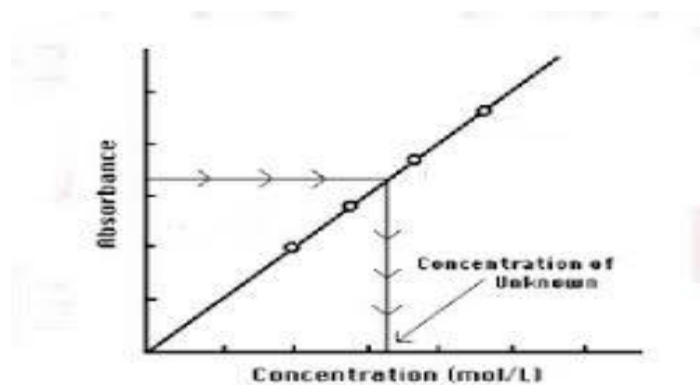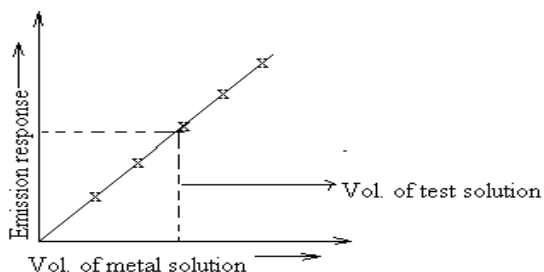

FLAME PHOTOMETRY

Principle:

The flame photometer is based on the determination of concentration of an element in a solution by measuring the intensity of the characteristic radiation emitted to the flame by the element when the element solution is aspirated to flame. Here the emission intensity is correlated with the concentration of the element forms the basis of flame photometry.

When a solution containing the sample element is aspirated into the flame, following changes takes place at that flame.

▪ First, the solvent gets evaporated leaving behind the salt in the flame.

- The salt then gets evaporated into vapors of the salt, which further undergo dissociation into the constituent atoms.

- The metal atoms formed in the flame may absorb heat energy from the flame and get electronically excited to their higher energy level.

- As they are unstable at this excited level, the atoms fall back to their ground state by emitting light radiations.

- The intensity of the light radiation emitted imparts characteristic color to the flame and intensity of light radiation emitted to the flame is proportional to the concentration of the element in the flame.

- Different metals emit their characteristic radiation at different wavelengths; they do not interfere with each other, even when they are present together.

Instrumentation:

Flame photometer consists of a nebulizer, mixing chamber, burner, filter, detector and a read out device. Sample is drawn into nebulizer where it mixes with the air stream as a fine mist and passes into the mixing chamber. In the mixing chamber, it mixes with fuel gas and then passes into the burner.
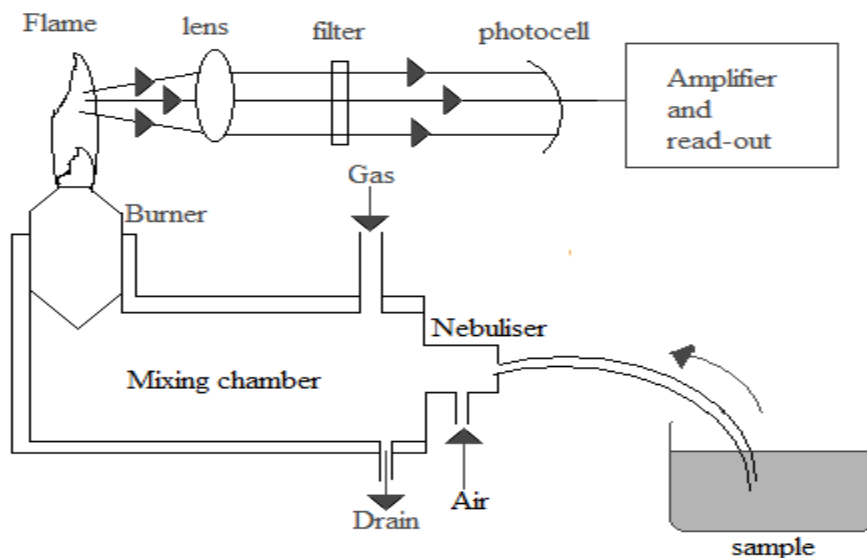
Where, the mixture is burnt and series of reaction occurs, radiation from the resulting flame passes through the lens and finally through a filter, which permits only the radiation characteristic of the element under investigation to pass through the detector. The output from the detector is read out on a suitable read out system.

APPLICATIONS:

- ✓ Concentration of sodium, potassium in urine.
- ✓ Determination of Alkali & Alkaline earth metals

POTENTIOMETRY

Potentiometry is an analytical method in which the amount of a substance in solution is determined, by measurement of the emf between two electrodes that are dipped into the solution.

PRINCIPLE:

When a metal M is immersed in a solution containing its own ions, M^{n+}, the electrode potential is given by Nernst equation,

$$E = E^o + \frac{0.0591}{n} \log \left[M^{n+} \right]$$

E can be measured by combining the electrode with a reference electrode and measuring the emf of the cell. The concentration can be calculated, provided E^o of the electrode is known.

The indicator electrode and calomel electrode are combined together to form galvanic cell and dipped into the solution of analyte and connected to potentiometer. A Potentiometer is used to measure cell potential to determine the concentration of ions present in solution. In the potentiometric titrations, a

known volume of analyte is titrated with a standard solution. During the course of titration, concentration of product will be continuously altered. As the potential of calomel electrode remains constant any change in cell potential is due to a change in the potential of indicator electrode during titration. Here indicator electrode is the electrode whose potential depends upon the concentration of ions present in the solution of analyte. Initially, the change in potential is very small. At the equivalence point, when the amount of titrant is added to analyte, there will be a sharp rise (jump) in potential. Beyond the equivalence point, there will be no significant change in potential. By plotting a graph of change in potential against the volume of titrant added, the equivalence point can be determined.

INSTRUMENTATION:

- A Known volume of an analyte solution is taken in beaker.
- Calomel and platinum electrodes are dipped into the analyte solution and connected to potentiometer. The solution is stirred well and initial cell potential (emf) is noted.
- The titrant is added in increments of 0.5ml from burette to the analyte solution and emf is measured each time after stirring the solution.
- The process is continued till equivalence point where emf increases rapidly.
- A few readings are taken beyond the equivalence point. Thus the changes in potential at different volumes of titrant are recorded.
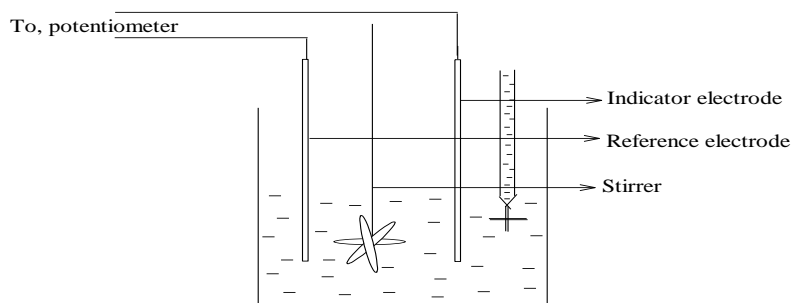
ADVANTAGES:

✓ It can be carried out for colored solutions where indicators cannot be used.

✓ It is possible to determine the end point in titrations of very weak acids or very weak bases.

Based on the nature of chemical reactions, potentiometric titrations are classified as

1. Neutralization titrations

2. Redox titrations

3. Precipitation titrations

1. Neutralization (Acid – Base) titrations:

If a solution of HCl is titrated against NaOH, electrode potential is dependent on H^+ ion concentration. Hence, here we can use glass electrode as an indicator electrode. A glass electrode is placed in HCl solution and coupled with a reference electrode to form a galvanic cell. The emf of the cell is measured potentiometrically, and is given by

$E_{cell} = E_{ref} - 0.0591 \log[H^+]$

$\quad = E_{ref} + 0.0591 \text{ pH}$

The titrant (NaOH) of known concentration is added in increments of 0.5 ml from burette to the analyte solution and emf is measured each time after stirring the solution. Sudden jump is seen at equivalence point. The equivalence point is found by plotting $\Delta E / \Delta V$ against volume as follows.
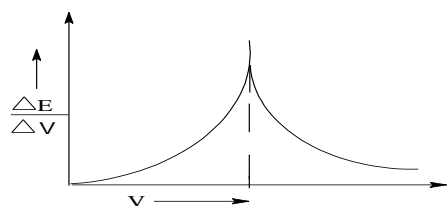

2. Red-ox titrations:

The titrations involving Mohr's salt solution and Potassium dichromate solution can be done by Potentiometry.

- The platinum electrode is used as an indicator electrode and coupled with a calomel electrode (reference electrode) and dipped in a solution of known volume of analyte (Mohr's salt solution) and connected to potentiometer and emf is measured.

- The titrant (Potassium dichromate) of known concentration is added in increments of 0.5ml from burette to the analyte solution and emf is measured each time after stirring the solution.

- FAS reacts with $K_2Cr_2O_7$ under acidic conditions, the redox electrode potential is set up at indicator electrode. $Pt/Fe^{2+}, Fe^{3+}$.

- The electrode potential of the redox electrode is given by Nernst equation

$$E = E^o + \frac{0.0591}{n} \log \frac{[\ Fe^{3+}\ ]}{[\ Fe^{2+}\ ]}$$

- The electrode potential depends upon concentration of Fe^{2+} and Fe^{3+} ,

- As the titration proceeds Fe^{3+} increases and Fe^{2+} decreases and redox electrode potential increases and emf of the cell goes on increasing and steep rise is seen at equivalence point.

- At equivalence point all the Fe^{2+} is converted to Fe^{3+} ions and redox potential of $Pt/Fe^{2+},Fe^{3+}$ stops and further addition of dichromate new redox potential comes into existence $Pt/Cr^{6+},Cr^{3+}$ because the solution contains Cr^{3+} ions produced due to reduction of dichromate by Fe^{2+} ions.

- This redox electrode $Pt/Cr^{6+},Cr^{3+}$ has higher potential than $Pt/Fe^{2+},Fe^{3+}$.
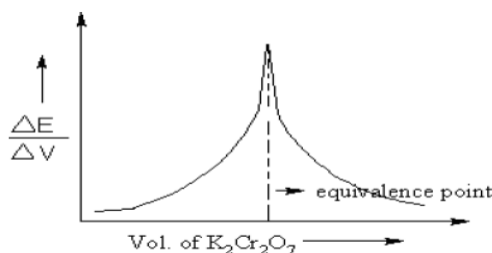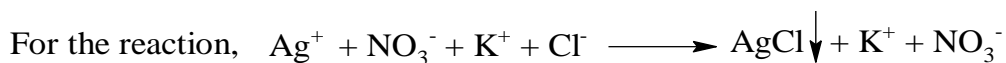

- Plot a graph of $\Delta E/ \Delta V$ versus volume of $K_2Cr_2O_7$ gives the equivalent point.
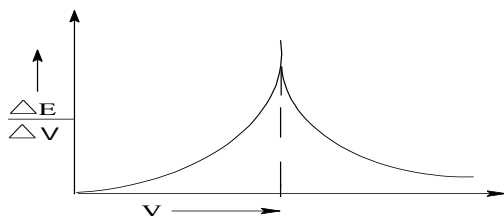
3. Precipitation titrations:

Consider a titration of $AgNO_3$ Vs. standard KCl, where Ag^+ ions are precipitated as AgCl. The silver electrode acts as indicator electrode & calomel as reference electrode, the potential can be measured as,

$$E = E^o + 0.0591 \ \log \ [Ag^+]$$

For the reaction, $\quad Ag^+ + NO_3^- + K^+ + Cl^- \longrightarrow AgCl\downarrow + K^+ + NO_3^-$

The titrant of known concentration KCl is added in increments of 0.5ml from burette to the analyte solution Ag^+ ions is precipitated as AgCl. i.e., concentration of Ag^+ ions decreases during the process and emf is measured each time after stirring the solution. A sudden jump (rise) is seen at equivalence point.

CONDUCTOMERTIC TITRATION

It is a analytical method of analysis based on measurement of electrical conductance of an electrolytic solution.

THEORY /PRINCIPLE

The conductance of a solution can be explained by Ohm's law, current **(I)** flowing in a conductor is directly proportional to emf **(E)** and inversely proportional to resistance **(R)**.

$$I = E/R \text{ or } E = IR.$$

The reciprocal of resistance is conductance = **1/R**. It is expressed as ohm^{-1}, mho or Siemen (S).

The resistance of conductor is directly proportional to its length **'l'** and inversely proportional to the area of cross section **'a'** of the conductor. Then,

$$R = S \, l/a, \text{ where S is specific resistance. } S = aR/l$$

The reciprocal of specific resistance is specific conductance **(K).**

$$C = 1/R, \text{ therefore } C = (1/S) \times (a/l) = K (a/l)$$

Specific conductance **(K)** is the conductance of a solution present between 2 parallel electrodes of area $1cm^2$ which are kept 1cm apart. It is given by,

$$K = (l/a) \times (C)$$

Where **l/a** is constant for a given Conductivity cell known as cell constant since **l** and **a** will be fixed for a conductivity cell **C**.

The conductance of the solution depends on mobility of ions, concentration of ions and temperature.

- ✓ Faster the mobility of ions greater the conductance.
- ✓ Larger the concentration of ions greater is the conductance.
- ✓ As temperature increases conductance increases.

Procedure:

Conductometric titrations are the titrations in which amount of the analyte present in the given solution is measured by the change in conductance. In these titrations there is replacement of ions of particular conductance by ions of different conductance and sudden change in conductance is seen at equivalence point. To determine the equivalence point in acid base titrations a graph is plotted of conductance versus volume.

INSTRUMENTATION:

- It consists of two platinum electrodes each of unit area of cross section placed unit distance apart connected to conductometry.
- The electrodes are dipped in analyte solution taken in beaker.

- The titrant is added from a burette to the analyte &solution is stirred.
- The conductance is measured after addition of titrant at regular intervals of 0.5ml.

ADVANTAGES:

- Mixture of acids can be titrated accurately.
- Accurate results are obtained in dilute and concentrated solutions.
- The method can be employed for colored solutions also.
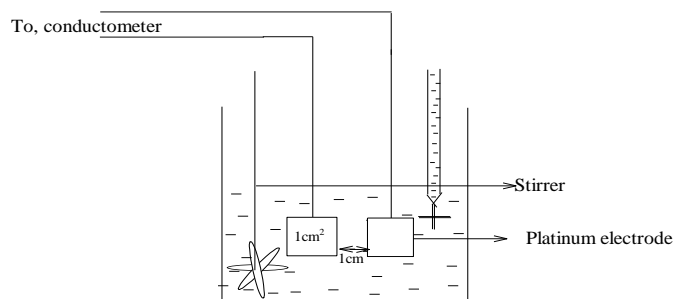
*APPLICATIONS***:**

1. Titration of strong acid with a strong base: eg HCl Vs. NaOH

- When strong acid is titrated with a strong base, conductance decreases till equivalence point since highly mobile H^+ ions are replaced by Na^+ of base.
- After the equivalence point, conductance rapidly increases with further addition of base due to increase in concentration of OH^- ions.
- The graph obtained on plotting conductance versus volume of base is as follows.
- Two straight lines are obtained. The point of intersection is the end point.
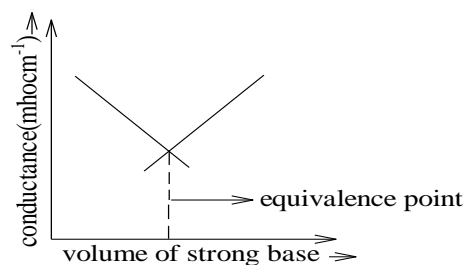
2. Titration of weak acid with a strong base: eg CH_3COOH Vs. NaOH

- In this titration on adding NaOH, the conductance of the weak acid increases till until acid is completely neutralized due to formation of salt (Sodium acetate).
- After the equivalence point, conductance rapidly increases with further addition of base due to increase in concentration of highly mobile OH^- ions.

- The graph obtained on plotting conductance versus volume of base is shown in fig.
- The point of intersection is the end point.
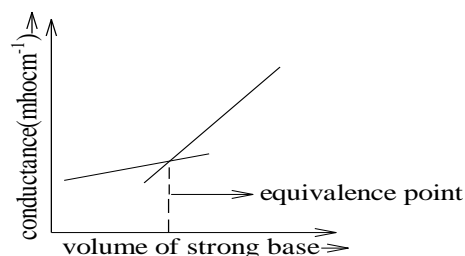
3. Titration of acid mixture with strong base:

- In the mixture of strong acid and weak acid, strong acid dissociates completely and consumed first by the base.
- After the neutralization of strong acid, the weak acid is neutralized. During neutralization of the strong acid (Ex: HCl) conductance first falls since highly mobile H^+ ions are replaced by Na^+ of base.
- Later, during the neutralization of weak acid (Ex: acetic acid), the poorly conducting acid is converted into a salt (Ex. CH_3COONa).
- The salt undergoes complete dissociation; therefore, the conductance increases gradually.
- After the complete neutralization, further addition of base NaOH introduces more and more Na^+ and OH^- ions into the solution, conductance again increases rapidly.
- When conductance of the solution is plotted against volume of base added, three straight lines will be obtained.
- First point of intersection corresponds to the volume of base required to neutralize strong acid and second point of intersection is for total acid.
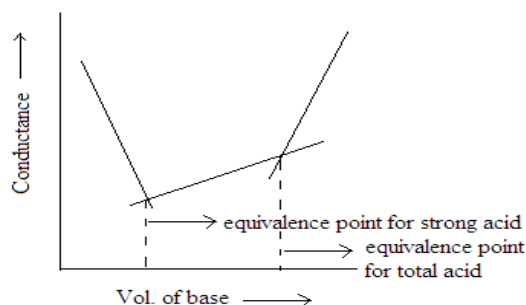
QUESTION BANK

1. *Explain the theory and instrumentation of Potentiometry.*

2. *Explain the theory and instrumentation of Colorimetry*

3. *Explain the theory, instrumentation and applications of Flame photometry*

4. *Explain the theory and instrumentation of Conductometry.*

5. *What is potable water. Mention any five characteristics of potable water.*

6. *Write the principles and requirement of volumetric analysis.*

7. *Explain the determination of hardness by EDTA method*

8. *Define the following units in standard solution.*

   (a) Molarity (b) Molality (c) Normality (d) PPM (e) Mole fraction

9. *Explain the determination of COD analysis.*

PSK