

ION EXCHANGE CHROMATOGRAPHY

Ion exchange may be defined as a reversible reaction in which free mobile ions of a solid called ion exchange are exchanged for different ions of similar charge present in solution.

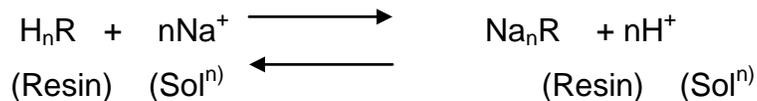
Most ion exchangers for practical use consist of an insoluble organic polymer into which a charged group has been introduced in some suitable manner. The backbone is generally styrene-divinylbenzene copolymer.

PROPERTIES:

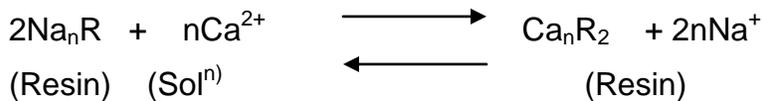
- 1.) They are almost insoluble in water & organic solvents such as benzene, CCl_4 etc.
- 2.) They are complex in nature i.e. they are polymeric.
- 3.) They have active or counter ions that will exchange reversibly the other ions in a surrounding solution without any substantial change in the material.

CATIONS EXCHANGERS:

It is a high molecular weight, cross-linked polymer having sulphuric, carboxylic, phosphonic etc. Groups as an integral part of the resin and an equivalent amount of Cations. Thus it is a polymeric anion to which active Cations exchanger is kept in a solution of a salt some H^+ ions of the resin enter the solution and in equivalent amount of Cations of the resin. It is represented as:



The resins having sodium ions produced in the above $\text{R} \times \text{N}$ can exchange these ions with other Cations.

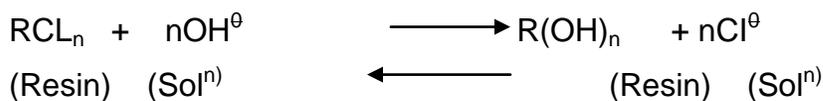
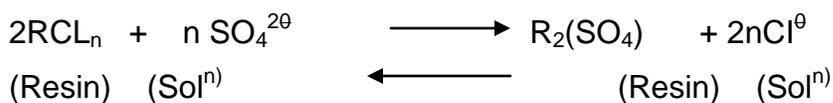


Some Commercial Available Cation Exchanges

Trade Name	Functional Group	Framework Material
1. Amberlite IR-120	SO ₃ H	Styrene/ divinylbenzene (Copolymers Homoporous)
2. Dowex	SO ₃ H	-Do-
3. Zerolit	SO ₃ H	-Do-
4. Amberlite – 200	SO ₃ H	Same Framework Material as above but lieteroporous
5. SE cellulose	C ₂ H ₆ SO ₂ H	Cellulose
6. Amberlite IR-50	COOH	Methacrylic Acid/ Divinyl
7. CM	CH ₂ COOH	Cellulose, fibrous

ANION EXCHANGERS:

It is a polymer having amine or quaternary ammonium groups amount of anions such as integral parts of the resin and an equivalent amount of unions such as Cl⁻, SO₄^{2θ}, OH ions etc. These anions are mobile and exchangeable. The anion exchange behaviour of these materials may be represented as follows:



Trade Name	Functional Group	Framework Material
1. Amberlite IR-400	Styrene/ divinylbenzene (Copolymers Homoporous)	-CH ₂ – N ⁺ (CH ₃) ₃
2. Zerolit FF – IP	Same as above but (heteroporous)	-DO-
3. Amberlite IR-410	Styrene/ divinylbenzene (Copolymers Homoporous)	
4. Zerolit N– IP	Same as above but isoporous	
5. QAE Sephadex A- 25	Dextran	

REGENERATION:

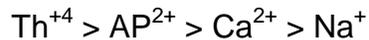
Anions exchangers are generally supplied in the form of salts amines in particular are stable only in this form. On the other hand Cations exchangers can be converted into the H⁺ form by treatment with aqueous asid followed by washing the ammonium base having hydroxyl groups form the strangle basic anion exchanger on treatment with sodium hydroxides while the weakly basic anion exchangers are converted into free amines. Resins must be complete full cycle of charging & discharging before use. Carrying out this step enhances its effective capacity.

ION EXCHANGE COLUMN IN CHROMATOGRAPHIC SEP:

The principle of ion-exchange chromatography is based upon the simple fact that different Cations (or anions) have different capacity to undergo exchange reaction on the surface of a given exchanger.

The capacity of an ion to undergo exchange R x N depends upon the charge and the size of hydrated ion in solution. Under similar conditions the capacity has been found to increase in the charge on the ion, but has been found to decrease with increase in the size of the hydrated ion.

If we compare the hydrated ions of the same size it is found that the ionic charge plays a role to determine their capacity to undergo exchange reaction. So the capacity amongst Cations has been found to decrease in the following order:



Likewise, the capacity amongst anions of same size has been found to decrease in following order:

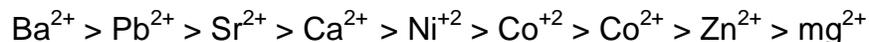


If we compare the ions carrying the same charge the size of the hydrated ions plays role in determining their capacity to undergo exchange reactions.

Thus amongst the univalent Cations the capacity has been found to decrease in order:



Amongst doubly charged the capacity has been found to decrease as:



Amongst the univalent anions the capacity has been found to decrease as:



If the active polyvalent ion in a resin is to be exchanged with an ion of lower valence, the exchange has been found to be favourable by using much higher concentration of the solution.

The quality of resin is determined by its capacity, which depends upon total number of ion active groups per unit weight of material. Greater the number

of ions the greater the capacity of the resin for exchange process and greater the cross-linking of resin, higher the efficiency.

SELECTION OF SUITABLE SOLVENTS:

It is useful to classify ion exchange according to their PK values of their ion group. For practical use the dissolved material must be present also in the dissociated form if it is to be retained by resin. It is most convenient to work at a PH where one of the components will be retained while the other does not interact with ion exchangers. The ions retained can be eluted with the aid of high concentrations of cations & anions without changing the PH.

APPLICATIONS:

1. SEPARATION OF SIMILAR IONS FROM ONE ANOTHER:

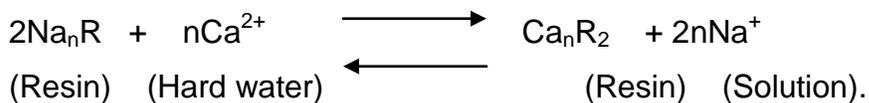
Ion exchange chromatography is being used to separate similar ions from one another because the different ions undergo exchange $R \times N$ to different extents for instance a mix. of Li^+ , Na^+ and K^+ ions can be separated by passing their solution through a cation exchanger. 0.1 N HCl has been used as an eluent. Similarly for Cl^- , Br^- , & I^- sodium nitrate is used as eluent.

2. REMOVAL OF INTERFERING RADIALS:

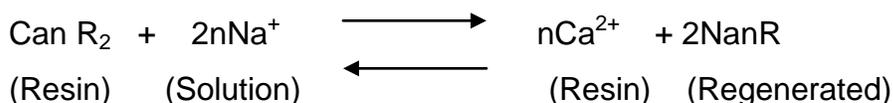
In the estimation of Ca^{2+} and Ba^{2+} ions by the oxalate or sulphate method, phosphate ion is found to interfere. Therefore its removal becomes necessary which is achieved by passing a solution of Ca^{2+} and Ba^{2+} ions having phosphate ions through sulphuric acid cation exchanges. The Ca^{2+} and Ba^{2+} ions got exchanged with H^+ ions while the phosphate ions will pass as such through the column. At last the Ca^{2+} and Ba^{2+} are removed by using suitable eluent.

3. SOFTENING OF HARD WATER:

Hardness of water is due to the presence of Ca^{2+} , Mg^{2+} and other divalent ions, which may be removed by passing hard water through cation exchangers charged with Na^+



The Ca^{2+} , mg^{2+} ions are retained in the column whereas the Na^+ ions pass into solution. After using the ion exchanger for long time it becomes inactive, and is revived by percolating through it a concentrated solution of NaCl , so reverse rxn take place.



4. COMPLETE DEMINERALISATION OF WATER:

It requires the removal of cations and anions. The water is first passed through an acidic cation exchanger when the metallic cations (Na^+ , Ca^{2+} , mg^{2+} etc) are exchanged with H^+ ions. The water obtained from cation exchanger is then passed through a basic anion exchanger where anions commonly present in water (Cl^- , NO_2^- , SO_4^{2-} etc) are exchanged by OH^- ions of the exchanger. The H^+ and OH^- which pass into solution in exchange for cations and anions, combine to form unionised water.

5. LANTHANIDE SEPARATION:

When solution-containing mixtures of lanthanides is passed through a column packed with particles of a suitable ion exchange resin, the cations present in solution undergo exchange with the hydrogen or only other cation that may be present in ion exchanger.

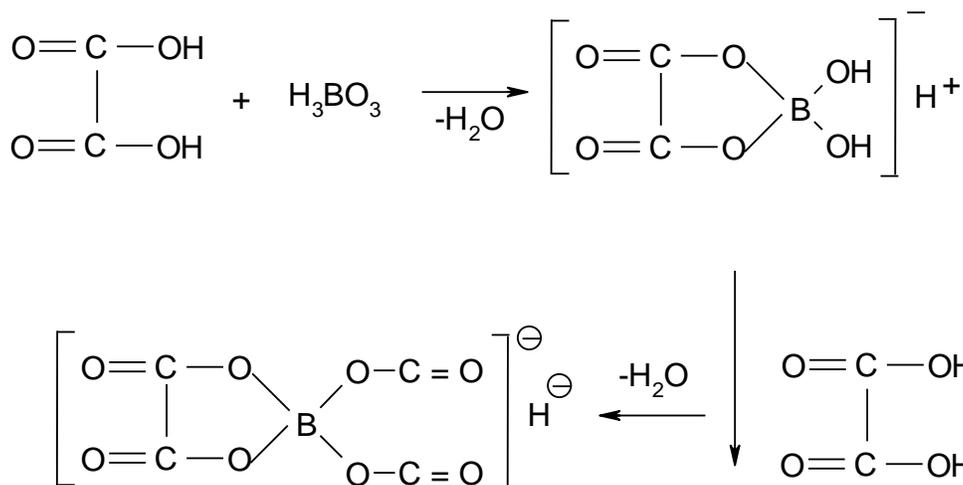
The cations having the maximum capacity to undergo exchange $R \times N$ gets held near the top while the other cations get held further down in the column in order of their decreasing capacities to undergo exchange.

6. PURIFICATION OF ORGANIC COMP-EXTRACTED IN WATER:

Many natural products extracted in water have been found to be contained with ions originally present in water.

7. SEPERATION OF SUGARS:

Sugar is first of all converted in to borate complexes. Similarly, disaccharides can be separated from the menosaccharide



8. SEPARATION OF AMINO ACIDS:

Ion exchange chromatography is used to separate the complex mix of amino acid obtained from acid hydrolysis of protein.

POTENTIOMETRIC TITRATION:

It includes, the direct measurement of on electrode potential ion may be found & the changes in E.M.F of an electrolytic cell brought about by addition of titrant.

The referenda electrode are expected to assume a potential which is independent of the composition of the solution, So the indicator electrode can give information about the nature of substrata capable of exchanging e^{\ominus} .

In potentiometer titration's the concentration of are or more species is measured potent one tribally. The titration beaker-becomes is of half-cells along

with a reference electrode for the other woolfells. In, this titration's, the change in the electrode potential upon the addition of the titrant are noted against the volume of the tyrant added. At the endpoint rate of change of potential is maximum. The end point is found by plotting a curve of potential versus the volume of titrant.

Three types of instruments are used to measure potentials:

- Non-electronic instomants
- Electronic instomants
- Automatic Instomants.

Types of potentiometric titration's:

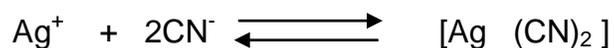
1.) Acid Base Titration:

The neutralization capacity of acids and bases is accompanied by charge in concc of H^+ and OH^- . The reference electrode used in this titration is N_2 colonel electrode.

A volume is acid to be titration is kept in a beaker along with a standard hydrogen electrode. It is connected to a N_2^- colonel electrode through a salt bridge. The hydrogen and colonel electrodes are connected to potentiometers, which records the EMF of solution. After each addition of base from burette into a beaker, the EMF is measured. The values of EMF are measured. The values of EMF are plotted against the volume of base added and the end point is obtained from graph.

2.) COMPLEXOMETRIC TITRATION'S:

They can be followed with an electrode of the metal whose ion is involved in complex formation. For e.g. a silver electrode may be used to follow the titration of a cyanide ion with a standard solution of silver. The silver ion concentration will be governed by the equilibrium constant for complex formation reaction.



At equivalence point

$$2[\text{Ag}^+] = [\text{CN}^-]$$

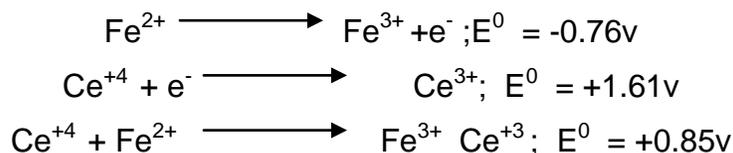
The solid silver cyanide begins to get precipitated seen after equivalence point. The further addition of silver neither changes the concentration of the complex nor changes the silver ion of any extent. So that the titration curve has an almost horizontal equivalent point.

3.) Oxidation-reduction Titrations:

Redox rxn can be followed by an inert indicator electrode. The electrode assumes a potential proportional to the logarithm of the concentration ratio of the two-oxidation states of the reactant or titrant which ever is capable of properly poisoning the electrode. These titrations involve the transfer of e^- from the substance being oxidised to substance being reduced.



The standard potential of the two half reactions are:



The equilibrium constant can be calculated by:

$$E^0 = \frac{0.0591}{n} \log_{10} K$$

4.) Precipitation Titrations:

Any Precipitation Titration that involves insoluble salts of metals such as mercury, silver, lead and copper may be followed potentiometrically. The indicator electrode may be made of the metal involved in the reaction or may be an electrode whose potential is governed by the conductance of the anion being precipitated. The magnitude of potential change at the end point depends on the solubility of the substance being Precipitated as well as conductance involved. The Titration of chloride ions with a standard solution of silver nitrate using a silver metal indicator electrode is an example.

Advantages: (over ordinary indicator method)

- I. The method can be used with coloured solution e.g. vinegar where ordinary titrations with suitable indicator fails.
- II. Used for analysis of dilute solution with accuracy.
- III. Used for titrating weak acid against weak base.
- IV. No need of external indicator in oxidation-reduction titrations.
- V. Made automatic by bringing relay into operations.
- VI. Titrations can be carried out on micro level i.e. dilution up to 10^{-5} is successful.
- VII. Differential titrations are possible.
- VIII. Along with end the information about sample and its rxn may be obtained by completely recording of potentiometric titration curve.
- IX. Method is considered to be very accurate.
- X. Apparatus used is not expensive & easily available.

APPLICATIONS:

- ✓ Used in titrations of amino acids, amines, zinc & manganese ions etc.

COLOUR METRIC ANALYSIS

Chemical systems which exhibit a selective light absorptive capacity are coloured and hence the term colour metric analysis are often applied to the measurement of such system when the object is to determine the concentration of the constituents responsible for the colour.

The variation of the colour of a system with change in concentration of the same component forms the basic of colour metric analysis; and it is concerned with the determination of the concentration of a substance by measurement of the relative absorption of light with respect to a known concentration of substance.

Colour metric analyses are of two types:

1. Visual Colorimetry:

This is the type of analysis in which natural or artificial white light is used as a light source and determinations are usually made with a colorimeter or colour comparator.

2. Visual Colorimetry:

In this type of analysis eye is replace by a photoelectric cell. The latter eliminates the error due to the personal characteristics of the observer. Photoelectric colorimeter is usually employed with light contained with in a comparatively narrow range of wavelengths obtained by passing white light through filters. Photoelectric colorimeter containing filters are also known as filter photometers.

➔ INSTRUMENTATION:

1) SOURCE:

The wavelength range of visible light lies between 4000 \AA^0 to 7500 \AA^0 . In this region a tungsten filament lamp is most widely used. Its construction is

similar to the household lamp. It contains a tungsten wire, which is heated in a controlled atmosphere. In order to get best results it is important that tungsten lamp should emit radiant energy, which should be constant over long periods of time, which can be achieved by constant power supply.

Requirement of radiation source:

- ✓ Must be stable.
- ✓ Must be of sufficient intensity for transmitted energy to be detected at the end of optical path.
- ✓ Must supply continuous radiation over entire wavelength region in which it is used.

2.) Filters and Monochromators:

- ✓ Filters: it is device, which allows light of required wavelength to pass but absorbs light of other wavelengths wholly or partially. A suitable filter and select a desired wave length band.

Filters are of two types:

a.) Absorption Filters:

It is a solid sheet of glass that has been coloured by a pigment, which is dissolved, or dispersed in glass. Dyed gelatine or similar materials can also be used.

B.) Interference Filters:

It is a semi transparent metal film on a plate of glass, and coated with a thin layer of some dielectric material followed by another coating of thin film of metal. When a ray of light is incident over on interference filter a part of light is incident over an interference filter a part of light reflects back where as the remaining light is transmitted, part of the incident radiation is reflected repeatedly by the metal layer but at each reflection some is transmitted outwards. The

several out-going rays undergo constructive interference for those wavelengths, which are exactly even multiples of distance separating the two.

B.) Monochromators:

It successfully isolated bands of wave lengths usually much more than a narrower filter, the essential elements of a monochromator are an entrance slit, a dispersing element and an exit slit. The function of a prism or a grating is to disperse the hetero chromic radiations into its component wavelengths.

3.) Slits:

There are two slits

- ✓ Entrance slit: Which provides a narrow source of light so that there is no over lapping of monochromatic images.
- ✓ Exit Slit: Which is a narrow band of dispersed spectrum for observation of detector.

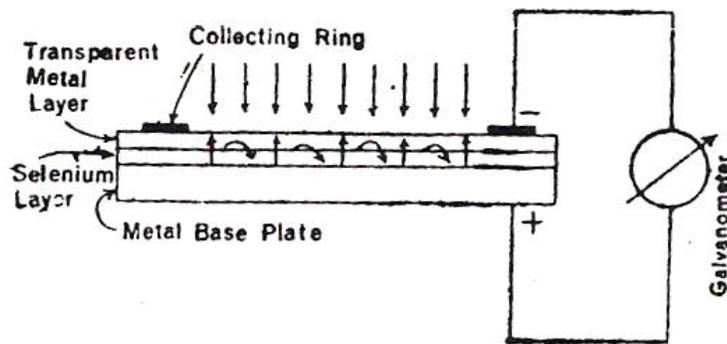
4.) Cells:

It should be transparent to the wavelengths region being recorded. The thickness is 1 cm (Internal Diameter) & made of colour corrected fused glass. May be rectangular or cylindrical in shape with flat ends.

5.) Detection of Radiation:

In order to detect radiations three types of photosensitive devices are photo voltaic cells, phototubes and photo multiplier tube

- a. **Photo voltaic cells:** It consists of a metal base plate like iron or aluminium which acts as one electrode on its surface a thin layer of a semi conductor metal like selenium is deposited. The surface of selenium is covered by a very thin layer of silver or gold, which acts as a second collector electrode.



When radiation is incident upon surface of selenium electrons are generated at the Se Ag interface, which are collected by silver and creates an electric voltage difference between silver surface and the base of cell. A photo current will flow which is directly proportional to the intensity of incident radiation beam.

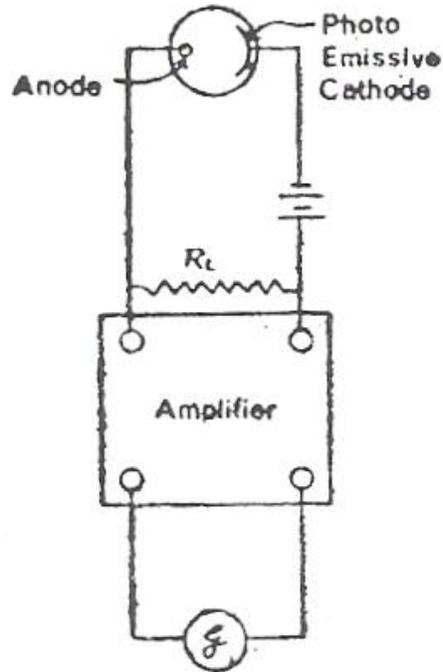
FACTS:

- 1) Photo voltaic cells are sensitive over the whole visible region but less sensitive in blue region than in green and yellow.
- 2) The Current output of the photo voltaic cell depends upon the wavelength of the incident light.
- 3) The Current produced by coal cannot be readily amplified by electronic circuits because of low internal resistance.
- 4.) They show fatigue effect. Initial photo current is high and it attains steady value after a few minutes.

b) Phototubes:

They are also called photo emissive cells. The choice of sample cell is based upon:

- a) The transmission characteristics at the desired wavelength
- b) The pathlength, shape & size



c) The relative expense

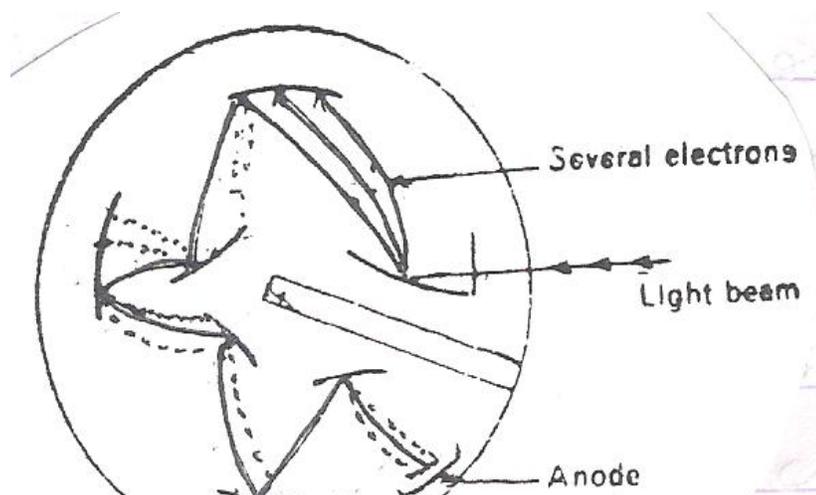
It consists of an evacuated glass bulb, which has a light sensitive cathode in form of half-cylinder of metal. The inner surface of cathode is coated with a light sensitive layer of caesium or potassium oxide and silver oxide, the metal ring inserted near the centre acts as anode.

When radiation is incident upon the cathode, photoelectrons are emitted, which are collected by anode.

Then returned via external circuit blue to the flow of these electrons there occurs an $I R$ drop across resistor, which is proportional to current. This current may be amplified. Phototubes are more sensitive than photovoltaic cells; as they have high internal resistance; their output currents can be easily amplified and these are employed for measuring low intensities of illumination.

C) PHOTOMULTIPLIER TUBES:

Employing photo multiplier tube can increase the sensitivity of photo emissive cells. It consists of electrode covered with a photo emissive material. This tube contains a large number of plates known as dynodes each dynode is covered with material, which emits several electrons for each electron striking on surface.



6.) POWER SUPPLY:

- ✓ Decreases the line voltage to the instruments operating level with a transformer.
- ✓ Converts A.C to D.C with a rectifier if D.C is requisite.
- ✓ Smothes out any ripple, which may occur in the line voltage in order to deliver constant voltage.

7.) VISUAL COMPARATORS:

Before photoelectric instruments were generally available colorimetric analysis were carried out by simple visual comparison methods.

The four important techniques for colour comparison are:

1. Multiple standard method
2. Duplication method
3. Dilution method
4. Balancing method

A) MULTIPLE STANDARD METHOD:

The unknown solution is taken in a 50 ml or 100 ml nessler tube and made up to the mark. The solution is thoroughly mixed. The colour of this unknown solution is compared with a series of standard solutions prepared with known amounts of ion under analysis. The concentration of the unknown solution will then be equal to that of the known solution whose colour it matches exactly. If exact match is not available one should prepare a further series of standard solutions with a narrower range of concentration until an exact match is available.

B). DUPLICATION METHOD:

The unknown solution is taken in one nessler tube followed by the development of colour with appropriate reagent and made up to mark. In another nessler tube the solution of developing reagent is taken and made up a little lower than the mark on the nessler tube from a burette a std. Solution is added to this nessler tube with constant agitation until a colour is unknown solution becomes duplicated in the tube.

C). DILUTION METHOD:

In this technique, two nessler tubes of equal diameter, height and made out of same quality of glass are used. To the first tube we add a std. Solution and to the second the solution with unknown concentrations. Light from the same source is allowed to pass through each cell and the emergent beams are compared. The more concentrated solution is progressively diluted until the intensity of light emerging from both cells becomes equal. At this point the concentrations per unit volume of solution in both the tubes should also be the same.

As the two beams are equal in intensity, the absorbance A is equal in each case: from beer's law;

$$A = \frac{-\log I_t}{I_0} = E l_1 C_1 \text{ (solution 1)}$$

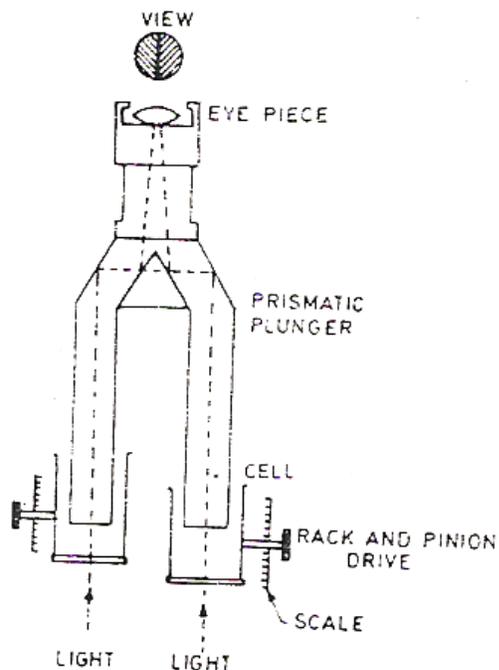
$$A = \frac{-\log I_t}{I_0} = E l_2 C_2 \text{ (solution 2)}$$

$$E l_1 C_1 = E l_2 C_2$$

$$\rightarrow C_1 = C_2$$

D.) BALANCING METHOD:

This is more elaborate arrangement for individually varying the length of the light path in two solutions so that a colour match may be secured visually.



Balance method is used for visual colour balancing. The unknown solution is taken into a cylinder or a tube with a flat transparent base. The standard solution is taken into a second cylinder. A transparent plunger is kept in each cylinder. The plungers are moved up and down until the colours seen from the top of each cylinder become identical from the reading of the depth of samples the concentration of the unknown can be evaluated.

TYPES OF PHOTO COLORIMETER:

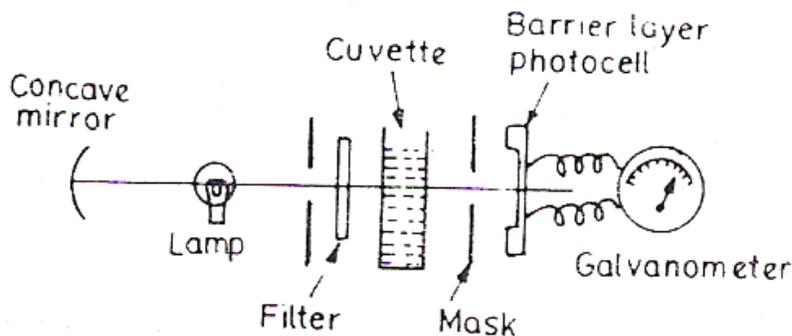
1. Single Beam Instrument:

The essential parts of a single beam instrument are:

- a.) Source of light with a concave reflector.
- b.) An adjustable diaphragm.
- c.) A coloured glass filter for monochromating light.
- d.) Cavetti for holding the adsorbing solution.
- e.) A single photocell to receive the radiation &
- f.) A directly connected galvanometer.

The current output of the cell is directly proportional to the radiant power falling upon it at a given wavelength.

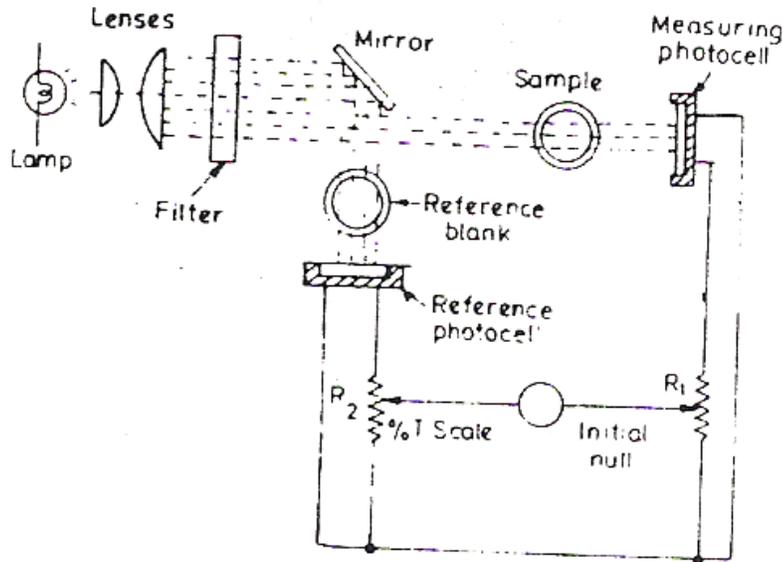
In order to determine the absorbance of the solution, the curette is filled up with pure solvent. Then the diaphragm is adjusted so that the meter reads full sealer. Now the solvent is replaced by solution without disturbing the diaphragm. Then the meter will read the percent transmittance from which the adsorbance of solution can be evaluated.



D.) DOUBLE BEAM INSTRUMENT:

In order to operate this instrument the null balana galvanometer is adjusted mechanically to bring the needle at midscale with lamp off. Then the lamp is switched on and blank solution is kept in both light beams. The potential dial R_2 is adjusted to read 100 percent Tran smittance and then slide wire contact R_1 is adjusted to null the galvanometer. Standard & unknown solutions are

introduced into the measurement beam and slide wire contact R_2 is adjusted to null the meter. The transmittance or absorbance can then be read off from the potentiometer dial.



ADVANTAGE OF DOUBLE BEAM:

- ✓ It is not necessary to can dually replace the blank with sample or to zero adjust at each wavelength as in the single beam.
- ✓ The ratio of powers of the sample and refe boom is constantly obtained & used. Any error due to variation in the intensity of source and fluctuation in the detector is minimized.
- ✓ Because of the previous two factors the double beam system lends it self to rapid seaming over a wide wavelength region and to the use of recorder or digital readout.

CODUCTOMETRY

Analysis based on measurement of conductivity in solution is called conduct metric analysis. The migrations of ions are responsible for the concentration of electricity in solutions. Hence two factors are involved speed of ions and their concentration.

MEASUREMENT OF CONDUCTIVITY:

a.) CONDUCTIVITY CELL:

The solution whose conductivity is to be determined is taken in a suitable cell. These cells are usually made of highly insoluble glass such as Pyrex or quartz and are fitted with platinum electrodes. The electrode consists of stout platinum plates.

Cells having short paths and large electrodes are employed for dilute solutions, while cells with long paths are used for concentrated.

b.) ELECTRODES:

Consists of two parallel sheets of stout platinum foil, that do not bend readily; their relative positions are fixed by sealing the connected tubes into sides of conductivity cells. In order to remove polarisation effects the electrode is coated with finely divided platinum black and these are called Platonised platinum electrode.

c.) CONDUCTIVITY WATER:

Absolute pure water has no conductance due to absence of dissolved impurities. Thus absolutely pure water is known as conductivity water.

d.) SOURCE OF ALTERNATING CURRENT:

Simple induction coil is generally found in operation, but doesn't give symmetrical alternating current. So a high frequency a-c generator or a Vreeland oscillator is used.

e.) METHOD OF MEASUREMENT:

Measure of conductivity is measurement of resistance so wheat stone bridge can be used.

APPLICATIONS OF CONDUCTIVITY MEASUREMENTS:

a.) SOLUBILITY OF SPARINGLY SOLUBLE SALT:

There are various substances such as AgCl, BaSO₄, Pb SO₄ etc. Which are regarded as insoluble or so sparingly soluble that their solubility cannot be determined by any chemical method. But this extreme small solubility of substance can be determined with help of conductivity.

b.) Ionic Product of water:

Pure water ionises to a very slight extent and so we have the equilibrium. The product of ionic concentration of H⁺ & -OH expressed in moles per litre is constant at constant temperature and is known as ionic product of water.

c.) Basicity of Acid:

According to Oswald the basicity of acid is given by

$$B = \frac{\lambda_{1024} - \lambda_{32}}{10.8}$$

Where λ_{1024} and λ_{32} denote the equivalent conductivities of sodium salts of the acid at dilutions of 1024 litres and 32 litres per gm equivalent.

d.) Conductometric titrations:

This method of analysis is applicable to ant titrations in which there is sharp change in conductivity at the end point. The determination of the end point of titration by means of conductivity measurement is known as conductometric titrations.

TYPE OF CONDUCTIVITY TITRATIONS

A.) Acid Base Titrations.

These are particularly well adapted to the conductometric end point because of very high conductance of reaction product.

- ✓ Strong acid with strong base.
- ✓ Strong acid with weak base.
- ✓ Weak acid with weak base.

B.) Acid Base Titrations.

When a stronger acid reacts with sodium or potassium salts of weak acid, the weaker acid will be replaced.



Only a slight increase in conductance is obtained up to the end point. This is because chloride ion has higher conductance than acetate ion. After end point it increases more rapidly owing to the addition of excess of hydrochloric acid.

C.) Precipitation Titrations:

These titrations cannot be carried out so effectively as the acid base titrations because acid base titrations are characterised by sharp breaks because both hydrogen and hydroxyl ions have very high equivalent conductance. It a cation is to be precipitated a titrant whose cation has the smallest possible mobility's selected. So maximum possible change in conductance during titration is assumed.



These titrations cannot be performed accurately because:

- ✓ Slow separation of precipitate.
- ✓ Absorption of ions on precipitate.

D.) Redox Titrations:

In these titrations there is a decrease in the hydrogen ion concentration.



Since the mobility of hydrogen ions is high, a sharp decrease in conductance is expected during the initial part of titration when initial concentration of acid is moderately high; the relative change in hydrogen ions conductance is very small.

E.) Complexometric Titrations:

In the titration of KCL with $\text{Hg}(\text{ClO}_4)_2$ Two breaks are obtained. The first break is due to formation of HgCl_4^{2-} and the second due to K_2HgCl_4



Conductometric titrations based upon precipitation or complex formation rxn are not so useful as those involving neutralisation process. Conductance changes during these titrations are generally not as large as those observed with acid base titrations. The factors such as a slowness of reaction and co precipitation are further source of difficulty with these titrations.

ADVANTAGES:

1. They can be used in case of coloured liquid where ordinary indicators cannot work.
2. They can be used for dilute solutions and also for very weak acids.
3. It is not necessary to measure the actual conductance value because we can use any quantity that is proportional to it.

DISADVANTAGES:

1. It becomes less accurate and less satisfactory with increasing total electrolytic concentration.
2. Although the method is potentially adaptable to all types of volumetric analysis the number is useful application to oxidation-reduction system is limited. The reason for this is that the substantial excess of hydronium ion typically needed for such reactions tends to mask conductivity changes associated with volumetric reactions.