M.Sc CHEMISTRY
(DISTANCE EDUCATION CENTRE – ACHARYA NAGARJUNA UNIVERSITY)

PAPER – V : ANALYTICAL CHEMISTRY
SYLLABUS

Unit – I
OPTICAL METHODS OF ANALYSIS PART-A

Ultraviolet rays and visible spectroscopy - Theory - Beer's law, limitations of Beer's law - different techniques to increase precision - instrumentation - applications - determination of stability constants - determination of pK values of an acid-base indicator - determination of molecular weight - simultaneous photometric determination - qualitative and quantitative analysis - phosphate, iron, ammonia, manganese, vanadium in complex matrices - photometric titrations .

Infrared spectroscopy - instrumentation - limitations - structure determination - quantitative analysis - base line technique.

Nephelometry and turbidimetry: Theory - instrumentation - differences between nephelometry and turbidimetry - turbidmetric titrations - applications.

Unit – II
OPTICAL METHODS OF ANALYSIS PART – B

Flourimetry and Phosphorimetry: Theory - fluorescence and phosphorescence - factors affecting flouroscence - relation between fluorescence and concentration - limitations - comparison of flourimetry and phosphorimetry – applications.

Flame Photometry: Principle - theory - instrumentation - experimental procedures - errors in flame photometry - applications.

Atomic Absorption Spectroscopy: Principle - theory - limitations - relation between atomic absorption spectroscopy and flame emission - instrumentation - interference of cation and anion - applications.

Unit – III
ELECTRO ANALYTICAL METHODS

Conducto metric analysis: Principle - measuring apparatus - applications to acid-base, precipitation and complexometric titrations.

Potentiometric methods: Principles and techniques - various types and complex formation reactions, types of electrodes, applications of pH, red ox, precipitation and complex formation reactions.

Polarography: Introduction, decomposition, potential and over voltage, instrumentation and general techniques, reaction at dropping mercury electrode, its uses in detection and determination of substances and amperometric titrations.

Electro analysis–Electrogravimetry: Constant current and controlled potential techniques

Coulometric analysis: Controlled potential and constant current techniques.

Unit – IV
SEPERATION TECHNIQUES

Solvent extraction: Introduction, principle, techniques, factors affecting solvent extraction, quantitative treatment of solvent extraction, equilibria - chelate and ion association system - synergism

Ion exchange methods: Introduction, action of ion exchange resins, separation of inorganic mixtures, applications.

CHROMATOGRAPHY: Part - A

Introduction - column, paper chromatography, thin layer chromatography

CHROMATOGRAPHY: Part - B

Introduction - Gas chromatography and High Performance (Pressure) Liquid Chromatography (HPLC)

Books suggested:

1. A.I. Vogel-A text book of quantitative Inorganic analysis-III Edition-ELBS,
2. D.A.Skoog, D.M.West and F.J.Holler—Fundamentals of Analytical Chemistry, Harcourt Asia
3. D.A.Skoog, F.J.Holler and T.A.Nieman-principles of Instrumental Analysis, Harcourt Asia
4. J.W.Robbinson, Undergraduate Instrumental Analysis, Marcel Decker
5. B.K.Sharma -- Instrumental Methods of Chemical Analysis, Goel publishers
6. H.Kaur – Instrumental Methods of Chemical Analysis, Pragathi Prakasan
7. G.R.Chatwal and S.Anand–Instrumental Methods of Chemical Analysis, Himalaya Publishing House
8. H.H.Willard, LL Merrit and JA Dean – Instrumental Methods of Analysis., Affiliated East West Press, New Delhi
9. R.A.day and A.L.Underwood – Quantitative Analysis, Prentice Hall India Pvt.
10. G.W.Eving – Instrumental Methods of Chemical Analysis, McGraw Hill Kogakusha
11. P.B.Janardhan, Physico – Chemical Techniques of Analysis (Vol I) – Asia Publishing House.
12. G.R.Chatwal – Analytical Chromatography, Himalaya Publishing House
13. J.J.Lingane, Electro Analytical Chemistry – Interscience Publishers
14. J.A.Barnard and R.Chayan – Modern Methods of Chemical Analysis, McGraw Hill ,London
15. M.N.Satri – Separation Methods, Himalaya publishing House.
16. G.H.Morrison and H.Freiser –Solvent Extraction in Analytical Chemistry, John Wiley & Sons Inc., London.
17. B.F.Pease –Basic Instrumental Analysis, D.Van Nostrand Company.
18. Subhash - Satish and V.P.Kudesia, Spectrum Analysis, Pragathi Prakasan.

Acknowledgements

The authors wish to thank with gratitude the various authors and publishers of the above mentioned books as they have used the figures, diagrams and data at times directly or in a modified form. They also wish to thank the services of Ms.B.Jyothirmai in the preparation of this study material in several ways.

CONTENTS

UNIT 1

COLORIMETRY AND VISIBLE SPECTROPHOTOMETRY

Lesson 1

Objectives of the lesson:
This lesson deals with General Introduction, Basis for colorimetric estimations, Developments in photometric determinations, instrumentation.

INTRODUCTION:

Absorption spectrophotometry is quite useful physical method for quantitative analysis.

Spectrophotometry is generally concerned with ultraviolet (400–200nm) and visible (800–400nm) region. Colorimetry is concerned with the visible region of the spectrum.

Approximate wavelength s of light

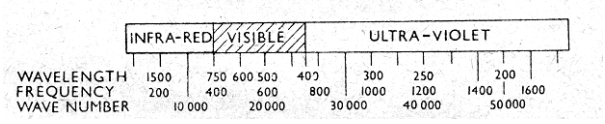
Colour	nm
Ultra violet	<400
Violet	400 - 450
Blue	450 -500
Green	500 - 570
Yellow	570 -590
Orange	590 - 620
Red	620 - 760
Infra red	> 760

Spectrometer is useful in producing coloured light of any selected colour (wave length) and when used as a part of spectrophotometer it is termed as a monochromator and it is generally calibrated in wavelength (nm) or nanometer. Photometer is a device for measuring the intensity of light. The combination of spectrometer and photometer i.e., the instrument can produce any selected light (i.e. of wavelength) and can measure the intensity of the said light.

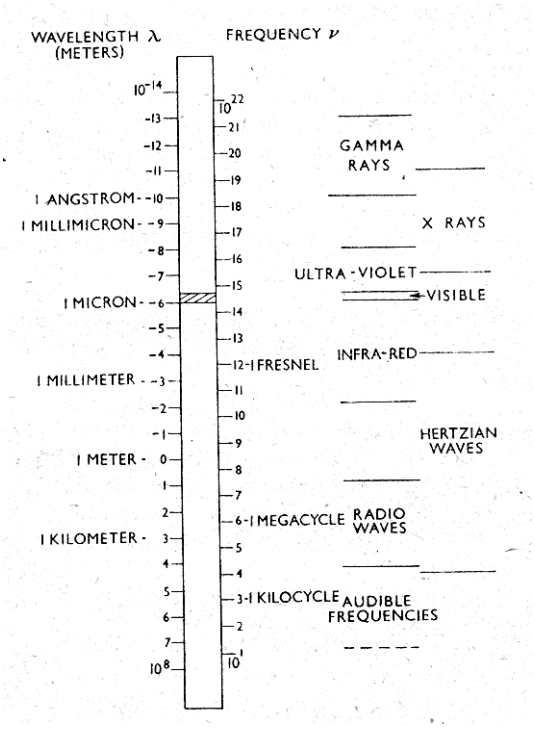
Electromagnetic Spectrum:

The approximate limits of wavelength and frequency of various types of radiations including the frequency range of sound waves will be as shown in figure.

The particular wave length region with which the present topic is connected is shown below:



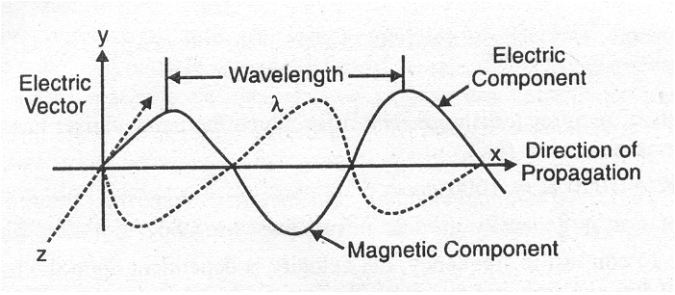
The electromagnetic waves are usually described in terms of wavelength (λ). It is the distance between two peaks or troughs in centimeters. Wave number ($\bar{\upsilon}$) tells about the quantity, that is number of waves in one centimeter. Frequency (ν) is the number of waves per second.



Electro Magnetic Spectrum

The above three quantities are interrelated

$$\frac{1}{wave..length} = \text{wave number} = \frac{frequency}{velocity}$$



1Angstrom unit = 10^{-10} metres = 10^{-8} cm

1 Micron (μ) = 10^{4} A = 10^{-6} m = 10^{-4} cm

1 Milli micron (mμ) = 10 A or 10^{-7} cm

The velocity of light generally represented as 'C' is equal to 2.99 x 10^{10} cm / second

Wave number ($\bar{\upsilon}$) = $\frac{1}{\lambda}$ waves cm^{-1}

Frequency (ν) = $\frac{c}{\lambda} = \frac{3x10^{10}}{\lambda}$ waves sec^{-1}

1 Fresnel unit (f) = $\frac{3x10^{-2}}{\lambda}$ waves sec^{-1}

We are able to say a particular thing is red, when all other colours are absorbed and only red colour is retransmitted. The black board is appearing black since it absorbs all colours. The black colour absorbs all light from the sun and radiates heat. When all colours are retransmitted then it will be white in colour.

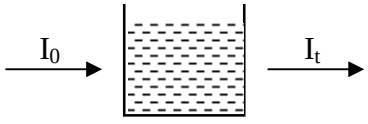
Basis of Colorimetry:

The variation of colour or its intensity of a system with change in concentration of one of the components forms the basis for colorimetric analysis. The colour is usually due to the formation of coloured compound by the addition of an appropriate reagent or it may be inherent in the desired constituent itself. The intensity of the colour can be compared with that obtained by treating the known amount of substance in the same manner. Colorimetry is concerned with the determination of the concentration of a substance by the measurement of the relative absorption of light with respect to known concentration of the substance.

When light falls on a system the incident energy may be transmitted, reflected and absorbed.

$$I_o = I_t + I_a + I_r \quad \ldots\ldots\ldots\ldots (1)$$

where I_o = intensity of the incident light
I_t = intensity of the transmitted light
I_a = intensity of the absorbed light
I_r = intensity of the reflected light



In practice when same cuvette is used for series of analyses (analytical measurements) the intensity of reflected light may be regarded as constant and small (about 4%) and hence may be neglected.

$$I_o = I_t + I_a \quad \ldots\ldots\ldots\ldots (2)$$

The relationship between the intensity of absorbed light / transmitted light and thickness of the medium has been given by Lambert (1760). The law states that "*when monochromatic light passes through a transparent medium the rate of decrease in intensity with the thickness of the medium is proportional to the intensity of light*". In other words it can be stated that- "*The intensity of the emitted light decreases exponentially as the thickness of the absorbing medium increases arithmetically*".

This can be expressed as

$$\frac{-dI}{dt} = kI \qquad \ldots\ldots\ldots\ldots (3)$$

where I is the intensity of the incident light of wave length (λ)

t is the thickness of the medium and k is a proportionality factor

Integrating equation (3) and substituting $I = I_o$ when $t = t_o$

we have $ln\ I_o / I_t = kt$

$$I_t = I_o .e^{-kt} \qquad \ldots\ldots\ldots\ldots (4)$$

where I_o = intensity of the incident light

I_t = intensity of the transmitted light

k = constant known as absorption coefficient

Converting natural logarithms to normal logarithms we get

$$I_t = I_o .10^{-0.4343\ k\ t} = I_o .10^{-K\ t} \qquad \ldots\ldots\ldots\ldots (5)$$

where K = 0.4343 k (or k / 2.3026) and it is the ***extinction coefficient*** and can be defined from the equation (5)

"It is the reciprocal of the thickness (t cm) which is required to reduce the light to $1/10^{th}$ of its intensity."

$$\therefore I_t / I_0 = 0.1 = 10^{-Kt} \qquad \ldots\ldots\ldots\ldots (6)$$

or $Kt = 1 \qquad K = 1/t$

The ratio I_t / I_o is the fraction of the incident light transmitted through a thickness 't' of the medium and is termed as ***transmittance*** (T). The ratio $\log I_o / I_t$ is termed as ***absorbance*** (A) or Optical Density (OD) of the medium. The ratio I_o / I_t is termed as ***opacity***.

Then $D = \log I_o / I_t \qquad \ldots\ldots\ldots\ldots (7a)$

Lamberts law shows the log relationship between the transmittance and the length of the optical path passing through the sample. Beer (1852) observed a similar relationship between concentration and transmittance. "The intensity of a beam of monochromatic light decreases exponentially with the increase in concentration of the absorbing substance arithmetically". Thus we can write

$$I_t = I_o .e^{-k' C} \qquad \ldots\ldots\ldots\ldots (7b)$$

$$I_t = I_o .10^{-0.4343\ k' C} \qquad \ldots\ldots\ldots\ldots (8)$$

$$I_t = I_o .10^{-K' C} \qquad \ldots\ldots\ldots\ldots (9)$$

C = concentration of absorbing substance, k' and K' are constants.

On combining equations (5) and (9)

$$I_t = I_o . 10^{-act} \qquad \ldots\ldots\ldots\ldots (10)$$

Thus the above equation is termed as the mathematical statement of Beer - Lamberts Law. This is of fundamental importance in spectrophotometry or colorimetry. In equation 10 the value of 'a' depends

up on unit of concentration. If 'C' is expressed in g mole / lit and 't' in centimetre, then 'a' can be replaced by symbol '$\in$' which is termed as ***molar absorption coefficient*** or ***molar absorptivity*** or ***molar extinction coefficient***.

$$OD = \text{Optical density} = \in Ct$$

where $OD = \log I_o / I_t = \log 1 / T = - \log T$

The specific extension coefficient E_s may be defined as the extinction or optical density per unit thickness (path length) and unit concentration.

Developments in photometric determination or measurements:

Standard Series Method:

Test solution contained in a Nessler's tube is diluted to a definite volume thoroughly mixed, and its colour is compared with a series of standards similarly prepared. The concentration of unknown is then of course equal to that of the known solution whose colour matches with it exactly. The accuracy may be ± 3% to as high as ± 8%.

Duplication Method:

A standard solution of the component under determination is added to the reagent until the colour produced matches to that of unknown sample in the same volume of sample.

Dilution Method:

The sample and standard solutions are contained in glass tubes of the same diameters and are observed horizontally through tubes. The more concentrated solution is diluted until the colours are identical in intensity when observed horizontally through same thickness of solution. The relative concentration of the original solutions is then proportional to the heights of the solution.

Balancing Method:

The comparison is made in two tubes and the height of the liquid in one tube is adjusted so that when both the tubes are observed vertically the colour intensities in two tubes are identical.

Photoelectric photometer:

Human eye is replaced by means of photoelectric detector.

Spectrophotometer:

It is a combination of spectrometer and a photometer. Spectro meter when used in the system is known as monochromator which is essential for the production of desired specific wave length of radiation for the process of measurement.

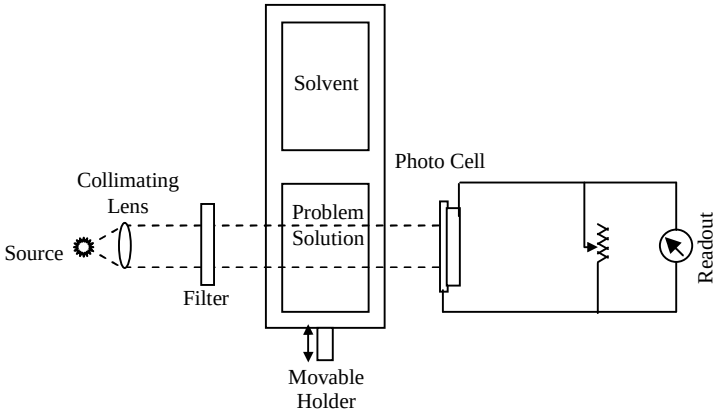
Photometer portion of this instrument is useful to measure the intensity of the light radiation transmitted or absorbed while passing through the solution. The following table illustrates the specific coloured light (hue transmitted) which is suitable for the measurement of the colour intensity of the solution mentioned as complimentary colour.

Complementary colours

Wave length	Transmittance	Complementary
400 - 435	Violet	Yellowish green
435 - 480	Blue	Yellow
480 - 490	Greenish blue	Orange
490 - 500	Bluish green	Red
500 - 560	Green	Purple
560 - 580	Yellowish green	Violet
580 - 595	Yellow	Blue
595 - 610	Orange	Greenish blue
610 - 750	Red	Bluish green

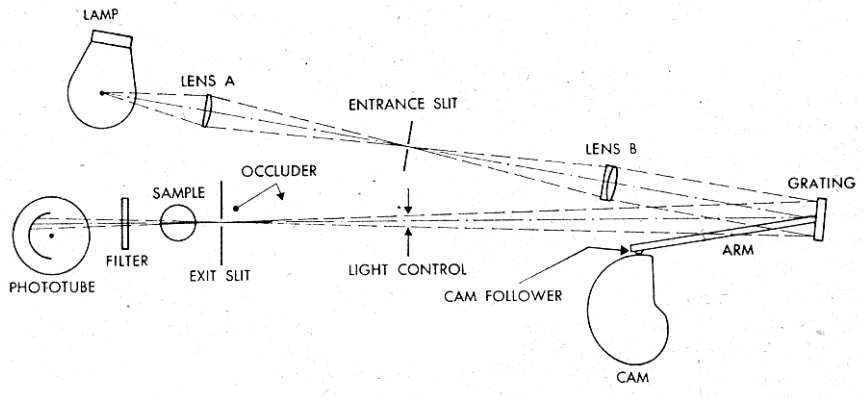
INSTRUMENTATION:

Photoelectric Colorimeter:



The instrument consists of a source, a collimating lens, a filter, a movable cell holder and readout mechanism. The light emerging from the source will be allowed to pass through the collimating lens to converge the beam and passes through the filter for the selection of a particular colour useful for the measurement of the colour of the problem solution. The readout mechanism is capable of giving out the transmittance or absorbance pertaining to both blank (solvent) and the sample (solution).

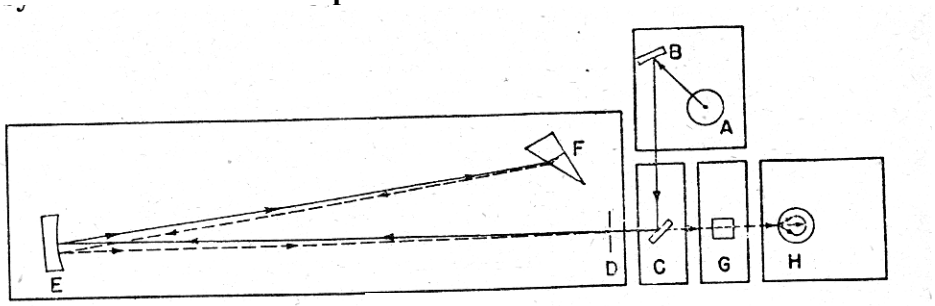
Bausch and Lomb Spectronic 20 colorimeter:



In the above instrument white light from the tungsten lamp is allowed to pass through lens A and the entrance slit. Lens B collects the light from the entrance slit and refocuses it onto the exit slit after it

has been reflected and dispersed by the diffraction grating. The grating has a provision for rotation by means of an arm which is moved when the cam is rotated in order to obtain various desired wavelengths. Provision for locating the wavelength is made through a scale fastened to the shaft. The monochromatic light passing through the exit slit goes through the sample to be measured and falls upon the filter and then passes to photo tube. Cuvettes or special type of test tubes are used as containers for the samples. For routine work, the wavelength control is rotated until the desired wavelength in nm indicated on the wavelength scale. The amplifier control is adjusted to bring the meter reading to zero on the percent transmission scale or ∞ on the optical density (OD) scale. The test tube or cuvette is then inserted in the cuvette holder having the blank (or solvent) and then rotated for 100% transmission. This indicates that the blank has no absorption and is capable of transmitting the light with 100% efficiency. Then the unknown sample is inserted in place of blank, the percent transmittance or OD is read directly from the meter without making any manipulation.

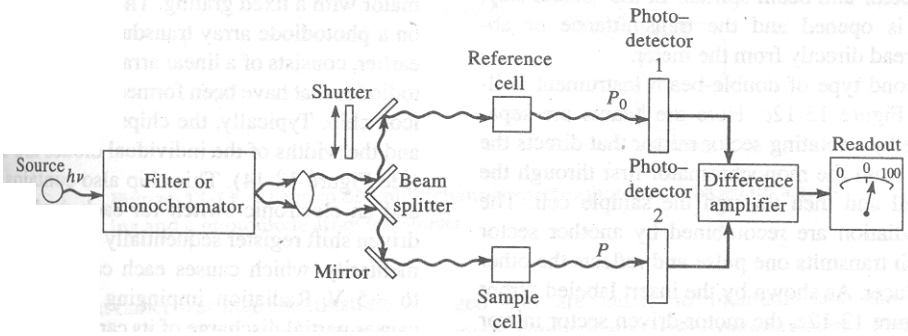
Beckmann DU ultra violet and Visible spectrometer:



This is a precision instrument. Two interchangeable light sources are used: a tungsten filament lamp and a hydrogen discharge lamp. Two photo cells are employed : a red sensitive photo tube for use above 600 mμ and a blue sensitive photo tube for use in the range 320 – 625 mμ (tungsten lamp) and 210-360 mμ (hydrogen lamp). It employs a quartz prism with a concave mirror. The wavelength range is from 210 to 1000 nm and the wavelength scale readings are accurate to 0.5 nm.

An image of light source (A) is focused by condensing mirror (B) and the diagonal mirror(C) and on the entrance slit (D). The entrance slit is the lower of the two slits vertically over each other. Light falling on the collimating mirror (E) is rendered parallel and reflected toward the Quartz prism (F). The back surface of the prism is aluminized so as the refracted light at the first surface is reflected back through the prism undergoing further refraction as it emerges from the outer surface of prism. The collimating mirror focuses the spectrum in the plane of the slits D, and the light of the wavelength for which the prism is set passes out of the monochromator through the exit (upper) slit, through the absorption cell (G) and to the photocell (H). The photocell response is amplified and registered on the null meter.

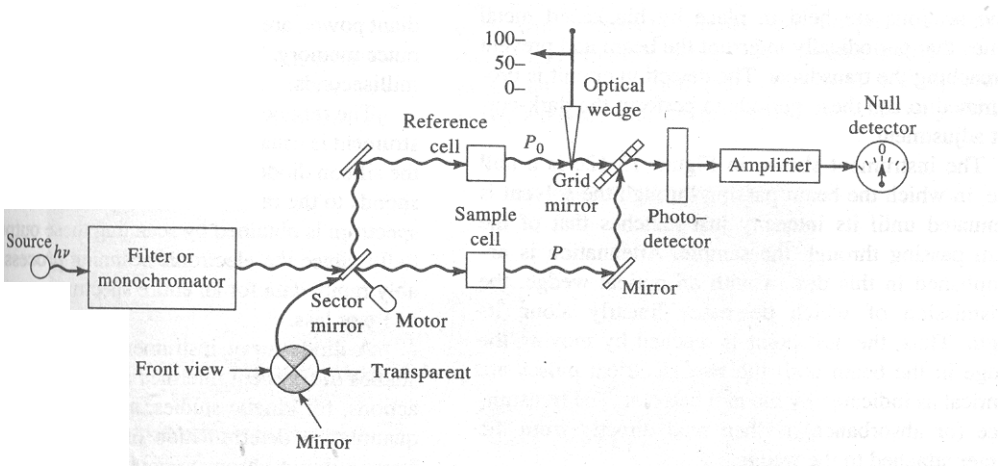
Double Beam instrument with beam separated in space:



In double beam separated in space instrument the beam hν from the monochromator is split into two equal parts, one half passes through the blank to the reference detector, the other through the sample to the sample detector. The output from the two detectors is electrically balanced, amplified if necessary, and the ratio of the two outputs is fed to the read out device.

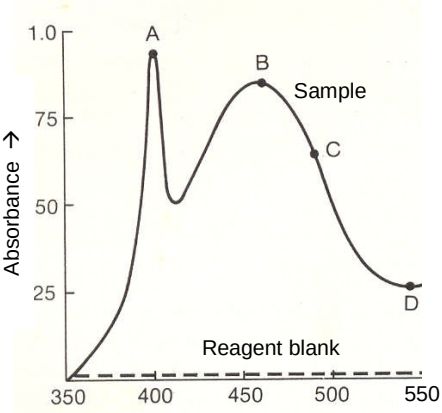
This design suffers from the disadvantage of requiring two detector units. In addition, the power of the beam from the monochromator hν is cut in half by the beam divider to form the respective powers of the reference P_0 and sample, P beams. This loss of power must be compensated for by the addition of either more sensitive detectors or more powerful amplifiers.

Double beam instrument with beams separated in time:



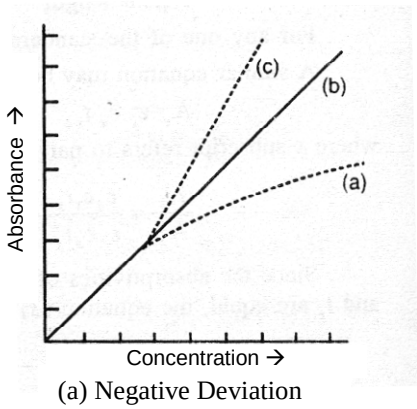
In the above beams separated in time design the full energy from the source lamp is alternated between the reference and sample beams at a fixed frequency. The reference power P_0 and sample power P, are alternatively read by the single detector, the required electrical corrections are made. The ratio of P / P_0 is determined, amplified if necessary and fed to the read out device.

Absorption Spectrum:



For adopting a colorimetric procedure for quantitative determination we must have knowledge about the absorption spectra. The absorption spectrum is nothing but a graphical representation of the optical density (OD) versus the wavelength. The purpose of taking the absorption spectrum is to have an idea about the absorption maximum (λ_{max}) at which place the various determinations pertaining to that complex can be taken. The bold line indicates the absorption spectrum of the sample while the dotted line indicates that of reagent blank. We can conclude that the λ_{max} is 460 nm from the figure since A is at 400nm which comes under ultraviolet region.

Importance of Beer's law:



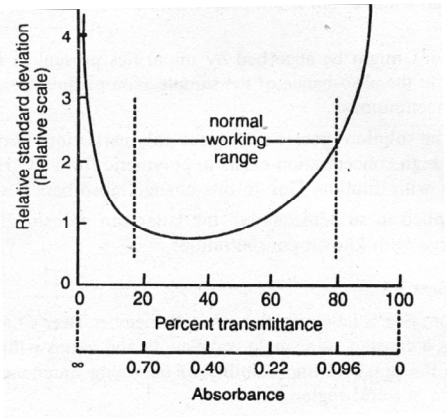
(a) Negative Deviation
(b) Without Deviation
(c) Positive Deviation

Beers law is a plot drawn for optical density versus the concentration where the colour intensity is measured at the absorption maximum (λ_{max}). As we know earlier the intensity of the beam of monochromatic light decreases exponentially with the increase in concentration of the absorbing substance arithmetically. In other words there is a direct proportionality between the concentrations of a particular species to the optical density measured. A plot for these two will generally give a straight line passing through the origin. However, there may be a positive or negative deviation in the curve as shown in the figure owing to the modifications and reorientations that are occurring with in the solution.

The deviations in the Beer's law may be due to the following reasons:

(i) The deviations may be due to the ionization, dissociation or association of the coloured solute in the solution.
(ii) Deviations may also occur due to the presence of impurities that may absorb at the same wavelength or due to the fluorescence behaviour of some of the impurities.
(iii) In the absence of the monochromatic light we can expect deviations in Beer's law. The deviations also depend upon improper slit width since it allows undesirable radiations to fall on the detectors.
(iv) Deviations may occur if the solute undergoes polymerization.
(v) Beer's law cannot be applied due to the presence of suspensions because it leads to errors in measurement of the colour.

Errors in spectrophotometric determinations:



We have OD = $\epsilon ct = \log 1/T$. In general the instruments read out scales are calibrated in both the absorbance and percent transmittance. Although it eliminates the laborious process of conversion of percent transmittance to the absorbance values, it may lead to an error, which is not readily apparent. Let us examine a relative error curve for single beam instrument.

The relative error reaches a minimum at 36.8% transmittance (OD=0.434). This means that the most precise readings will be obtained at near these values. The curve also shows that relative error increases sharply on either side of the scale. In general, it is advisable to have the measurements between 15% transmittance (OD = 0.824) and 80% transmittance (OD = 0.097) to have good photometric determinations.

General remarks on colorimetric determinations:

(i) It will give more accurate results at low concentrations than the corresponding volumetric or gravimetric procedure. Colorimetric procedures are simpler to carryout the experiment.
(ii) It can be applied there where no gravimetric or volumetric procedures exists. For example, for certain biological substances.
(iii) It is useful for routine type of work.
(iv) The technique is rapid without scarifying accuracy.

Criteria for satisfactory colorimetric analysis:

(i) *Specificity*: By utilizing such devices as introduction of complex forming compounds, altering the oxidation states, control of pH, specificity may be attained. Hence can be considered as selective.
(ii) *Proportionality between colour and concentration:* System should follow Beer's law.
(iii) *Stability of colour*: It should be stable for sufficient time to take readings.
(iv) *Reproducibility*: They must give reproducible results.
(v) *Clarity of the solution*: The solution must be free from precipitate. Turbidity scatters as well as absorbs the light.
(vi) *High sensitivity*: It is highly desirable particularly when minute amounts of substances are to be determined.

Other processes to render colour reactions specific and / or to separate one individual substance.

(a) Suppression of the action of interfering substance by the formation of complex ions or non-reactive complexes.
(b) Adjustment of pH.
(c) Removal of interfering substance by extraction or by some other chemical processes.
(d) Isolation of substance.
(e) Separation by volatilisation.
(f) Separation techniques like ion exchange or chromatography.

UNIT 1

APPLICATIONS OF COLORIMETRY AND VISIBLE SPECTROPHOTOMETRY

Lesson 2

Objectives of the lesson:

This lesson deals with the applications of the method for establishment of composition in complexes, their determination, and other applications of specific nature.

I. Determination of composition of a complex:

Organo metallic compounds, in general, shows selective absorption in the visible and ultraviolet regions. This property has been widely used in determining their composition as well as their stability constants. This can be determined by using three methods.

1. Continuous variation method
2. Mole ratio method
3. Slope ratio method

1. The method of Continuous Variations:

This method was first proposed by Job and later modified by Vosburgh and Cooper in 1941. In this method the equimolar concentration solutions of metal (M) and ligand (L) are used. A series of solutions are prepared in which the sum of formal concentrations of M and L is the same while their ratios vary. The absorbances are recorded at each mole fraction either with respect to metal or with respect to ligand.

The absorption is then plotted against the mole fraction of one of the reactants, that is,

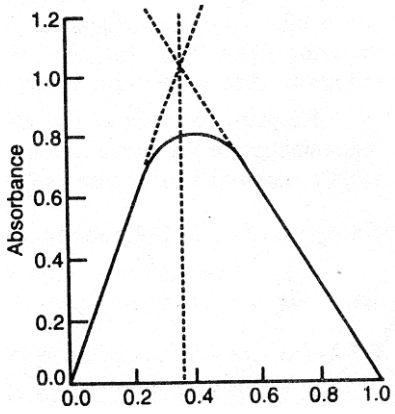
$$\frac{[M]}{[M]+[L]} \quad \text{or} \quad \frac{[L]}{[M]+[L]}$$

where [M] = concentration of cation in solution

[L] = concentration of ligand

The resulting curve will show a maximum at a mole ratio corresponding to the ratio of metal and the ligand in the complex.

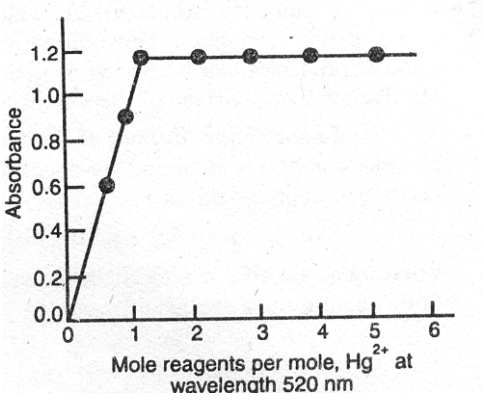
Ex: Complex of formula ML_2 is shown in the figure



Since the maximum is occurred when $\frac{[M]}{[M]+[L]}$ = 0.33, the above experiment suggests that the formula of complex is ML_2.

2. Mole Ratio Method:

This method is introduced by Yoe and Jones. In this method, the absorbances are measured for a series of solutions, which contains varying amounts of one constituent say (L) with a constant amount of the other (M). A plot is prepared for absorbances as a function of moles of ligand while keeping the concentration of metal constant. This is expected to give a straight



line from origin till the point, where sufficient number of moles of ligand was supplied to the metal to form a complex of the type ML_n where 'n' is an integer. Then the curve becomes horizontal since one of the constituents (M) is totally used up. Further addition of ligand will not enhance the intensity of the colour. The point of intersection or the intersection of the extrapolated lines of these two lines will indicate the number of moles of ligand (L) required for the formation of a complex with the metal (M). In present case the figure indicates a 1**:**1 complex.

3. The Slope Ratio Method:

The slope ratio method of Harvey and Manning is applicable only to systems in which a single complex is formed and is particularly useful for weak complexes. According to this method complex formation reaction can be forced to completion in the presence of a large excess of other reactant and Beer's law is followed.

For the reaction $mM + nL = M_mL_n$

The method becomes inapplicable if more than one complex is formed at the same time.

II. Determination of instability constants:

Mole ratio method can be used to evaluate the instability constants of the complexes. If the complex contains metal ion (M) and the ligand (L) in the ratio 1**:**n the reaction may be written as follows:

M	+	nL	= ML_n	
0		0	C	------- (initial concentrations)
$C\alpha$		$nC\alpha$	$C(1-\alpha)$	------- (equilibrium concentrations)

The instability constant (β) is given by

$$\beta = \frac{(C\alpha)(nC\alpha)^n}{C(1-\alpha)}$$

where C is the concentration of the complex in moles/lit

α is the degree of dissociation.

The value of α can be evaluated from the following expression

$$\alpha = \frac{E_m - E_s}{E_m}$$

where E_m is maximum absorbance in the presence of large excess of reagent sufficient for complexing the total metal and

E_s is the value of absorbance when the metal and ligand are present in the stoichiometric ratio (1**:**n).

The values of E_m and E_s are deduced from the mole ratio plot and the value of β can be evaluated.

III. Determination of stability constants (by Bent and French method):

The stoichiometric ratio of metal to ligand in case of free complexes is frequently determined by logarithmic method of Bent and French.

Let us assume

$$M + nLH = ML_n + n\,H^+$$

Where M stands for the metal LH stands for the ligand and n is the integral number. The formation constant K can be written as

$$K = \frac{[ML_n][H^+]^n}{[M][LH]^n} \quad ; \quad K[LH]^n = \frac{[ML_n][H^+]^n}{[M]}$$

On taking logarithm on both the sides we have

$$\log K + n \log [LH] = \log \frac{[ML_n][H^+]^n}{[M]}$$

In presence of large excess of ligand, the equilibrium concentration of the ligand is practically the same as added. From the above equation it is seen that a plot of log [LH] vs $\frac{[ML_n][H^+]^n}{[M]}$ will give a straight line with a slope equal to n i.e., the number of the ligand species involved in the complex formation, the intercept is equal to log K. Thus, the stability constant can be calculated from such a plot.

IV. Determination of Molecular weight:

If an unknown compound be treated to form a derivative in which a chromophore of known '$\in$' value is incorporated, the molar concentration of the chromophore may be obtained spectrophotometrically. This provides a simple method for determining molecular weight. Although the molar absorptivity of the absorption band remains constant in all the derivatives, the absorbance (A) will depend upon the molar concentration and hence the molecular weight of the molecule of interest can be determined. The molecular weight (M) may be determined spectrophotometrically from the relation

$$M = \frac{wb}{A}$$

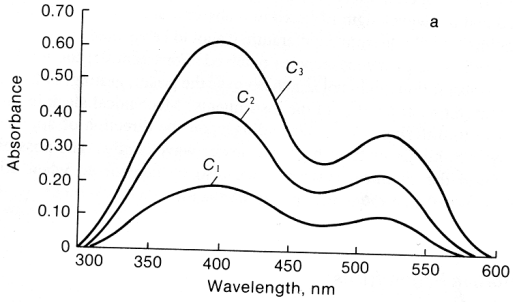
where w = weight of the compound in grams per litre

b = thickness of the medium

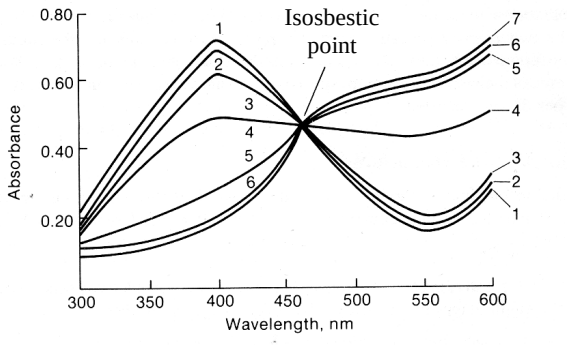
It is assumed in this method that '$\in$' is not affected by intra or intermolecular forces, and that no interfering bands exist. Picric acid and picrate salts of amines absorb at 380nm. With a molar absorption of 13,400 and an accuracy of ± 2% was obtained for the spectrophotometric determination of molecular weights of amines. Molecular weight determinations have been reported for sugars from the absorption spectra of their osazones of aldehydes and ketones from the absorption spectra of their 2,4- dinitro phenyl hydrazones and of saturated alcohols from the absorption of their β - 2,4-dinitro phenyl propionyl esters.

Comparison of Spectra:

The absorption spectra for various concentrations of a hypothetical compound are shown in the figure. In this ***family of curves*** it is difficult to qualitatively compare two curves in view of the change in the shapes with the change in concentration.



Proof of two equilibria:



In a solution of an acid -base indicator HX

$$\underset{\text{acid}}{HX} = H^+ + \underset{\text{base}}{X^-}$$

where HX is acidic and X^- is the basic form of the indicator. With pH change there will be a family of curves as depicted in the figure provided both HX and X^- absorb over the wave length region under study. The common point at which all these curves cross is known as ***isosbestic point.*** At this point of wavelength the absorbance of all the curves is one and the same. This is a proof of two absorbing species. Generally it happens when we come across two inter convertible species which can absorb in the same spectral region i.e., in case of oxidation reduction, chelation as well as acid base equilibria.

Determination of pK and pH value of an acid base indicator:

In a solution of an acid - base indicator HX

$$\underset{\text{acid}}{HX} = H^+ + \underset{\text{base}}{X^-}$$

where HX is acidic and X^- is the base form of the indicator,

Total concentration of the indicator is constant and the ratio of acid to base ([HX] to $[X^-]$) changes with pH. At relatively low pH (high acidity) the above equilibrium shifts to the left. Curve - 1 represents HX (acid); and curve -7 that of basic form. X^- would be obtained from highly basic solutions.

The equilibrium constant is

$$k = \frac{[H^+][X^-]}{[HX]}$$

Taking logarithms on both sides

$$\log k = \log [H^+] + \log \frac{[X^-]}{[HX]}$$

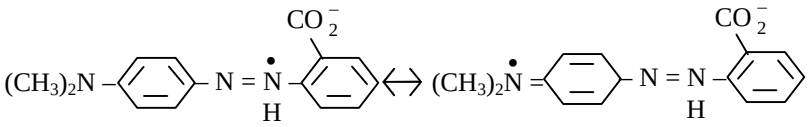
when the ratio $[X^-] / [HX]$ is one, it becomes $\log k = \log [H^+]$ and hence pK = pH

The absorbance values at 400nm reflect the concentration of HX and decreases as the concentration of HX decreases (pH increases). Where as those at 550nm reflect the concentration of $[X^-]$ and increases as $[X^-]$ increases (HX decreases)

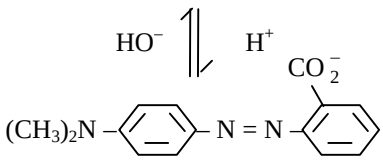
Spectro photometric determination of pK value of an indicator:

Discussion:(Acid dissociation constant of Methyl Red)

The dissociation of an acid-base indicator is well suited to spectrophotometric study. The procedures involved will be illustrated by the determination of the acid dissociation constant of methyl red (MR). The acidic (HMR) and basic (MR^-) forms of methyl red are shown below.



ACID FORM (HMR) RED



BASIC FORM (MR^-) YELLOW

The acid dissociation constant K is given by equation:

$$K = \frac{[H^+][MR^-]}{[HMR]} \dashrightarrow (1)$$

$$pK = pH - \log \frac{[MR^-]}{[HMR]} \dashrightarrow (2)$$

Both HMR and MR^- have strong absorption peaks in the visible portion of the spectrum; the colour change interval from pH 4 to pH 6 can be conveniently obtained with sodium acetate - acetic acid buffer system. The determination of pK involves three steps:

a) Evaluation of the wavelength at which HMR (λ_A) and MR^- (λ_B) exhibit maximum absorption.

b) Verification of Beer's law for both HMR and MR^- at wavelengths λ_A and λ_B.

c) Determination of the relative amounts of HMR and MR^- present in the solution as a function of pH.

By using the same concentration of indicator in each of the measurements at different values of pH and measuring the optical density for each solution at λ_A and λ_B, the relative amounts of HMR and MR^- in solution can be calculated from the two equations

$$D_A = d_{A.HMR}[HMR] + d_{A.MR^-}[MR^-] \text{-----3}$$

$$D_B = d_{B.HMR}[HMR] + d_{B.MR^-}[MR^-] \text{-----4}$$

Where $d_{A.HMR}$, $d_{A.MR^-}$, $d_{B.HMR}$, $d_{B.MR^-}$ are derived from the Beer's law plots plotted for both HMR and MR^- at wavelengths λ_A and λ_B. By solving these two simultaneous equations, the ratio $[MR^-]$ / [HMR] can be obtained and hence pK with the aid of equation (2). Equations (3) and (4) imply that the observed optical densities at λ_A and λ_B are simple additive sums of the absorbance's (optical densities) due to HMR and MR^-.

Simultaneous Photometric Determination:

Criteria:

The pre condition is that both the systems should not interact with each other. Then it can be granted for that optical densities are additive, they should have different absorption maxima provided

$$D_{\lambda_1} = \lambda_1 D_1 + \lambda_2 D_2 \text{------1}$$

$$D_{\lambda_2} = \lambda_2 D_1 + \lambda_2 D_2 \text{------2}$$

where D_{λ_1} and D_{λ_2} are the measured optical densities at the two wavelengths λ_1 and λ_2 and the subscripts 1 and 2 represent different substances, and the λ_1 and λ_2 refer to the two different wavelengths. The wave lengths are selected to coincide with the absorption maxima of the two solutes: the absorption maxima of the solutes should not overlap appreciably, so that substance'1' absorbs strongly at wavelength λ_1 and weakly at λ_2 and substance '2' absorbs strongly at λ_2 and weakly at λ_1 (for example two different species chromium and manganese).

This can be converted to the form $D = \epsilon ct$

where ϵ is the molar extinction coefficient or molar absorptivity, 'c' is the concentration expressed in g moles / litre, and 't' is the thickness of the absorbing solution expressed in cm. If 't' remains constant

$$D_{\lambda_1} = \lambda_1 \epsilon_1 c_1 + \lambda_1 \epsilon_2 c_2 \text{ ------3}$$

$$D_{\lambda_2} = \lambda_2 \epsilon_1 c_1 + \lambda_2 \epsilon_2 c_2 \text{ ------4}$$

solutions of these simultaneous equations give

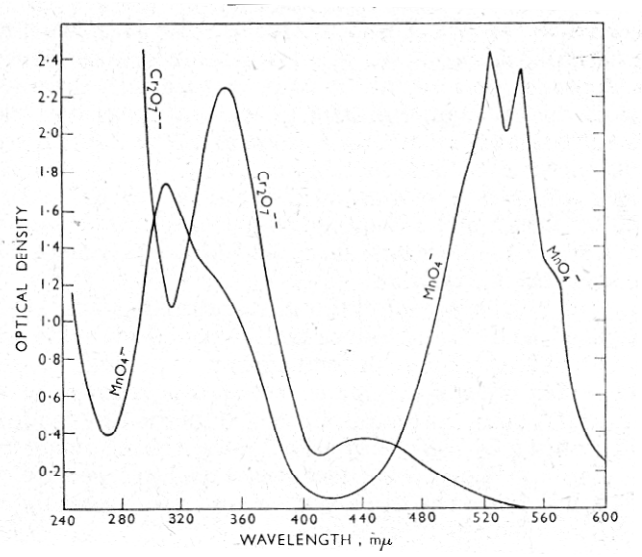
$$c_1 = \frac{\lambda_1 \epsilon_2 . D_{\lambda_1} - \lambda_2 \epsilon_2 . D_{\lambda 2}}{\lambda_1 \epsilon_1 \cdot \lambda_2 \epsilon_2 - \lambda 1 \epsilon_2 \cdot \lambda_2 \epsilon_1} \text{ ------5}$$

$$c_2 = \frac{\lambda_1 \epsilon_1 . D_{\lambda 2} - \lambda_1 \epsilon_2 . D_{\lambda 1}}{\lambda_1 \epsilon_1 \cdot \lambda_2 \epsilon_2 - \lambda 1 \epsilon_2 \cdot \lambda_2 \epsilon_1} \text{ ------6}$$

The values of molar extinction coefficients ϵ_1 and ϵ_2 can be deduced from measurements of optical densities of pure solutions of substances 1 and 2. By measuring the optical density of the mixture at wavelength λ_1 and λ_2, the concentration of the two components can be calculated.

The above consideration can be illustrated by the simultaneous determination of manganese and chromium in steel and other ferrous alloys. The absorption spectra of 0.001M permanganate and dichromate ions in 1M sulphuric acid, determined with a precision spectrophotometer using spectral band- widths less than 5mμ at all wavelengths and against water in the reference cell are shown in figure

The peak at 350mμ for dichromate solutions cannot be used because ferric ion absorbs strongly below 425mμ; at a wavelength of 440 mμ near the weaker band maximum the correction for ferric ion absorption is small. For permanganate the absorption maximum is at 545mμ, a small correction must be applied for dichromate absorption. Optical densities for these two ions, individually and in mixtures obeys Beer's law provided the concentration of sulphuric acid is at least 0.5M. Ferric iron, Ni, Co, V absorb at 425mμ and 545mμ and hence corrections must be made.



APPLICATIONS OF COLORIMETRY:

DETERMINATION OF IRON:

Two procedures are in use where in the following reagents will be employed

1. Thiocyanate and 2. o - Phenanthroline

1. Thiocyanate Method:

Ferric iron reacts with thiocyanate to give a series of intensely red - coloured compounds, which remain in true solution. Ferrous iron does not react. Depending upon the thiocyanate concentration, a series of complexes can be formulated as $[Fe(SCN)_n]^{3-n}$ where n = 1,2,3--6. At low thiocyanate concentration the predominant coloured species is $[Fe(SCN)]^{2+}$, ($Fe^{3+} + SCN^- = [Fe(SCN)]^{2+}$), at 0.1M thiocyanate concentration $[Fe(SCN)_2]^+$ and at very high thiocyanate concentration it is largely $[Fe(SCN)_6]^{3-}$.

In the colorimetric determination a large excess of thiocyanate should be used, since this increases the intensity and also the stability of the colour. Strong acids (HCl or HNO_3, 0.05 - 0.5M) should be present to suppress hydrolysis. Sulphuric acid is not recommended because it has a tendency to form complexes with ferric ions.

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$$

Procedure**:**

Reagents**:**

Standard solution of ferric iron and approximately 2 M potassium thiocyanate solution.

A standard series of different concentrations of Iron (III) solutions are required for the preparation of calibration curve. About 10 to 12, 50ml standard volumetric flask numbered in a serial order are taken. To each flask 5ml of hydrochloric acid (4N), 2ml of potassium thiocyanate (2M)are added. Then about 25ml of distilled water is added to all the flasks such that the total volume in each flask ranges from 30 to 35ml. Then iron (III) solution is added to each one of the flasks staring from 1.0ml. Then immediately the contents are made upto the mark, thoroughly mixed and the optical density is measured at 480nm (λ_{max}) against the reagent blank. A reagent blank is one in which both 5ml of hydrochloric acid (4N), 2ml of potassium thiocyanate (2M) are taken and the flask is made upto the mark with distilled water. The successive measurements are done with incremental additions of different concentrations of iron(III) solution to the rest of the flasks.

A calibration curve is constructed taking amount of iron(III) on x axis and corresponding optical densities on y-axis and the curve is checked whether the Beer's law is obeyed or not. The unknown solutions are similarly taken and the colour intensity (optical density is measured) from which the concentration of iron(III) present in unknown solutions are computed.

Note: The iron solutions are to be added to the volumetric flask just before the measurement of the optical density in view of the expected complexity of iron-thiocyanate complexes at different concentration ratios of iron(III) to thiocyanate.

2. o - Phenanthroline Method:

Ferrous iron reacts with o- phenanthroline to form an orange- red complex $[C_{12}H_8N_2)_3Fe]^{2+}$. The colour intensity is independent of the acidity in the pH range 2-9, and is stable for longer periods. Ferric iron is present may be reduced with hydroxyl ammonium chloride or with hydroquinone. The iron phenanthroline complex (as perchlorate) may be extracted with nitrobenzene and measured at 515mμ against a reagent blank.

Reagents: o-Phenanthroline, sodium acetate, hydroxyl ammonium chloride, or hydroquinone.

Procedure: Take an aliquot portion of the unknown slightly acidic in nature solution containing 0.1-0.5 mg of iron and transfer it to a 50ml volumetric flask. Determine by use of similar aliquot portion containing a few drops of bromophenol blue, the volume of sodium acetate solution required to bring the pH to 3.5 ± 1.0. Same volume of acetate solution to the original aliquot part is added and then 4ml each of the hydro-quinone and o- phenanthroline solutions are added. The contents were made up to the mark with distilled water, mixed well, and allowed to stand for one hour to complete the reduction of iron.

The intensity of the colour produced is compared with standards, similarly prepared. If the measurements are made by a colorimeter a filter showing maximum transmission at 480-520mμ is used. On the other hand if a spectrophotometer is used, the measurements are made at a wavelength of 510mμ.

II. DETERMINATION OF MANGANESE:

Principle: Manganese in small quantities can be estimated by oxidation to permanganate acid. The oxidizing agent is potassium periodate. In hot acid solution periodate oxidises manganese ion quantitatively to permanganic acid.

$$2\ Mn^{2+} + 5IO_4^- + 3H_2O \rightarrow 2MnO_4^- + 5\ IO_3^- + 6H^+$$

Permanganic acid is pink coloured and the colour produced is proportional to the Mn^{2+} present.

Procedure: A standard series of different concentrations of Mn^{2+} solutions are taken in say 9 volumetric flasks of capacity 50ml. Then to each flask 1ml of sulphuric acid (1N) and 5ml of phosphoric acid (manganese free) are added. Then 2mg of potassium periodate is added to each of them. A blank solution is also made in a similar manner without Mn^{2+} solution. The contents of the flasks are made approximately say 40ml. Then they are heated in a water bath for 10min and suddenly cooled and made upto the mark. Then optical densities are measured for different concentrations to draw a Beer's law plot. The wave length is set at 545nm.

A graph is drawn by taking amount of Mn^{2+} present on X-axis and optical density on Y-axis. A straight line is obtained. Same procedure is adopted for the given unknown samples also and the amount of Mn^{2+} in unknown samples is computed from the graph.

III. DETERMINATION OF PHOSPHATE:

Theory: Orthophosphate and molybdate ions condense in acidic solution to give phosphomolybdic acid which upon selective reduction say with hydrazine sulphate produces blue colour due to molybdenum blue of uncertain composition. The intensity of the blue colour is proportional to the amount of phosphate initially incorporated in the heteropoly acid. If the acidity during the time of reduction is 1N in sulphuric acid and hydrazine sulphate is the reductant, the resulting blue complex exhibits a maximum absorption at 840nm.

Reagents:

1. Molybdate solution - 12.5g in 10N H_2SO_4 (500ml)
2. Hydrazine sulphate - 1.5 g in 1 litre deionised water
3. Standard phosphate solution - 0.2197g of potassium dihydrogen phosphate in deionised water and diluted to one litre.

Procedure:

The standard phosphate solutions are taken in different concentrations in clean 50ml volumetric flasks and then 5ml of molybdate solution and 2 ml of hydrazine sulphate solution are added to each volumetric flask. The contents are made upto roughly 2/3rds of the flask with distilled water. A blank solution is also prepared by taking 5ml of molybdate solution and 2 ml of hydrazine sulphate solution in a 50ml volumetric flask and similarly filled with distilled water to 2/3rds of the volumetric flask. The solutions are heated on a water bath for 10 minutes uniformly in case of both the blank and standards and cooled suddenly. Then the volumes are made upto the mark in each flask with distilled water and their optical densities are measured at 840nm (λ_{max}).

A graph is drawn taking the amount of phosphate on x-axis and optical density on y-axis. The straight line graph which is obtained is examined whether Beer's law is obeyed or not. Same procedure is adopted for the unknown samples also. The amount of phosphate in unknown samples are computed from the graph.

IV. DETERMINATION OF AMMONIA:

An alkaline solution of mercuric iodide in potassium iodide is used as a reagent for the colorimetric determination of ammonia.

When Nessler's reagent is added to a dilute ammonium salt solution, the liberated ammonia, reacts with the reagent fairly rapidly but not instantaneously to form of an orange-brown product, which remains in colloidal solution but flocculates on long standing. The colorimetric comparison must be made before flocculation occurs. The reaction with Nessler's reagent may be represented as

$$2K_2[HgI_4] + 2NH_3 \rightarrow NH_4Hg_2I_3 + 4KI + NH_4I$$

The reagent is employed for determination of ammonia in very dilute ammonia solutions and in water. A photoelectric colorimeter or spectrophotometer is used. When 1ml of the Nessler's reagent is added to 50ml of the sample, a blue colour filter in the wavelength region 400-425mμ allows measurements with a 10mm path in the nitrogen range 20-250μg. Nitrogen concentrations approaching up to 1mg can be determined with a green colour filter or in the wavelength range near 525mμ. The calibration curve should be prepared under exactly the same conditions of temperature and reaction time adapted for sample.

V. DETERMINATION OF VANADIUM:

When hydrogen peroxide is added to the solution containing small quantities of vanadium in sulphuric acid solution, a reddish- brown coloration is produced, this is thought to be due to the formation

of a compound of the type $(VO_2)_2$ ($SO_4)_3$. A large excess of hydrogen peroxide tends to reduce the colour intensity and to change the colour from red-brown to yellow, this may be due to the formation of $(VO_2)(OH)_3$.

With a hydrogen peroxide concentration of 0.03%, the sulphuric acid concentration can vary between 0.6 and 6N without any appreciable effect on the colour. With higher concentrations of hydrogen peroxide the acidity must be increased to permit development of the maximum colour intensity.

Procedure: For each 10 ml of the test solution in 1-2 N sulphuric acid, 0.25 ml of 3% hydrogen peroxide are added. The colour intensity (O.D.) is measured against a reagent blank at 450 nm. If titanium is present in samples, 5-10% v/v hydrofluoric acid are added which will decolourise the ferric iron also. If titanium is absent phosphoric acid is used for decolourisation of iron. It is better to use the standard series method with inexpensive tubes for comparison.

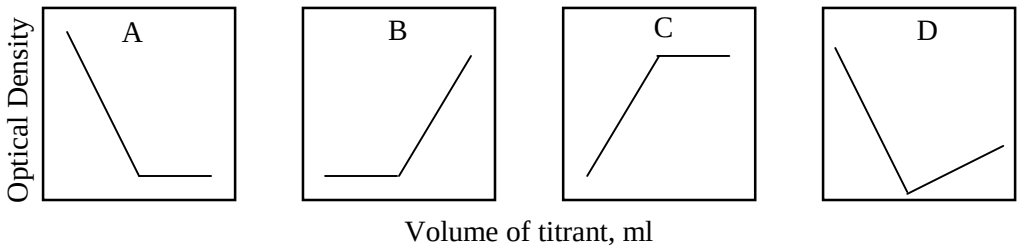
PHOTOMETRIC TITRATIONS:

Photometric or spectrophotometric measurements are used in locating the equivalence point in a titration. If one of the ions has a specific absorption proportional to its own concentration, this method becomes applicable. In other words, a direct photometric titration is the result of a change in the concentration of reactant or a product, or both. At least one of the species must absorb radiation. This technique has several advantages over the usual colorimetric estimations.

Some important advantages of photometric titrations are

1. The determination of end point is sharp, that is slight changes in colour are readily detected by spectrophotometer.
2. Since only changes in absorbance are taken into consideration other absorbing species do not interfere with the actual titration.
3. The method can be applied to solutions that are highly coloured and would interfere with usual indicators.
4. Since the end point determined by extrapolation of points far away from the end point region, any incompleteness of reaction at the end point causes no serious difficulty.
5. Indicator changes can be easily detected.

In this technique a graph is drawn between absorbance and volume of titrant. The plot consists of two straight line portions of different slopes. The end point is detected by the intersection of the extrapolated straight line portions.



The shape of the photometric titration curve depends on the optical properties of reactant, titrant and products of the reaction at the selected wavelength. Some typical titration plots are given above.

A – where the substance titrated is converted into a non-absorbing product

B – where the titrant alone absorbs

C – where the substance titrated, titrant are colourless and the product alone absorbs

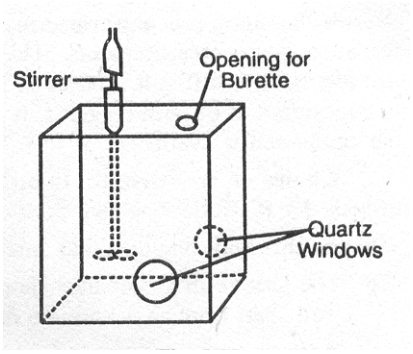
D – when the coloured reactant is converted into a colourless product by a coloured titrant

Moreover, in order to get good and satisfactory end point it is necessary that absorbing system must obey Beer's law (other wise the titration curve will lack the linear portions needed for end point extrapolation) and wavelength for analysis must be chosen with a great care. The effect of dilution can be made negligible by the use of a sufficiently concentrated titrant. If relatively large volume of titrant are added the effect of dilution may be corrected by multiplying the observed optical density by a factor $\frac{V+v}{V}$, where V is the initial volume and the v is the volume added.

Photometric titrations are ordinarily performed with spectrophotometers or filter photometers. But spectrophotometers are preferred, because their narrow bandwidths enhance the probability of adherence to Beer's law.

Procedure:

A special titration cell will be used which will be quite suitable for the titrations without removing the solution from the reaction vessel for the purpose of measurement of optical density. The cell will directly fit into the spectrophotometer.



The spectrophotometer is adjusted to the wavelength at which experiment is to be carried out. The instrument is now set preferably to read zero absorbance. The tip of the burette is adjusted into the cell and titration is started.

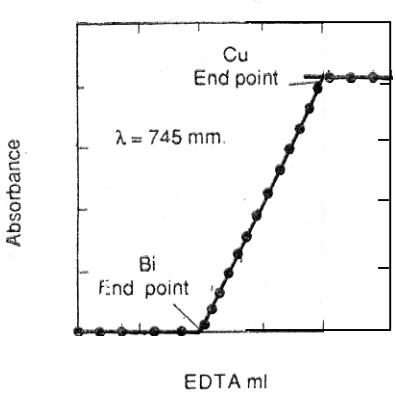
The solution is constantly stirred slowly by a mechanical stirrer when the reagent is added from the burette and subsequently absorbance is noted. The absorbance after each added increment is plotted against added volume of titrant. The equivalence point is subsequently determined by the intercept of two straight lines.

Applications:

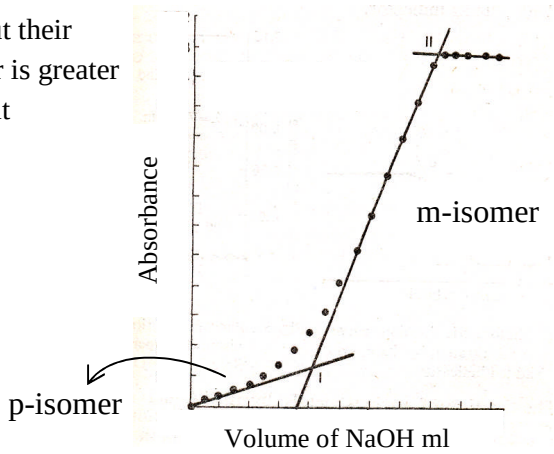
Photometric titrations often provide more accurate information than a direct photometric analysis.

1. Photometric titrations are applicable for all types of reactions. The method is quite useful in cases where ordinary procedures could not provide a determination.

2. The titration of various metals by EDTA and similar complexogens is one of the most important applications of photometric titrations. Underwood (1954) titrated bismuth and copper successfully in a single titration at 745nm, where Cu-EDTA complex absorbs strongly but Bi-EDTA does not.



3. Titration of phenols with sodium hydroxide: The titration of m- and p- nitrophenol can be performed with sodium hydroxide which is not possible by ordinary titrimetric procedures. Measurements are made at 545 nm during the course of titration. At this wavelength both m- and p- nitrophenols absorb but their corresponding acids do not . The absorptivity of m-isomer is greater than that of the p- isomer. Since p-isomer is stronger acid it undergoes neutralization first.



Note: The two acids cannot be estimated in presence of each other by usual titrations with or without any Indicator, as the colour change corresponding to the first end point would be very gradual.

UNIT 1

INFRARED SPECTROSCOPY

Lesson 3

Objectives of the lesson:

This lesson deals with the utility infra red spectroscopy as an analytical tool giving a brief introduction, instrumentation, and applications.

INTRODUCTION:

The range of Infra red Radiations:

The wavelength of infrared (IR) radiations falls in the range 750mμ to 25μ while visible light falls between 400mμ to 750mμ. The infrared radiation refers broadly to that region of electromagnetic spectrum, which lies between the visible and microwave regions. However, this region may be divided into four sections.

a) The Photographic Region : Ranges from visible to 1.2μ
b) The very near IR Region : Ranges from 1.2μ to 2.5 μ
c) The near IR Region : Ranges from 2.5 μ to 25 μ
d) The far IR Region : Ranges from 25 μ to 300-400 μ

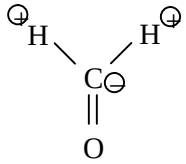
By virtue of large wavelength, IR has less energy than visible radiation. At longer wavelengths, the far IR can be considered to extend to 200μ. We have relationship between velocity of light (c), frequency (ν) , and wavelength (λ). Using the equation $\upsilon = c / \lambda$, we can calculate the frequency of IR radiation. The frequency range of IR radiations is from 2.2×10^{14}cps to 7.5×10^{15} cps (cycles per seconds). Further we have $E = h\nu$ hence, when the frequency is high (i.e., when wave length is short) the energy of radiation is high.

Requirements of IR radiation:

The major requirements are correct wavelength and electric dipole.

(i) Correct wavelength of radiation:

The molecules absorb radiation when some part of molecule (i.e., the atoms or groups of atoms comprising it) vibrates at the same frequency as the incident radiant energy. After absorbing radiation, the molecules vibrate at an increased rate. The atoms comprising a molecule can vibrate in several ways. For example, the carbon and hydrogen atoms in formaldehyde can vibrate towards and away from each other.

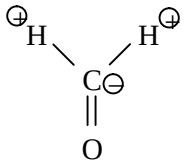


The rate at which these component atoms vibrate is quantised and can take place only at well defined frequencies that are characteristic of the atoms concerned. That is formaldehyde absorbs radiation that causes its carbon, oxygen or hydrogen atoms to vibrate in this manner.

If we measure the molecular absorption to record the frequencies at which the HCHO absorbs, this record is the basis of the IR spectrum of HCHO. Its complete IR spectrum however is modified by the molecules rotational energy.

(ii) Electric Dipole:

For a molecule to be able to absorb IR radiation, it must have a changeable electric dipole. A molecule has an electric dipole when there is a slight positive and slight negative electrical charge on its component atoms. These slight charges are not equal to the charge of a whole electron or proton, but represent a slight excess or depletion of electrons in some area. This excess or depletion of electrons has the effect of producing a fractional charge. Two adjacent fractional (but opposite) charges create a dipole. The dipole must change as a result of a vibrational transition resulting from IR absorption.



If the slightly charged parts of a vibrating molecule move, the dipole changes. It has been observed, with regard to the rate of change of the dipole during vibration, that when this rate is fast, the absorption of radiation is intense. The strength of the dipole and rate of change of dipole will be fast when the atoms of the molecule will be close to each other. Thus if the charge is high and the vibration is rapid, the absorption of radiation is intense. On the other hand if the rate of change of dipole is slow the absorption will be weak, this is because of distance (far apart) between the atoms.

Requirements for IR absorption can be summarized as follows:

1. Natural frequency of vibration of molecules must be equal to the frequency of incident radiation.
2. The frequency of radiation must satisfy $E = h\upsilon$
3. Change in vibration must be effected by the change in dipole of the molecule.
4. The intensity of absorption must be proportional to the square of rate of change of dipole.

Movement of molecules:

When a molecule vibrates it usually rotates at the same time. If the radiation of the molecule is slow, rotational energy will be less. If the rotation of molecule is fast rotational energy is high. Rotational energies are small when compared with vibrational energies. The rotational energy is usually simply added or subtracted to/ from the vibrational energy during absorption. When the molecule has no rotational energy, it absorbs the energy of the radiant energy would be the simple difference between the vibrational energy levels of the molecule. Since molecules usually rotate, however they may rotate faster (or) slower after being vibrated, the energy required for the rotation of the molecule must be obtained by the radiation. Hence the molecule absorbs that wavelength, which causes them to vibrate more quickly and to rotate at different rate. Once the vibration is taking place the system is transferred to rotation. Thus the total radiational energy absorbed by the molecule is equal to the algebraic sum of the molecule's vibrational and its rotational energy.

1. Vibrational Movement:

A molecule is made up of a number of atoms joined by chemical bonds. Such atoms vibrate about each other in the same way that the weights held together by the spring would vibrate. It has been shown that two masses joined by a spring vibrate according to the equation

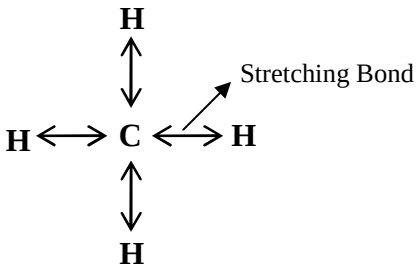
$$\upsilon = k\sqrt{\frac{f}{\mu}}$$

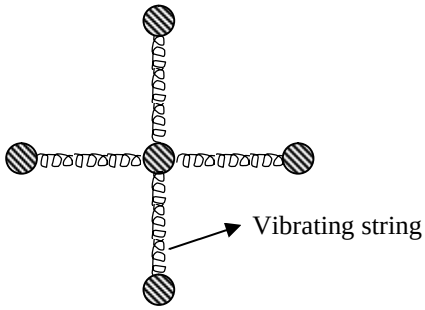
where υ = frequency of vibration; k = constant; f = binding strength of the spring

$$\mu = \text{reduced mass} = \frac{M_1 M_2}{M_1 + M_2}$$

where M_1 and M_2 are masses of the vibrating bodies.

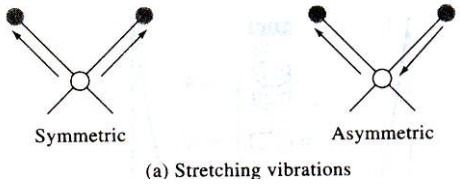
Example:



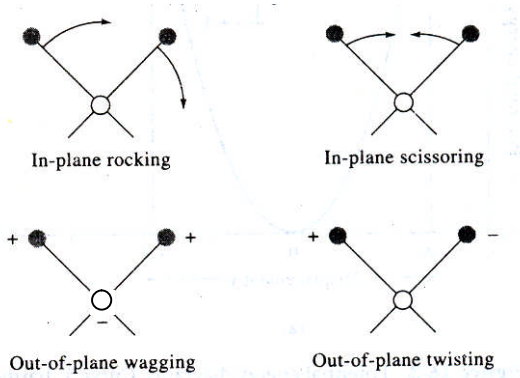


Two atoms joined by a neutral bond vibrate according to the same equation, where f is binding force of chemical bond and μ is reduced mass of vibrating atoms. Since f and μ are constants among given set of atoms and chemical bonds, the frequency of vibration is also constant.

There are several ways in which two atoms of a large molecule can vibrate in relation to a third atom. A typical example is the vibration of 'H' atom apart from carbon in organic compounds. Principal modes of vibration of carbon and hydrogen include:



(a) Stretching vibrations

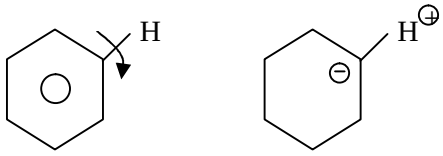


(b) Bending vibrations

The arrows indicate the direction of the motion of H nucleus on the plane of the paper; the signs (+) and (-) indicate motion perpendicular to the plane of the paper {(+) Approaching towards the reader and (-) Receding i.e., away from the reader}. In wagging both hydrogens move together while in twisting they move in opposite direction. Each of the modes of vibration absorbs radiation at different wavelengths.

Rotational Movement:

The parts of a molecule vibrate towards each other at the same time molecule as a whole may rotate in the same way that the ball spins.



This rotation may be fast or slow and may take place about different axes of the molecule.

It is a fact when the molecule or atom moves from one energy state to higher energy state, its energy changes from E_1 to E_2. Difference in energy $E_2 - E_1 = E$, which is related to the frequency of absorbed radiation by the equation $E = h\nu$, where ν is the frequency of absorbed radiation and 'h' Planck's constant. Usually when molecules are caused to vibrate there will be change in rotational energy as well. A molecule absorbs radiation with energy equal to its own vibrational and rotational energy.

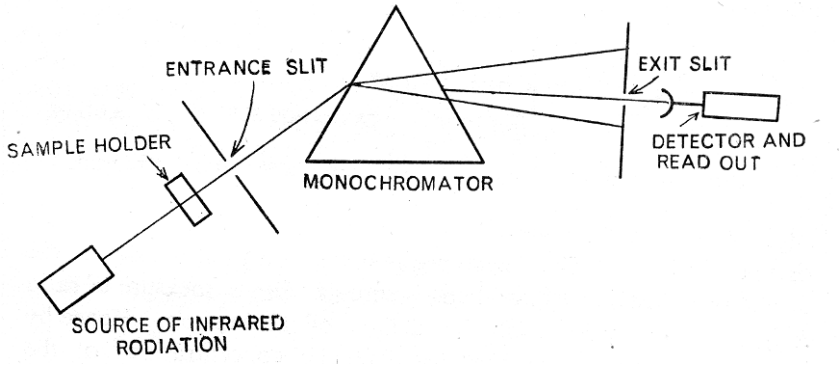
Molecules vibrate at many rates of vibration with the result that there are many values of 'E'. Hence instead of a single absorption line, we observe many absorption lines all close together. These closely packed lines are called absorption bands. The absorption bands for any particular pair of vibrating functional group, may extend over a wide absorption(wavelength) range.

IR positions of various vibrations:

Bond	**Mode**	**Wave number (cm^{-1})**
C – H	stretching	2700 – 3300
C – H (in CHO)	generally 2 bands which are nearer to 2720cm^{-1}	2900 – 2700
Alcohol (– OH)	Stretching	3710
Free – OH	Sharp – OH Stretching	3650 – 3590
– OH	O – H bending	1410 – 1260
 C – OH	C – O stretching	1150 - 1040
Water of crystallization	weak band 1640 –1615	3600 - 3100

Instrumentation

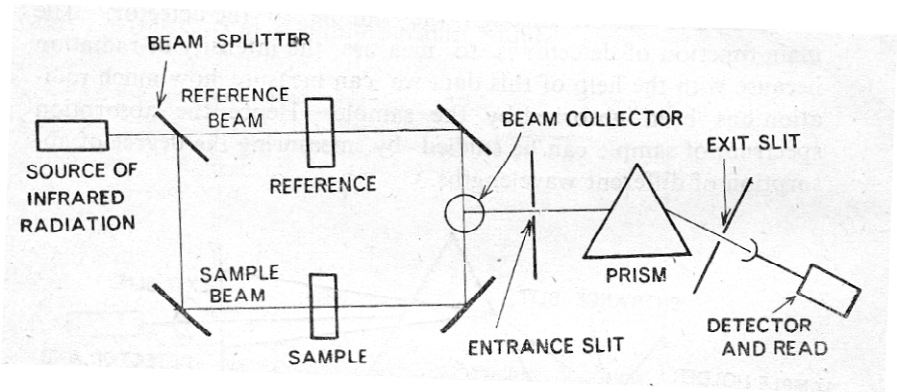
Single Beam IR Spectrophotometer:



Radiation from the source passes through the sample and then through the entrance slit to the monochromator. The desired wavelength is chosen and passed through the monochromator to the exit slit and to the detector. The detector measures the intensity of radiation left over after it passed through the sample. Knowing the original intensity of radiation, we can measure how much radiation has been absorbed by the sample. By measuring the degree of absorption at different wavelengths the absorption spectrum of sample can be obtained.

The intensity of radiation (I_0) is measured with no sample in the light path. The reading from the detector or read out system is taken as I_t. The sample is then placed into the light path, which absorbs radiation. The intensity of radiation falling on the detector is the measure of I_t. The ratio I_t/I_0 is the transmittance (T) of the Beer – Lambart's equation. By measuring this ratio, quantitative analysis of the sample can be made. In practice a major problem that frequently arises is that the intensity of the radiation source varies slowly over long periods of time or even rapidly over short period of time. In these circumstances the value of I_0 is varying constantly and it is difficult to measure I_t/I_0 accurately. Quantitative results are therefore subjected to error.

Double Beam IR Spectrophotometer:



The instrument separates the source beam into two half beams, the sample beam and the reference beam. The sample is placed in the sample beam path and a reference material such as solvent used in the sample is placed in reference beam path. The two half beams are brought over to one point (recombined)

and passed on to the optical path of the detector. Since there is no IR absorbing medium in the reference beam path it reaches the detector unabsorbed and is measure of I_0.

On the other hand the other portion of the beam passes through the sample, a portion of it is being absorbed and hence there will be decrease in the intensity. The difference can be attributed to intensity transmitted. After the two half beams are brought together they produce an oscillating signal. The greater the absorption of sample the greater the degree of oscillation. The detector system is designed to measure the degree of oscillation, which then becomes the direct measure of degree of absorption by the sample and the ratio I_t / I_0. From this ratio, the concentration of the sample can be determined.

Radiation Sources:

IR instruments require a source of radiant energy, which provides a means for isolating narrow frequency bands. The two most popular sources of IR radiation are **Nernst Glower** and **Globars.**

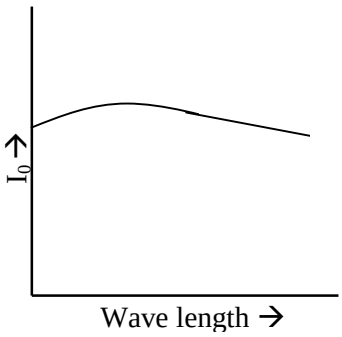
Nernst Glower: It is bar composed of rare earth oxides of zirconium, cerium oxide and thorium oxide. It can be operated in air since it is not subjected to oxidation. Its size is 2mm in diameter, 30mm in length. This can be heated electrically to a temperature between 1000 to 1800^oc.

Globar: It is a bar of sintered silicon carbide and can be heated electrically to similar temperatures as above. Its dimensions are 50mm in length and 4mm in diameter.

Others:

A simple nichrome wire heated by passing a current also serves as a source where required wavelength range and intensity are too high. A rhodium wire sealed in a cylinder can also be employed as a source. Tungsten filament lamp is also found satisfactory for near IR region. At these elevated temperatures each source strongly emits IR radiation, and also fulfills two important requirements of radiation source namely that the intensity of radiation be steady and consistent over long periods of time.

In addition, the radiation from these sources extends over a wide wavelength range (1.4-25μ). Unfortunately, the intensity of radiation from them is not the same at all frequencies. The behavior of the intensity of radiation of wavelength range of 1.4 to 25 μ is not uniform but considered to be uniform for most practical purposes. This variation is no handicap because compensation can be made if necessary. Also, it should be remembered that the absolute value of the radiation is seldom measured. Usually it is the fraction of the radiation absorbed that is important. This is determined by measuring the ratio I_t / I_0. .



Monochromators :

The radiation emitted by the source covers a wide frequency range. However, the sample absorbs only at certain characteristic frequencies. In practice it is important to know what these frequencies are. To do this we must be able to select any desired frequency from the source and eliminate the radiation at other frequencies. This can be achieved by use of a monochromator, the two main types of which are **Prisms** and **Gratings**.

Prism Monochromators:

The material used for making the prism must be transparent to IR radiation. This requirement eliminates common materials such as glass and quartz, which are not transparent to IR at wavelengths longer than 3.5microns. Secondly, the material used must be strong enough to be fabricated and polished. The most common materials used for making the prism are metal salts such as potassium bromide, calcium fluoride, sodium chloride (rock salt) or thallous bromide. The final choice among these compounds is determined by the wavelength range to be examined.

Compound	Range of transmission	Useful wavelength region
LiF	0.2 - 6μ	2.5 – 5.9 μ
Calcium fluoride	0.2 - 9μ	2.4 – 7.7μ
Sodium Chloride	0.2 - 17 μ (rock salt region)	2 – 15.4μ
Potassium Bromide	0.2 μ - 26μ	9 – 26μ
Cesium bromide	1 - 38μ	9 – 26μ
KRS-5 (Tl Br+Tl I)	0.6 - 40μ	25 – 40 μ
Quartz	0.8 - 0.3μ	

Sodium chloride is the most common prism material for the range 2 – 15 μ while for the region 12 – 25 μ , potassium bromide prism is generally used.

Most of the metal salts used for making prisms are water-soluble. For this reason it is necessary to keep salt prisms dry. Installing the instrument in an air-conditioned room is very advantageous. If this is not possible, the prism should be kept in a desiccated atmosphere. Commercial equipments will be generally provided with small heaters, to keep the prism above room temperatures at all places, thus preventing condensation of water vapour from the atmosphere on the surface of the prism. If water comes in contact with prism its surface becomes rough and etched. Radiation would be no longer being reliable. For this reason many IR instruments are left on ‘stand -by’ but not switched off when not in use.

Grating Monochromators:

The advantage of grating is that they can be made with materials such as aluminum that are stable in the atmosphere and are not attacked by moisture. Another advantage is that they can be used over considerable wavelength range. This is in contrast to salt prisms, which have reduced wavelength range. The only problem lies with grating is that different orders of wavelength can and will travel through the same light path on leaving the face of the grating. Since several wavelengths are superimposed on each other in this way, several displaced spectra are super imposed on each other. The problem can be solved by using a grating in conjunction with a small prism. This prism acts as an order sorter. The prism that is used is much smaller and less expensive, when it is used as a principal monochromator.

Slit Systems:

The radiation from the source is dispersed by the monochromator into a fan shaped beam, only a small part of which is used. This small section is separated from the rest of the beam by the exit slit. Generally the slit will be like jaws. The physical distance between the jaw widths is called mechanical slit width.

Instruments will have the provision for measuring the mechanical slit width directly. In U.V. the slit width is of the order 0.1mm where as in IR spectroscopy it is 0.1cm to 2cm (U.V. radiation will have high energy when compared to IR which is of lower energy). The wavelength range of radiation that passes through exit slit is called the spectral slit width, the width of which can be measured by passing emission light of very narrow band width through the slit to the detector.

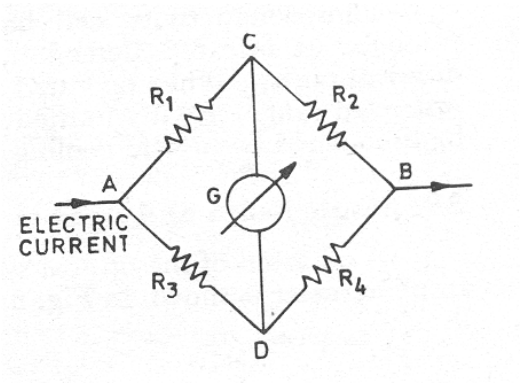
Detectors:

The most common types of detectors used in IR spectroscopy are:

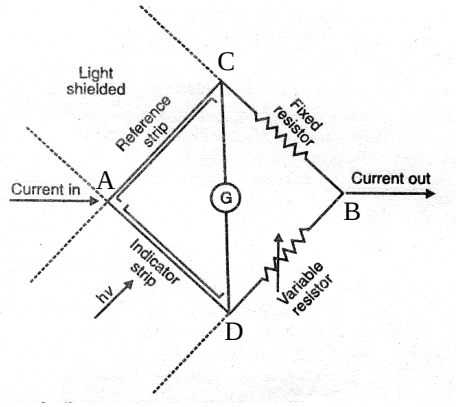
1.Bolometers 2. Thermocouples and 3. Thermistors

Bolometer:

A Bolometer is a very sensitive resistance thermometer that is used to detect and measure feeble thermal radiations, which are best suitable for IR study. It is analogous to Wheatstone bridge. The principle involved here is "When radiations such as IR radiations fall on this conductor it becomes warmer. As its temperature changes its electrical resistance also changes. The degree of change in resistance is a measure of the amount of radiation that has fallen on the detector."



Wheatstone Bridge



Bolometer

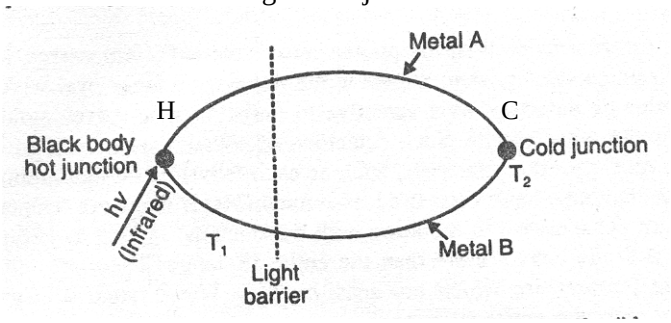
Bolometer consists of four arms like in case of Wheatstone's bridge with a provision of null deflection galvanometre 'G' connected across the joint C and D, when used, as detector in IR spectroscopy the radiation from IR source will be allowed to fall on the arm AD. When radiations fall on the detector however, the change in electrical resistance causes the bridge to become imbalanced. Thus it alters the resistance of the arm 'AD' which creates an imbalance between the resistance of the arm AD and DB (adjacent arms). However, the resistance of the arms AD and DB are always kept balanced.

The imbalances of the resistances between the arms AD and DB causes a flow of current through galvanometre 'G'. The galvanometre measures the current flow, which is a measure of the degree of imbalance of the bridge. This in turn is a measure of the change in resistance of the detector, which is a measure of the intensity of the IR radiation falling on the detector. When there is no sample the total radiation falls on the arm AC and is consider as I_0. When there is sample on the path of radiation less IR intensity radiation reaches the arm AD and by virtue of it the intensity of absorbed radiation can be calculated.

Thermocouples:

A thermocouple is made by welding together two wires made from different metals. One junction is named as 'H' and the other junction as 'C'. IR radiations are allowed to fall on junction 'H' when it becomes hot due to absorption of IR radiation. Care should be taken that no radiation falls on the cold junction (C), which should be carefully screened and kept at constant temperature. The hot junction (H), which is exposed to IR radiation, becomes hotter and hence there will be rise in temperature of that junction H.

In such circumstances one junction is hotter while the other is colder and a potential difference will be generated in the wire, which depends upon the temperature difference between the junctions and therefore gives a measure of IR radiation falling on the junction.



Thermistors:

These detectors are made of a fused mixture of metal oxides. As their temperatures increase, their electrical resistance decreases. This relationship between temperature and electrical resistance enables us to use thermistors for IR radiations measurement in the same way as bolometers.

Other detectors:

Among the other detectors, Golay detector is one which depends on the change of pressure of a gas in an enclosed sphere. The other being photocell, which is a resistor whose electrical resistance is very sensitive to light falling on it. However, semiconductors can also be used, whose resistance changes when radiation falls on it. The latter is very fast and sensitive detector.

Sample Cells: The sample cells for different phases of solid, liquid and gases will be of different nature.

Solid Samples:

Three techniques are available for preparing solid samples for IR spectrometry.

1. The sample must be made to a powder. The powder can be made into thick slurry or a null, by grinding it with a greasy viscous liquid such as Nujol (paraffin oil). It is good for qualitative but not for quantitative analysis.
2. *KBr Pellet Method*: This involves mixing of a finely ground solid sample with powdered potassium bromide. The mixture is pressed under very high pressure (at least 25,000 psig) to form a small disk about 1cm in diametre and 1-2mm thickness. The disk is transparent to IR radiation and may be analysed directly.
3. In third method, the sample is deposited on the surface of a KBr or NaCl cell by evaporation of a solution of the solid. IR radiation is then passed through the thin layer deposited.

Cells for Liquid Samples:

The easiest samples to handle are liquid samples. These may be poured, frequently with no preparation into rectangular cells made of NaCl, KBr etc., and their IR spectrum is determined directly. For double beam work matched cells are used. One cell is used to contain the sample, the other cell for a reference material (eg., solvent).

Matched cells are similar in total thickness and in cell wall thickness. All cells must be protected from water because they are water soluble. Organic liquid samples should be made moisture free before pouring into cells, otherwise cell surface become opaque and cause erroneous results.

Gas Samples:

The gas sample preparation is similar to liquid sample in as much as the ends are made of KBr, NaCl. To compensate for the small weight of sample that is contained in a gas, they are made larger. Usually they are 10cm long, but multiple reflections can be used to make the effective path length as long as 40mts so that constituents of the gas can be measured.

Analytical Applications:

1. IR spectroscopy is used for qualitative and quantitative analysis of organic compounds and mixtures. It helps to identity many functional groups that are important in organic chemistry.
2. We can acquire information about its geometry by analyzing the molecule's IR spectrum. This provides the qualitative basis for IR absorption spectroscopy. The spectra that are obtained as it pertains to different functional groups that are there in the unknown sample will be matched with characteristic absorption frequencies or wavelengths of different functional groups available in the form of manual or directory.

IR spectroscopy is useful as a quantitative tool enables us to measure the concentration of the components in various samples. The height or the intensity of the absorption peaks or absorption bands give the information about the concentration of particular component.

<u>Qualitative Analysis</u>:

This is done by matching the frequencies that the spectrum shows to be absorbed with the relevant functional groups.

Groups	**Absorption (wave number)**
CH group	3000 cm^{-1}
Alkane group CH-stretching)	< 3000 cm^{-1}
Alkenes and aromatic	> 3000cm^{-1}
Alkanes	1380cm^{-1}
(indicates the presence of terminal methyl group)	
Gem dimethyl group	1380 & 1365cm^{-1}
H-C-H (Scissor motion)	1460cm^{-1}(indicates the presence of methylene group)

If four or more methylene groups present in a linear arrangement it gives rise to the rocking methylene band at about 720cm^{-1}.

The substitution pattern of the benzene ring can be deduced from a series of weak but very useful band in the region 2000- 1670cm^{-1}.

Coupled with the positions of the strong bands between 900 and 650cm^{-1}, which are due to the out -of-plane C-H bending vibration.

Hydroxyl group - 3600- 2000cm^{-1}

Carbonyl group - position depends on chemical environment

Aldehydes and Ketones - 1725 - 1690cm^{-1}

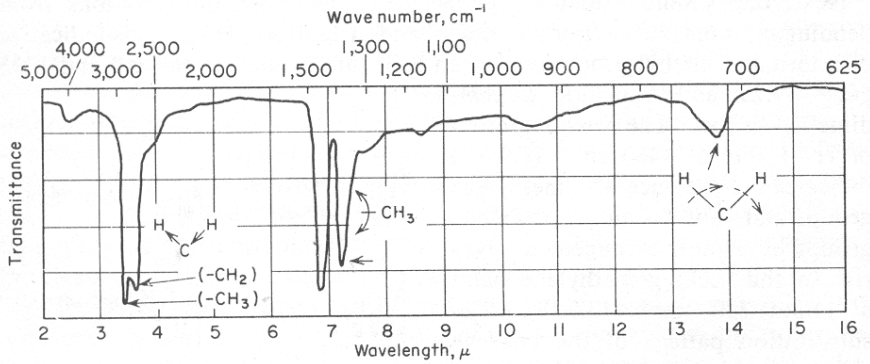
If an OH group is attached as in a carboxylic acid, the carbonyl frequency will be higher (1700- 1670cm^{-1})

If an amide group is attached the frequency will be 1690 - 1600cm^{-1}

Ester Carbonyls 1750 - 1725 cm^{-1}

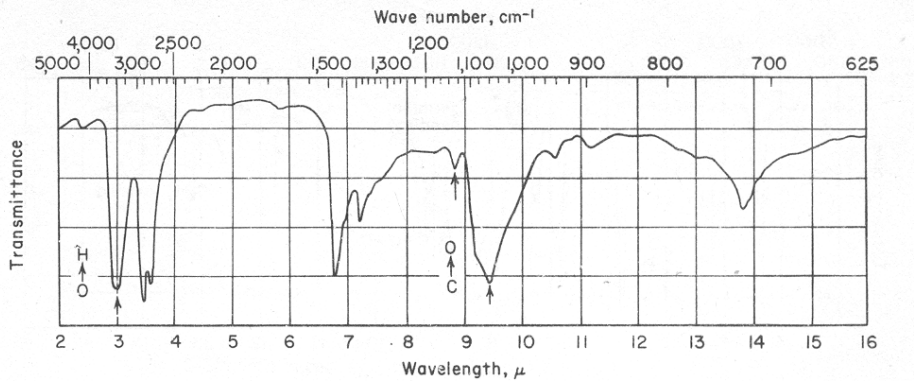
Anhydrides show double adsorption band (One Band at 1850-1800cm^{-1}, second band at 1800 - 1750cm^{-1})

Typical Spectrum of Saturated Alkane CH_3 (CH_2)$_8$ CH_3



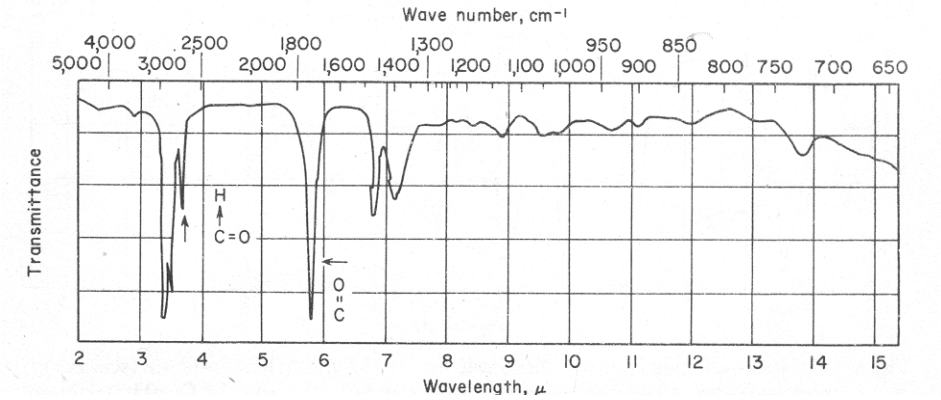
The figure shows the spectrum of a saturated alkane (NUJOL), a compound which contains only carbon and hydrogen in a straight chain. The four prominent absorption bands arise from the C-H and C-C linkages, at about 2940cm^{-1} (3.4μ) from C-H stretching: at 1460cm^{-1} (6.85μ) from a scissors - like bending of H-C-H groups; at 1380cm^{-1} (7.25 μ) from a symmetrical deformation of the terminal methyl groups and at 720cm^{-1} (13.85μ) from a rocking vibration of the methylene hydrogen attached to the carbon atoms in the chain when four or more methylene groups are aligned linearly.

IR spectrum of Lauryl Alcohol CH_3(CH_2)$_{10}$ CH_2OH



Replacing a hydrogen by OH group on the end of an aliphatic chain introduces two modes of vibration that is O-H stretching at 3400cm^{-1} (2.95μ), C-O stretching at 1110cm^{-1} and 1060cm^{-1}(8.9-9.45μ). The latter modes occur also in ethers but reversed in intensity. Phenols exhibit similar bands.

IR spectrum of n- Octaldehyde: $CH_3(CH_2)_6CHO$

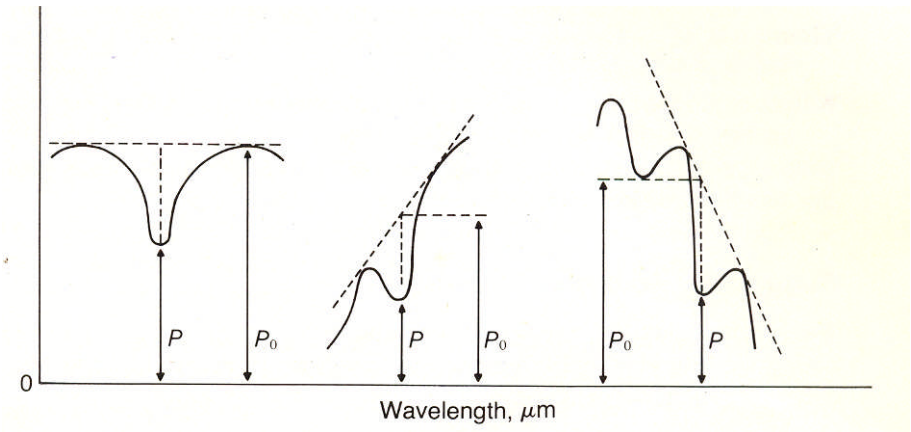


Introduction of carbonyl group produces a number of new bands, the figure shows the effect of an aldehyde group at the end of the chain, the strong C=O, stretching frequency at 1730cm^{-1} (5.77μ) is the usual location of an aldehyde and ketone. A short band at 2720cm^{-1} (3.68μ) is the C-H stretching frequency of the aldehyde group, shifted to a lower frequency due to the adjacent carbonyl group.

Quantitative Methods:

Base Line Method / Technique:

Quantitative analysis in the IR is often feasible provided the problems are recognized and conditions are standardized.



In this procedure the spectrum of the sample is analysed as follows.

1. An absorption band of the standard, which is isolated from those of the other matrix components, is selected.
2. A straight line (base line) is drawn tangent to the spectral absorption curve on both sides of the chosen absorption peak (transmittance minimum)
3. The transmitted energy P, and the incident energy P_0, are determined from the graph. P_0 is the interception of the frequency line and P is the point of maximum absorbance (Minimum transmittance).
4. Absorbance (log P_0/ P) is calculated and a Beer's law plot of standards is obtained. The concentration of the sample is then determined from the graph.

Because of close or overlapping bands and the continually changing base line, the choice of a base line is not always as easy as it first seems.

Applications:

1. It is used for the identification and determination of organic materials especially in the identification of many functional groups of organic compounds.
2. Atmospheric pollutants can also be identified when still in atmosphere.
3. Another interesting application is the examination of old paintings and artifacts (old articles of historic interest). It is possible to identify the varnish used on the painting and the textile comprising the canvas, as well as the pigments in the paint. From this information fake masterpieces can be detected.
4. In industry, IR spectroscopy has three important uses. It can be used to determine impurities in raw material; it can also be used for quality control. The third use is for the identification of materials made in their own research laboratories or of materials made by competitors.
5. From the IR spectrum it is possible to identify the odour and taste compounds of food, distinguish one polymer from another, determine the composition of mixed polymers or the solvent in paints.

Limitations:

1. It is not possible to determine molecular weight by IR spectroscopy.
2. It does not give possible information on the relative positions of different functional groups of a molecule.
3. Another limitation is that simple IR spectrum of an unknown substance will not differentiate between mixtures of compounds and pure compounds.

For example a mixture of paraffin and alcohols will give the same spectra as higher molecular weight alcohols.

UNIT 1

NEPHELOMETRY AND TURBIDIMETRY

Lesson 4

Objectives of the lesson:

This lesson deals with general introduction to the method, theory, instrumentation and applications.

Introduction:

The optical properties of each suspension will vary with concentration of the dispersed phase. When light is passed through the suspension, part of the incident radiant energy is dissipated by absorption, reflection, refraction, while the remainder is transmitted.

$$I_o = I_{absorbed} + I_{reflected} + I_{refracted} + I_{transmitted}$$

Measurement of the intensity of the transmitted light as a function of the concentration of the dispersed phase is the basis of the turbidimetric analysis (on line measurement).

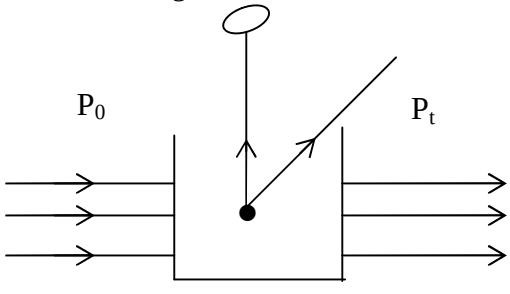
When the suspension is viewed at right angles to the direction of the incident light the system appears opalescent due to the reflection of light from the particles of the suspension (Tyndall effect). The light is reflected irregularly and diffusely and consequently the term scattered light is used to account for this opalescence or cloudiness. The measurement of the intensity of the scattered light (at right angles to the direction of the incident light) as a function of the concentration of the dispersed phase is the basis of nephelometric analysis (Nephle = cloud). Nephelometric analysis is most sensitive for very dilute suspensions (not greater than 100mg per litre). Techniques for turbidimetric analysis and nephelometric analysis resemble those of filter photometry and fluorimetry respectively.

Nephelometry, turbidimetry and Raman spectroscopy are the methods, which are based on the scattering of radiation. With respect to instrumentation nephelometry and turbidimetry are more closely related.

TURBID SOLUTION:

A turbid solution is one, which is a suspension of solid particles in a liquid. The term scattering is another one, which is of equal importance in those systems, which implies a more or less random change in the direction of propagation. The mechanism involved depends upon the wavelength of radiation, the size and shape of the particles responsible for scattering and sometimes of their arrangement. Scattering by relatively large particles is called Tyndall scattering.

When such a suspension is brought to the light path of photometer less radiant power reaches the photo detector than if the clear liquid were in the light path. This reduction is due to the scattering of light i.e., due to reflection of light and refractivity due to the suspended particles. Since the light



is scattered in all directions and consequently the radiant power of the beam directed towards the detector is reduced and as a consequence of the mixture, which was turbid or has a cloudy appearance. The concentration of these particles, which are responsible for this loss in radiant power, may be related to each other if other parameters are kept constant.

All the measurements are carried out generally with visible light. Let us consider an example of turbid solution in a beaker, a beam of light is allowed to pass through it (P_O). The transmitted power (P_t) can be measured just as in spectrophotometry or the power scattered at a specific angle (say right angles) (P_{90}) may be determined.

The ratio P_t / P_0 decreases with increasing number of particles while ratio such as P_{90} / P_0 will increase. For very dilute suspension, measurement at an angle is much more sensitive than in the on line measurement, as it involves observation of faint, scattered light against a black background. The on line measurement is called turbidimetry which can be performed with any standard spectrophotometer or filter photometer. Thus turbidimetric analysis is based upon the measurement of diminution in power of a collimated beam as a result of scattering. Thus the measurement of the intensity of the transmitted light as a function of the concentration of the dispersed phase is the basis of turbidimetric analysis.

According to the Tyndal effect when a beam of light passes through a suspension and the later is viewed at right angles to the direction of the incident beam the system appears opalescent due to the reflection of light from the suspended particles. Since the reflection of light is irregular and diffuse, the term-scattered light is introduced to account for this opalescence or turbidness.

Colour of the turbid solution depends upon the particle size. If turbidity is to be produced by mixing two reactants, the following conditions should be standardised.

1. The concentration of the solutions mixed.
2. The manner, order and rate of mixing of reactants.
3. Agitation.
4. Temperature.
5. The presence and absence of inert electrolytes and protective colloids.

Generally we experience low accuracy and precision in turbidimetric methods. While we measure intensity of transmitted light in turbidimetric methods, the intensity of scattered light is measured to gain sensitivity, in case of nephelometry.

The nephelometric analysis is based on the measurement of intensity of scattered light at right angles to the direction of incident light as a function of the concentration of dispersed phase. In other words, Nephelometry is based on the measurement of the power of scattered light at right angles to a collimated beam. As fluorescence measurement is more sensitive than absorption, nephelometric analysis is sensitive than turbidimetric method. The nephelometric measurement is more sensitive for dilute solutions and for moderately heavy particles both are applicable. The choice between a nephelometric and turbidimetric analysis depends upon the amount of scattered light. Turbidimetric analysis gives

satisfactory results, if the scattering is extensive due to the presence of many particles. A nephelometric analysis is suitable when the suspension is less dense and decrease in power of the incident beam is small.

THEORY:

It should be kept in mind that scattering associated with these measurements involves no net loss in radiant power. The only change, which takes place, is in the direction of propagation. The intensity of radiation appearing at any angle depends upon the following factors.

1. Number of particles.
2. Size and shape of the particles.
3. Wavelength of the radiation
4. The relative refractive indices of the particles and medium.

Effect of concentration on scattering:

In a dilute suspension the attenuation of parallel beam of radiation can be expressed by the relation,

$P = P_o\ e^{-T\,b}$ (similar to $I_t = I_o\ e^{-kt}$)

Where P_0 = Power of the incident beam

P = Power of the beam after passing through the length 'b' of turbid solution

T = Turbidity or Turbidity coefficient

The value of T has been found to be linearly related to the concentration of the scattering particles. Hence,

$$S = \log \frac{P_0}{P} = KbC$$

where S = Turbidence
K = Proportionality constant
b = Path length
C = Concentration in g/litre

A linear relation between $\log_{10} P_o/P$ and 'C' is established with standard samples, the solvent being used as a reference to determine P_o. The calibration curve that is obtained in this manner is used for determining the concentration of the samples in turbidimetric analysis. In nephelometric analysis a linear relationship is obtained by plotting the power of the beam scattered at right angles to the incident beam against concentration.

On the other hand, intensity of scattered light by small particles obeys Rayleigh's equation.

$$I_r = I_0 \left\{ \frac{\eta_1^2 - \eta^2}{\eta_1^2} . \frac{NV^2}{\lambda^4 r^r} \left(1 + \cos^2 \beta\right) \right\} \quad \text{..... (1)}$$

where η = Coefficient of refraction of medium
η_1 = Coefficient of refraction of particles
N = Total number of particles
V = Volume of one particle

λ = Wavelength of incident light
r = Distance to observer
β = Angle between incident and scattered light

For nephelometric investigations, quantities η, η_1, β and r are constant and hence Rayleigh's equation reduces to

$$I_r = I_o \frac{KNV^2}{\lambda^4} ----2$$

where K is the proportionality constant.

On the other hand, for the turbidimetric measurements the transmitted intensity (I_t) can be determined from the equation,

$$\log \frac{I_0}{I_t} = k^1 \frac{Cld^3}{d^4 + \alpha\lambda^4} \quad \text{---------- (3)}$$

where Io = intensity of incident beam.
I_t = Intensity of transmitted beam.
λ = Wavelength
C = concentration of absorbing particles in the solution
d = mean diameter of absorbing particles
l = thickness of absorbing layer of solution

k^1 and α are constants depending upon the nature of suspension and method of measurement. If d, λ, α and k^1 are constants, we have

$$\log \frac{I_0}{I_t} = K^1 lc \quad \text{---------- (4)}$$

This equation (4) is know as the basic equation of turbidity and is similar to Bouger-Lambert - Beer's equation $I_t = I_0\, 10^{-K^1 lc}$, Where K^1 is molar turbidity coefficient of solution.

Effect of particle size and shape:

The fraction of light scattered depends on the size and shape of the particles responsible for scattering.

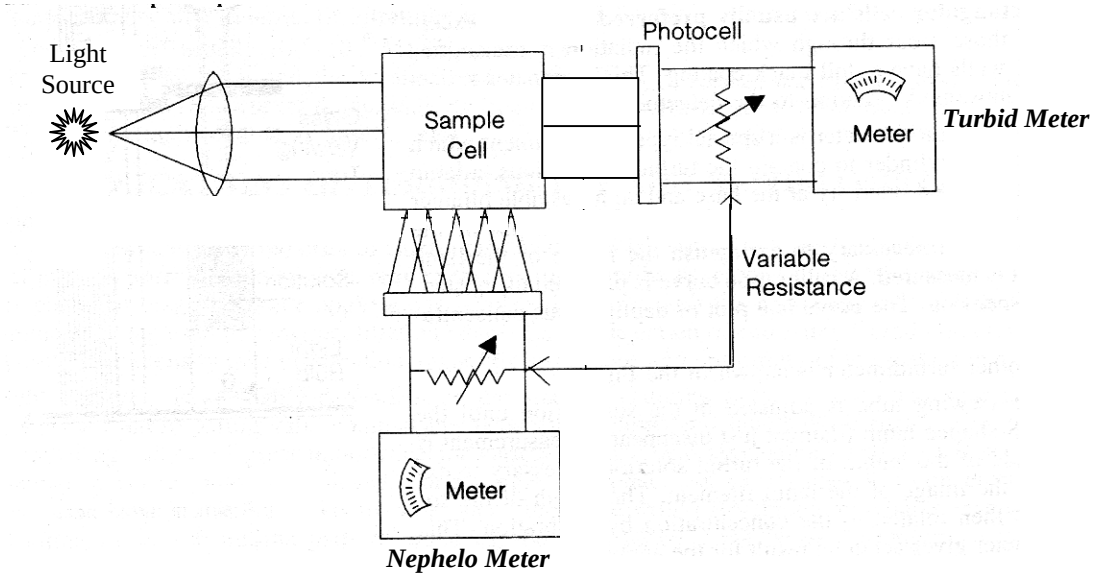
Effect of wave length on scattering:

It has been observed that turbidity is related to the wavelength by the expression

$$T = S\,\lambda^{-t}$$

where S is a constant for a given system. The quantity 't' depends upon size of the particle and its value is equal to 4, when the scattering particles are smaller than the wavelength of the radiation that is Rayleigh's scattering.

INSTRUMENTATION:



Nephelo Meter

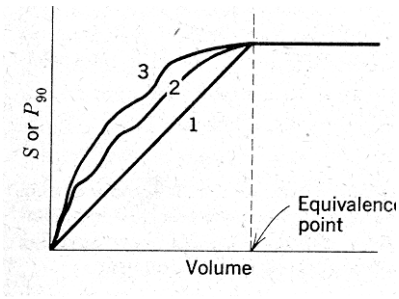
Any filter photometer or spectrophotometer can be utilized for turbidimetric measurements but with severely limited accuracy and sensitivity. If the solvent and dispersed particles are both free from colour, then the wave length in the blue or nearly uv should be selected for maximum sensitivity. To be operated as nephelometers, the instruments must have provisions for getting the illumination at right angles.

TURBIDIMETRIC TITRATIONS:

Reactions in which the equivalence point is revealed by the appearance or the dissolution of a precipitate have long been part of the analyst's domain. A method for determining silver by a chloride titration to the point where no further precipitate forms was introduced by Gay-Lussac in 1832 and although time - consuming, it is capable of giving excellent results.

This type of procedure can be carried out in the cuvette of a photoelectric turbidimeter or nephelometer with lessened eyestrain, and no doubt in many instances with increased sensitivity.

Titrations of the form A+B→C, where 'C' is insoluble, might be expected to give a curve of either turbidance or scattered intensity which would consist of two intersecting straight lines (curve 1), as the amount of precipitate must increase to a maximum and then stay constant. That is curve (1) is ideal and curve (2) and (3) might result from precipitate with mixed particle sizes and poor stirring.



The titration curve (1) can be true only if the number of particles increase linearly to the equivalence point while all remain the same in size. But in practice it will not happen because more probably, added reagent will simultaneously form some new particles and add to those nuclei previously

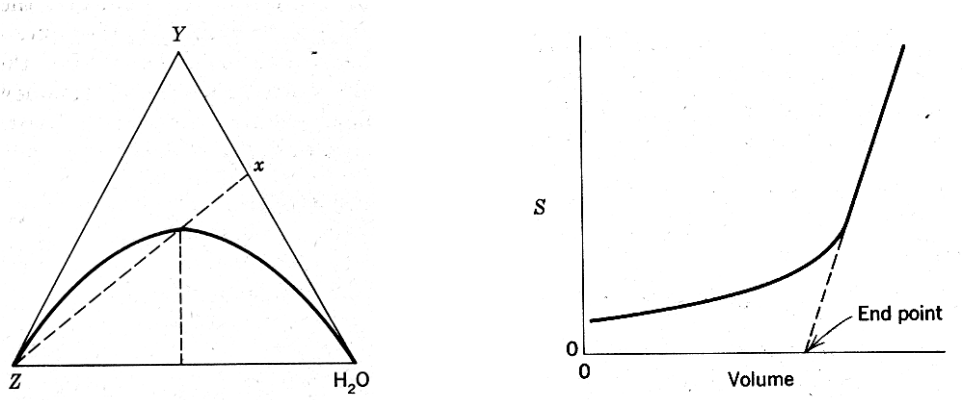
formed (in fact, the latter tendency is the more likely). In this, the prediction of curve becomes complicated. If the particles become too large, a poorly defined equivalence point or none at all like curves (2) and (3) will result. A complicating factor is that unless the suspension is very dilute the particles will continue to grow between added increments of titrant, so that excessively long times must be allowed between additions (6 or 7 minutes).

The method is useful in 10^{-5} – 10^{-6} formal range, with an average relative error of $\pm$5%. Bobtelsky and his coworkers have been successful in carrying out many hundreds of turbidimetric titrations at some what higher concentrations usually 10^{-3} to 10^{-4} formal. They made no attempt to control the particle size, and ran the titrations at normal speed. The curves cannot give meaningful data on turbidity as such, but Bobleksky method has given useful and reproducible results. As no linear relation between actual quantity of precipitate and apparent absorbance can be assumed, Bobtelsky is careful and hence not used the term turbidimetry, but calls his method heterometry and his simplified photometer, a heterometer (instrument)

PHASE TITRATIONS:

This explains, the titration of a mixture of two liquids by a third one, which is miscible with one but not the other. Addition of a sufficient quantity of third liquid will cause the separation of phases visible as turbidity.

In order to interpret results, either the three component phase diagram must be known or the unknown must be titrated in comparison with known mixtures. This following figure illustrates the titration of water-pyridine mixtures by chloroform.



The titration curve resulting when a pyridine - water solution of composition 'x' is titrated with $CHCl_3$.

The method could just as well be utilized for titrating chloroform-pyridine mixtures by water, or reversed, and a turbid mixture of chloroform and water titrated with pyridine to the point of clarity. A representative curve for H_2O – Y – Z, where Z might be $CHCl_3$ and Y might be pyridine, which is completely miscible with $CHCl_3$ and water.

APPLICATIONS:

1. Phosphorus can be detected at a concentration of one part in 300 million parts of water as a precipitate with strychnine molybdate reagent.
2. Ammonia in 160 million parts of water can be detected by a mercuric chloride complex (Nessler's reagent). The reactions can be made by adding protective colloids such as gelatin to produce suspension which are stable for such a long times to facilitate measurements precise.
3. Sulphur can be determined turbidimetrically by converting to barium sulphate by shaking a dilute solution of sulphate containing sodium chloride and hydrochloric acid with excess barium chloride. For getting reliable results, the quantity and grain size of the crystalline barium sulpate and the duration of stirring must be uniform for samples and standards.
4. Turbidimetric (or) Nephelometric analyses are of great importance in the analysis of water for the determination of clarity and for control treatment processes. Further the concentration of a variety of ions can be determined by using precipitating reagents.
5. Nephelometry is an important tool in the measurement of smokes, smog and other aerosols in understanding the environmental pollution problems. As the particles are smaller and farther apart one can expect better results.
6. The diameter of scattering particles can be determined with good precision provided they are less than about one twentieth of the wavelength.

They are also useful in sewage work, in power and steam generating plants, in beverages, bottling industries, in pulp and paper manufacturing units, in petroleum refineries, and pharmaceutical industries.

7. Determination of Carbon dioxide: The gas is passed through alkaline solution of barium salt and then analysed as barium carbonate suspension.
8. Benzene in alcohol can be determined by dilution with water by getting immiscible suspension.
9. It is also used for the analysis of turbidity in sugar products and clarity in citrus juice and fluorides as CaF_2, Chlorides as AgCl, Cyanides as AgCN, Calcium as calcium oxalate and zinc as ferrocyanide.

UNIT 2

FLOURIMETRY AND PHOSPHORIMETRY

Lesson 1

Objectives of the lesson:

This deals with introduction, theory, and instrumentation.

INTRODUCTION:

It is a fact that a molecule gets rid of excess energy following absorption of electromagnetic radiation. The process of excitation by electromagnetic radiation and as a consequence, reemission of radiation either of the same wavelength or of different wavelength is known as photoluminescence. Fluorescence and phosphorescence are the two important manifestations of photoluminescence. The lifetime for fluorescence is of the order 10^{-8} to 10^{-4} seconds, where as for phosphorescence it varies from 10^{-4} sec to 10 seconds or more. These two can be distinguished by their spectra.

When an electromagnetic radiation is absorbed by a system, one or more of different phenomena may occur. Since the light is a form of energy, the absorption of light means absorption of energy. Hence the primary effects in all photo processes are (a) An increase in thermal energy of system. (b) Activation or electronic excitation in which process the electrons in the atoms or molecules of the system rise to higher energy levels. If sufficiently energetic light is absorbed by a system, the later will raise the electrons of the atoms not only through one or two energy levels, but it will eject them completely and ionise the atoms. This type of phenomenon is known as **Photoelectric Effect.**

On the other hand when the light absorbed is not sufficiently energetic to eject electrons it will raise it to a higher energy level from which level it may return to its normal position either instantaneously or in steps with the emission of light energy. When this emission is instantaneous the phenomenon is also known as **Fluorescence**. However when there is a time lag the process is known as **Phosphorescence.** But when the absorbed light energy is stored i.e. fluorescence and phosphorescence are absent the resulting chemical reactions are known as photochemical reactions.

Fluorescence: When a beam of light is incident on certain substances, they emit visible light or radiations. The phenomenon is known as fluorescence, which is instantaneous and starts immediately after the absorption of light and stops as soon as the incident light is cut off.

Phosphorescence: When light radiation incident on certain substances, they emit light continuously even after the incident light is cut off. This delayed fluorescence is known as phosphorescence.

The fluorescence may be of two types 1. Resonance Fluorescence 2. Sensitized Fluorescence. Frank and Cario observed that mercury vapour absorbs radiation of wavelength 2536 A^0 but is not ionised by it. The vapour simply glows with that radiation and the light is emitted at the same wavelength at which it was adsorbed. This is called ***Resonance Fluorescence***. If the vapour of either thallium, zinc,

cadmium or of an alkali metal is added to the mercury vapour and then exposed to the radiations of wavelength 2536A^{o} the vapours of the foreign metal fluoresce. This phenomenon is known as **Sensitised Fluorescence**.

The phenomenon of fluorescence is of common occurrence and is shown mainly by fluorite, anthracene, and solutions of certain dye stuffs, eosin, fluorescein, chlorophyll, uranyl sulphate and the vapours of iodine, mercury, sodium and acetone.

In analytical work fluorescence is important because of the fact that the intensity of light emitted by a fluorescent material depends upon the concentration of that material. In this manner the measurement of fluorescent intensity permits the quantitative determination of traces of many inorganic species particularly for biological systems.

Among organic molecules fluorescence is to be expected in those species with large rigid multi cyclic structures. Rigidity is some times brought about by complexation with a transition metal and in such instances fluorescence is likely to provide a highly sensitive and often specific analytical tool for the metal.

Fluorescence is more common and more widely applied in analysis than in phosphorescence.

THEORY:

The terms singlet and triplet arise from multiplicity considerations of atomic spectroscopy and simply define the number of unpaired electrons (n) in the absence of a magnetic field. Therefore, if n is the number of unpaired electrons, the multiplicity is (n+1). Thus, if no unpaired electrons are present (n=0), then the spin state is singlet state (n+1 = 0+1=1). Similarly, systems having 1,2,3,---unpaired electrons refer to doublet, triplet, quartet, etc., states respectively.

Most of the molecules in their ground state do not have unpaired electrons (singlet state). When such a molecule absorbs u.v. or visible radiation of the proper frequency, one or more of the paired electrons (generally a Π-electron) get raised to an excited singlet state. In this excited state, the spin of the electron does not undergo any change and the net spin is still zero. One more possibility is that one set of electron spins may have undergone unpairing, resulting in two unpaired electrons with same spin which make an excited triplet state.

When molecules are irradiated with light of the appropriate frequency, it will be absorbed in about 10^{-15} second. In the process of absorption, the molecules may move from the ground to the first excited singlet electronic state. Although at room temperature molecules may be present in their ground vibration level, after absorption the ***excited*** molecules can end up in any one of the vibrational levels in the first excited electronic state. From the excited singlet state, one of the following three phenomena will probably occur, depending on the molecule involved and the conditions.

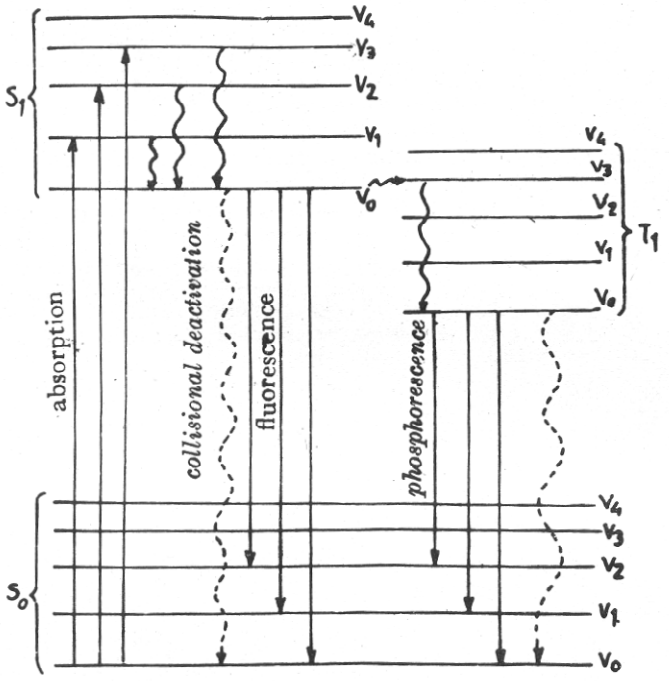
1. The first possibility is that the excited singlet state is relatively unstable. In such a situation, the excited molecules will return to the ground state by collisional deactivation without emitting any radiation.

2. The second possibility is that the molecule in the excited singlet state may emit an ultraviolet or visible light photon. This process is called ***fluorescence***. If we compare the absorption and fluorescence spectrum of the same compound, they do not superimpose on each other as expected but they are mirror images of each other with the fluorescence spectrum shifted to longer wavelengths. The reason for this is that as the time required to execute a vibration is about 10^{-13} second which is much shorter than the decay or ***mean life of 10^{-9} second***, most of the excess vibrational energy will be given to the surroundings and then excited molecules will decay in their ground vibrational levels.

3. The third possibility is that the molecule with relatively stable excited singlet state may undergo transition to a metastable triplet state and some time thereafter returns to the ground state, usually by emission of a u.v. or visible light photon. This is known as phosphorescence emission. And the process of crossing from a singlet state (no unpaired electron) to a triplet state (two unpaired electrons) is termed as intersystem crossing.

The decay from the triplet to the ground state singlet is forbidden by spin symmetry and is therefore slow. Thus, the life-time of phosphorescence is much longer than fluorescence. This mechanism of phosphorescence involving singlet – triplet decay scheme has been confirmed by the magnetic susceptibility and ESR measurements.

According to Hund's rule, the triplet level always lies lower than the corresponding singlet level and for this reason phosphorescence spectrum is not the mirror image of the absorption spectrum and it always occurs at long wavelengths compared with the absorption and fluorescence spectrum.



Factors affecting fluorescence and phosphorescence:

1. All the molecules cannot show the phenomenon of fluorescence and phosphorescence. Only those molecules show these phenomena that are able to absorb u.v. or visible radiation. In general, the greater the absorbency of a molecules, the more intense its luminescence. It means that molecules having conjugated double bonds (Π-bonds) are particularly suitable for this study while aliphatic and saturated cyclic organic compounds are not suitable.

2. Substances often exhibit a marked effect on the fluorescence and phosphorescence molecules. Few generalizations may be useful:

a. Electron donating groups like $–NH_2$ and –OH often enhance fluorescence. On the other hand, groups like $–SO_3H$, $-NH_4$ and alkyl groups do not have much effect on both these processes.

b. If a large atomic number is introduced into a Π - electron system, it enhances phosphorescence and decreases fluorescence.

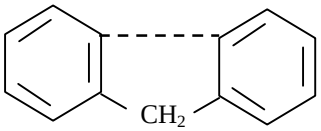
3. *Effect of pH:* The pH exhibits a marked effect on the fluorescence of compounds. For example, the neutral or alkaline solution of aniline shows fluorescence in the visible region. But if this solution is acidified, the visible fluorescence disappears.

   The pH value does influence the fluorescence of an aromatic compound with acidic or basic ring constituents. For ionized and unionized species the values of wavelength and emission intensity are different. Phenol and phenolate fluoresce in the ranges 285 – 365 nm and 310 –400 nm and the corresponding fluorescence intensities are 18 and 10 respectively.

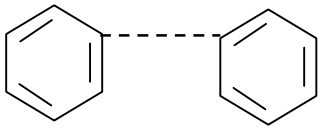
4. *Effect of dissolved oxygen:* The presence of dissolved oxygen reduces emission intensity of a fluorescent solution due to photo chemically induced oxidation of the fluorescent species. The paramagnetic nature of molecular oxygen do promote ***intersystem crossing*** and convert molecules to the excited state resulting into quenching of fluorescence.

5. *Effect of Temperature:* The quantum efficiency of most of the molecules decreases with increasing temperature because the increased frequency of collisions at higher temperature enhances the probability of deactivation by external conversion.

6. *Effect of structural rigidity:* It has been seen that compounds with rigid structure fluoresce to a great extent. The quantum efficiency of biphenyl and fluorine are 0.2 and 1.0 respectively when measured under same conditions. The presence of methylene group in fluorine results in enhanced structural rigidity.



Fluorene



Biphenyl

When fluorescence dyes are absorbed on solid surfaces, the emission intensity is enhanced on account of increased rigidity. Structural rigidity also accounts for increased fluorescence of certain chelating ligands when they undergo complexation with metals. For example, the zinc complex of 8-hydroxy quinoline fluoresces better than organic ligand.

7. *Quantum Efficiency:* The quantum efficiency, Φ, for a highly fluorescent compound like fluorescein, approaches unity under some conditions. The value of Φ leads to zero for species that do not

fluoresce. The value can be determined by the relative rates for the process by which the lowest excited singlet state is deactivated. Thus,

$$\Phi = \frac{K_f}{K_f + K_i + K_{ex} + K_{in} + K_{pd} + K_d}$$

Where K_f, K_i, K_{ex}, K_{in}, K_{pd}, and K_d are the rate constants of fluorescence, intersystem crossing, external, internal, pre-dissociated and dissociation processes. The magnitude of K_f, K_{pd}, and K_d depend upon chemical structure while other constants are strongly dependent upon environment and to a little extent on structure.

Relation Between Intensity of Fluorescence and Concentration:

The following relationship has been developed

$$F = K (I_o - I_t) \quad \ldots\ldots\ldots\ldots\ldots (1)$$

where F = intensity of Fluorescent radiation energy
I_0 = intensity of Incident radiation energy.
I_t = intensity of Transmitted radiation energy
K = proportionality constant

'F' is assumed proportional to the intensity of the radiant energy absorbed ($I_0 - I_t$).

But we have from Beer - Lambert Law

$$I_t = I_o \, . \, e^{-\in Ct} \quad \ldots\ldots\ldots\ldots\ldots (2)$$

$$(I_o - I_t) = I_o - I_o \, e^{-\in Ct} = I_o \, (1 - e^{-\in Ct}) \quad \ldots\ldots\ldots\ldots\ldots (3)$$

$$\therefore \quad F = K I_o \, (1 - e^{-\in Ct})$$

$$F = F_o (1 - e^{-\in Ct})$$

$$F = F_o - F_o \, e^{-\in Ct}$$

$$F_o \, e^{-\in Ct} = F_o - F$$

$$e^{-\in Ct} = (F_o - F) / F_o$$

Taking logarithm on both sides

$$\ln e^{-\in Ct} = \ln \frac{F_0}{F_0 - F}$$

(or)
$$\in Ct = \ln \frac{F_0}{F_0 - F}$$

$$\in Ct = 2.303 \log \frac{F_0}{F_0 - F} \quad \ldots\ldots\ldots\ldots\ldots (4)$$

where F_0 is the fluorescence intensity of the standard .

For very dilute solutions, it can be proved that $F \alpha C$

we have $F = F_0 \, (1 - e^{-\in Ct})$

when 'C' is small $e^{-\in Ct} = 1 - \in Ct$ (since $e^{-x} = 1-x$)

$F = F_0 \, (1 - 1 + \in Ct) = F_0 \, \in Ct$; Here F_0, $\in$, t are constants,

hence $F \alpha C$

Similar relationship holds good for the relation between phosphorescence intensity and concentration as in the case of fluorescence. Radiation power of the excitation source should be as large

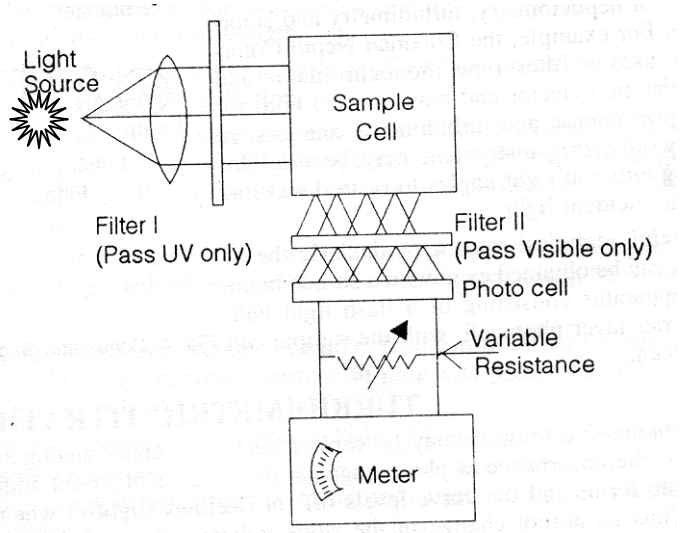
as possible and the time of excitation should be as long as possible to fully populate the triplet state. The interval of time following *cessation* (termination) of excitation is an important factor in phosphorescence. The influence of impurity in molecules leading to deactivating collisions is significant; hence a need for a rigid medium is essential.

Instrumentation:

Instruments for the measurement of Fluorescence are known as Fluorimeters. They are comparable to absorptiometers in that the sample is subjected to irradiation, and measurement is made of the power of the radiation having the sample.

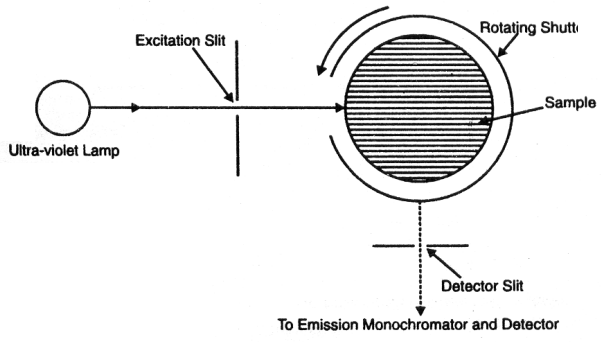
In the majority of the instruments the illumination is at right angles to the direction of the observation. The 90^0 construction is not particularly favorable, except for convenience in the lay out of parts.

The cells, receptors and filters are identical with those present in a filter photometer. The choice of an appropriate filter depends upon the wavelength of the emitted light and on the exciting mercury line or lines. It has been observed that a combination of filters work appreciably than a single filter. Mercury vapour lamp is widely used as a source. Fluorimeters resembles nephelometers in that the illumination is at right angles to the direction of observation. Infact that the same instrument can be used for either purpose provided that the lamp produces both U.V. and Visible radiation.



The primary filter, which transmits U.V but not visible radiation, is inserted between the source and the sample. The second filter is placed between the sample and photocell (detector). This second filter transmits visible and absorbs U.V. radiation. Compounds which phosphoresce are likely to fluoresce as well and a phosphoremeter must be able to distinguish between two.

This can be achieved by means of rotating shutter, such that a definite delay is introduced between the times during which the sample is irradiated and observed. A large number of organic compounds with conjugated ring systems phosphoresce intensely.



UNIT 2

APPLICATIONS OF FLOUROMETRY AND PHOSPHORIMETRY

Lesson 2

Objectives of the lesson:

This lesson deals with applications of fluorimetric and phosphorimetric methods as analytical tools besides the comparison of the methods.

APPLICATIONS OF FLUORIMETRIC ANALYSIS:

Fluorimetric methods are inherently applicable to lower concentration ranges than are spectrophotometric determinations and are thus among the most sensitive analytical techniques available to the scientist.

1. Morin and 8-hydroxy quinoline are the most important reagents in inorganic analysis. The determination of berilyum, aluminium, galium and zinc can be carried out by making use of morin. The later was also used by Bishop for the determination of citrate, fluoride, oxalate, phosphate, tartarate etc. 8-hydroxy quinoline yields a fluorescence in chloroform with aluminium, galium, indium in aqueous suspension with zinc and in alcohol with lithium.

2. Another inorganic fluorometric application is the determination of traces of boron in steel by means of the complex formed with benzoin. The boron present in an acid solution of the sample is first converted into boric acid which is then separated from other constituents by co-distillation with methyl alcohol. The resulting distillate containing boric acid is neutralised by NaOH and the methyl alcohol is evaporated off. The residue is dissolved in alcohol to which benzoin (alcoholic solution) is added. After two minutes the fluorescent intensity of the mixture is measured. Beer's law obeyed upto 2 μg of boron. Platinum ware should be used in place of common laboratory Borosilicate glass apparatus.

3. Aluminium in alloys can be determined fluorimetrically using Eriochrome Blue Black -R. The pH being maintained at 4.8. The sensitivity is one part in 108 parts.

4. For the determination of uranium the sample is first boiled with nitric acid and then fused with sodium fluoride such that a melt containing sodium fluoride and uranium fluoride is obtained. Upon cooling the melt solidifies to glass which can be directly examined in a specially designed fluorimeter. The sensitivity is of the order of 5×10^{-9} g of uranium in 1g sample.

5. Ruthenium can be determined in the presence of other platinum metals using 5- methyl, 1,10-phenanthroline at pH 6. The limit of identification of Ru (II) being 0.3μg / ml while the other ion may be present in 100 folds excess. Among fluorescent compounds dependence upon the pH of solution is often marked and procedures generally call for careful buffering. The amount of fluorescence also depends on temperature to a greater extent.

6. Estimation of vitamin B_1 (Thiamine):

Thiamine (vitamin B_1) is commonly estimated by the blue fluorescence of its oxidation product thiochrome. The sample is treated with phosphatase an enzyme which causes hydrolysis of the phosphate esters of thiamine which are frequently present in food materials. The phosphotase and other insoluble matter are filtered off and the filtrate diluted to a known volume. Two equal aliquots are taken, one for analysis and another for blank. To the first an oxidising agent (potassium ferricyanide) is added and then equal quantities of sodium hydroxide and isobutyl alcohol are added to both.

After shaking and subsequent removal of the aqueous layer, the alcoholic solution is examined in the fluorimeter. The whole procedure including blank is repeated with standard thiamine solution. If other coloured or fluorescing substances are present purification can be effected by passing the solution through a column of adsorbent (following the phosphatase treatment)

Thiamine is preferentially adsorbed, where as the contaminants pass through. The thiamine is then eluted with an acidified potassium chloride solution, made upto volume and treated as above.

Determination of Vitamin B_2 (Riboflavin):

The fluorimetric analysis also provides a good procedure of determining riboflavin. The power of fluorescence depends upon the specified conditions, the nature and the amount of impurities present. A method known as standard increment has been employed in order to make sure that the effect of impurities is same upon the standard and unknown.

In this method fluorescence of a portion of the standard is measured in the same solution with the unknown. The principle underlying this method is the fact that riboflavin can be oxidised by a non-fluorescing material which in turn easily reduced to regenerate the vitamin quantitatively.

The samples such as foodstuffs, after extraction with acid is treated to precipitate interfering salts and is oxidised with dilute $KMnO_4$ solution. The residual fluorescence is determined as blank. A reducing agent sodium dithionate (solid) $Na_2S_2O_4$ is now added and the fluorescence is again determined. A known volume of the standard is then added and the fluorescence is measured again. The results are calculated as follows.

Solution	Designation	Fluorescence
10ml oxidised sample + 1ml water	A	F_A
(A) + Dithionate	B	F_B
(B) + 1ml of standard riboflavin	C	F_C

since the power of fluorescence is proportional to the concentration of fluorescent material.

Thus $$\frac{F_B}{F_C - F_A} = \frac{m_x}{m_x + m_{s\tan dard}}$$

where m_x and $m_{standard}$ are respectively the masses of riboflavin from sample (to be determined) and standard in the cuvette.

Quenching:

This is the name given to any reduction in the intensity of fluorescence due to specific effects of constituents of the solution it self. Any material that causes the intensity of fluorescence to be less than the expected value is known as **Quencher** and the effect is termed **Quenching**.

Quenching may occur simply as a result of partial absorption of the fluorescent light by some component of the solution. However if the fluorescent substance itself is responsible for this absorption it is known as **Self Quenching**. Quenching may occur as the result of excessive absorption of either primary (or) fluorescent radiation by the solution. This is called **Concentration Quenching** (or) the **Inner Filter Effect**.

Quenching can also be caused by non radiative loss of energy from the excited molecules. The quenching agent may facilitate conversion of the molecules from the excited singlet to triplet level from which emission cannot occur. The quenching of many aromatic compounds by dissolving oxygen follows this mechanism.

Electron transfer from or to the excited molecule can cause fluorescence quenching in some systems such as the fluorescence of methylene blue which is quenched by ferrous ions. **Chemical quenching** is a term some times applied to the reduction in emission due to actual changes in the chemical nature of the fluorescent substance. A common observation is pH sensitivity. For example aniline shows blue fluorescence in the range of pH 5 to 13 when excited at 290 nm. At lower pH aniline exists as the anilinium cation and in highly alkaline media as the anion, neither ion is fluorescent.

APPLICATIONS OF PHOSPHORIMETRY:

Phosphorimetry finds applications in biology and medicine. But these applications are not accepted for routine analysis. Some interesting applications are

1. **Determination of Aspirin in Blood Serum:** Aspirin in blood serum can be determined with high sensitivity by phosphorimetry at liquid nitrogen temperatures. By this method 0.02 – 1.00mg aspirin per ml of serum can be analyzed. The metabolic product of aspirin, i.e., salicylic acid, does not exhibit appreciable phosphorescence but is quite strongly fluorescent where as aspirin is exhibiting strong phosphorescence but not fluorescence. Therefore it becomes possible to carry out a simple chloroform extraction of the serum and then analysis is done for both the drug (aspirin) and its metabolite (salicylic acid) in the presence of one another by using these two complementary techniques (fluorimetry and phosphorimetry).

2. Low concentrations of procaine, cocaine, phenobarbitol, and chlorpromazine in blood serum have been determined by phosphorimetry in combination with extraction procedures.

3. Cocaine and atropine in urine have been determined by employing phosphorimetry in combination with extraction procedures.

4. Phosphorimetry has been employed in combination with thin layer and paper chromatography. An interesting example is given by Winefordner and Moye. They have separated three tobacco alkaloids (nicotine, nornicotine and anabasine) from crude tobacco by thin layer chromatography on alumina. The R_F values of three alkaloids are 0.80, 0.26 and 0.48 respectively. The separated drugs were scrapped from the plate and determined by phosphorimetry.

Comparison between Phosphorescence and Fluorescence:

S. No.	Phosphorescence	Fluorescence
1.	When light radiation is incident on a substance, they emit light continuously even after the incident light is cut off. This is called Phosphorescence or Delayed Fluorescence	When light radiation is incident on a substance instantaneous emission of light starts immediately after absorption of light and stop after the incident light is cut off. This is called Fluorescence.
2.	The substance which emits phosphorescence is called Phosphorescent substance.	The substance which emits Fluorescence is called Fluorescent substance
3.	The instrument used is Phosphorimeter, with an arrangement called rotating shutter to provide time lag for irradiation of the sample.	The instrument is called a special Fluorimeter.
4.	Life time is 10^{-4} to 20 seconds.	It is of order 10^{-8} to 10^{-4} seconds.
5.	More complicated experimentally	Less complicated
6.	More sensitivity than Fluorimetry	Less sensitivity
7.	Quantum efficiencies are great	Quantum efficiencies are less when compared to phosphorimetry
8.	Scattering problems do not exist	Scattering problems are severe in Fluorimetry
9.	At low temperatures Quenching does not pose a serious problem	Quenching is a serious problem when compared to phosphorimetry.

Limitations of Fluorimetry and Phosphorimetry:

1. The quantum efficiency of a luminescent process must be the same and reproducible. If quantum efficiency decreases, it leads to the phenomenon of quenching.
2. Heavy atoms and paramagnetic species affect intersystem crossing and quantum efficiency, especially in fluorimetry. Even oxygen contributes its paramagnetism and leads to quenching.
3. A drift or change in source intensity and position of the cell leads to wrong results.
4. The inner filter effect which originates due to difference in intensity of fluorescence will lead to incorrect measurements.

UNIT 2

FLAME PHOTOMETRY

Lesson 3

Objectives of the lesson:

This lesson deals with introduction, instrumentation, methods of determination and applications.

INTRODUCTION:

Flame Photometry also called as **Flame Emission Spectroscopy** is a special technique in which excitation is caused by spraying a solution of the sample in a hot flame. A flame can serve effectively as a source of atomic emission lines and also as an absorbing medium for the same lines. Flame photometry is concerned with the emission of characteristic radiation in flames by individual elements and the correlation of its emission intensity with the concentration of the element introduced into the flame. Flame photometry, coupled with simple read- out devices, produces high sensitivity and reliability for the determination of several elements. The technique is most widely acceptable for the analysis of sodium and potassium, especially in fluids and tissues. Flame photometry is different from atomic absorption spectroscopy in that former is concerned with those particles that are electronically excited in the medium where as the later is based upon the behavior of particles that exist in the ground state in the flame.

Emission Spectra:

An electron is said to be in ground state, when it is in the lowest energy level. But when it gains thermal or radiant energy it jumps to the higher energy level and is said to be in exited state on the other hand, when electron drops from higher level to lower level, the radiant energy or light is emitted which depends upon the frequency or wave length of the radiation. These wavelengths of different radiations give spectrum which is measured by the spectroscope. Now this spectrum of emitted radiations is called **emission spectrum**.

The quantitative separation and determination of the alkali and the alkaline earth metals by wet chemical test has always been a difficult analytical problem. Emission spectroscopy deals with the examination of the energy emitted from a substance when suitably excited which is an obvious instrumental approach to the determination of these elements. It is a well known fact that a characteristic yellow light is emitted when a small amount of sodium salt is introduced into the flame of a Bunsen burner and the brightness of the flame varies with the amount of sodium or other metal introduced.

PRINCIPLE:

The sample to be analyzed is dissolved in water or in an inorganic solvent and introduced into the flame by means of atomizer under controlled conditions. The radiation from the flame enters a dispersing device in order to isolate the desired region of the spectrum. The intensity of isolated radiation can be measured by sending through a photocell. The out put from the photocell is measured by a suitable galvanometer. After carefully calibrating the photometer with solution of known composition and concentration, it is possible to measure the intensity of spectral line of an element present that emits the particular radiation.

Atomization of solution permits the uniform distribution of sample through out the body of the flame. The most important application of flame photometry will be the analysis of sodium and potassium particularly in biological fluids and tissues.

Flames and Flame Spectra:

The most important characteristic of a flame in flame emission spectroscopy is that it serves

1. To convert the constituents of the liquid sample into the vapour state.
2. To decompose these constituents into atoms (or) simple molecules.
3. To excite a fraction of the resulting atomic (or) molecular species by thermal energy of the flame.

The excited atoms emit photons and return to the lower energy state. The emitted photons are measured. If E_2 and E_1 are the energies of higher and lower energy levels respectively then the radiation emitted can be obtained by the equation.

$$E_2 - E_1 = h\nu \quad \text{---------- (1)}$$

where h = Planck's constant, ν = frequency of emitted radiation.

But we have $\nu = c\lambda$ ---------- (2)

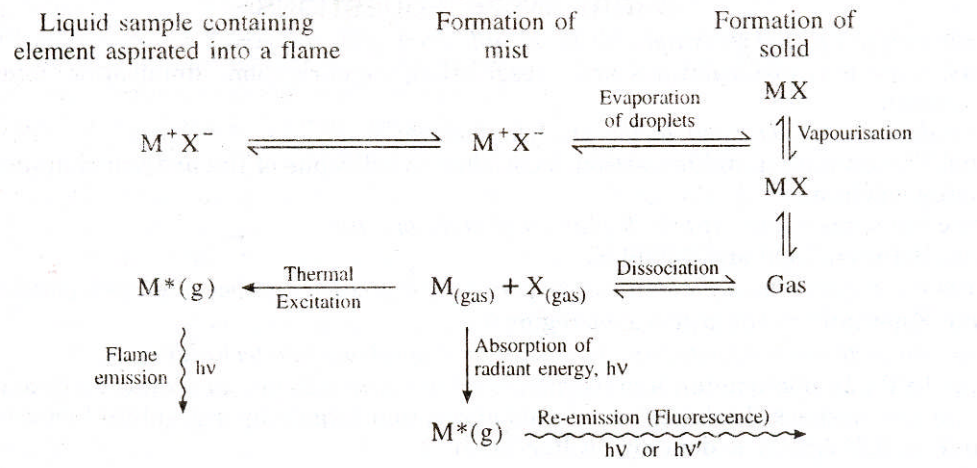
c = velocity of light, λ = wavelength of emitted radiation.

Hence combining equations 1 and 2, we have

$$E_2 - E_1 = hc/\lambda \quad \text{or}$$

$$\lambda = \frac{hc}{E_2 - E_1} \quad \text{---------- (3)}$$

From the equation (3) it is possible to evaluate the wavelength of the emitted radiation, which is characteristic of the element. The intensity of radiation corresponds to the amount of element, which is present in the flame. The temperature of the flame usually lies between 1000^{o}C to 3000^{o}C. The following sequence of events normally occurs in flame photometry.



A portion of neutral atoms or radicals in the flame may combine to form new gaseous compounds. The fraction of free atoms that are thermally excited is governed by a Boltzmann distribution which is as follows. The ratio of number of atoms which becomes excited (N^*), to the number which remains in ground state (N_o) is given by Boltzmann Distribution

$$\frac{N^*}{N_o} = A.\exp^{-E/KT}$$

. ---------- (4)

where A = Constant for a particular system

E = Activation energy

K = Universal constant (1.3805×10^{-16} ergs /deg)

T = Kelvin temperature

N^* = Number of excited atoms

N_o = Number of atoms remaining in ground state.

Effect of Temperature:

From equation (4) it follows that the formation of excited atoms depends upon the temperature of the flame. Therefore for higher number of excited atoms the temperature of the flame must be increased. Thus the fraction of atoms excited depends on the temperature of the flame. The temperature of the flame lies between 1000^oC to 3000^oC. Mixtures of coal gas and air do not give very hot flames because of the presence of nitrogen.

The following table shows the various common fuels employed in flame photometry and maximum temperatures resulting from their combustion with oxygen / air as oxidant.

Fuel	In presence of Oxygen	In presence of air
Illuminating gas	2800	1800
Methane	2700	2000
Propane	2800	1925
Butane	2900	1900
Hydrogen	2780	1800
Acetylene	3050	2200
Cyanogen	4580	-

The highest energy flame reported is produced by combustion of cyanogen gas in presence of oxygen.

$$C_2N_2 + 3O_2 \rightarrow 2CO + 2NO_2$$

The cyanogen gas produces spectra that are nearly arc like in quality and permits the determination of elements with high excitation energies. But because of its toxicity and other disadvantages, it is not likely to be used. Acetylene and Hydrogen are the most frequent choice in flame photometry.

Thermodynamic Function:

The theoretical as well as experimental evidences have shown that the reactions taking place in the mouth of the flame are in approximate thermodynamic equilibrium. As a consequence, burnt gases of the flame may be regarded as a solvent medium to which thermodynamic calculations can be applied.

Characterization:

Flame spectra are often characterized by appearance of bands originating from excitation of metal oxides and hydroxides. Nearly one third of the elements including rare earths, alkaline earth metals have been determined by using flame photometry.

Solvents: Alcohols, ketones, and esters alone or mixed with water can be used to spray the sample into the flame. These solvents usually increase the sensitivity of the flame photometric analysis. They also increase the likelihood of interferences.

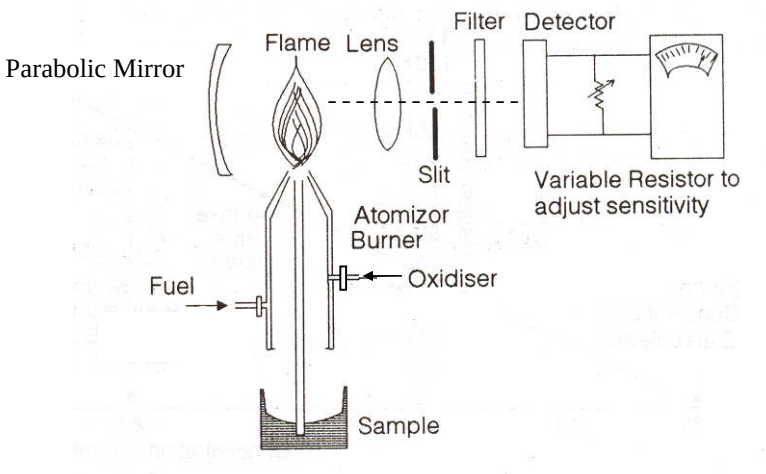
INSTRUMENTATION:

Two types of instruments are used

1. Flame photometer
2. Flame Spectrophotometer.

Flame photometer:

The various components of the flame photometer are shown below.



Generally the flame photometer has following parts

1. Pressure Regulator:

When the instrument is in operation suitable gases are provided. Pressure regulator is useful for the proper adjustment of these gases.

2. Atomizer: There are two types of atomizers

i) In one type it introduces the spray into the condensing chambers for removing large droplets.

ii) Another one which introduces spray directly into flame.

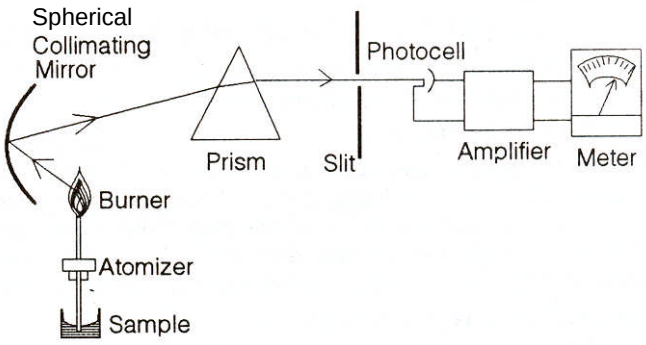
3. Burner: The burner must produce a steady flame. For low temperature flames Mecker type burner is generally used.

Optical system: The main aim of the optical system is to collect light from the steadiest part of the flame, make it monochromatic and then focus it on to photosensitive surface of the detector. The emitted light is

collected by a parabolic mirror and a lens, it is then allowed to pass through monochromator or filter. The light of the approximately selected wavelength strikes a photodetector and magnitude of electrical signal developed is read on a meter.

The other parts include photosensitive detector and instrument for recording the output of the detector.

FLAME SPECTROPHOTOMETER:



In flame spectrophotometer light from burner passes into a monochromator incorporating a spherical mirror and 60^{o} prism. This is in conjunction with a photomultiplier tube and a sensitive photocell is suitable for measurement from 250 - 1020mμ.

Calibration curve:

The concentration of a substance can be determined by making use of the calibration curve. The later can be established with different known concentrations of solutions containing the element and under identical instrumental arrangements and conditions. A correction must be applied for the flame background. The reading of the output meter is then plotted against the concentration.

The unknown concentration of the element can also be determined by

1. Emission intensity Vs concentration.
2. Standard Addition Method
3. Internal standard Method

1. EMISSION INTENSITY VS CONCENTRATION:

When interferences are absent and under proper experimental conditions i.e., having proper burning of the flame and correct filter / monochromator, deionized water is introduced into the flame and background emission is recorded. Similarly the possible highest concentration of test element is also fed to the instrument to know the range. Then different concentrations of standard solutions are introduced into the flame and the corresponding emission readings are recorded. Thus a plot is drawn for emission intensity vs concentration of standard element in mg / ml on x-axis which serves as the calibration curve. Then the unknown if it is not having any interference elements will be fed to the flame and emission intensity is noted. From this the amount of unknown can be computed.

2. STANDARD ADDITION METHOD:

In this method, net emission readings are obtained on two solutions. Solution 'A' containing an aliquot of the unknown solution (X) and solution 'B' containing the same quantity of unknown solution (X) plus a measured amount of standard solution of the test element (k_1).

The quantity of the test element in each of these solutions is then determined from their measured emission intensities and the standard calibration curve. Subtracting the amount of unknown found in solution 'A' from that found in solution 'B' yields the amount of test element equal to that added, when there is no depression or enhancement. When one of these effects is present, however, the quantity of test element found by subtraction is greater or lesser than that added. In such cases true metal content of solution 'A' is found by multiplying the observed metal content by a factor, which corrects for the interference. The factor is found by dividing the quantities of the metal added to solution 'B' by the amount of metal found (S_{found}) by subtracting the observed metal content of solution 'B' from that of the solution 'A'.

The concentration of unknown is found as follows.

L_1 = Emission reading of A (unknown)

L_2 = Emission reading of B (unknown + standard)

$(L_1 - H)_A = K X_{found}$ ----------1

$(L_2 - H)_B = K (X+S)_{found}$ ----------2

Subtracting 1 from 2

$$L_2 - L_1 = K . S_{found}$$

$$X_{\text{actually present}} = X_{found} \frac{S_{added}}{S_{found}}$$

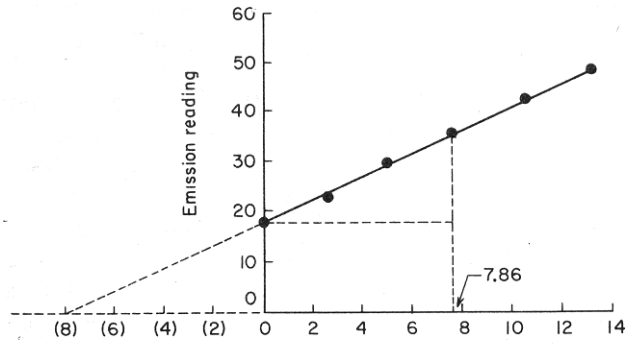
where H = Back ground reading

S = Amount of standard added (considering dilution factor)

X = Concentration of unknown

As discussed earlier improved results can be obtained by using different concentrations of the solution (i.e., k_2, k_3 etc.) Generally the amounts added may be 2 times or half of the original amount will yield good results. The resulting net emissions are plotted against the increments of standard solutions as shown in the figure.

The extrapolated line intersecting the x-axis indicates the amount of the unknown present in the sample.



Graphical representation of the standard addition method of evaluation

3. INTERNAL STANDARD METHOD:

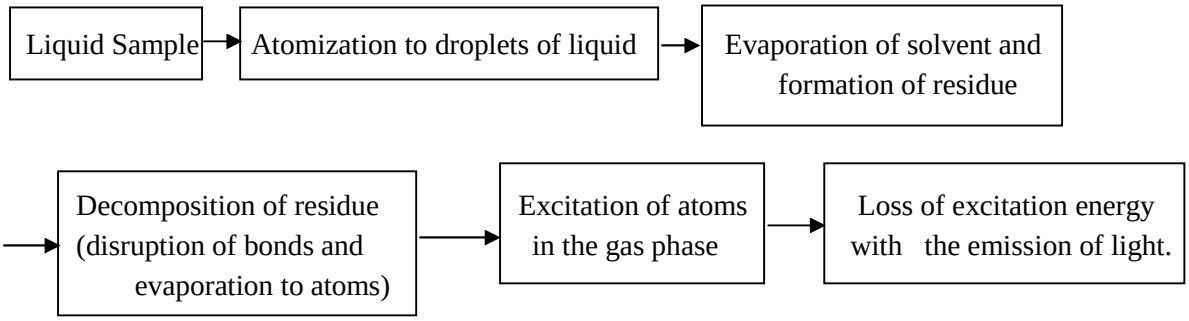
An internal standard method can also be used for determining the unknown concentrations of the element. In this method a foreign element not connected with the determinable element will be added both to the unknown and standards. It is preferable if the added element will have readily excitable

spectral lines. Lithium which shows a readily excitable spectral line and is rarely present in practical samples will be quite useful for this purpose.

A fixed quantity of internal standard element is added to both samples and standards alike. After excitation, radiant energy (emitted) by standard and by test element is measured simultaneously by dual detectors. The ratio of emission intensity of sample line to that of internal standard line is plotted against concentration of sample element (test element) on log - log paper to prepare calibration curve for a series of standards. This can be achieved by double beam instruments. The intensity of each line is corrected for back ground radiation in which it lies. The plot of log (emission ratio) vs log (concentration of test element i.e., sample) give a straight line of slope 45^{o} over a limited concentration intervals. On most double beam instruments the ratio is given by reading of the balancing potentiometer. Calibration curves are linear

ERRORS IN FLAME PHOTOMETRY:

Sources of error exist with emission flame photometry as with other analytical methods. The various events that take place are



If all these processes take place in an appropriate manner, very good results are obtained. But it was actually not so because of several interferences like chemical, spectral, ionization etc. Flame temperatures also influence the determinations.

Chemical Interferences:

Analytical errors arise when other compounds present in the sample as impurity and radiations of wavelengths that are not completely removed by a monochromator system. The magnitude of this effect depends on the following important factors.

1. Quality of the monochromator
2. Temperature of the source
3. Concentration ratio between the contaminants and of element sought.

The chemical interferences may be reduced to a greater extent by adding organic solvents or complexing agents or both to the sample.

Spectral Interferences:

The first type of spectral interferences arises when two elements or compounds may exhibit different spectra but their spectra may partly overlap and both are emitting at some particular wavelength. In this case, the detector cannot make distinction between the sources of radiation and will record the total signal. Thus an incorrect answer will be obtained. This type of interference is more common at high flame temperatures because numerous spectral lines are produced at high temperatures. An interesting example is that iron line at 3247.28A^o overlaps the copper line at 3247.54A^o and the iron line at 2852.13A^o overlaps the magnesium line at 2852.12A^o. This type of error can be eliminated by removing the effect of interfering elements either by using extraction methods or using calibration curves which are prepared from a solution having similar quantities of the interfering element.

The second type of spectral interference can occur if spectral lines of two or more elements are close but their spectra do not overlap. This type of interference is especially trouble some when a filter is used as the spectral isolation device. With a filter, spectral lines separated by as much as 50 -100A may be passed through the filter to the detecting unit, thus resulting in an incorrect read out signal. Such possibilities can be decreased to some extent by increasing the resolution of the spectral isolating system.

The third type of interference occurs between a spectral line and a continuous back ground. This type of interference arises due to high concentration of salts in the sample. This occurs especially in salts of alkali and alkaline earth metals. Some of the organic solvents will produce a continuous background. An example of which is methyl isobutyl ketone, which is particularly trouble some in flame photometry. This can be avoided by scanning technique.

Ionisation Interferences:

It has been noticed that in few cases the metal ionizes at high temperatures of the flame.

$$Na \rightarrow Na^+ + e^-$$

The sodium has emission spectra of its own. Hence ionisation decreases the radiant power of atomic emission. This interference can be removed by adding an excess quantity of potassium salts to all solutions of un known as well as known solutions.

Flame Temperatures:

No lines or very weak lines are usually obtained when the temperature of flame is too low. Too low temperatures are insufficient to cause dissociation of the salt to effect vapourisation and to excite the atoms of the metal. However, very high temperatures may also have detrimental effects. Hence for good precession the temperature of the flame must be appropriate.

APPLICATIONS:

1. Flame photometry can be applied to the analysis of wide variety of materials including biological fluids, soil, plant materials, cement, glasses, and natural waters.
2. Determination of sodium, potassium, and calcium in such diverse samples as blood serum, urine, soil extractions and industrial and natural water is common in many laboratories.
3. The determination of Li, Na, K, Cs, Rb, Ca, Sr, Ba, Cu, Cr, Ga, In, Fe, Pb, Mg, Mn, Tl, and boron etc has been carried out by this technique.

UNIT 2

ATOMIC ABSORPTION SPECTROSCOPY

Lesson 4

Objectives of the lesson:

This lesson deals with introduction, principle and theory, instrumentation, applications.

INTRODUCTION:

Atomic absorption spectroscopy has proved to be the most powerful instrumental technique for the quantitative determination of trace metals in liquids. This method provides the determination of total metal content of the sample and is almost independent of the molecular form of the metal in the liquid. This method can be used to determine about 60-70 elements, including most of the common rare earth metals in the concentration range from trace to macro quantities.

By this technique the determination can be made in the presence of many other elements. Hence there is no need for separation of test element from others, which saves lot of time and the process also eliminates error. The method is not only restricted to aqueous solutions, but also applicable to non aqueous solutions. The method needs no sample preparation and hence it is an ideal tool for non chemists also.

PRINCIPLE AND THEORY:

The absorption of energy by ground state atoms in the gaseous state forms the basis of atomic absorption spectroscopy. When the solution containing metallic species is introduced into a flame, the vapours of metallic species will be obtained. Some of the metal atoms may rise to an energy level sufficiently high to emit the characteristic radiation of the metal, which was considered in flame emission spectroscopy or Flame photometry. A large percentage of metal atoms will remain in the non-emitting ground state. These ground state atoms of particular element are receptive of light radiation of their own specific resonance wavelength. (In general the same wavelength as they would emit if excited).

Thus when a light of this wavelength is allowed to pass through a flame having atoms of the metallic species, part of that light will be absorbed and absorption is proportional to the density of the atoms in the flame. Thus in atomic absorption spectroscopy we determine the amount of light absorbed. Once this value of absorption was known the concentration of the metallic element can be determined because the absorption is proportional to the density of atoms in the flame. Mathematically - the total amount of light absorbed may be given by expression as follows.

At a particular frequency ν, the total amount of light absorbed = $\frac{\pi e^2}{mc}.Nf$ …….. (1)

e = charge of the electron of mass ‘m’

c = velocity of light

N = the total number of atoms that can absorb at frequency ‘ν’

f = oscillator strength or ability of each atom to absorb frequency ‘ν’

In above equation π, e, m and c are constants, the equation reduces to the following form

Hence, Total amount of light absorbed = constant x N f …….. (2)

Thus from equation (2) it follows that

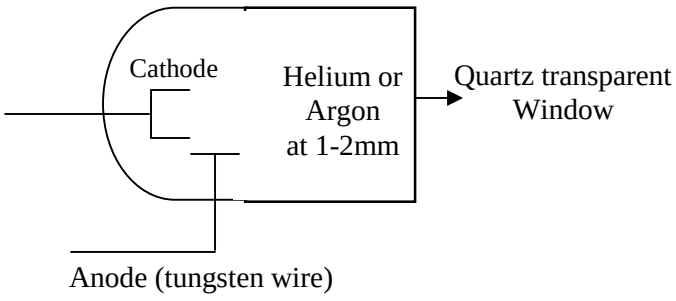
a) There is no term involving wavelength of absorption other than the indication of the actual absorption wavelength.
b) There is no term involving the temperature

From the above it follows that absorption by atoms is independent of wavelength of absorption and the temperature. These features provide distinct advantages over flame emission spectroscopy.

INSTRUMENTATION:

The basic components of instrument for atomic absorption measurements are similar to those of a spectrophotometer for the absorption of solutions. The equipment consists of a source, a monochromator, a detector, a sample container (i.e., a flame in this case) and an amplifier indicator.

Both single beam and double beam instruments have been designed for atomic absorption spectroscopy. The hallow cathode tube is the most common source of radiation which has widely been used in atomic absorption spectroscopy.

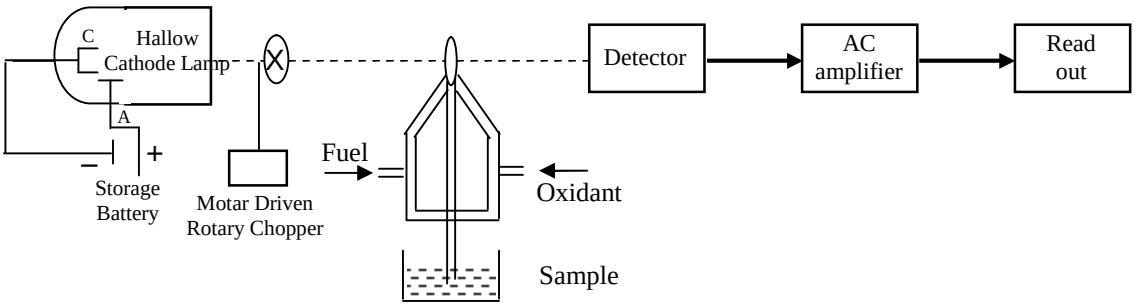


Construction of hallow cathode lamp:

This is a thick walled glass tube, which has a quartz transparent window at one end. Two tungsten wires are sealed (fused) into the other end of the tube. One end of the tungsten wire is attached with a hallow metal cylinder, the diameter of which would be 10-20mm. This cylinder acts as a cathode, while other tungsten wire acts as an anode. The tube is filled with inert gases like pure helium or argon at 1 to 2mm pressure. The cathode cup is made up of such an element whose spectrum is desired or it may be constructed from an inert element, in which the desired element or its salt can be kept. When a potential is applied across the electrodes, the gas filled in the tube ionizes and the flow of current occurs, as a result of flow of ions to the electrode. If the applied potential is sufficiently large, the gaseous cations will acquire kinetic energy sufficient to dislodge some of the metal from the surface of the cathode and produce an atomic cloud. This process of dislodging is known as **Sputtering.** Portions of the sputtered metal atoms are in excited state and thus emit their characteristic radiation in the usual way. As the process proceeds the metal atoms diffuse back to the surface of the cathode or to the glass walls of the tube and are re-deposited.

The cylindrical shape of the cathode concentrates the radiation in a limited region of the tube. The geometry and applied potential are the two important factors upon which the efficiency of the hallow cathode tube depends. High potentials and thus high current lead to greater intensities.

The schematic diagram of AAS will be as follows.



Devices used for the formation of an atomic vapour

Ovens: Sample is brought rapidly at high temperatures

Electric arc and sparks: In this device highest currents of high potential will be supplied to solid or liquid samples.

Sputtering devices: The sample held on cathode is bombarded with positive ions of inert gas.

Flame Atomization: In this case liquid sample is atomized with positive ions of inert gas.

Monochromators: It is extremely important that instrument must be capable of providing a sufficient narrow band width to separate the line chosen for determination from other undesirable lines that may either interfere with the measurement or reduce the sensitivity of the analysis. A glass filter has been employed for most alkali metals. Most instruments however incorporate a good quality U.V. visible monochromator.

Detector and Indicators:

These components are same as for a typical UV visible spectrophotometer.

Oxidants and fuels:

Natural gas, hydrogen, propane, butane, acetylene are important fuels, which have been employed for production of flame in AAS. The most widely used were acetylene. The common oxidants have been air, air enriched with O_2 , oxygen and nitrous oxide.

Low temperature flame such as natural gas - air produce satisfactory results for elements which are readily converted into atomic state (Cu, Zn, Pb, Cd). High temperature flame such as acetylene - air mixture is used for elements which form refractory oxides which require some what high temperatures for decomposition.

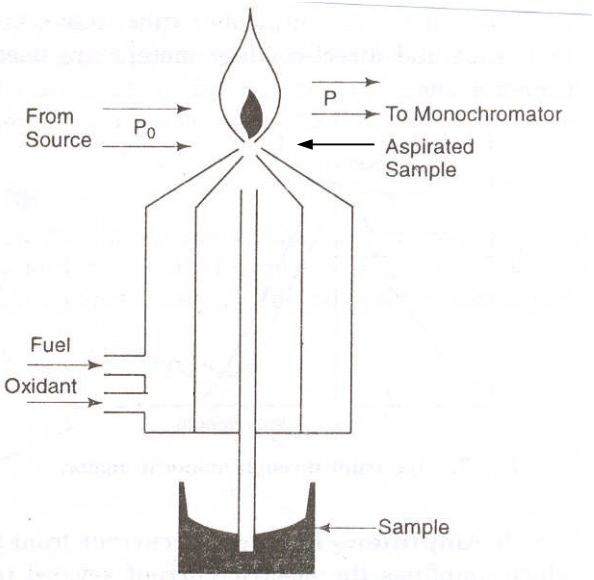
An oxygen – acetylene or nitrous oxide - acetylene flame may be employed for elements which form stable oxides (Al, Be and rare earths). However the ratio of fuel to oxidant influences the extent of formation of atoms.

Types of Burners:

Two common types of burners are being used

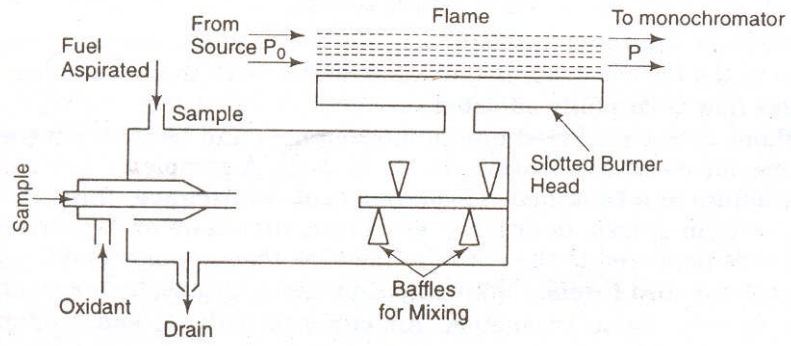
1. Total combustion burner
2. Pre- mixture Burner

Total combustion burner:



In this burner the sample is aspirated into a large chamber by means of a stream of the oxidant. Here the mist of the sample, oxidant and the fuel supply are mixed and then forced to the burner opening.

Pre- mixture Burner: The burner is also named as Laminar Flow burner. The fuel and oxidant gases are mixed in the body of the burner assembly along with the aspirated sample. The mixture then passes through an area containing one or more baffles to complete the mixing before entering the burner head. The large drops from the aspirator impinge on the walls of the mixing chamber and baffles are drained off, so that only the fine droplets find their way to the flame. The burner orifice consists of a long narrow slit, which produces a non turbulent, quite and ribbon shaped flame.



The premix burner will be designed with particular attention for the prevention of strike back, which may produce a sharp explosion in the enclosed mixture.

INTERFERENCES:

Anion Interference:

Phosphate ion interferes with the determination of magnesium and calcium. If the phosphate ions are present, the absorptions due to magnesium and calcium are weaker than if phosphate ions were absent. The reason is almost certainly the formation of stable phosphates of calcium and magnesium that do not easily break up into atoms in the flame. The interference may be reduced by adding a salt of lanthanum or thorium to the sample solution. These ions combine preferentially with phosphate ions. Interference can be avoided by the addition of EDTA.

Cation Interference:

In certain cases cations also interfere in atomic absorption measurements but this effect is less pronounced than in flame emission work. For example, aluminium interferes with alkaline earth elements where as boron interferes with calcium, and magnesium with calcium. Al interference with Mg. It is due to the formation aluminium, magnesium (heat stable) metalloids. Also Be, Al, and Mg interferes with Ca. They are rare

APPLICATIONS:

1. It has been applied for the sensitive determination of Na, Mg, Zn, Ag, Au, K, Pt, Rh, Fe, Mn, Ca, Sr, and other elements.
2. The technique may also be used for
   i) Determination of zinc in copper alloys and aluminium alloys
   ii) Determination of noble metals such as Ag, Au, Pt, and Rh.
   iii) Analysis of Bronze

3. Estimation of Silver in Lead deposits:

The sample will be digested with HCl – HNO_3 mixture (approximately 2**:**3 ratio) evaporated to dryness. Then the residue is dissolved in small amount of HCl and the contents transferred to standard flask are made upto the mark with dilute ammonium acetate. The pH is kept at 5 or more to make sure that silver remains in the solution.

Standards are prepared in

1. HCl - Ammonium acetate - KCN mixture.
2. Air - acetylene flame is used.

4. Determination of Metallic Elements in Food Industries:

Copper, Zinc and Nickel are the most common toxic elements of interest to food analyst. For solid foodstuffs the most common procedure is to extract the trace metals by digestion with the dilute sulphuric acid or with nitric acid or with 50% hydrogen peroxide and then fed to the instrument for estimation.

5. Determination of Lead in Petrol:

In petrol the two anti knocking additives were tetraethyl lead and tetra methyl lead. In order to apply atomic absorption spectroscopy to the analysis of lead in petrol, the analytical chemist must know which of these (tetraethyl lead and tetra methyl) or what mixture of two has been included in the sample

to be analysed. If there is no clear information about the nature of the lead additive direct method is not applicable instead of that indirect method can be used.

Direct Method:

If nature of the anti knocking additives is known, one can determine lead directly in petrol by atomic absorption spectroscopy. This involves the following steps

i) First of all standard solutions containing tetraethyl and tetra methyl lead (known concentrations) are prepared in cyclohexanone. The standards should cover the range 0-5μg/ml lead if the tetramethyl lead is being estimated, and 0-50 μg/ml lead if the tetraethyl lead is to be assessed. Then the standards are aspirated to the atomic absorption spectrophotometer at 2833^{o}A using air - acetylene flame and the response curves for solutions of tetraethyl lead, tetra methyl lead and mixtures of these compounds are drawn between the absorbance and μg/ml.(Standard curves are obtained).

ii) The petrol sample is diluted with cyclohexanone and is then aspirated into the absorption spectrophotometer at 2833^{o}A. The value of absorption is noted and is then compared with the standards curves. In this way one can obtain the lead content of petrol.

Indirect Method:

If the analyst posses no information about the nature of the lead additive, indirect method is used. This method involves the following steps.

i) Standard samples of lead containing 50, 25, 10, and 5 μg/ml are prepared in the deionised water. Then, the standard samples are aspirated to the atomic absorption spectrophotometer at 2833A^{o} to note down the absorbance corresponding to each standard sample.

ii) The petrol sample is treated with bromine to convert the lead to lead bromide which is extracted with dilute nitric acid. Then the extract is aspirated to the atomic absorption spectrophotometer to record the absorbance. Finally, the lead content in the petrol sample is calculated by employing the following expression:

$$\text{Pb as } \mu \text{ g/ml}(W_i/W_t) = \frac{S_2 - S_1}{S_0 - S_2} \times C \times \frac{1}{10 \times \text{S.g of original sample present in sample}}$$

where S_o = scale reading for blank, i.e., 1% nitric acid

S_1 = scale reading for sample extract

S_2 = scale reading for standard

C = concentration of standard Pb μg/ml (Wi / Wt)

s.g. = specific gravity

6. Calcium in blood serum:

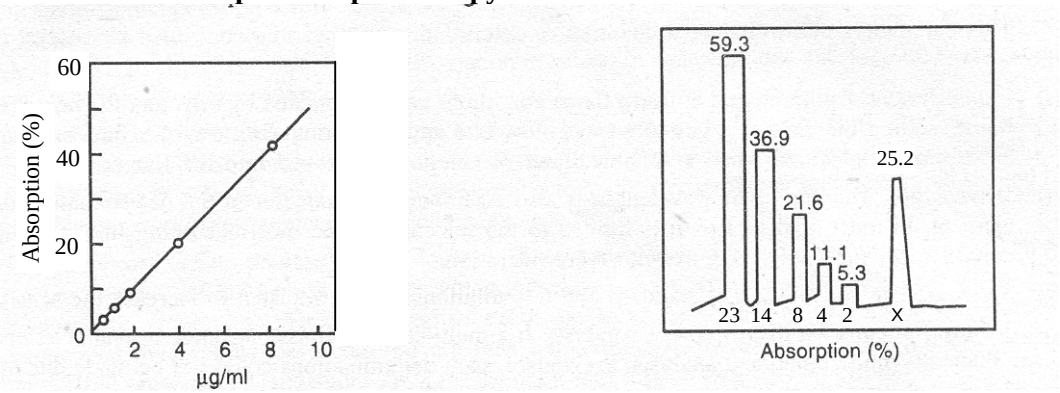
To an aliquot of blood serum a small amount of strontium and 4% trichloro acetic acid are added and the contents were stirred well and then centrifuged for 5 minutes.

Standards are prepared in a similar manner

7. Chromium in steal:

Sample is digested in phosphoric acid – sulphuric acid with the addition of HNO_3. an acetylene flame is used and the measurements are made at 3579^0A for chromium.

Operation of atomic absorption of spectroscopy:



For this purpose standard calibration curves are employed. The strip charts are generally used. The instrument is set for 100% transmittance. The numbers at the top indicate percentage absorption. The numbers below each absorption band indicates the concentration of standard sample. From the chart the value of absorption will be known, then the concentration (c) can be determined using A = mc where m is the slope of the line and A is the absorption.

Advantages:

1. The most important advantage of this technique over other procedures (flame photometry) is its high degree of freedom from interferences from environments.
2. More sensitive than emission flame photometry.
3. The technique is independent of flame temperatures.

Disadvantages:

1. The main disadvantage of this method is the need of a separate lamp source for each element to be determined. Attempts are being made to use a continuous source with a very high resolution monochromator.
2. The method can not be applied successfully for estimations of elements like Al, Ti, W, Mo, V, Si etc., because these elements give rise to oxides in the flame.
3. If aqueous solution are used the predominant anion affects the signal to a noticeable degree.

Differences between Atomic absorption and Flame emission Spectroscopy:

Flame emission	Atomic absorption
1. In flame emission, the atoms when put in the flame become excited The excited atoms return to the ground state emitting radiations The measurement of radiation forms the basis of flame emission spectroscopy. Signal in flame emission is the sum of all energies emitted as excited atoms drop to ground state. The signal is of total emitting atoms.	In AAS the signal is obtained from the difference between intensity of the source in the absence of metallic elements present in the liquid and the decreased intensity due to the presence of metallic elements present in the optical path.
2. In this technique radiation emitted by the excited atoms is related to the concentrations.	In this technique radiation absorbed by the unexcited atoms is related to the concentration.
3. Since emission intensity is dependent upon the number of exciting atoms; it is greatly influenced by the temperature variations.	AAS depends upon the number of unexcited atoms and the absorption intensity does not depend upon the temperature of the flame directly. However measurements are influenced by temperature fluctuations.
4. This is not true in the case of flame spectroscopy.	In AAS the relation between emission absorbance and concentration is nearly linear, that is Beer's law is obeyed over a wide range of concentrations.

UNIT 3

CONDUCTOMETRY

Lesson 1

Objectives of the lesson:

This lesson deals with introduction, principle, instrumentation, and applications.

INTRODUCTION:

Ohm's law states that the current i (amperes) flowing in a conductor is directly proportional to the applied emf E (volts) and inversely proportional to the resistance R (ohms) of the conductor.

$i = E / R$

The above law is obeyed by metallic as well as by electrolytic conductors.

The resistance 'R' depends upon the area of cross section (a) and length of conductor (*l)* which can be stated that "the resistance 'R' of a conductor of a uniform cross sectional wire is directly proportional to its length (*l)* and inversely proportional to area of cross section (a)".

$R \alpha l$, $R \alpha 1/a$, $\therefore R \alpha l/a$ or $R = \rho l/a$

Where ρ is a constant called Resistivity or Specific resistance and may be defined as follows:

"The resistance in ohm's of a specimen of one centimetre length and one square centimetre in area of cross section or it is the resistance between opposite faces of 1 cm^3 of the metal".

$\rho = Ra / l$ ohm cm^2 /cm $= Ra / l$ ohm cm.

The specific resistance ρ of a liquid is defined in the same way as for a solid conductor. The reciprocal of specific resistance is called specific conductance (k) .

When l = 1cm, and a =1sq.cm , we have specific conductance is equal to conductance. Conductance is expressed in ohm^{-1} or mhos.

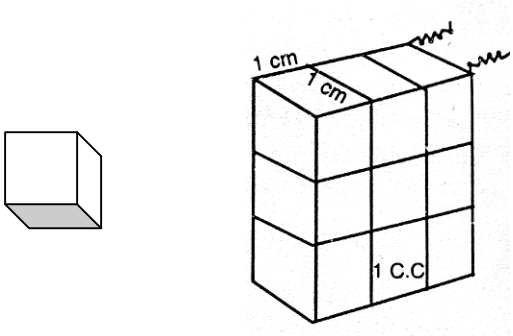
Thus the **specific conductivity** is defined as "the conductivity of one centimeter cube of the solution of an electrolyte". If one gram equivalent of solute is present in an aliquot the conductance of such solution is termed as the **Equivalent conductance (λ).**

The equivalent conductance will be specific conductance multiplied by volume V in cc. containing one gram equivalent weight (or)

$\lambda = k.V$

$$\lambda = \frac{1000.k}{c}$$

Where c is the concentration of the solution expressed in gram equivalents per litre. The equivalent conductance may be defined as "the conductivity in mho's of a solution containing one gram equivalent of the solute when placed between two sufficiently large electrodes which are one centimetre apart".



Let us consider a rectangular tank with two opposite sides made up of a metallic conductor and acting as electrodes exactly one centimetre apart. Now 1cc of solution is placed in the tank and the conductivity is measured. Evidently the measured conductivity will also be the specific conductivity of the solution, because specific conductivity is the conductivity of one centimetre cube of the solution. If this 1cc of the solution contains one gram equivalent of the solute, then the measured conductivity is also the equivalent conductivity.

Now dilute 1cc of solution to 9cc by adding water. In this case the measured conductivity is still equivalent conductivity since 9cc of solution contains one gram equivalent weight of the solute. But measured conductivity will not be equivalent to the specific conductivity, because now there are nine cubes each of which has specific conductivity (k). Thus the total conductivity of solution will be 9k.

Similarly the solution is diluted to Vcc and then the later form V cubes, thus total conductivity is given by kV. Hence the equivalent conductivity at any dilution is the volume 'V' in cc containing one gram equivalent weight of electrolyte is given by

$$\lambda = k.V$$

The equivalent conductivity may be defined as "equivalent to the product of specific conductivity and volume V cc of the solution containing one gram equivalent of the electrolyte".

For strong electrolytes the equivalent conductance increases as the dilution is increased. But it appears to approach a limiting value known as the equivalent conductance at infinite dilution (λ_∞). This quantity is sometimes written as λ_0 when concentrated rather than dilution is considered

The quantity λ_∞ can be determined by extrapolation for dilute solutions of strong electrolytes. For weak electrolytes the extrapolation method cannot be used for the determination of λ_∞ but it may be computed from the equivalent conductance at infinite dilution of the respective ions. By using the " Law of independent migration of ions" at infinite dilution the ions are independent of each other and each contributes its part to the total conductance, thus

$$\lambda_\infty = l_+^0 + l_-^0$$

l_+^0 and l_-^0 are ionic conductances (or) ionic mobilities at infinite dilution of the cation and anion respectively.

The values for the limiting ionic conductance for some ions in water at 25^0c are given below:

Cation	l_+^0	Anion	l_-^0
H^+	349.8	OH^-	198.3
Na^+	50.1	F^-	55.4
K^+	73.5	Cl^-	76.3
NH_4^+	73.5	CH_3COO^-	40.9
Ag^+	61.9	Br^-	78.1
$1/2Ba^{+2}$	63.6	ClO_4^-	67.4
Li^+	38.7	NO_3^-	71.5

The increase of mobility of most ions is about 2 % for each 1^o C rise in temperature. It is therefore important to allow the contents of the conductivity cell to attain thermal equilibrium before proceeding with the conductance measurement. The conductance of weak electrolytes is largely dependent upon the degree of ionisation, which itself also dependent upon the temperature.

MOLAR CONDUCTANCE (μ) :

This may be defined "as conductivity of solution containing one gram mole of the solute when placed between two sufficiently large electrodes which are exactly one centimetre apart". This is denoted by μ and is numerically equal to the product of specific conductivity and volume V in cc of the solution containing one gram mole of the electrolyte.

$$\mu = k.V$$

Measurement of Conductivity:

The prime requirements for measuring the conductivity of a solution are

1. Electrodes
2. Conductivity cells
3. Conductivity Water

Electrodes:

In general practice the electrodes usually consists of two parallel sheets of stout platinum foils that do not bend readily and their relative positions are fixed by sealing their connective tubes into the sides of the conductivity cell. In order to remove the polarisation effects the electrodes are coated with finely divided platinum black and these are called platinised - platinium electrodes.

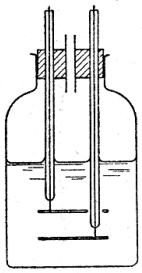
The following procedure may be used for platinising the electrodes. The conductivity vessel and electrodes are thoroughly cleaned by immersing in a warm solution of $K_2Cr_2O_7$ in concentrated sulphuric acid. After washing with distilled water until free from acid, the electrodes are plated with platinum from a solution containing 3g of chloroplatinic acid (3%) and 0.025g of lead acetate per 100ml (or 0.02 to 0.33%) by passing an alternating current for some time.

Electrolysis of chloroplatinic acid takes place. It is continued until both the electrodes are covered with jet- black deposit. The electrodes get blackened due to the coating of finely divided platinum. The lead salt favours the formation of the platinum deposit in a finely divided adherent form.

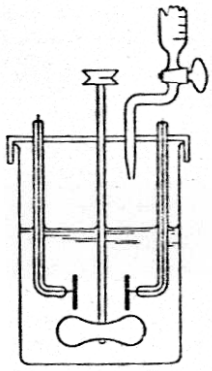
Conductivity cells:

The solution whose conductivity is to be determined is taken in to a beaker along with a cell known as conductivity cell. There are of various forms and are usually made up of high quality glass such as pyrex glass (or) quartz and are fitted with platinum electrodes.

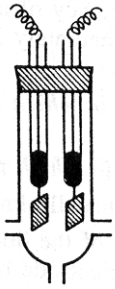
Various forms of conductivity cells are shown in the following figures A, B, C.



Fig(A)



Fig(B)



Fig(C)

A: It is a pyrex glass bottle of suitable capacity, closed by a stopper which carries the two electrode leads and has a third opening through which the reagent may be added, mixing is done by gentle shaking the contents of the bottle in a thermostat. The electrodes are stout horizontal platinum discs; previously platinised and the glass tube carrying the lower electrode passing through a hole in the upper one. The tubes holding the electrodes are kept in the same relative positions for as long as is required.

B: A cell in which the electrodes are firmly fixed in the ebonite lid. This cell is usually provided with a mechanical stirrer.

C: It is a schematic diagram of an immersion type of cell for dipping into the test solution. It consists of glass container with apertures at the side and bottom for the circulation of the liquid under test.

In usual conductivity vessel the geometry of the electrodes is not convenient to measure and it is customary to replace the ratio (l/a) by a single symbol θ , which has constant value by the given pair of electrodes (cells) and is termed as cell constant experimentally determined by equation.

$\theta = kR$ { $k = l / aR = \theta / R$; since ($l / a = \theta$) or $\theta = kR$ }

The conductance measurements are carried out on solutions of known 'k'. Conductance values of solutions of KCl are commonly known and employed at 25^0 C. The concentration of KCl per kg of a solute is k mho cm^{-1}

Conc. of KCl / Kg of solution	71.352	7.41913	0.74526
Conductance k mho cm^{-1}	0.11134	0.021286	0.001409

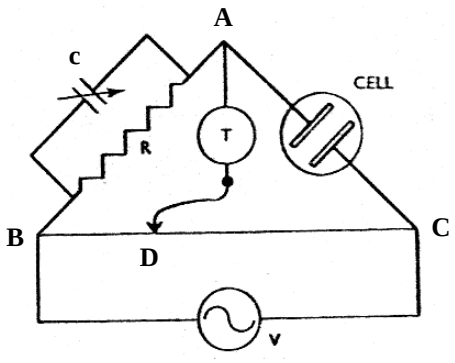
Conductivity Water:

Laboratory distilled water will have appreciable conductivity due to dissolved CO_2 and traces of laboratory gases. The storage containers may also contribute to the conductivity of distilled water. Water for conductance measurement should show a conductivity of less than 0.01×10^{-6} mho.

For accurate work, solutions must be prepared in absolutely pure water, which has no conductance due to dissolved impurities. For this purpose ordinary distilled water is not suitable. Thus absolutely pure water known as conductivity water is used. This can be prepared by distilling acidified solution of $KMnO_4$ in ordinary distilled water through an alkaline solution of $KMnO_4$.

Measurement:

The passage of current through a solution of an electrolyte may produce changes in the composition of the solution in the vicinity of the electrodes; potentials may thus arise at the electrodes, with the consequent introduction of serious errors in the conductivity measurements. This is due to polarisation effect. Unless such polarisation effects can be reduced to negligible proportions measurements can not be made. These difficulties can be eliminated by the use of alternating currents for the measurement so that the polarisation is constantly reversed.



The platinum electrodes are covered electrolytically with a light coating of finely divided platinum known as platinum – black. This greatly increases the surface area and materially reduces polarisation. The resistance (or conductance) can be measured with the aid of **Wheatstone bridge.**

The conductivity cell form one arm AC of a Wheatstone bridge, a standard variable resistance box 'R' forms another arm (AB) and a calibrated slide wire resistance (BC) constitutes the third and fourth arms, DB and DC.

Alternating current is supplied (ex., at 1000 cycles) to the bridge by a volve oscillator 'v' across BC, and a telephone T (or equivalent device) is connected across (AD) which serves to detect the point of balance. A variable condenser 'c' is connected in parallel with the resistance 'R'. When the position of the contact 'D' is adjusted as well as possible for a minimum sound in the telephone T. Various capacitances are inserted until the best setting is obtained.

When once the bridge is balanced we can write

$$\frac{R_{Cell}}{DC} = \frac{R}{DB}$$

From which resistance of the cell (R_{cell}) can be calculated.

A disadvantage of this method for measuring resistance is that one must work in a quiet room undisturbed by noises; this may be largely overcome by the use of an additional amplifier.

For conductometric work it is best to replace the telephone detector by a visual device, such as the magic – eye electronic device. The Mullard conductivity bridge incorporates a circuit of this kind. For conductometric work a Cambridge conductivity bridge is a more accurate instrument.

APPLICATIONS OF CONDUCTOMETRIC TITRATIONS:

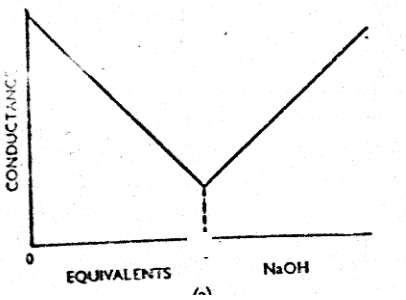
ACID BASE TITRATIONS:

These are particularly well adapted to the conductometric end point because of very high conductance of the hydroxide and hydronium ions compared with conductance of reaction products.

i) <u>Strong Acid with Strong Base</u>:

Let us consider the titration of HCL with NaOH.

$$[H^+ + Cl^-] + [Na^+ + OH^-] = (Na^+ + Cl^-) + H_2O$$
$$350 \quad 76.3 \quad 50.9 \quad 198.3$$



The conductance first falls due to the replacement of the hydrogen ion (mobility 350) by the added cation (mobility 50) and then, after the equivalence point is reached, conductivity rapidly rises with further additions of strong alkali due to the large mobility of the hydroxyl ion (198). The two branches of the curve are straight lines provided the volume of the reagent added is negligible, and their intersection gives the end point.

Thus, the titration is carried out at constant temperature and the conductivity is plotted against the volume of sodium hydroxide added. This titration is of practical interest when the solutions are dark or deeply coloured or if the solutions are dilute ($10^{-3} – 10^{-4}$N), in the later case CO_2 must be excluded.

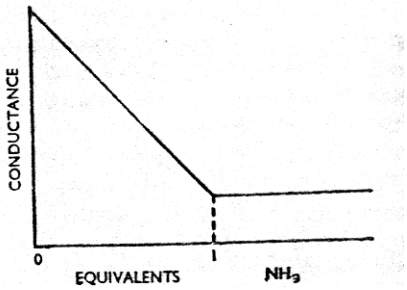
ii) <u>Strong acid with a Weak Base</u>:

Let us consider the titration of HCl (strong acid) with NH_4OH (weak base)

$$[H^+ + Cl^-] + [NH_4^+ + OH^-] = NH_4^+ Cl^- + H_2O$$
$$350 \quad 76.3 \quad 73.5 \quad 198$$

When ammonium hydroxide is added to hydrochloride acid, the conductivity decreases because of the replacement (disappearance) of the fast moving H^+ ions by the slow moving NH_4^+ ions.

The first branch of the graph reflects the disappearance of the hydrogen ions during the neutralization, but after the end point has been reached the graph becomes almost horizontal, since the excess of aqueous ammonium is not appreciably ionised in presence of ammonium chloride.



iii) <u>Weak acid with a Strong base</u>:

Example-1

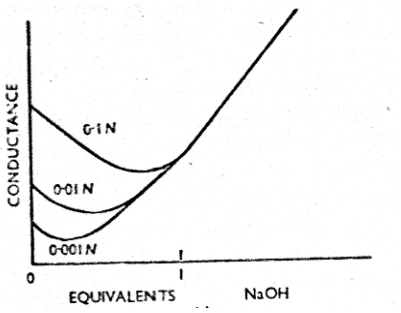
Let us consider the titration of weak acid (CH_3COOH) with a strong base (NaOH)

$$(CH_3COO^- + H^+) + (Na^+ + OH^-) = (CH_3COO^- + Na^+) + H_2O$$

40.9 350 50.1 198

In titration of weak acid with strong base, the shape of the curve will depend upon the concentration and the dissociation constant K of the acid.

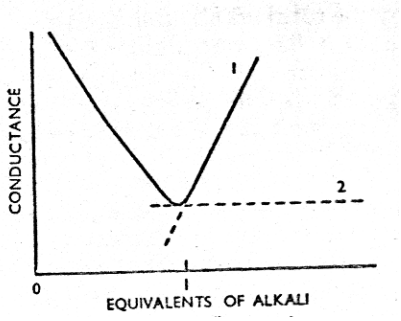
Thus in neutralisation of acetic acid ($K_a=1.8x10^{-5}$) with NaOH solution, the neutral salt (CH_3COONa) which is formed during the first part of the titration tends to repress the ionisation of acetic acid still present and hence its conductance decreases. The rising salt concentration will however, tend to produce an increase in conductance. As the titration proceeds, an indefinite break will occur at the end point, and the graph will become linear after all the acid has been neutralised.



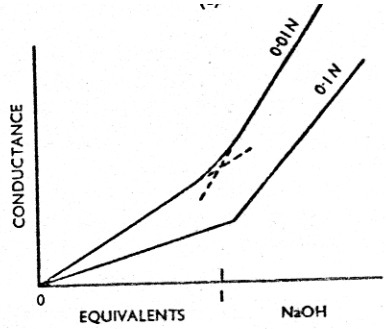
Example-2 O-nitro benzoic acid with KOH and NH_4OH:

Curve 1 is obtained as a result of titration of 0.005N o-nitro benzoic acid with 0.130N potassium hydroxide. The neutralization line is slightly curved in the vicinity of the end point. The acid is first titrated with aqueous ammonia solution; in case the end point is not satisfactory as desired a second titration is carried out using potassium hydroxide solution of the same concentration. The two curves are practically identical up to the neutralization point, and beyond this straight lines are obtained in both titrations, the intersection of which gives the end point.

Curve 2 is obtained with 0.130N aqueous ammonia solution. If the end point is required with great accuracy, a correction should be applied since the conductance of ammonium salt is approximately 0.6% lower than that of the potassium salt solutions, and the point of intersection should therefore be found when the final section of curve 2 is raised by this amount.



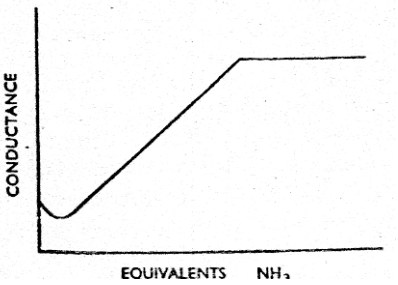
iv) <u>Very Weak acid with Strong base</u>:



At the beginning conductance is very small, but increases as the neutralization proceeds owing to the formation of salt. Due to hydrolysis the conductance values near the equivalence point are high; beyond the equivalence point the hydrolysis is considerably reduced by the excess of alkali.

Ex: Titration of Boric acid and Sodium hydroxide.

v) <u>Weak acid with Weak base</u>:

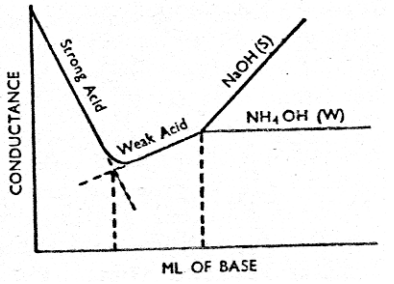


The conductivity is governed by the extent of ionization and concentration of the base used before the end point. In the first instance it decreases since the ionization is suppressed due to anion formation passes through a minimum and increases upto the end point. This is due to the conversion of non conducting weak acid into its conducting salt.

$CH_3COOH + NH_4OH \rightarrow CH_3COONH_4 + H_2O$

It has an advantage over the strong base. The endpoint is easily detected and in dilute solution the influence of CO_2 may be neglected.

***vi)* Mixture of Strong acid and a Weak acid with a Strong base:**

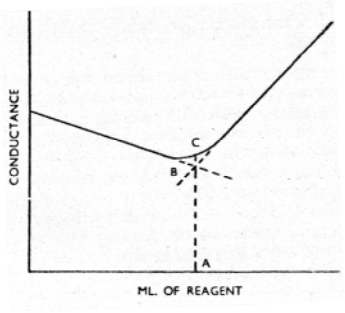


Upon adding a strong base to a mixture of a strong acid and a weak acid Ex: Hydrochloric acid and acetic acid; the conductance falls until the strong acid is neutralised, then rises as the weak acid is converted into its salt and finally rises more steeply as excess of alkali is introduced.

The other applications of conductometry include

1. Precipitation titrations
2. Redox titrations
3. Complexometric titrations
4. Replacement or displacement titrations
5. Determination of solubility of sparingly soluble salt
6. Ionic product of water

1. Precipitation titrations:



Many precipitation titrations can be carried out conductometrically. In general case of a titration of electrolyte A^+B^- with electrolyte C^+D^- to give insoluble AD and electrolyte C^+B^-

$$A^+B^- + C^+D^- \rightarrow AD + C^+B^-$$

(insoluble)

The net ionic results at equivalence point is replacement of A^+ by C^+. If 'C' has lower mobility than A, a downward sloping line is obtained for the conductance graph. Since beyond the equivalence point the addition of C^+D^- increases the conductance. The net result is a V- shaped curve with the equivalence point at the interception of 2 straight lines. A similar result is obtained in the titration

$$A^+B^- + C^+D^- \rightarrow CB + A^+ D^-$$

Here the anion B^- is replaced by D^- which has a low mobility. A 'V' shaped curve is again obtained. Since lithium ions (38.7) and acetate ions (40.9) have exceptionally low mobilities. It is best to precipitate cations with lithium salts and to precipitate anions with acetate. The titration to the equivalence point of an equivalent weight of barium chloride can be expressed as follows.

$$\underset{63.6\ \ 76.3}{1/2\ Ba^{2+}\ Cl_2^-} + \underset{38.7\ \ 79.8}{1/2\ Li_2^+\ SO_4^{2-}} \rightarrow 1/2\ Ba\,SO_4 + \underbrace{Li^+\ Cl^-}_{38.7 + 76.3 = 115}$$

Generally conductometric precipitation titrations are not accurate as neutralization titrations.

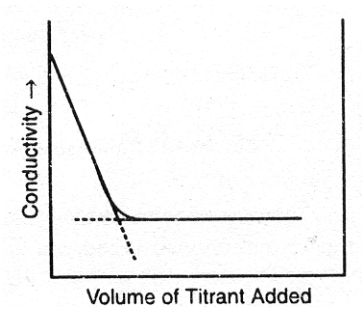
2. Conductometric redox titration:

In case of oxidation reduction titration, there is a decrease in the hydrogen ion concentration.

E.g. Iron(II) Vs dichromate.

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

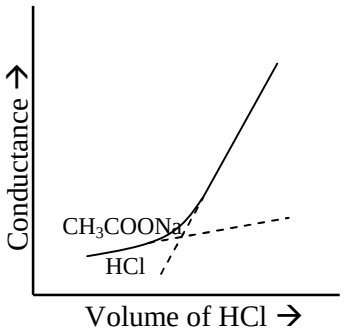
Since the mobility of hydrogen ion is high a sharp decrease in conductance is expected during the initial part of the titration.



3. Conductometric replacement titrations:

Salts of strong base and weak acid can be conductometrically titrated with a strong acid and salts of strong acid and weak base can be conductometrically titrated with a strong base. For example in the titration of

$$\underset{50\ \ \ 40.9}{Na^+CH_3COO^-} + \underset{350\ \ 76.3}{(H^+\ \ Cl^-)} \rightarrow \underset{50\ \ 76.3}{Na^+\ Cl^-} + CH_3COOH$$



only a slight increase in the conductance is noticed upto the equivalence point. Beyond the equivalence point, further addition of HCl gives sharp increase in conductance.

4. Complexometric titration:

An interesting complex formation reaction is the determination of mercury by cyanide ion. Mercury(II) ions in the solutions as perchlorate exists almost entirely as free ions. It may be titrated with potassium cyanide solution. Two breaks in the curves are obtained one at the formation of $Hg(CN)_4^{-2}$ and the principal one at the end of the completion of the reaction.

$$(Hg^{++} + 2ClO_4^-) + 2(K^+ + CN^-) \rightarrow Hg(CN)_2 + 2\,(K^+ + ClO_4^-)$$

Before the equivalence point one mercuric ion is replaced by 2 potassium ions and the conductance varies only slightly. Beyond the equivalence point the addition of potassium and cyanide ions causes the conductivity increase sharply. The end point is readily determined.

5. Determination of solubility of sparingly soluble salt:

There are various substances such as silver chloride, barium sulphate, lead sulphate etc. which are regarded as insoluble (or) so sparingly soluble in water, that their solubility can not be determined by any chemical method.

But this extremely small solubility of substances can however be determined with the help of conductivity measurements. Suppose if it is required to find out the solubility of sparingly soluble salts AgCl at 25^0C. The substance is readily washed with conductivity water in order to remove soluble impurities and it is then suspended in conductivity water warmed and cooled to 25^0C.

A small of amount of substance will go into the solution. The solution thus obtained may be regarded as saturated solution of AgCl at 25^0C. The specific conductivity k of the solution at 25^0C can be measured by means of conductivity cell by usual method. Since minute salt is present in the solution it will be almost completely dissociated into ions and hence the values of λ_v may be equal to λ_∞, the equivalence conductivity at infinite dilution, thus

$$\lambda_v = \lambda_\infty, = k.v$$

where v is volume containing 1g equivalent of the solute. But according to Kohlrausch law the value of λ_∞, is given by

$$\lambda_\infty, = l_+^0 + l_-^0$$

where l_+^0, l_-^0 are limiting ionic conductances (or) ionic mobilities of the cation and anion respectively.

$$\lambda_\infty, = \lambda_{Ag^+} + \lambda_{Cl^-}$$
$$= 61.9 + 76.3 = 138.2 \text{ mhos}$$

Thus by knowing the values of λ_∞, k, the volume V containing 1g equivalent, the solubility S can be calculated.

Since V cc of solution contains 1g equivalent weight of solute

1000 cc of solution contains ……..?

$$= \frac{1000}{V} \text{ g.eq./lit.}$$

Hence solubility

$$S = \frac{1000}{V} E \quad \text{g/lit.}$$

E = Equivalent weight of the substance

$$S = \frac{1000 \times E \times k}{\lambda_\infty} \quad [\because V = \frac{\lambda\infty}{k}]$$

$$\text{Solubility of AgCl at } 25^0\text{C} = \frac{k \times 143.5 \times 1000}{138.2}$$

from which the solubility of AgCl can be determined.

6. Ionic product of water:

Pure water ionizes to a very slight extent and so we have equilibrium

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

$$\frac{[H^+][OH^-]}{[H_2O]} = K$$

where K is ionization constant of water.

Since water is supposed to be slightly ionized the concentration of unionized water may be considered as practically constant. In other words

$$[H^+]\ [OH^-] = K_w$$

where K_w is ionic product of water

"The product of ionic concentrations of H^+, OH^- expressed in gram moles per liter is constant at constant temperature and is known as ionic product of water". The specific conductivity of pure water at 25^0C is found to be 5.54 x 10^{-8}mhos by Kohlrauch.

Assuming water to be completely ionized

$$\lambda_\infty = \lambda_{H^+} + \lambda_{OH^-} = 349.8 + 198.3 = 549.1$$

Thus when the conductivity of water is 5.54 x 10^{-5} mhos, the number of gram equivalents of H^+ ions/litre will be given by $\frac{5.54 \times 10^{-5}}{549.1}$ = 1.01 x 10^{-7}

Similarly, the number of gram equivalence for OH^- will also be equal to 1.01 x 10^{-7}.

Hence $K_w = [H^+]\ [OH^-]$

$= 1.01 \times 10^{-7} \times 1.01 \times 10^{-7}$

$\therefore K_w$ = ionic product of water = 10^{-14} at 25^0C

UNIT 3

POTENTIOMETRY

Lesson 2

Objectives of the lesson:

This lesson deals with introduction, theory, instrumentation, and applications.

INTRODUCTION:

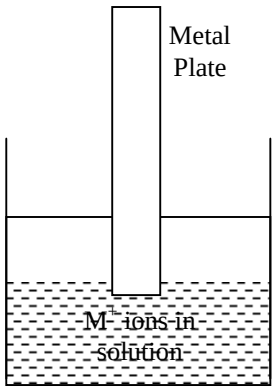
The Electro Chemical Cell:

When a metal strip is immersed in a solution of its own ions a potential difference (voltage) is developed between the metal and the solution. The potential difference is caused by the tendency of the metal atom to go into the solution as ions, liberating electrons in the process. The system constitutes a half-cell. The metal strip in the solution is called an Electrode. The reaction between the metal strip and ionic solution can be represented as

$$M^o \rightarrow M^+ + e^- \quad \text{-------1}$$

where M^0 is an uncharged metal atom, M^+ is a positive ion and e^- is an electron. This is an oxidation reaction, because in the process the metal has been oxidised, the metal ions enter the solution (dissolve), which becomes positively charged. The electrode retains the electrons and therefore becomes negatively charged. This is an oxidation step and the electrode is called an anode.

Expressing this differently, we say that at the anode, oxidation of metal occurs according to the reaction (1). It should be noted that the reaction is reversible. In practice a state of equilibrium is reached between the system components, M^o, $M^+$and e^-. Further more, the reaction is not restricted to systems where only one electron is involved. More probably, the reaction should be represented as



$$M^o \rightarrow M^{+n} + n\,e^- \quad \text{-------2}$$

Where ‘n’ is a whole number

It has been found that with some metals at equilibrium it is in the opposite direction and metal ions tend to become metal atoms, taking up the electrons. This reaction can be represented as

$$M^+ + e^- \rightarrow M^o \quad \text{----3}$$

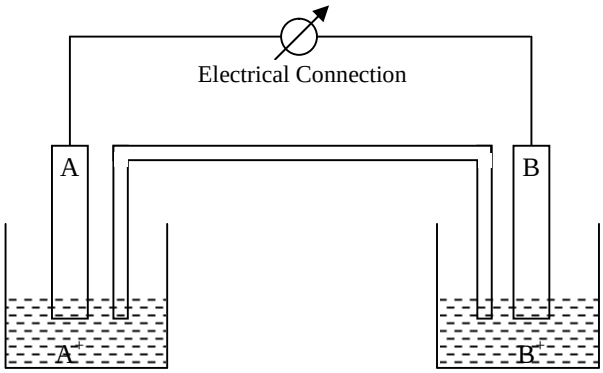
This is a reduction reaction because the positively charged metal ions lose their charge and become neutral atoms. In this process, the metal ion, already in the solution, takes an electron from the electrode and becomes a neutral atom M^o, the neutral atom deposits on the electrode. In the course of this reaction, the solution losses a positive charge and thus becomes more negative; the electrode loses a free electron (or gains a positive ion) and becomes less negative. This is a reduction of metal ion and the

electrode is termed cathode. At the cathode, reduction of the metal takes place. As in case of oxidation reactions the components here also are in equilibrium, further more than one electron may be involved.

$$M^{n+} + ne^- \rightarrow M^o$$

Each of these systems constitutes a half-cell. It is not possible to measure directly the potential difference between the metal and the solution in either case. In fact the observations of a half-cell would give no measurable sign of interaction. When we join two half cells together, however the potential differences generated at each half cell combine to form a complete cell with a potential difference manifested by a current flowing across the connections. This is the basis of an electrical cell or a battery.

Salt Bridge:



Completion of the circuit is effected through the galvanometer and the salt bridge. The salt bridge, which makes the electrical connection, is usually a gel in which an inert electrolyte is dissolved. For example, a salt bridge can be made by dissolving potassium chloride in hot agar-agar gel. The solution is transferred to a glass tube. After it has cooled, the bridge is physically strong enough to provide a connection. The advantage of this connection is that it is electrically inert.

An inert salt-bridge must be used to connect the two solutions (two half cells) electrically. If we were to use a metal wire, the wire itself would constitute a pair of half-cells at each end and would complicate the calculations. Another advantage of this gelatinous salt bridge is that it prevents mixing of two solutions in the two half-cells. It has been explained earlier that it is not possible to measure absolute voltage difference between the metal strip and the solution of its ions. However, we can compare the difference between one half-cell and the other.

In practice, the voltage difference between hydrogen and hydrogen ions under standard conditions is defined as zero. In other words, the cell utilizing the reaction has zero voltage.

$$H \rightarrow H^+ + e^-$$

By connecting this half cell to any other half-cell and measuring the voltage difference developed, we can obtain the relative voltage developed by the second half-cell.

Let us consider for example, a cell made up of the two half cells

$$Zn^o \rightarrow Zn^{2+} + 2e^-$$

and

$$2H^+ + 2e^- \rightarrow 2H^o$$

By definition, the voltage of second cell is zero. The total voltage developed is -0.763V. But hydrogen half cell's voltage is zero. Hence the voltage of zinc half-cell is -0.763V. Similarly we can determine the voltage of other half-cells.

Now, let us consider copper-zinc cell

$Zn^0 \rightarrow Zn^{2+} + 2e^-$ – 0.763V
$Cu^{2+} + 2e^- \rightarrow Cu^0$ + 0.337V

The total voltage developed by the two half cell's is the difference between the two half cells and is equal to

- 0.763 - (+ 0.337) = - 1.10V or
0.337 - (- 0.763) = 1.10V

Here Zn metal becomes anode and copper metal becomes cathode.

Nernst equation:

The potential of a galvanic cell depends upon the activities of the various species, which undergo reaction in the cell. The equation which expresses this relation ship is called the Nernst equation, after the physical chemist Nernst, who in 1889 first used the equation to express the relation between the potential of metal - metal ion electrode and concentration of ion in the solution. In a chemical reaction such as

$$aA + bB \rightarrow cC + dD \qquad \ldots\ldots\ldots\ldots (1)$$

The change in free energy is given by the equation

$$\Delta G = \Delta G^0 + 2.3RT \log \frac{a_C^c \times a_D^d}{a_A^a \times a_B^b} \qquad \ldots\ldots\ldots\ldots (2)$$

where ΔG^o is the free energy change when all the reactants and products are in their standard states (unit activity), 'R' is the gas constant, 8.314 joules / degree mole and 'T' is the absolute temperature. The free energy change or work done, by driving Avagadro's number of electrons through a voltage 'E' is (Ne)E, where 'N' is Avagadro's number and 'e' is the charge on the electron. The product (Ne) is 96,500 coulombs, called as one Faraday, or F and hence

$$\Delta G = - n FE \qquad \ldots\ldots\ldots\ldots (3)$$

where n is the number of moles of electrons involved in the reaction. If all the reactants and products are in their standard states, this becomes

$$\Delta G^o = -nFE^o \qquad \ldots\ldots\ldots\ldots (4)$$

Hence equation 2 can be written as

$$-n\,FE = -n\,FE^{o} + 2.3\,RT \log \frac{[C]^{c}.[D]^{d}}{[A]^{a}.[B]^{b}} \text{------5}$$

where concentrations are substituted for activities .This can be written as

$$E = E^{0} - \frac{2.3RT}{nF} \log \frac{[C]^{c}[D]^{d}}{[A]^{a} + [B]^{b}} \qquad \text{…….. (6)}$$

At 298^{0} K the equation becomes (at 25^{o} C)

$$E = E^{0} - \frac{0.0591}{n} \log \frac{[C]^{c}[D]^{d}}{[A]^{a} + [B]^{b}} \qquad \text{…….. (7)}$$

Now, we can extend the equation for a system, where the equilibrium can be represented as

$$M^{n+} + ne^{-} \rightarrow M^{0} \quad \text{or} \quad Ox + ne^{-} \rightarrow Red$$

where n is the number of electrons transferred

$$E = E^{o} - \frac{1}{n}\ 0.0591\ \log\ \frac{[Red]}{[Ox]} \qquad \text{---------- (8)}$$

where [Red] = concentration of reduced form of the metal ion

[Ox] = concentration of oxidised form of a metal ion

This brings us to a very important relation between E, the emf of the half-cell, and the concentration of the oxidised and reduced forms of the components of the solution. Several analytical techniques are based on this relationship.

$$Zn^{o} \rightarrow Zn^{2+} + 2e^{-}$$

$$2H^{+} + 2e^{-} \rightarrow H_{2}$$

$$\overline{Zn^{o} + 2H^{+} \rightarrow Zn^{2+} + H_{2}}$$

In place of zinc, by substitution of various metal element ion half-cells, the potentials of variety of half cell reactions against standard hydrogen half cell can be determined. The resulting data are arranged in order of reducing capabilities of various metals. It is called **Activity series**.

Activity series of some metals

Metal		Reduction potential E^0V	Chemical reactivities
K	–	–2.93	Active with water, steam or acids
Ba	–	–2.90	
Ca	–	–2.87	
Na	–	–2.71	
Mg	–	–2.37	Active with steam or acids
Al	–	–1.66	
Mn	–	–1.18	
Zn	–	–0.763	
Fe	–	–0.44	
Cd	–	–0.403	Less reactive with acids
Ni	–	–0.246	
Sn	–	–0.136	
Pb	–	–0.123	
H_2	–	0.00	
H_2	–	0.00	Active with strong oxidizing acid. No hydrogen is formed
Cu	–	+0.337	
As	–	0.234	
Sb	–	0.212	
Bi	–	0.320	
Ag	–	0.799	
Hg	–	0.854	
Pt	–	1.20	Active with only aquaregia and no hydrogen is formed
Au	–	1.42	

The rules which are followed in the representation of electro chemical cells are:

1. Conventional chemical symbols are used to designate different chemical species such as ions, atoms, molecules, gases etc.
2. Partial pressures of gases and ionic concentrations are written in parenthesis ( ), immediately following the respective gas or ionic symbol.
3. Two ions placed in the same solution are separated by a comma (,) , but the order in which the ions are given are not specified.

4. A single vertical line (|) designates phase boundary. The boundary may be between two different states such as a solid and a liquid (or) between the same salts such as between two solutions. The emf developed across the boundary is included in the emf of the cell.

5. A double vertical line (||) denotes a salt bridge or equivalent. It indicates that the junction potential at this location is minimized and may be ignored in calculations.

   (i) Zn | Zn^{2+} (1M) || Cu^{2+} (0.5M) | Cu

   Metal strip zinc is immersed in 1M Zn^{2+} solution and metal copper is immersed in 0.5M Cu^{2+} solution joined with a salt bridge.

   (ii) Zn | $Zn(NO_3)_2$ (1M) || $CuSO_4$ (0.5M) | Cu

   (iii) Zn | $Zn(NO_3)_2$ (1M) ▌ $CuSO_4$ (0.5M) | Cu

   Thick line indicates thin membrane permitting electrical conduction but prevents physical mixing. Noble metals such as platinum are widely used in many applications.

   Pt, Cl_2 (0.5 atm) | HCl (1M) || HCl (0.1M) | H_2(0.3 atm), Pt

   Platinum electrodes do not enter chemical reaction but form an interface at which reaction takes place. Phase boundary on left hand side is in between Pt, Cl_2 and HCl and on right hand side HCl and H_2, Pt. If the same concentrations of HCl say 1M is used on both sides of the cell, it can be represented as

   Pt, Cl_2 (0.5 atm) | HCl (1M) | H_2, Pt

   Here no salt bridge is required.

   Pt | Fe^{3+} (0.1M), Fe^{2+}(0.2M), H^+(0.5M) || H^+ (1M) | H_2(0.5atm) | Pt

   With respect to the ions Fe^{3+}, Fe^{2+} and H^+ (0.5M) the order is immaterial. On left hand side simple line is shown for phase boundary between Pt and Fe(III) – Fe(II) system.
   On right hand side the optional vertical line instead of a comma has been used.

6. Standard potentials:

$$E = E^o - \frac{0.0591}{n} \log \frac{[Red]}{[Ox]}$$

In the Nernst equation, the expression E^o is the emf of the half-cell under standard conditions. A half-cell is said to be under standard condition when it is either

1. A pure liquid or pure solid (eg. a metal electrode in the standard state.)
2. A gas at a pressure of 1 atm (760 mm Hg) and a temperature of 0^oc
3. A soluble solute at 1M - concentration (more accurately at unit activity)

At very low temperature, the activity will be unity. At very high concentration, the activity is less than one. A half-cell is also under standard conditions when it is

i) A saturated solution of a sparingly soluble solute eg: AgCl

ii) A saturated solution of a dissolved gas at 1 atm pressure and 0^oC

When applying the simplified form of Nernst equations, we get

$$E = E^o - \frac{0.0591}{n} \log \frac{[Red]}{[Ox]}$$

But [oxidised] = [reduced] and also both Ox and Red are at unit activity, then

$$E = E^o - \frac{0.0591}{n} \log 1$$

since log 1 = 0

$$E = E^o - \frac{0.0591}{n} \times 0$$

$$E = E^o$$

REFERENCE CELLS:

In order to measure the emf of a half-cell, it is necessary to compare it with a second half-cell and measure the voltage produced by the complete cell. The second half-cell serves as a reference cell. Although the hydrogen half cell serves as the standard reference in the activity series, in practice it is not always convenient to use a hydrogen half cell as a reference cell; hence other more stable cells have been developed. In principle, any metal ion system could be used under controlled conditions to provide a standard half-cell. In practice many metals such as sodium, potassium, are subjected to chemical attack by the electrolyte.

Other metals such as iron are difficult to obtain in pure form. With some metals, the ionic forms are unstable to heat or exposure of the air. Also it is frequently difficult to control the concentrations of the electrolytes accurately. As a result, only a few systems provide satisfactory stable half-cells.

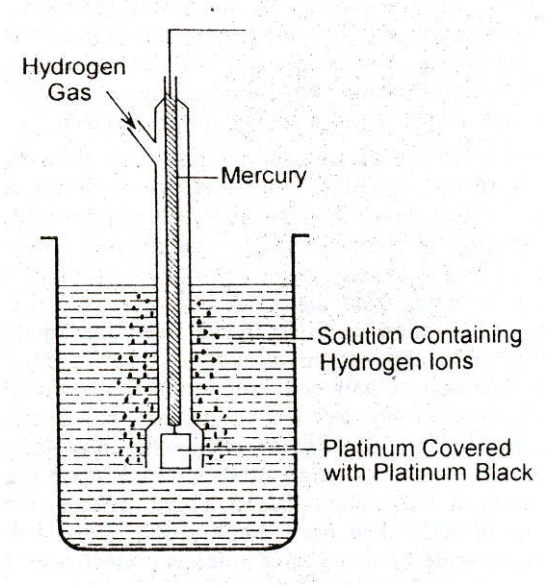
That is how reference cells were of two types

1. Primary reference electrode such as hydrogen electrode

2. Secondary or subsidiary reference electrode such as
   i) Calomel Electrode
   ii) Silver - Silver chloride electrode
   iii) Mercury - Mercurous chloride electrode and others

Primary Reference Electrode - Standard Hydrogen Electrode:

It consists of a small piece of platinised platinum foil, surrounded by hydrogen gas at one atmosphere and immersed in a solution containing H^+ ions, say HCl of unit activity.



A platinum wire is connected to the electrode and sealed through a glass tube makes electrical contact with outer circuit. The platinum foil is surrounded by an outer glass tube which has an inlet for hydrogen gas at the top and a number of holes at the base for escape of excess hydrogen gas. Hydrogen gas in contact with a solution containing H^+ ions functions as a reversible electrode of a metal ion in contact with ions of the metal. The platinized platinum electrode adsorbs a part of the hydrogen. This combination functions as solid hydrogen electrode and it results in equilibrium between the adsorbed hydrogen on the electrode surface and the hydrogen ions in solution. Thus the fundamental reaction for the hydrogen electrode is

$$H_2 \rightarrow 2H^+ + 2e^-$$

The hydrogen dissolved in the solution also makes it normal with respect to hydrogen ion. Thus the electrode works as normal hydrogen electrode, and by convention the potential of this standard hydrogen electrode is arbitrarily fixed at zero .Now since the activity of hydrogen at relatively low pressures is equal to the pressure p_{H_2}, of the gas in atmospheres, the single electrode potential of the hydrogen electrode can be determined both by the pressure of the hydrogen above the electrode and the activity of hydrogen ions in solutions namely,

$$E_{H_2} = E^0_{H_2} - \frac{RT}{F}\log_e \frac{a_{H^+}}{p^{1/2}_{H_2}}$$

But $E^0_{H_2}$ (i.e., the emf of hydrogen electrode at one atmospheric pressure and at unit activity of H^+ in the solution) is equal to zero. Thus $E_{H_2} = -\frac{RT}{F}\log\ a_{H^+}$ (where hydrogen pressure is one atmosphere, $\log_e P^{1/2}_{H_2}$ is negligible). Thus the potential of hydrogen electrode depends upon the activity of H^+ ions in solution.
The cell is usually written as

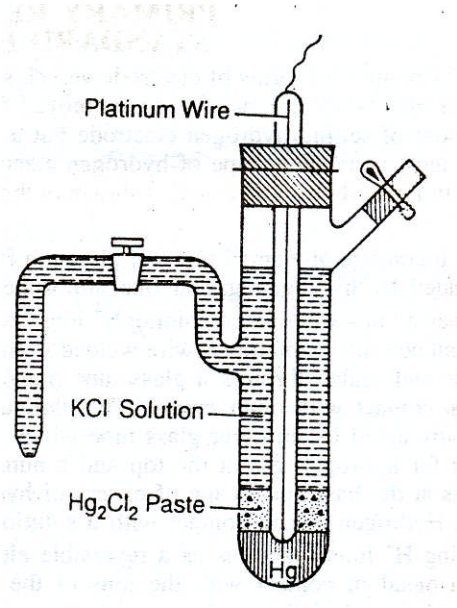
$$Pt, H_2\ (a=1)\ \|\ M^{n+}\ (a=1)\ |\ M$$

Calomel Electrode:

The half-cell is composed of metallic mercury in contact with a saturated solution of mercurous chloride, or calomel, Hg_2Cl_2. The chloride concentration of the solution is controlled by placing the calomel in contact with a potassium chloride solution of known concentration.

$$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$$

The oxidised form is Hg_2Cl_2 and the reduced form is $2Hg + 2Cl^-$



Applying the equation

$$E = E^o - \frac{0.0591}{n}\log\frac{[Red]}{[Ox]}$$

$$E = E^0 - \frac{0.0591}{n}\log\frac{[Hg]^2 \times [Cl^-]^2}{[Hg_2Cl_2]}$$

But Hg_2Cl_2 and Hg are in standard state

$$E = E^o - \frac{0.0591}{2}\log\frac{1\times[Cl^-]^2}{1}$$

$$E = E^o - \frac{0.0591}{2}\log[Cl^-]^2$$

The potential of the calomel electrode depends upon the concentration of KCl solution used. Generally, three different concentrations of KCl are being employed Viz., 0.1N, 1.0N and a saturated solution.

The potential differs as follows

$Hg \mid Hg_2Cl_2(s)$, 0.1N KCl -0.3338 +0.00007 (t-25)

$Hg \mid Hg_2Cl_2(s)$, 1.0 N KCl - 0.2800 + 0.00024 (t-25)

$Hg \mid Hg_2Cl_2(s)$, saturated KCl -0.2415 + 0.00076 (t-25)

The calomel electrode when connected with hydrogen cell can be symbolised as

$$(-)\ Hg \mid Hg_2Cl_2, N\ KCl \parallel H^+, H_2 \mid Pt\ (+)$$

Silver- Silver Chloride Cell:

Silver wire coated with silver chloride immersed in a solution containing chloride ions such as NaCl . The half cell potential is -0.2224 volts at 25^oc

Mercury -Mercurous sulphate electrode:

$$Hg \mid Hg_2SO_4\ (s)\ ,\ SO_4^{2-}$$

The electrode consists of mercury in a solution containing sulphate ions which has been saturated with mercurous sulphate. The half cell potential is -0.6141 volts at 25^oc

Mercury - Mercuric oxide electrode:

It consists of a pool of mercury in contact with a solution NaOH or KOH which is saturated with HgO. The reaction will be

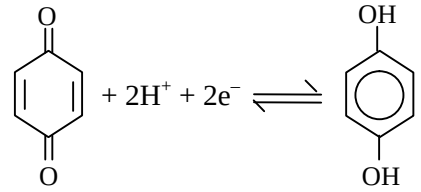
$$HgO(s) + H_2O + 2e^- \rightarrow Hg + 2OH^- \text{ (at } 25^oC \quad 0.098 \text{volts)}$$

Quinhydrone electrode:

Quinhydrone electrode acts as a reference electrode. The preparation of this electrode is very simple when compared with preparation of hydrogen electrode, which has certain limitations. E.Bill mann (1921) has introduced quinhydrone electrode; this renders the determination of pH a rapid and simple process and does not require hydrogen gas. Quinhydrone is a compound of quinone and hydroquinone, and in solution it is decomposed into equimolar quantities of these substances.

$$\underset{\text{Quinhydrone}}{C_6H_4O_2 \,.\, C_6H_4(OH)_2} \rightleftharpoons \underset{\text{Quinone}}{C_6H_4O_2} + \underset{\text{hydroquinone}}{C_6H_4(OH)_2} \qquad \text{--------- (1)}$$

Quinone and hydroquinone form a reversible oxidation- reduction system, which may be represented as



Quinone Hydroquinone

---------- (2)

If an inert electrode such as platinum is immersed in the system we can use it as a half cell.

$$E = E^0 + \frac{RT}{2F}\log_e \frac{a_Q a_{H^+}^2}{a_{H_2Q}} \qquad \text{--------- (3)}$$

$$E = E^0 + \frac{RT}{2F}\log_e \frac{a_Q}{a_{H_2Q}} + \frac{RT}{F}\log_e a_{H^+} \qquad \text{--------- (4)}$$

where a_Q, a_{H^+}, a_{H_2Q} are the activities of quinone, hydrogen ions and hydroquinones respectively and E^o is the standard potential referred to the molar hydrogen electrode. Under these conditions quinhydrone dissociates to give equimolar quantities of quinone and hydroquinone, the ratio of activities may be regarded as constant

$$E = E^0 + \frac{RT}{F}\log_e a_{H^+} \qquad \text{--------- (5)}$$

E^o has been determined in usual manner by direct reference to the normal (standard) hydrogen electrode and has a value of 0.6998 V at 25^oC. Substituting these values in equation (5)

$$E = 0.6998 + 0.0591 \log a_{H^+}$$

Thus the potential of quinhydrone electrode changes with the hydrogen-ion activity.

The half-cell can be represented as

$$Pt \mid QH(s), H^+ \mid H_2\ (1atm)$$

and the complete cell can be represented as

$Hg \mid Hg_2Cl_2$, KCl (Satd) || solution, quinhydrone | Pt

Antimony Electrode:

The so called antimony electrode is really antimony - antimony trioxide electrode.

The electrode reaction is

$$Sb_2O_3\ (s) + 6H^+ + 6e^- \rightleftharpoons 2Sb\ (s) + 3H_2O$$

the electrode is generally prepared by casting a stick of antimony in the presence of air, sufficient oxidation occurs in this way to render further addition of oxide unnecessary. The potential at 25^oc is

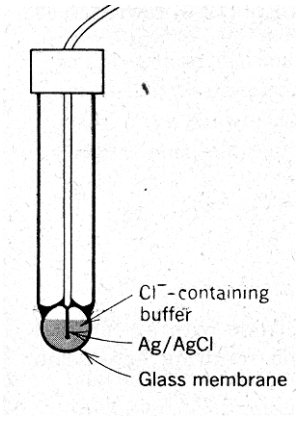
$$E = E^0_{Sb_2O_3,Sb} - \frac{0.0591}{6}\log\frac{1}{a^6_{H^+}}$$

$$E = E^0_{Sb_2O_3,Sb} - 0.0591\ pH$$

There are certain limitations in using antimony electrode. The antimony electrode cannot be applied

a) In the presence of strong oxidising agents or of complexing agents such as tartrates and organic hydroxy acids.
b) In presence of metals more noble than antimony.
c) In solutions with pH lower than 3, since oxide then becomes appreciably soluble.

Glass Electrode:



It is most widely used hydrogen- ion responsive electrode. Hard glasses like pyrex, are not suitable but special soft glasses of the soda lime type are pH responsive. ex; Corning glass (72% SiO_2, 22% Na_2O and 6% CaO). This glass has the desirable properties of low melting point, relatively with high electrical conductivity and high hygroscopicity. Two simple types of glass electrodes are known

a) A tube of special glass is blown at the lower end into a extremely thin bulb (a few tenths of mm thickness)

b) A very thin membrane of the special glass is sealed on to end of a glass tube, which is smooth and square.

To measure H^+ ion concentration of a solution the glass electrode must be combined with reference electrode and a saturated calomel electrode is most commonly used for this purpose.

$$Ag, AgCl\ (S)\ \mid\ HCl\ (0.1M) \mid glass \mid test\ solution \parallel KCl\ (sat), Hg_2Cl_2(S) \mid Hg$$

Owing to high resistance of glass membrane a simple potentiometer can not be employed for measuring the cell emf and specialized instruments must be used. The emf of the cell may be expressed as

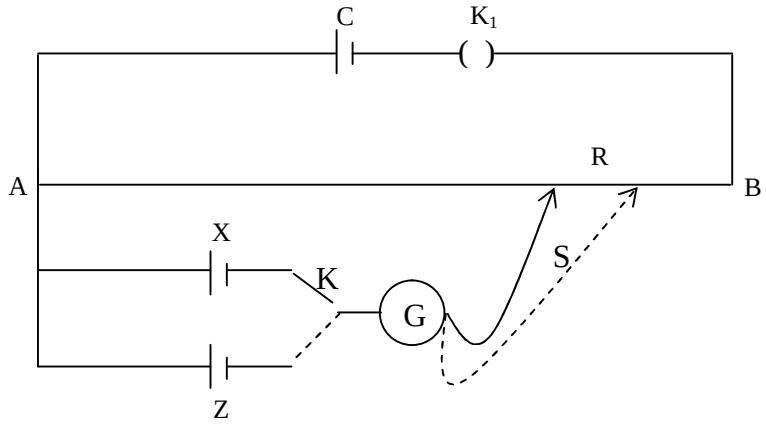
$$E = K + \left(\frac{RT}{F}\right)\ln a_{H^+}$$

(or) at 25^0C temperature, E = K + 0.0591 pH

Where K is constant dependent upon glass electrode.

Potentiometer - Principle of emf measurement (Poggendorff's principle):

The most satisfactory method for measurement of emf of the cell is given by Poggendorff's compensation method. It depends on Poggendorff's principle: the passage of an electric current from one electrode of a cell to the other clearly shows that an electrode potential exists between the two electrodes of the cell. This potential difference responsible for the flow of electric current from one electrode of higher potential to the other of lower potential is called electromotive force (emf). This is generally expressed in volts. The principle is that the emf of the cell is just obtained by an equal and opposite difference so that no current flows through the galvanometer is therefore employed as a null instrument.



AB is a uniform platinum iridium wire of high resistance, which is stretched tightly along a metal scale. 'C' is a working cell generally a storage battery of constant emf, which must be larger than that of the cell whose emf is to be measured. 'C' is connected across the ends A and B of the wire through a plug key K_1. The positive pole of the cell 'X' (whose emf is to be determined) is connected to A and its negative pole is connected to B through a two way key K, and a sensitive galvanometer 'G', to a sliding contact 'S' that can be moved along the wire 'AB'. The plugs are inserted at K and K_1 and by moving the sliding contact S along the wire AB, a point R is reached so that no current flows through the galvanometer. This indicates that fall in potential along AR due to the battery 'C' is exactly balanced by the emf of the cell X, say E_X. Now with the help of suitable switch (double way key) at K,X is replaced by Z which is a standard cell, of accurately known emf, say E_Z like Weston standard cadmium cell (1.0183 volts at 25^oC) and the sliding contact is adjusted until a point of balance is reached at R_1 when the galvanometer shows null deflection . The fall of potential along AR_1 is naturally equal to E_z. Since the wire AB is of a uniform nature, we have

$$\frac{E_X}{E_Z} = \frac{AR}{AR_1}$$

On the other hand, emf of unknown cell $E_X = \frac{AR}{AR_1}.E_Z$

from which E_X can be determined.

Advantages of potentiometric titrations over ordinary indicator methods:

i. The method can be used with the coloured solutions where ordinary titrations with suitable indicator fail.
ii. The method can be used for the analysis of dilute solutions with a high degree of accuracy.

iii. The method can be used for titrating weak acid against weak bases.
iv. There is no need for external indicator in oxidation reduction titrations.
v. The method can be made automatic by bringing relay into operation. It will stop the liquid running from the burette when e.m.f reaches a certain value.
vi. Potentiometric titrations can be carried out on micro level, if electrodes of the type necessary for titration can be constructed or in sufficiently small size and dilution (10^{-5}M) can be used successfully.
vii. Another important advantage is that differential titrations are possible. Hence individual components of a mixture can be determined provided they sufficiently differ in oxidizing power.
viii. Potentiometric titrations are generally considered to be most accurate. This accuracy mainly depends upon the acidity of the experiment to measure titration values accurately and the equilibrium constant of the titration reaction. Thus for accurate results a reaction must go for completion in a normal way.
ix. These titrations have been used extensively due to the fact that apparatus used is not very expensive and are readily available.

Potentiometric Redox Titration:

The following experiment will clearly explain how the potentiometric titration can be understood.

Suppose 30.0ml of 0.1M $FeSO_4$ solution containing H_2SO_4 are diluted to 100ml and titrated potentiometrically at 25^{o}C with 0.1M Ce $(SO_4)_2$ solution.

$$Fe^{2+} + Ce^{4+} \rightleftharpoons Fe^{3+} + Ce^{3+}$$

During the first stage of titration ferrous and ferric ions are present and the ratio of the later to the former is progressively increasing with a normal calomel cell in conjunction with solution being titrated. The circuit at any stage of this part of titration is represented as follows

$$Pt \mid Fe^{3+}, Fe^{2+} \parallel \tfrac{1}{2}\, Hg_2Cl_2, Cl^- (1M) \mid Hg$$

Normal potential of Fe^{2+}- Fe^{3+} system in H_2SO_4 is 0.68V and 1.44 for Ce^{3+} - Ce^{4+} system.

Redox potential will change with type of acid used and the concentration of the acid used. The details are given in the following table. Eg. Ce(IV) – Ce(III) system

Acid Conc.(N)	$HClO_4$	HNO_3	H_2SO_4
1	+1.70	+1.61	+1.44
2	1.71	1.62	1.44
4	1.75	1.56	1.43
8	1.87	1.56	1.42

Commencement of Reaction

The potential is determined by Fe^{2+}- Fe^{3+} ion ratio.

$$E = E^0 - \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

$$E = 0.68 - 0.0591 \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

How ever we do not know the ferric ion concentration, this being dependent upon how the ferrous salt was prepared, how much has been oxidised by air etc. Let us assume that not more than 0.1% of the iron remains in the ferric state that is the ferrous to ferric ion ratio is 1000: 1.

a) $E = 0.68 - 0.0591 \log \frac{[1000]}{[1]}$

$= 0.68 - 0.0591 \log 10^3$

$= 0.68 - 0.1773$

$= 0.5V$

b) 10.0 ml of ceric solution is added , 33% of Fe (II) might have been converted to Fe (III)

$E = 0.68 - 0.0591 \log \frac{66.66}{33.33}$

$= 0.68 - 0.0591 \log 2$

$= 0.68 - 0.0591 \times 0.3010$

$= 0.68 - 0.0177$

$= 0.6623V$

c) 20.0 ml of ceric solution is added. Now 2/3rd or 66% of Fe(II) is in the form of Fe (III)

$E = 0.68 - 0.0591 \log \frac{33.33}{66.66}$

$= 0.68 - 0.0591 \log \frac{1}{2}$

$= 0.69V$

d) when 30.0 ml of ceric sulphate is added, then

$E = 0.68 - 0.0591 \log \frac{1}{1000}$

$= 0.68 + 0.0591 \log 1000$

$= 0.8573V$

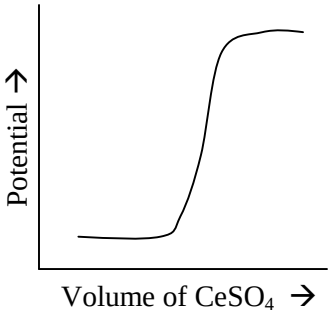
when Fe(II) is completely oxidised to ferric. If we consider the concentration of Ce(III) and Ce(IV) after the completion of titration the potential of the cell will be as follows:

$$E = E^0 - \frac{0.0591}{1} \log \frac{[Ce^{3+}]}{[Ce^{4+}]}$$

$$E = 1.44 - \frac{0.0591}{1} \log[1000]$$

$= 1.44 - 0.177 = 1.26V$

Thus we observe a jump in the potential from a lower value to higher value as shown in the figure.



At equivalence point

Using the equilibrium constant in order to calculate the potential

$$E_{Fe^{2+}, Fe^{3+}} = 0.68 - 0.059 \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

$$E_{Ce^{3+}, Ce^{4+}} = 1.44 - 0.059 \log \frac{[Ce^{3+}]}{[Ce^{4+}]}$$

However if the two equations are added giving

$$2E = 2.12 - 0.059 \log \frac{[Fe^{2+}][Ce^{3+}]}{[Fe^{3+}][Ce^{4+}]}$$

The logarithmic term will be zero since at the equivalence point $[Fe^{2+}] = [Ce^{4+}]$ and $[Fe^{3+}] = [Ce^{3+}]$

hence $2E = 2.12$ (or)

$E_{\text{equivalence point}} = 1.06$ volts

For any reaction in which the number of electrons lost by reductant is the same as the number gained by the oxidant, the potential at equivalence point is simply the arithmetic mean of the two standard potentials

$$E_{\text{equivalence point}} = E_{ep} = \frac{E_1^0 + E_2^0}{2} = \frac{E^0{}_{Ce^{4+}, Ce^{3+}} + E^0{}_{Fe^{3+}, Fe^{2+}}}{2}$$

$$E_{ep} = \frac{0.68 + 1.44}{2} = 1.06V$$

Equivalence is simply the arithmetic mean of two standard potentials between the reductant and the oxidant reacting in 1:1 mole ratio. Consequently the magnitude of potential and the curve is independent of the concentration of ferrous solution but depends only on the ratio of oxidized and reduced states.

APPLICATIONS:

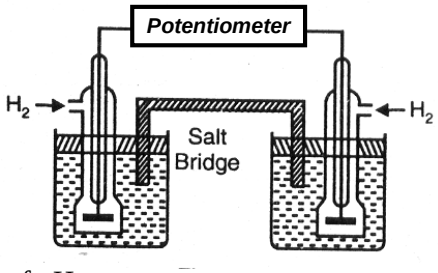
1. Determination of pH:

The most accurate method used to determine pH of a solution is potentiometric method. Hydrogen electrode is used mainly for this purpose. A normal hydrogen electrode can be setup by bubbling pure hydrogen gas at a pressure of 1 atmosphere through a solution of an acid in which activity of hydrogen ions is unity. For detection of electrode potential an inert metal like gold or platinum is placed so that it dips partly in the acid and the hydrogen gas bubbles on it at a slow rate (a platinised platinum plate is preferred as it permits the equilibrium value of potential to be reached quickly).

If a hydrogen electrode is immersed in a solution, and the half cells are coupled with a normal hydrogen electrode by means of a saturated KCl bridge in order to eliminate the liquid junction potential, the e.m.f of the resulting cell can be calculated potentiometrically.

$$Pt \mid H_2,\ H^+ (a=1) \parallel H^2, H^+(a=x) \mid Pt$$

The e.m.f. of the concentration cell at 25^0C is given by



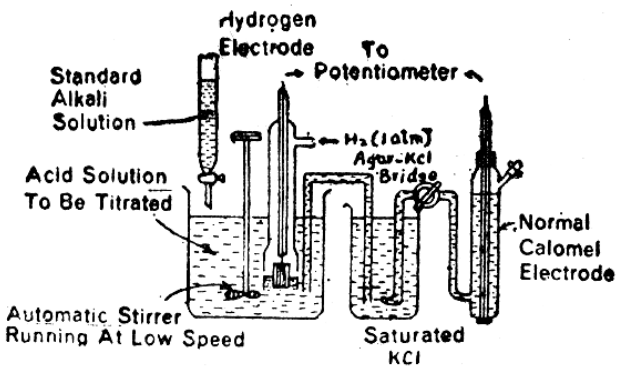
$$E = E0 - \frac{RT}{F}\ln\frac{C_2}{C_1} = 0 - \frac{0.0591}{1}\log\frac{1}{[H^+]} = -0.0591\ pH$$

$$pH = -\frac{E}{0.0591}$$

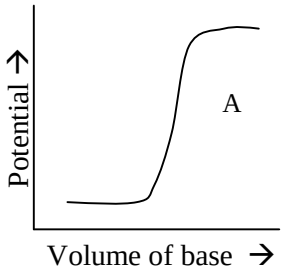
Thus by simply measuring the e.m.f of a cell we can find out the value of pH.

2. Acid base titrations (or) Neutralisation reactions:

In case of acid base titrations i.e., neutralization reactions change in the concentration ratios of H^+ and OH^- is involved. Hence hydrogen electrode may be employed for this purpose. Normal calomel electrode is used as reference electrode. The experimental hook up will be as follows

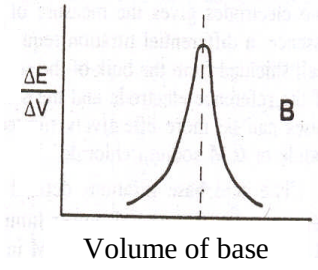


The known volume of a acid whose concentration is to be determined is taken in a beaker having stirring facility. A standard hydrogen electrode is also placed in the beaker. It is connected to a calomel electrode through a salt bridge. The hydrogen electrode and calomel electrodes are connected to a potentiometer having a facility to record the e.m.f of the solution after each addition of base from a burette.



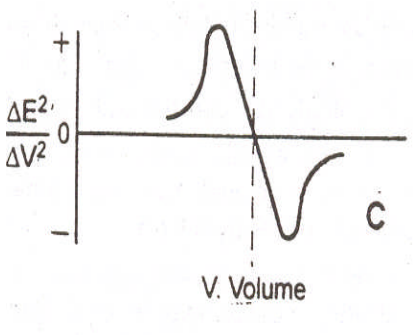
The values of e.m.f are recorded for each addition until the neutralization is completed and a few more readings are taken. The values of e.m.f are plotted against volume of base which is taken on x-axis. The curve is as shown in the figure (A).

The potential of hydrogen electrode is given by $E = E_0 - 0.0591 \log a_{H^+}$ at 25^0C where E_0 is standard electrode potential and $-\log a_{H^+}$ is nothing but pH and since t = 0 we can rewrite the above equation as E = 0.0591 pH thus change in electrode potential is directly proportional to change in pH during titration. The point where there will be sudden jump in potential gives the end point.



More sensitive results can be obtained by plotting $\frac{\Delta E}{\Delta v}$ against volume of the base. An inverted "V" shaped curve is obtained as shown in the figure. The apex indicates the end point on x-axis (Fig. B).

Instead the results can be manipulated for the second derivative i.e., $\frac{\Delta^2 E}{\Delta v^2}$ in which case the graphical representation will be as shown in the figure (C). It is clear that for locating endpoint only the experimental figures in the vicinity of equivalence point are required.



3. Complexometric Titration:

Complexometric titrations can be followed by using the electrode by the metal whose ions are involved in complex titrations. For example a silver electrode is used to follow titration of cyanide ion with standard solution of silver. The silver ion concentration will be governed by equilibrium constant for the complex formation reaction

.

$$Ag^+ + 2CN^- \rightleftharpoons [Ag(CN)_2]^- \qquad \ldots\ldots\ldots\ldots (1)$$

$$K_c = \frac{[Ag^+][CN^-]^2}{[Ag(CN)_2^-]} \qquad \ldots\ldots\ldots\ldots (2)$$

At the equivalence point

$$2[Ag^+] = [CN^-]$$

Thus equation (2) can be rewritten for concentration of $[Ag^+]$ as follows

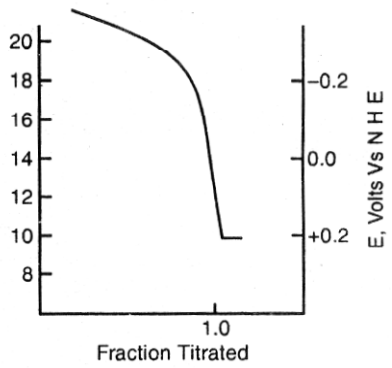
$$K_c = \frac{Ag^+[2Ag^+]^2}{[Ag(CN)_2^-]}$$

$$K_c = \frac{Ag^+ 4[Ag^+]^2}{[Ag(CN)_2^-]}$$

$$K_c = \frac{4[Ag^+]^3}{[Ag(CN)_2^-]}$$

$$[Ag^+]^3 = \frac{K_c[Ag(CN)_2^-]}{4}$$

$$[Ag^+]^3 = \sqrt[3]{\frac{K_c[Ag(CN)_2^-]}{4}}$$



In this case the solid silver cyanide gets precipitated soon after the equivalence point. Further addition of silver will not change either the concentration of complex or silver ion. Thus the titration curve has an almost horizontal portion shortly after the equivalence point.

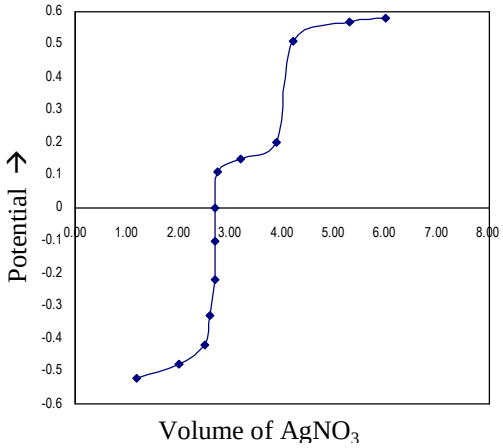
4. Precipitation Titration:

Principle:

When two ions A^-, A_1^- are present in a solution together and both form sparingly soluble salts BA and BA_1. Then the salt BA will be precipitated first upon the addition of B^+ if it is less soluble of the two precipitates. Thus for example in case of chloride and iodide the solubility of silver chloride and silver iodide are $S_{AgCl} = 1.2 \times 10^{-10}$ and $S_{AgI} = 1.7 \times 10^{-16}$ respectively.

Since the solubility product of silver iodide is less than silver chloride, silver iodide will get precipitated first which refers to the potential jump from negative potential to positive potential in the graph. After the first equivalence point silver chloride gets precipitated and hence the second break.

Chloride and Iodide verses Silver nitrate:



Equal volumes (5.0ml) of both KCl and KI of 0.01N solutions are taken in a 250ml beaker and the solution is diluted to 50ml with water. A bright silver electrode is used as an indictor electrode, which is connected to negative terminal of potentiometer through agar- agar, NH_4NO_3 salt bridge. Calomel electrode is connected to positive terminal of potentiometer. The beaker should be wrapped with carbon paper. The solution is titrated with $AgNO_3$ solution (0.01N). As the titration proceeds, the potential changes from negative to positive near the equilibrium point. The change of potential from negative to positive indicates the complete formation of AgI precipitate. As titration proceeds, AgCl gets precipitated and one drop of $AgNO_3$ at end point gives a sudden jump, which corresponds to the complete precipitation of AgCl.

A graph is drawn by taking volume of $AgNO_3$ solution on x-axis and potentials on y- axis.

UNIT 3

POLAROGRAPHY

Lesson 3

Objectives of the lesson:

This lesson deals with the study of the methods polarography and amperometric titrations as analytical tools.

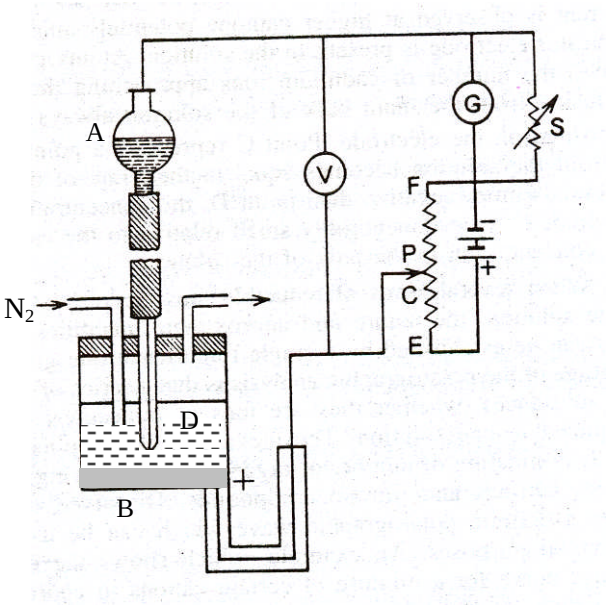
INTRODUCTION:

Polarography is a process where in electrolysis is carried out using a micro- electrode and a current -voltage curve is recorded. The current -voltage curve is called Polarogram. The technique has been invented by **Heyrovsky** a Czechoslovakian scientist in 1922.

Let us imagine a small electrode (cathode) placed into a solution with a second large electrode and a voltage is applied across the two. When the voltage is high enough, the reaction (reduction) can take place at the small electrode, this can be depicted as,

$$M^+ + e^- \rightarrow M^o$$

The electrode is a reducing electrode in this case. The concentration of the M^+ ions in the immediate vicinity of reducing electrode decreases as these ions are reduced to M^o atoms. With time, the concentration of M^+ ions in this space approaches zero, even though the concentration of M^+ ions in the main bulk of the solution is unaltered. Under these conditions the electrode is said to be polarised. It is very important to note that the size of the electrode must be small so that reduction of M^+ ions at its surface does not cause an appreciable change of M^+ in the bulk of the liquid.



The instrument is known as polarograph. In this equipment there is a dropping mercury electrode 'D' which consists of mercury reservoir (A) from which mercury drifts down as small drops through a capillary. This acts as a cathode and is known as indicator or microelectrode. The anode consists of a mercury pool at the bottom of the vessel (B), whose area is large, so that it is not polarized.

Both cathode and anode are connected across the appropriate ends of the battery. The applied voltage can be changed by adjusting the sliding contact (C) along the potentiometer wire EF. 'P'is a potentiometer by which emf upto 3V may be readily applied to the cell. 'G' is a galvanometer, which measures the current strength and 'S' is a shunt for adjusting the sensitivity of the galvanometer. The cell is provided for blowing nitrogen gas through the sample, which removes dissolved oxygen from the sample. Among

several micro electrodes, the dropping mercury electrode (DME) is found to be the best for obtaining the current -voltage curves due to the following advantages:

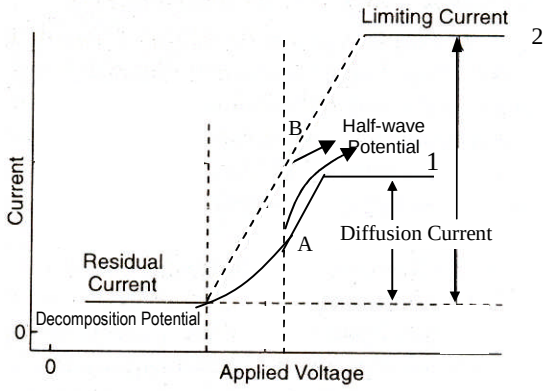
1. Its surface is reproducible, smooth and continuously renewed, which is quite useful for reproducing the current - potential curve and eliminates passivity or poisoning effects.
2. Mercury forms amalgams (solid solution) with many metals and therefore lowers their reduction potentials.
3. The diffusion current assumes a steady value immediately after each change of applied potential and is reproducible.
4. High over voltage of hydrogen on mercury makes possible deposition of ions which are difficult to be reduced.
5. The surface area can be calculated from the weight of the drops.

The DME may be used over the range + 0.4 to about -2.0V with reference to SCE. Above +0.4v mercury dissolves and gives an anodic wave, it begins to oxidise to mercurous ions. At potential more negative than -1.8V verses SCE, visible hydrogen evolution occurs in acid solutions and the usual supporting electrolyte commences to discharge.

Working:

Consider a polarographic cell, containing a solution to which an external emf is applied. The positively charged ions present in the solution will be attracted to the DME by a combined process of electrical force and diffusive force. Of these two processes, that of diffusion is far greater in effect, since the ions of the relatively large quantity of inert electrolyte present bear most of the burden of carrying the current.

As the emf is increased, the current is recorded and a graph will be obtained as shown.



If the applied emf is increased gradually, the amperes of current remains nearly zero and increases only slightly until the decomposition potential of the reducible ions is reached. At this point electrolytic reduction starts at the mercury cathode and increased emf causes a sharp increase in amperes in accordance with Ohm's law.

$$E = IR$$

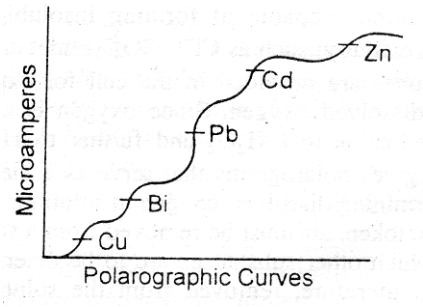
As the emf is further increased, a point is reached where there is practically complete state of concentration polarization at the DME occurs and increasing emf therefore causes almost no increase in amperes. This limiting current is called **diffusion current**. These three steps are plotted in a solid curve where micro amperes are plotted on Y- axis against voltage (v) on X- axis. Point 'A' on the curve represents the so called **half-wave potential** or the potential at which the current is one half of the diffusion current. It is independent of the size of the drop, its time of formation and the concentration of solution. The importance of half wave potential is seen from the dotted curve which applies to the electro reduction of the same ions at higher concentration.

Here it is seen that

i) The half wave potential 'B' of solution (2) corresponds to the same point on the X-axis as the half-wave potential 'A' of solution (1).
ii) The diffusion current for solution of higher concentration (2) is greater than that of the solution containing the ions at lower concentration (1).

The facts can be summed up as follow:.

1. Half wave potentials are independent of concentration and with properly calibrated apparatus, which serves as a means of determining the nature of the substance being reduced.
2. The amperes of the diffusion current are a measure of the quantity of the substance present in the solution.



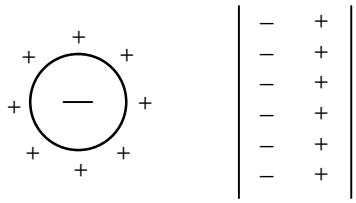
When reducible ions of several metals present in the same solution and the respective half-wave potentials are not too close together, the nature and approximate quantities of the ions can be established in a single run. The current voltage curve for a mixture of certain cations in an appropriate supporting medium is given in the figure.

Factors affecting the Liming Current:

The factors which effect current - voltage curve are

1. Residual current 2. Migration current 3. Diffusion current 4. Kinetic current

1. Residual current:



The current is not zero when no reducible ions are present. As the mercury drop grows, ions from supporting electrolyte gather around it. If the drop is negatively charged, these ions are positively charged. Consider KCl solution i.e., potassium ions in it will be attracted to the drop. They are not reduced to potassium atoms, but remain close to the mercury surface forming the electrical double layer. The effect is like charging up a condenser. When the drop falls off a new drop forms, a new condenser is charged up. This causes a continuous flow of electric current, which increases as the potential of the drop is increased. It is observed that the charging current is zero at the point at which the surface tension is maximum. This happens at about 0.52v more negative than SCE. In case of electrolytes containing traces of impurities, a small Faradic current is also super imposed on the condenser current. It is a practice to include this in residual current. Thus the residual current is the sum of condenser current and Faradic current.

2. Migration Current:

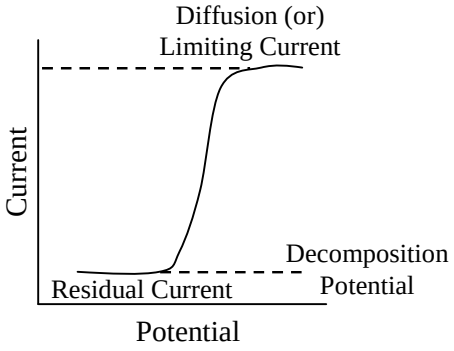
Electro active material reaches the surface of the electrode largely by two processes. One is the migration of charged particles in the electric field caused by the potential difference existing between the electrode surface and the solution; the other is concerned with the diffusion of particles. The current required for the above two processes is called migration current.

Heyrovsky proved that the migration current could almost be eliminated if an indifferent electrolyte is added to the solution in a concentration so large that its ions carry almost all the current.

The following example illustrates the concept very clear. Suppose a solution contains 0.1M KCl and 0.01 M cadmium ions. The current is carried through the cell by all the ions present. The fraction of total current carried by each ion depends upon its relative concentration compared with the other ions and transport number. In present case about 90% of the current will be transported to the cathode by the K^+ ions. If the concentration of the K^+ ions increased to be more than 99% of the total cations present the relative current carried out by other cations is reduced practically to zero. Thus all the current through the cell will be transported by the potassium ions. The discharge potential of K^+ ions is so high that it cannot be discharged at the cathode and form a positively charged cloud which no longer allows the electrostatic attraction to be operative to attract the reducible ions from the bulk of solution. Under such conditions the electro active species can reach the electrode only by diffusion.

3. Diffusion Current:

When an excess of supporting electrolyte is present in the solution, the electrical force on the reducible ions is nullified, this is because the ions of the added salt carry practically all the current and the potential gradient is compressed or shortened to a region so very close to the electrode surface that it is no longer operative to attract reducible ions. Under these conditions the limiting current is almost solely diffusion current.



D.Ilkovic (1934) examined the various factors which govern the diffusion current and derived the following equation.

$$i_d = 607\ n\ D^{1/2}\ C\ m^{2/3}\ t^{1/6} \quad \text{--------} \quad 1$$

where i_d = the average diffusion current in micro amperes during the life of the drop

n = number of. Faradays of electricity required per mole of the electrode reaction.

D = diffusion coefficient of the reducible or oxidisable substance expressed as cm^2 / sec

C = concentration in milli moles/ litre

m = rate of flow of mercury from the dropping electrode expressed as mg / sec.

t = drop time in seconds

The constant 607 is a combination of natural constants including Faraday. It is slightly temperature dependent and the value 607 is at 25^oc

From the Ilkovic equation it follows that "The observed diffusion current is directly proportional to the concentration of the electro active material". This is the basis of **quantitative polarographic analysis.** The original Ilkovic equation neglects the effects on the diffusion current because of the curvature of the mercury surface;

Hence Lingane and Loveridge (1950) modified the above equation as follows

$$i_d = 607\ n\ D^{1/2}\ C\ m^{2/3}\ t^{1/6}\left(1 + 39D^{1/2}m^{-1/3}t^{1/6}\right) \quad \text{--------} \quad (2)$$

The correction is not large. The expression in parenthesis usually has a value between 1.05 and 1.15 and need only to be taken into account in very accurate work.

The diffusion current depends upon

i) Temperature
ii) Viscosity of the medium
iii) Concentration of base electrolyte
iv) Dimension of capillary
v) Molecular or ionic state of the electro active species
vi) Pressure of dropping mercury

4. Kinetic Current:

This current is a result of slow reaction processes occurring between adsorbed ions at the surface of the DME prior to electron exchange.

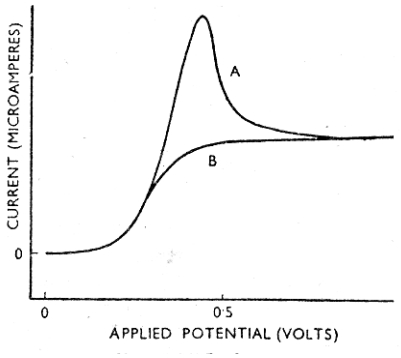
The limiting current may be affected by the rate of non- electrode reaction called the kinetic current. The kinetic current will be proportional to the rate constant and to the volume of the interface, and therefore is a direct function of size of the mercury drop but independent of the velocity of the flow of mercury from the capillary.

This current results if oxidised or reduced form of electro active species is involved in a chemical equilibrium with other substances. It means that these are rate processes. Therefore the current resulting from such processes is called the kinetic current.

Polarographic maxima:

Current-voltage curves obtained with DME frequently exhibit pronounced maxima which are reproducible and which can usually be eliminated by the addition of certain appropriate "maximum suppressors". These maxima vary in shape from sharp peaks to rounded humps which gradually decrease to the normal diffusion current curve.

For example curve 'A' is that of copper ions in 0.1M potassium hydrogen citrate solution and curve 'B' is same polarogram in the presence of 0.05M acid fuchsine solution. To measure the true diffusion current the maxima must be eliminated or suppressed. Fortunately this can be done easily by the addition of very small quantity of surface active substances such as dye stuffs (e.g. sodium methyl red), gelatin or other colloids.



Half Wave potential: (Qualitative Polarographic analysis)

Polarography is concerned with electrode reactions at the indicator electrode or microelectrode; that is with reactions involving a transfer of electrons between the electrode and the components of solution. These components are called oxidants, when they can accept electrons and reductants when they loose electrons. The electrode is a cathode when a reduction can take place at its surface and an anode

when an oxidation occurs at its surface. During the reduction of an oxidant at the cathode electrons leave the electrode and react in solution with the formation of an equivalent amount of a reductant. Similarly during the oxidation of a reductant at the anode electrons pass from the solution to the electrode and form an equivalent amount of the oxidant in the solution.

Free electrons cannot exist in solution; consequently any process of reduction at the cathode is accompanied by a simultaneous oxidation. We may summarize the above discussion as

oxidant + n electros → reductant

(or) $ox + ne^- \rightarrow red$

The reversible potential of the system as it can exist at the electrode // solution, interface of the drop will be recorded on the polarogram. The electro chemical equilibrium may be represented as

$$E = E^o + \frac{0.0591}{n}\log\frac{[ox]_0}{[red]_0} \qquad \ldots\ldots\ldots\ldots\ldots (1)$$

where the subscript represent concentrations at the electrode // solution interface.

Let us now assume that before the commencement of the current - voltage curve the solution at the electrode // solution interface consists entirely of oxidant. As soon as the applied potential is increased, some of the reducible substances (i.e., oxidant) at the interface are reduced, and the concentration of the oxidant at the electrode surface begins to decrease. Some ions will move in from the bulk of the solution by means of diffusion, as the concentration gradient builds up between the electrode surface and the bulk of the solution. The current ' i ' at any point on the wave is determined by the rate of diffusion of the oxidant from the bulk of the solution to the electrode surface under a concentration gradient [ox] to $[ox]_o$, Thus

$$i = k([ox] - [ox]_o) D_{ox}^{1/2} \qquad \text{--------- (2)}$$

where 'k' is evaluated from Ilkovic equation

when $[ox]_o$ is reduced to almost zero, equation 2 may be written as

$$i = k[ox] D_{ox}^{1/2} = i_d \qquad \text{--------- (3)}$$

where i_d is diffusion current

From equations 2 and 3 it follows that

$$i_d = k[ox] D_{ox}^{1/2}$$

$$i = k([ox] - [ox]_0) D_{ox}^{1/2}$$

$$i_d - i = k([\cancel{ox}] - [\cancel{ox}] + [ox]_0) D_{ox}^{1/2} = k[ox]_0 D_{ox}^{1/2}$$

$$\text{or } [ox]_o = \frac{i_d - i}{kD_{ox}^{1/2}} \qquad \ldots\ldots\ldots\ldots (4)$$

If the reduced form [red] is soluble in water and none was originally present at the electrode surface, it will diffuse from the surface of the electrode to the bulk of the solution. The concentration of $[Red]_0$ at the surface of the electrode at any value of 'i' will be proportional to the rate of diffusion of the reduced form from the surface of the electrode to the bulk of the solution under a concentration gradient $[red]_0$, thus

$$i = k [Red]_o \; D_{red}^{1/2} \qquad \text{…….. (5)}$$

If the reductant is insoluble in water but soluble in mercury phase (amalgam formation) equation 5 still holds. Substituting in equation 1, along with equation 4 we have

$$E = E^0 + \frac{0.0591}{n} \log \frac{i_d - i}{i} + \frac{0.0591}{n} \log \left[\frac{D_{red}}{D_{ox}} \right]^{1/2} \qquad \text{…….. (6)}$$

But by definition, half wave potential is the point where

$i = i_d - i$ or $i = 1/2 \; i_d$

Then the equation (6) reduces to the form

$$E_{1/2} = E^0 + \frac{0.0591}{n} \log \left[\frac{D_{red}}{D_{ox}} \right]^{1/2} \qquad \text{…….. (7)}$$

where $E_{1/2}$ is known as half - wave potential. It is clear from this equation that half wave potential is characteristic property of the given oxidation - reduction system and can be used for its identification as well as for other purposes. Eg : determination of pH, estimation of standard potential etc.

EVALUATION METHODS IN POLAROGRAPHY

1. Standard addition method:

When a single analysis is to be contemplated the polarogram of the unknown solution is recorded then the known volume of the standard solution of test ion is added and polarogram is repeated. From the increase in diffusion current the original concentration can be computed by interpolation. For unknown solution

$$i_d = KC_x = h$$

where 'h' is the height of the curve

And after the addition of 'v'ml of standard solution (the concentration of test ion is C_s) to V ml of unknown, we have

$$KC_x \left(\frac{V}{V+v} \right) + KC_s \left(\frac{V}{V+v} \right) = H$$

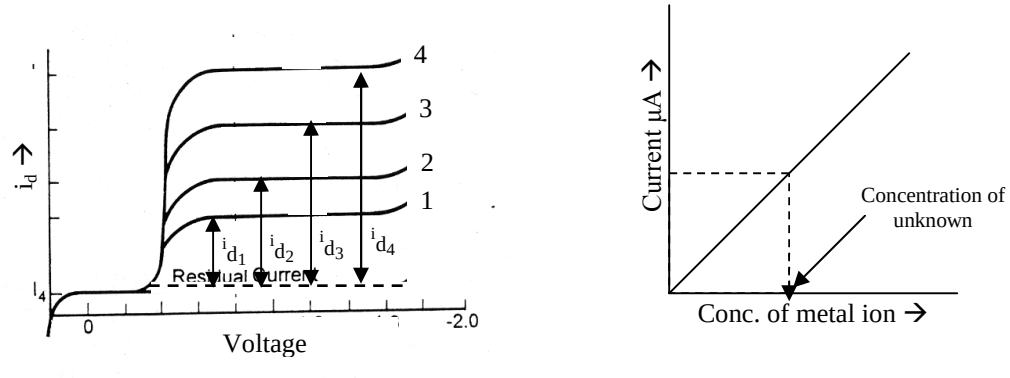
Solving the equation for concentration of unknown (C_x)

$$C_x = \frac{-vC_s h}{hV - H(V+v)}$$

It is admissible that the amount of standard solution be added should be able to bring about double the original wave height.

2. Direct comparison method:

The method is highly useful when analyzing large number of similar samples. In the direct comparison method the current voltage curve of a standard solution of the test ion under the same conditions as well as for the unknown would be recorded. Using the Ilkoic equation in the simplified form, the diffusion current coefficient (i_d/C) can be computed while measuring the heights of the curves. Just like in case of Beer's law in spectrophotometry another curve is constructed for diffusion current (i_d) against the concentrations of metal ion. Thus the diffusion current for the unknown will be recorded and from the linear graph the concentration of the unknown can be determined.



3. Internal standard method:

The internal standard method is also known as *pilot ion method* is based on the fact that the relative wave heights of two substances (i.e., the test ion and another electro active metal ion). As all other conditions remaining constant including supporting electrolyte it is only necessary to add a known concentration of the reference ion to unknown concentration of the test ion. Thus the concentration of the unknown can be computed since we have the information with regard to the concentration of reference ion (C_r); Diffusion currents of the standard and reference as well as the test ion

$$C_x = \frac{i_{d_x}}{i_{d_r}} . C_r$$

where C_x, C_r, i_{d_x}, i_{d_r} are concentration of unknown, concentration of reference, diffusion current for unknown and diffusion current for reference respectively.

4. Absolute method:

The method utilizes the original Ilkoic equation that is

$$i_d = 607\ n\ D^{1/2}\ C\ m^{2/3}\ t^{1/6} \quad \text{--------} \quad (1)$$

$$C = \frac{i_d}{607 n D^{1/2} . m^{2/3} . t^{1/6}}$$

$$I = 607\ n\ D^{½}$$

I is called diffusion current constant

So the temperature must be rigidly controlled at 25^0C. The Galvanometer must be accurately calibrated since the measurement employs absolute current measurements. Thus the concentration of unknown can be determined with the knowledge of available data in respect of concentration of the standard. i_d values of the standard known and unknown are measured.

Advantages:

The most important advantages of Polarography are

(i) It has a wide applicability and the method is non destructive.

(ii) In one experiment both qualitative and quantitative determinations of various species can be performed

(iii) The method is applicable for relatively larger concentration ranges (10^{-2} to 10^{-6}M.)

(iv) The technique is very rapid i.e. the experiment can be performed in a few minutes.

Applications:

Polarographic technique can be applied to both organic and inorganic species, molecular or ionic provided they can under go reduction at the surface of DME.

AMPEROMETRIC TITRATIONS

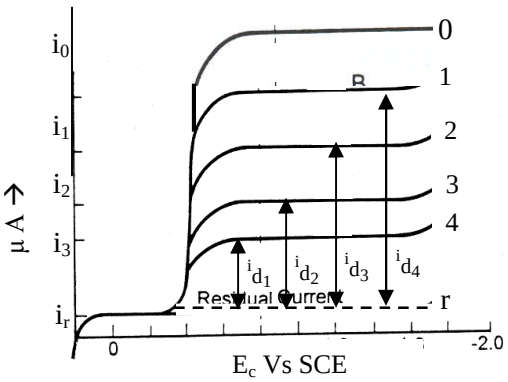
Polarography can be used as the basis of an electrometric titration method comparable with conductometric and the potentiometric method. It is known that limiting current is independent of the applied voltage impressed on the DME or any other indicator or microelectrode.

Suppose the migration current is eliminated by the addition of excess of supporting electrolyte, then the only factor which effects the limiting current is the rate of diffusion of electropositive material from the bulk of the solution to the surface of the electrode. Hence diffusion current (equal to limiting current) will be proportional to the concentration of the electro active material in solution. If some of the electro active material is removed by the interaction with some other reagent the diffusion current will naturally decrease. This forms the fundamental basis of amperometric titrations (derived from ampere, the unit of current).

In amperometric titration the voltage applied across the indicator electrode (ex. DME, rotating platinum electrode etc.,) and reference electrode (SCE) is kept constant and the current passing through the cell is measured and plotted against the volume of the reagent added. In other words, in these titrations, the current passing through the cell between an indicator electrode and a reference electrode at a suitable constant voltage is measured as a function of the volume of titrating reagent. As the diffusion current is a consequence of polarisation at a microelectrode, the technique is also known as Polaographic or Polarometric titrations.

The technique may be clear by an example. Let us consider the titration of lead ions (reducible substances) against sulphate ions (non reducible reagent). Lead ion is being reduced at the cathode gives a diffusion current while the sulphate ion being non-reducible shows no diffusion current. The concentration of reducible ions Pb^{2+} ions is denoted by curve '0' in the figure.

Suppose that the initial concentration of lead ions be C_0 and the value of limiting current corresponding to this concentration will be i_0. The titration exhibits maximum diffusion current at the applied emf. Incremental addition of sulphate remove some electro active lead ions and consequently as the concentration of lead ions decreases (from C_0 to C_1, C_2, C_3, C_4 …. C_r) the current also decrease from i_o t_0 i_1, i_2, i_3, i_4 and finally i_r at which point the lead ions have completely exhausted. When this condition is reached, the current value remains constant at its residual value characteristic of the supporting electrolyte and flat portion of the curve (residual current) is obtained as shown in figure-2.



E_c Vs SCE

Figure : 1

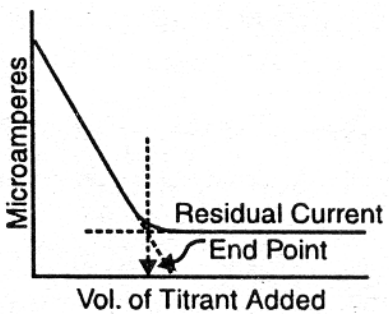


Figure : 2

When the titrated is non reducible and titrant is reducible Eg., the titration of sulphate ion against lead ion (reverse of above titration) the amperometric curve will be of the type shown in Figure-3. When both the titrated ion and titrant ion are reducible at the cathode (i.e., both give diffusion current at the applied voltage chosen). The curve will drop to the end point and then increases again to give a 'V' shaped curve as shown in Figure-4.

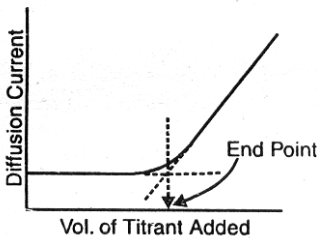


Figure : 3

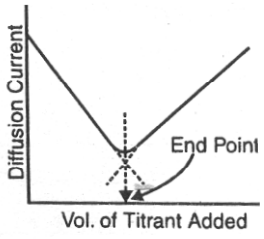


Figure : 4

Ex: Nickel with DMG, Cu^{2+} ion with α -benzoin oxime.

Applications:

1. Iodide, Bromide, and Chloride can be successfully titrated in mixtures with Ag, using a rotating electrode. In 0.1 - 0.3N solution of ammonia only AgI will be precipitated when Ag^{+} solution is added. The indicator reaction is the reduction of complex diamine silver ion. During the titration of iodide the current remains constant at zero or nearly until iodide ions are consumed and then rise sharply. After three or four points have been recorded past the end point, the solution is acidified to make it 0.8N in nitric acid. Immediately the silver ions added in excess are now released from the amine complex to combine with the bromide ions and precipitate Br^{-} as AgBr and current drops to zero.

   Chloride does not interfere with the titration of Br^{-} because AgCl particles cause a cathode current even in the presence of large excess of chloride. Therefore a second rise in the current indicates the end point of the bromide titration. A chloride end point can be obtained by adding gelatin, which suppresses the current due to AgCl and continuing the titration until the current again rises after the chloride end point.

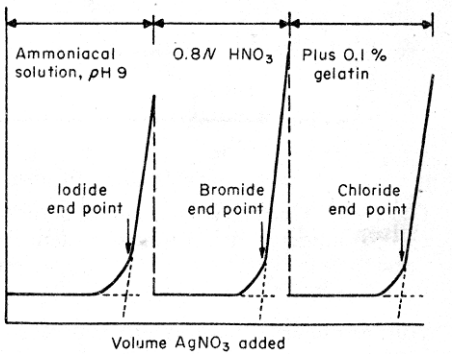


Figure : 5

2. The titration of a mixture of Pb^{2+} and Ba^{2+} by means of a chromate solution at an applied voltage of -1.0V. At this potential lead as well as chromate ions gives a cathodic diffusion current. This method is based on the difference in solubility of lead chromate and barium chromate. Upon the addition of CrO_4^{2-} to a solution of Pb^{2+} and Ba^{2+} ions, the diffusion current due to Pb^{2+} decreases practically to zero. Only after the end point of the titration of Pb^{+2} does the added chromate precipitate Ba^{2+}. Since the solubility product of $BaCrO_4$ is small, the concentration of Ba^{2+} and CrO_4^{2-} in the solution remains low and the diffusion current remains practically at zero,

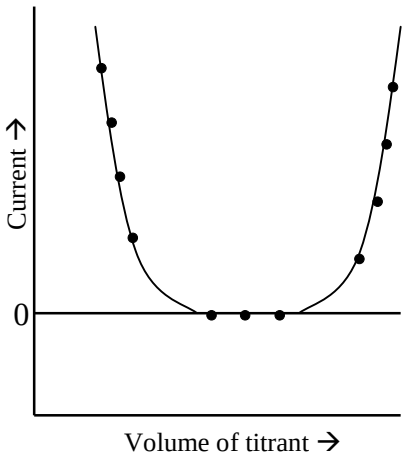


Figure - 6

until all the Ba^{2+} is precipitated. Only then the diffusion current due to chromate ion increases linearly with volume (Figure-6).

The other determinations in an amperometric technique are:

1. Phosphate with uranyl acetate.
2. Lead with dichromate.
3. Sulphate with lead nitrate.
4. Nickel with DMG.
5. Co, Cu, Pd with α-nitroso β-naphthol.
6. Iodide with mercuric nitrate.
7. Para amino salicylic acid with bromide.
8. Fluoride with thorium or lanthanum.

Advantages:

1. Amperometric titrations can usually be carried out rapidly, because generally two measurements before and two after the end point need be taken. Moreover, end point is found graphically using a simple equipment.
2. The results of the titrations are independent of the characteristics of the capillary.
3. Highly diluted solutions can be titrated with a high degree of precission.
4. Precipitation titrations can be performed in most cases even when the solubility is relatively high and under conditions where potentiometric and indicator methods do not yield good results.
5. Foreign electrolytes the presence of which is harmful in conductometric titrations do not interfere.
6. Substances that are not reduced or oxidized can be titrated if the reagent yields a diffusion current which is proportional to the concentration.
7. The titration can be carried out rapidly because only a few measurements need be recorded.
8. It is immaterial whether the reaction which takes place during the titration is reversible or irreversible.
9. In routine work the essential instruments needed is a sensitive galvanometer with a variable sensitivity.

Disadvantages:

1. These titrations are subject to ordinary sources of errors of volumetric determinations such as co-precipitation effects.
2. The foreign substances that do not interfere in the titration must not be present in concentration many times larger than the substances to be titrated. In their presence relative changes of the current during the titration becomes smaller.

UNIT 3

ELECTROGRAVITOMETRY AND COULOMETRY

Lesson 4

Objectives of the lesson:

This lesson deals with introduction to the techniques, theory, instrumentation and applications.

ELECTROGRAVIMETRY

Introduction:

Electrolysis may be used in analytical chemistry to separate substances from one another. Some substances may deposit during electrolysis where as others do not. The electric current may be regarded as precipitating agent and the procedure is called **Electrogravimetry**. Another application of electrolysis is called Coulometric analysis, where in the quantity of electricity required to oxidise or reduce a substance is measured and the method in which electrons act as the titrant may be regarded as titrimetric method.

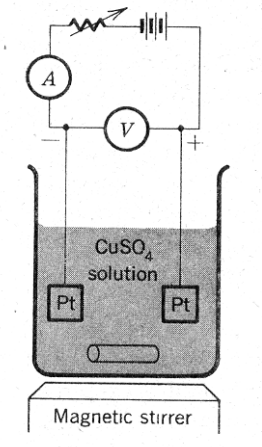
Electrolysis or Electrogravimetry:

Potentiometry is based upon a galvanic cell process, that is one in which there is out put of electricity and also no current will flow at the time of measurement. The change if any, in the composition of the solution, is brought about by a spontaneous chemical reaction and not by instruments. In contrast to this, electrolytic techniques require

1. The input of electricity and bring about a marked change in the composition of the solution.
2. Any electrolytic cell requires enough electricity to over come
   a) Nernst potential of the cell
   b) The resistance of the system (IR drop)
   c) Any over potential which may exist at electrodes.

In an electrolytic cell we consider the significance of the potential of two completely non-polarised electrodes i.e., potentiometry. In polarography we investigate the diffusion current phenomenon which arises when one of the electrodes is polarized.

In electrogravimetry we are concerned with the analytical applications of the electrolysis involving the passage of considerable currents such that both electrodes are polarized.



Let's consider an electrolytic cell set up as shown in the figure with a pair of platinum electrodes immersed in a solution of $CuSO_4$. As the applied potential is increased from zero initially no current flows until the decomposition potential is reached. Beyond this point large amount of current flows and copper deposits on the cathode and oxygen liberated at anode. The total potential V across the cell during the passage of the current may be written as

$$V = (E_a + \omega_a) - (E_c + \omega_c) + IR$$

$E_{applied} = E_a - E_c + IR$

In which E_a and E_c are the reversible half-cell emfs of the anode and cathode respectively. ω_a and ω_c represent the added potentials of the two electrodes partly due to over voltage with respect to the deposition of copper and oxygen and partly due to the concentration polarization resulting from passage of current and IR is the potential drop through the solution itself.

Since we are primarily interested in cathodic deposition of metals, it is convenient to maintain the conditions such that the reaction occurring at the anode is always the same. Then the values of E_a and ω_a will not change appreciably during the experiment. The deposition at the cathode is determined by the quantity $E_c + \omega_{c\,;}$ E_c is calculated from Nernst equation and the tabulated value of E^0 or E^{0^1} (this is valid if one can assume that the platinum cathode has become covered with copper and hence acts as a copper cathode). In much electro deposition work (in contrast with Polarography) comparatively concentrated solutions are encountered and therefore for precise work the activity corrections can not be neglected.

The most important requirements for electro gravimetric technique may be summarized as follows:

1. The deposition of the substance in question must be complete.
2. The reaction taking place in cell must be allowed to go to completion.
3. The electrode must be inert i.e., it should not undergo any change in the weight during the process of electrolysis
4. The deposition must be of known composition.
5. The deposition must adhere firmly so that electrode can be rinsed dried, and weighed without any loss.

The important terms that are to be considered during electrogravimetric analysis are

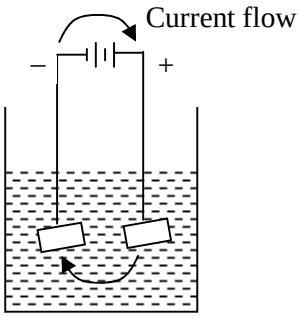
1. Polarisartion
2. Over voltage.
3. Potential drop (or) IR drop.
4. Decomposition potential.

Polarisation:

When a cell consisting of zinc and copper electrodes in sulphuric acid is setup and a current is taken off from it, the emf of the cell rapidly decreases. It is so happen because the copper electrode becomes covered with the bubbles of the gas which make a gas electrode with emf opposite to that of the cell. If the bubbles of the gas are removed mechanically (or) chemically the emf of the cell remains constant. It is said to exert a back (or) counter (or) polarization emf since it acts in the opposite direction in the opposite direction to the applied potential.

An electrode (hence a cell) is said to be polarized if its potential shows any departure from the value which should be predicted from the Nernst equation. On the other hand changes in the potential due to the actual change in the concentration of ions at the electrode surface are some time referred to as a form of polarization known as **concentration polarization.**

This phenomenon of back emf brought about by the products of electrolysis is termed as polarization. For a given concentration of electrolyte, the polarization emf for any given type of cell is constant. However exactly the same phenomenon takes place within the electrolysis in which the reactions are just the reverse of those occurring in the cell. Thus when the current of electricity is allowed to pass between two platinum electrodes dipped in a solution of dilute sulphuric acid electrolysis takes place, hydrogen and oxygen gases are evolved at the cathode and anode respectively.



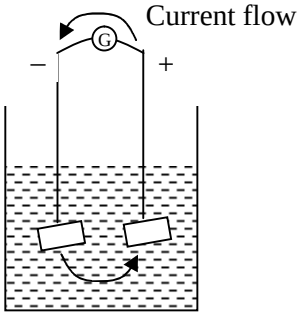
At the cathode $2H^+ + 2e^- \rightleftharpoons H_2$ (acidic medium)

$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$ (basic medium)

At anode $2H_2O \rightleftharpoons O_2 + 4H^+ + 4e^-$ (acidic medium)

$4OH– \rightleftharpoons O_2 + 2H_2O + 4e^-$ (basic medium)

Outside the solution the current flows from cathode to anode while inside the solution the direction of current flow is reverse i.e., it flows from anode to cathode.



Now if the battery is removed and two electrodes are joined through a galvanometer, it will be noticed that a small amount of current flows between two electrodes and the direction of current flow in this case will be opposite to that during the process of electrolysis i.e., current flows from anode to cathode outside the solution.

This is due to the fact that the platinum electrodes employed during the electrolysis become covered with the bubbles of hydrogen and oxygen gases, which give rise to new electrodes with emf opposite to that of the cell. Since these new electrodes have emf just opposite to that of the cell, it is called back emf or equilibrium decomposition voltage (potential) of the cell. Thus unless the applied emf is greater than the polarization / back / counter emf electrolysis almost stops.

Over voltage:

It has been observed that the decomposition voltage of the electrolyte varies with the nature of electrodes employed for the electrolysis and is in many incidences higher than that computed from the differences of the reversible electrode potentials. The excess voltage over the calculated back emf is termed ***over voltage*** (the term over voltage should strictly be used to a cell and over potential for a single electrode).

Over voltage may occur at the anode as well as at the cathode. The decomposition voltage (E_D) is therefore

$$E_D = E_{cathode} + E_{Oc} - (E_{anode} + E_{Oa})$$

Where E_{Oc} and E_{Oa} are the over potentials at the anode and cathode respectively.

The over voltage at anode (or) at cathode is dependent upon the following factors:

1. *The nature and physical state of metal employed for the electrodes:* Increase of large surface area decreases over voltage. It is observed that the reaction involving gas evolution usually require less over voltage at platinised electrode than at polished platinum electrode due to the much large surface area of the platinised electrode and smaller current density at a given electrolytic current.
2. *The physical state of the substance deposited:* If it is a metal the over voltage is usually small. If it is a gas, such as oxygen or hydrogen, the over voltage is relatively high.
3. *The current density employed:* For the current densities upto 0.01 amp / sq.cm the increase in over voltage continues but less rapidly.
4. The change in concentration (or) concentration gradient existing in the immediate vicinity of the electrodes to that in the bulk of the solution. As this increase, the over voltage rises. The concentration gradient depends upon the current density, the temperature and the rate of stirring of the solution.
5. The over potential decreases often considerably with increase in temperature

The IR drop (or) Potential drop:

The loss of potential in galvanic cell which was due to the IR factor was avoided in potentiometric measurements by the simple device of opposing the cell potential with an outside source in order to prevent any current flowing at the time of measurement. However, since the electrolysis process requires that current flow in order for the reaction to occur, the total applied potential must be adequate to overcome this IR factor.

Assuming deposition starts at 0.18 amperes and the resistance of the cell is 0.5 ohms, the IR factor may be regarded to be calculated as 0.09V. (IR factor = 0.18 x 0.5 = 0.09v). Thus the calculated minimum applied potential necessary to initiate deposition of copper will be.

$$E_{applied} = E_{galvanic} + IR$$
$$= 0.893 + 0.09$$
$$= 0.983$$

Over potential:

In practice an applied potential equal in magnitude but opposite in sign to the (E_{cell} + IR=0.983V) would be inadequate to initiate the deposition of copper.

Experimentally it is found that 1.5V or more are required to commence deposition. The difference between the calculated applied potential and the experimental applied potential necessary to bring about the desired reaction is due to over potential. This may arise from several changes.

(i) Concentration over potential:

The application of the Nernst equation assumes a homogeneous solution and a reversible reaction. If the concentration of a specific ion at the immediate surface of any electrode differs from its concentration in the bulk of the solution, a concentration gradient and concentration polarization occurs.

The potential difference brought about by this gradient is concentration overpotential. It may be considered as a hurdle (impediment) to the deposition process and suitable voltage must be applied to overcome it.

For example:

If the concentration of Cu^{2+} in the above cell is 0.05M at the surface of electrode while it is 0.5M in bulk due to inadequate stirring then, the cathode potential would be

$$E_{(Cu,Cu^{2+})} = E^{0}_{(Cu,Cu^{2+})} - \frac{0.059}{2}\log(Cu_s^{2+})$$

where (Cu_s^{2+}) is the concentration of the Cu^{2+} at the surface of electrode

$$\therefore E_{(Cu,Cu^{2+})} = -0.345 - 0.0295 \log 0.05 = -0.307V$$

and the galvanic cell potential when ignoring the IR term becomes

$$-0.307 + 1.229V = 0.922V \text{ instead of } 0.893 \text{ calculated earlier.}$$

(Anode)

The concentration gradient may be diminished (reduced) by mechanical (or) conventional stirring. The applied EMF necessary to continue deposition of copper when considering both the concentration gradient and the IR factor becomes 0.09 (i.e., 0.18 x 0.5)

$$0.922V + 0.09V = 1.012V \text{ instead of calculated } 0.893V$$

(ii) Activation over potential

In addition to over potential which arises due to concentration gradients, it is often necessary to apply an additional potential to over come the activation energy of the electrode reaction.

This over potential increases with current density and is dependent upon many factors such as

1. Surface of electrode.
2. Current density.
3. Temperature.
4. Chemical composition of the electrode.
5. Allotropic form of the electrode.

For practical purposes we will combine the two, and call it overpotential and define overpotential as “the difference between theoretical potentials (as calculated from Nernst equation and IR drop) and experimental potential necessary to initiate an electrolytic process”.

$E_{applied} = E_{galvanic} + IR + \text{overpotential}$

If 0.5 M Cu2+ half cell has total overpotential of 0.512 V , the minimum necessary applied potential to initiate the deposition must be

$E_{applied} = 0.893V + 0.09V + 0.512V$

$E_{applied} = 1.495V$

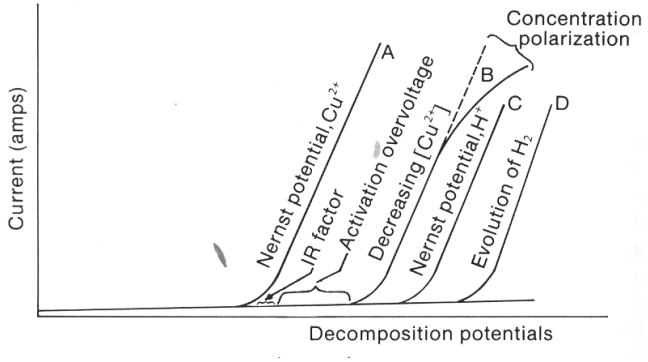
(iii) Decomposition potential

The experimental sum of all the potentials necessary to bring about the electrolysis (i.e., the Nernst potential, the IR factor, the over potential) is called the ***decomposition potential***.

This is determined experimentally by increasing the applied cell potential in increments measuring the resulting amperes and plotting the current against the applied cathode (or) cell potential.

The resulting graph is shown in the figure. There will be a slight flow of current with the increase of applied potential in the beginning. This may be due to some impurities

When applied potential is zero, the initial current will also be equal to zero since the two electrodes are at identical potentials.



Increased applied cathode potentials

First Cu^{2+} commences to be reduced to metal at cathode, the potential at which this reduction initiates is the decomposition potential of 'Cu' (A).

Further increase in applied potential will meet the needs of IR factor, overvoltage and then finally causes further reduction of 'Cu' at cathode and hence lowers the concentration of Cu^{2+} ion in solution (B). At the hydrogen decomposition potential the gas will be simultaneously evolved as 'Cu' is deposited (C,D)

Principles involved in electro-gravimetric analysis:

The decomposition of electrolyte by the passage of an electric current is known as electrolysis and it depends upon the following factors which form the basis for electro-gravimetric analysis

1. Applied voltage.
2. Electrode potential of the electrode.
3. Current flowing through cell.
4. Amount of electricity consumed during the process of electrolysis.

Most common methods used are

1. Electrolysis in simple cells.
2. Electrolysis at constant current.
3. Electrolysis at constant voltage.
4. Electrolysis at controlled potential.

Electrolysis in simple cells:

Applied voltage must be greater than the emf of the cell. The reactions occurring at cathode and anode of the cell are

$$Pt,\ Cu / Cu^{2+}\ (0.05M),\ H^+(1.0M) / O_2\ (0.20\ atm)$$

$$Cu \longrightarrow Cu^{2+} + 2e^-$$

$$4H^+ + 4e^- + O_2 \longrightarrow 2H_2O$$

The net reaction is $2Cu + O_2 + 4H^+ + 4e^- \longrightarrow 2Cu^{+2} + 2H_2O$

An external voltage must be applied opposing the potential of the cell. If the copper is to be precipitated (deposited) the applied voltage must be greater than the emf of the cell and in the case of above reaction it must be more than 1.5 volts. When electrolysis is carried out the concentrations of both copper and hydrogen decrease while that of oxygen remains constant. Since it remains in equilibrium with air the conditions in the cell will be so maintained that the change in hydrogen concentration is too small and can be neglected. Thus the decrease in voltage is mainly due to decrease in Cu^{+2} concentration in bulk of the solution.

Let us consider a common electrolytic cell, containing a platinum gauze cathode. Gauze electrodes are preferred since the interstices in the gauze lead to a good circulation of the electrolyte as far as conditions at the surface are concerned, and reduce the local depletion of the electrolyte that tends to occur with foil electrodes. The effective area will be the total foil area or the length of the wire, calculated from the number of meshes and dimensions of the electrodes, multiplied by πd, where 'd' is the diameter of the curve and a platinum spiral anode with an efficient stirring mechanism and a means of applying a definite potential. It can be represented as

$$Cu \mid Cu^{2+}(0.5M),\ H^+(1M) \mid O_2\ (1\ atm) \mid Pt$$

Having standard potentials

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad E^o = 0.345\,V \text{ in } H_2SO_4$$

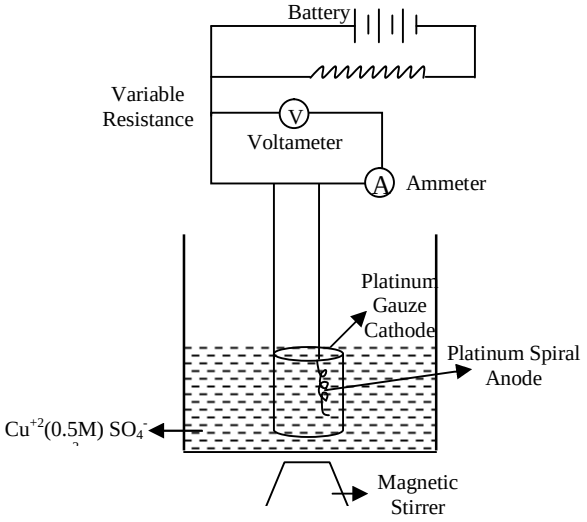
$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad E^o = 1.229\,V$$

Using the assumptions that the solution is 0.5M in Cu^{2+} and 1M in H^+, and also assuming the oxygen, which is being evolved at the anode, is at one atmosphere partial pressure, the true cell potential is calculated by Nernst Equation.

$$E_{cell} = \left[E^o_{(Cu,Cu^{2+})} - \frac{0.0592}{2}\log(0.5)\right] + \left[E^o_{(O_2\ H_2O)} - \frac{0.0592}{2}\log\frac{(1)}{(1)^4(1)}\right]$$

$$E_{cell} = [-0.345 - 0.0295 \log 0.5] + [1.229]$$

$$E_{cell} = -0.336 + 1.229V = 0.893V$$



This potential of 0.893V is the theoretical minimum, which must be applied in order to reverse the direction of the cell reactions, to deposit copper at the platinum gauze and evolve oxygen at the anode according to the reaction.

$$2H_2O + 2Cu^{2+} \rightarrow O_2 + 4H^+ + 2Cu$$

Since by definition, reduction always occurs at the cathode and oxidation at the anode in any electrochemical cell, the cathode of the previous galvanic cell becomes anode of the electrolytic cell and the anode of galvanic cell becomes the cathode of the electrolytic cell.

Electrolysis at Constant current:

When the applied potential of the previous cell is large enough to exceed the decomposition potential of the hydrogen, the current becomes constant and process is referred to as *Constant Current Electrolysis.*

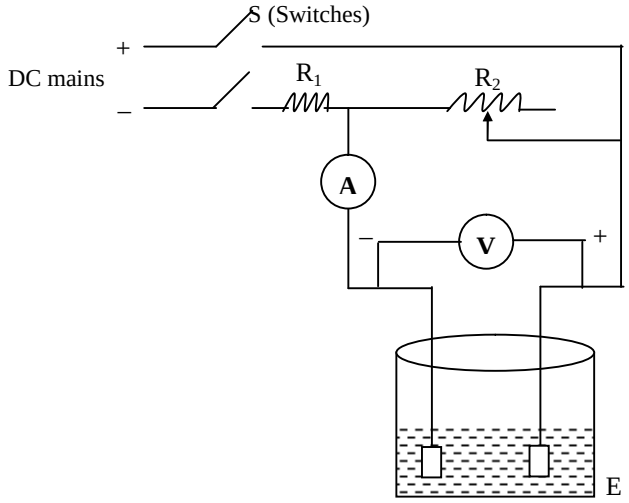
In this process, the current remains constant and voltage is allowed to increase otherwise, the rate of mobility of Cu^{2+} ion towards cathode will become zero. The major portion of the current will then be carried by the hydrogen ions. Copper will continue to deposit and hydrogen will be simultaneously evolved at cathode. These reduced hydrogen ions are being replaced in the solution at the anode by the reaction

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

The evolution of hydrogen simultaneously with the deposition of a metal may lead to poor metallic deposits. This is commonly prevented by the introduction of a substance, which is more easily reduced at the cathode than is hydrogen. The nitrate ion acts as a cathodic depolarizer.

$$NO_3^- + 10H^+ + 8e^- \rightarrow NH_4^+ + 3H_2O$$

Since the potential in constant current electrolysis by the evolution of hydrogen, the procedure is limited to those metals which are deposited at a potential which is less negative than is hydrogen. On the other hand it offers a rapid and convenient method of separating the metals which come out at a reduction potential more positive than hydrogen from those which separate at a more negative reduction potential than hydrogen for example in the separation of copper and nickel.



R_1 fixed resistance; R_2 Variable resistance; A-ammeter; V-voltammeter; E-electrolysis vessel;

Copper is determined in strong acid solution at a potential not exceeding 4 volts (above this potential nickel may plate out). The solution is evaporated to fuming in order to remove excess of nitric acid, the iron if present is precipitated with ammonia solution and nickel is deposited from the filtrate after the addition of large excess of ammonia solution 1/100 percent copper will deposit at the cathode at a potential of 1.4V (0.893 +0.512) beyond this hydrogen will evolve.

Constant voltage electrolysis:

In this system, the applied potential is set high enough to lower the metal ion concentration to its desired level and low enough to prevent the evolution of hydrogen or decomposition of another metal.

It is not possible to evolve hydrogen below 2.2 volts, hence the voltage is maintained between 1.43 and 2.2 volts. Copper is deposited without hydrogen evolution. However the method is not used due to some technical difficulties. After initiation of the deposition of copper, continuation of electrolysis will simultaneously cause a decrease in $[Cu^{2+}]$ and increase in $[H^+]$.

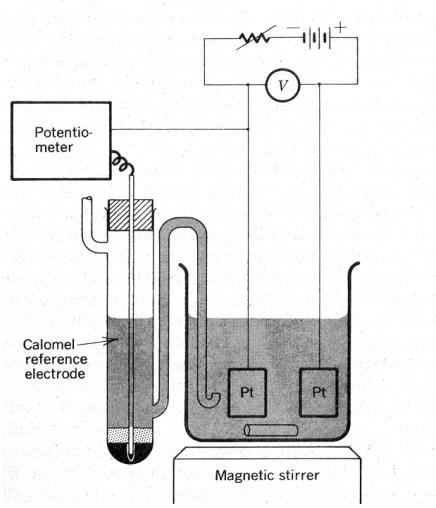
$$2Cu^{2+} + 2H_2O \rightleftharpoons 4H^+ + O_2 + Cu^0$$

These concentration changes will cause a shift in the Nernst potential and a change in the cell amperage.

This in turn changes the over potentials and the IR factor. Hence, after some time Cu^{2+} cannot be brought to the surface of the cell in sufficient quantity and thus concentration polarization occurs and current drops off.

Controlled Potential Electrolysis:

The problems in constant voltage electrolysis may be avoided if the cathode potential is held constant. It is exclusively the cathode potential which determines whether or not the cathode reaction of interest as well as possible interfering cathode reactions will occur.



A third electrode, the reference electrode usually SCE, is added to other type. The potential difference between reference electrode and the working cathode is maintained and applied potential of the complete system continually changed to compensate for any change in this difference.

Controlled Cathode Electrolysis:

In controlled cathode electrolysis, at a potential where only a single species is reducible, the current is limited by diffusion, and hence is proportional to the concentration of reducible species. It is therefore evident that both concentration and current will fall of exponentially with time. We can write

$$\frac{C_t}{C_o} = \frac{i_t}{i_o} = 10^{-kt}$$

where C_t represents concentration at time 't'

C_0 represents concentration at time = 0

i_t and i_0 the corresponding currents and k is a constant.

It can be shown that 'k' is proportional to

$$k \alpha \frac{DAS}{V}$$

Where

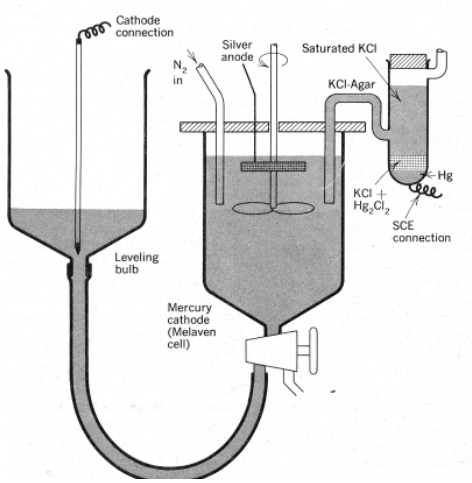
D= Diffusion coefficient A= Area of cathode

S= Rate of stirring V= Volume of solution

Thus a plot of log i against 't' will give a straight line with a negative slope equal to 'k'. From such a plot one can determine the time required to deposit any given fraction of the desired species.

Mercury Cathode Electrolysis:

A particularly convenient and important technique for the separation of metals is electrodeposition upon a mercury cathode. Since, the hydrogen over voltage on mercury is very high (greater than 1V), any metal with a deposition potential less than this can be deposited on a mercury surface, but those requiring a more negative potential will remain in solution. The elements not deposited include aluminium, tungsten, uranium and the metals of scandium, titanium, vanadium sub groups.



The alkali and alkaline earth metals are deposited only if the solution is basic. The method is applied with great success to the removal of iron and similar metals from solutions of aluminium alloys prior to the determination of that element by gravimetric or by other means. It has also been extensively applied to the purification of uranium solutions.

COULOMETRY

Introduction:

Coulometric procedures are concerned with the quantity of electricity which flows in any given electro-chemical cell and the relationship between this quantity and the amount of the reactants or products consumed or produced respectively.

Coulometry is based upon Faraday's laws which states that one faraday of electricity will react with one equivalent weight of a reactant and will yield one equivalent weight of product. A current of one ampere which flows at a given point for one second (i.e., amp- sec) is a coulomb 'Q'.

A Faraday 'F' is 96,487 coulombs (A-sec)
Coulometric techniques require

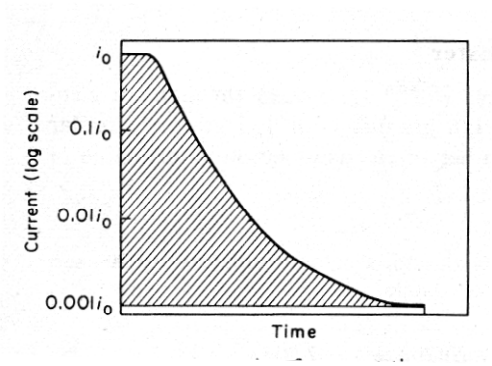
1. A reaction which proceeds at a reproducible current efficiency at the working electrode
2. An exact measurement of utilized coulomb

Coulometric procedures are usually classified as either constant current or controlled potential. The type of the curves that one can expect in both the types is as follows when we follow the current with respect to time.

Controlled potential:

In controlled potential the current decreases exponentially with time and thus the current is proportional to the area under the curve at any given time. The reaction can be assumed to be complete when the current value reaches its minimum (i.e., of its initial value). In constant current procedures current at any time will be kept at the same value, since it is constant no integration is necessary. However, an independent determination of end point is required.

Coulometers:



Let us consider measurement of coulomb, which is applied in both the technique.

Faraday law states that

Equivalent of electricity = Equivalents of reactants
= Equivalents of products

we have

$$\frac{Q}{F} = \frac{W}{m/n}$$

where Q = quantity of electricity in coulombs
F = Faraday (96,487 A- sec)
W = Weight of the reactant or product
m /n = equivalent weight of the reactant or product that is atomic weight or molecular weight 'm' divided by the number of electrons 'n' gained or lost in the reaction.

This can be rearranged as follows

$$W = Q\,M / F\,n$$

Working:

For calculating the quantity of electricity imposed on the solution of unknown (oxidant/reductant) a second electrolytic cell will be introduced which is known as coulometer. Insertion of another electrolytic cell, which controls the unknown, will eliminate the tedious and inaccurate process of obtaining and interpreting current - time data.

The second electrolytic cell, which operates at 100% efficiency with well defined electrode process, is called a coulometer. The most common coulometer (silver) is composed of a silver anode and a platinum cathode in a solution of silver, usually as perchlorate or nitrate.

The silver is plated at the cathode according to the reaction

$$Ag^{+} + e^{-} \rightarrow Ag$$

The cathode is weighed prior to and after electrolysis and number of coulombs required for electrolysis are determined by dividing the added weight by the equivalent weight of the silver. Hence, 96,490 coulombs are required to precipitate 107.9g silver. Because of large equivalent weight 107.9 accurate results are obtained.

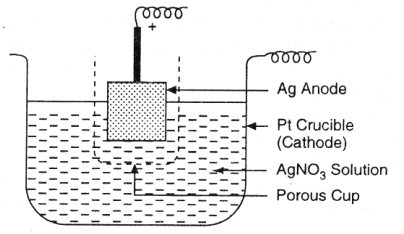


Fig. 2. Silver coulometer.

Example: How many seconds are required to reduce 0.0150 g(W) of Ag+ with a current of 18 milli amperes .

Equivalents of consumed electricity = equivalents of silver deposited

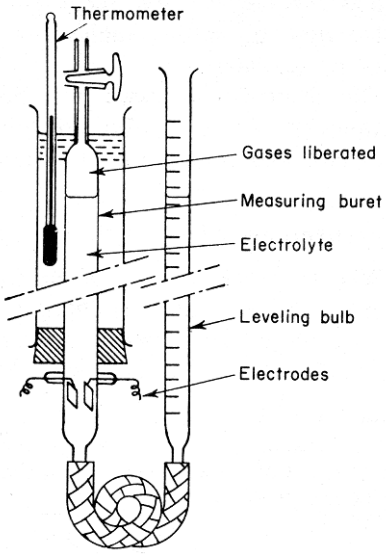
Q = ampere x seconds

$$\frac{ampere \times \sec ond}{F} = \frac{W}{M/n}$$

$$\text{Second} = \frac{W}{M/n}.\frac{F}{amperes} = \frac{W}{M}.\frac{nF}{amperes}$$

$$= \text{p}\frac{(0.015g)(96{,}487\,ASec/equivalance)\times 1}{(107.9g/equivalance)(18\times 10^{-3}A)} = 745 \text{ Sec}$$

As an alternative to this an iodine coulometer may be used. The cell consists of a solution of iodine - potassium iodide in a two-compartment container with platinum electrodes. Iodine is produced at anode and consumed at the cathode. The change in iodine concentration with one or other is determined by chemical titration with standard reducing agent. Similarly hydrazine sulphate can be used where nitrogen and hydrogen are evolved.



Another type of chemical coulometer depends upon the volume of gas (at known temperature and pressure) produced by passing the current through a cell where electrolysis of water takes place.

This gas coulometer or water coulometer is highly sensitive device (1ml of combined hydrogen and oxygen at STP corresponds to 0.0595meq or 16.8 ml per milli equivalent). The coulometer consists of a graduated tube with two platinum electrodes sealed into its lower end.

In gas coulometer the volume of the gas produced is related to the number of equivalents of electricity. The water coulometer consists of two platinum electrodes immersed in an inert electrolyte such as potassium sulphate. Hydrogen and oxygen are evolved at two electrodes.

Cathode	$4H^+ + 4e^- \rightarrow 2H_2$
Anode	$2H_2O \rightarrow 4H^+ + O_2 + 4e^-$
over all reaction	$2H_2O \rightarrow 2H_2 + O_2$

The over all reaction yields three moles of gas for every 4 moles of electrons. Since a mole of any gas occupies the same volume under identical conditions, it is necessary to determine only the total volume of the evolved gas. The relationship between the number of moles of gas and the volume is given by the ideal gas law.

$$PV = nRT$$

where P = pressure in atmospheres
V = volume in litres
n = number of moles
R = gas law constant (0.082 lit atm /deg / mol)
T = absolute temperature

For most accurate result a number of precautions such as pre saturating the electrolyte with the respective gases, controlling the temperature and vapour pressure corrections are necessary.

Example: How many ml of gas are evolved at standard conditions from the water coulometric per coulomb of electricity?

$$\frac{Q}{F} = Equivalent.of\ .electricity = 4/3(moles.of\ .gas)$$

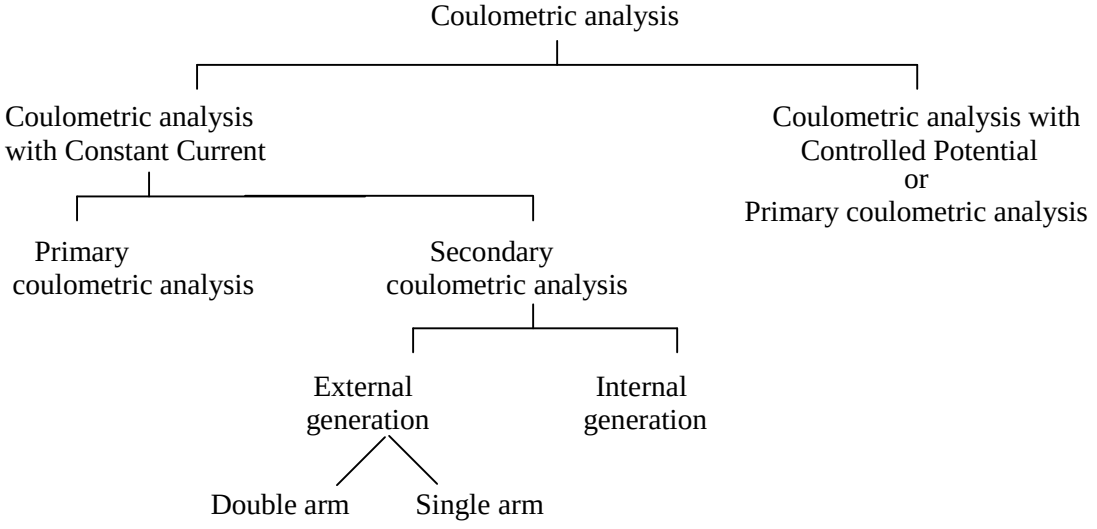
$$\text{and moles of gas } n = \frac{PV}{RT}$$

$$\therefore V = \frac{nRT}{P}$$

$$V = \frac{(3moles)(1coloumb)(0.082litatm/deg/moles)(273°c)}{(4equivalents)(96{,}487coulombs/Equ)1atm \times 10^3 ml/lit}$$

V = 0.1740 ml.

Coulometric analysis depends upon exact measurement of quantity of electricity passed through solution during the occurrence of an electrochemical reaction.



CONSTANT CURRENT COULOMETRY:

Primary constant current coulometry:

In case of primary constant current coulometry the relationship is $Q = i\,t$

where Q = total number of coulombs

i = current in amperes

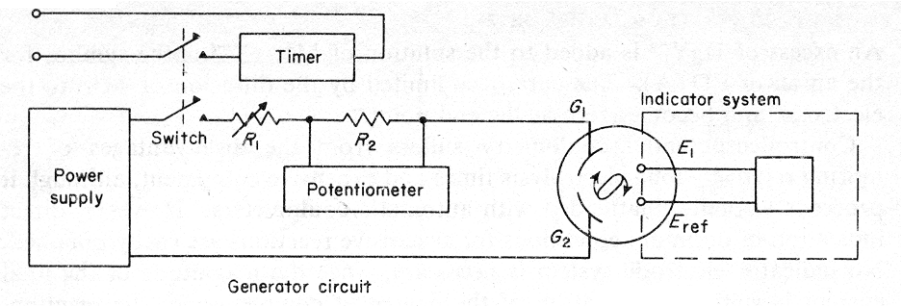
The necessary components of a constant current coulometric set up are

a) A constant current supply and monitor

b) Timer

c) A method of end point detection

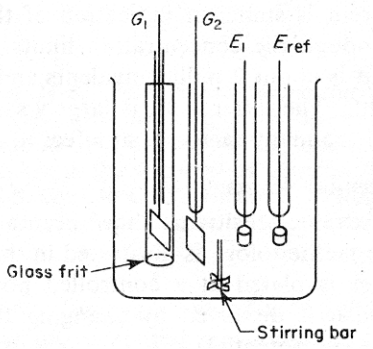
i) Visual indicator ii) Potentiometer iii) Amperometer



R_1 = series resistor R_2 = Precission resistor

G_1 and G_2 are generator electrodes (are sleeved in a jacket)

E_1 and E_{ref} are electrodes for end point detector system.



Any change in the concentration of the solution will change the resistance of the cell and resistance of the total circuit. Throwing the primary switch simultaneously starts the stopwatch and the electrolysis reaction. End point detection is done by potentiometer, here alternatively other procedures like amperometry, and photometry can also be used.

Primary constant current coulometry:

In primary coulometric titrations the titrant is generated by either an oxidation or a reduction process at the working electrode. This generated titrant reacts directly with the sample. For example, chloride may be determined by electro generated silver ions at the silver electrode according to the electrode reactions.

$$Cl^- + Ag \rightarrow AgCl + e^-$$

Secondary constant current coulometry:

In this technique one of the titrant is quantitatively produced at one of the electrodes, which is then stoichiometrically reacts with the ion to be determined.

Ex: Oxidation of Fe (II) to Fe (III) by Ce (IV) which is produced by the oxidation of cerium (III) at anode.

$$\begin{array}{lll} Fe(II) & \rightarrow & Fe(III) + e^- \quad -0.68\text{volts} \\ Ce(III) & \rightarrow & Ce(IV) + e^- \quad -1.44\text{volts} \\ \hline Fe(II) + Ce(IV) & \rightarrow & Ce(III) + Fe(III) \end{array}$$

This is more advantageous since oxidation of Fe(II) to Fe (III) at platinum electrode acting as anode does not proceed due to side reaction and liberation of oxygen.

This is because when oxidation started to some extent concentration of Fe(II) ion around the anode increases and diffusion of iron (II) from bulk of solution decreases. But as current remains constant, so that anode assumes more and more positive value of the potential as a result of oxygen being evolved at anode.

This can be countered by maintaining large excess of Ce(III) which goes to 100% completion. Ce(IV) diffuses and reacts with Fe(II) to form Fe(III).

Internal Generation:

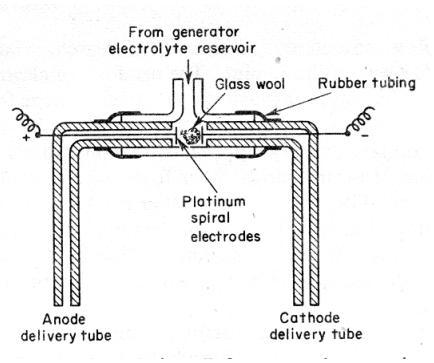
Estimation of thiosulphate with iodine liberated from KI at anode. Excess of KI is added to hypo in solution taken in an electrolytic cell and constant current is allowed. Iodine liberated at anode reacts immediately with hypo. Titration can be performed by adding starch indicator.

Amount of hypo consumed = current used for generation of iodine

External Generation:

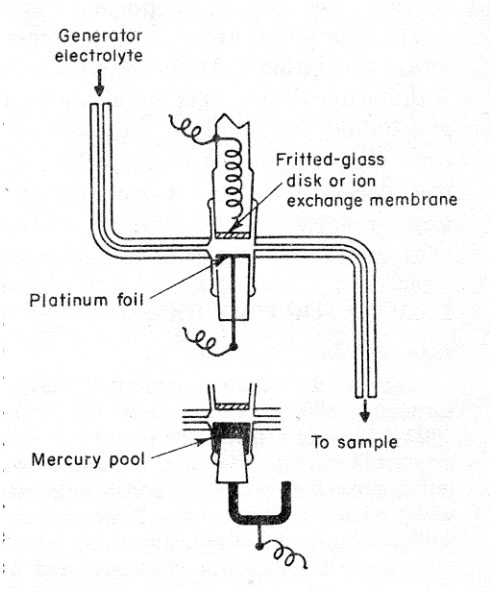
Double arm electrolytic cell:

The supporting electrolyte is fed continuously from a reservoir into the top of the generator cell. The incoming solution is then divided at the centre of 'T' joint in the two arm design, so that about equal quantities flow through each of the arms of the cell. Platinum electrodes are sealed on either side of the T- joint.



At the other end the beaker containing the sample to be titrated is placed beneath the appropriate delivery tip (tube). This hardly differs with ordinary volumetric titration. The only difference is that the titre is referred to unit of time and not unit of volume. Naturally, one half of the liquid continuously discharged is conducted to waste. When a solution of Na_2SO_4 is supplied sulphuric acid is formed at the anode and NaOH at the cathode. For bromination a solution of KBr is used.

Single arm electrolytic cell:



The single arm generator cell is useful for the generation of reagents in those cases in which mixing of the cathode and anode electrolysis products can be tolerated. The flow of supporting electrolyte is usually 6ml / minute or larger.

In titration of azodyes against titanium(III) (titanous ion), the titanous ion is produced externally and then it is delivered into the titration cell. Since the reaction between titanous ion and dye is very slow at room temperature, the titanous ion is produced externally at room temperature and then delivered into vessel (cell) at higher temperatures.

However elevation of temperature leads to gasification of the contents and decreases the current efficiency. It can be used successfully for titrations involving hydrogen, hydroxyl, iodine, chlorine and bromine.

APPLICATIONS:

1. *Netralisation Reactions:*

Acid-base titration can be carried out with a high degree of accuracy, using electro generated OH^- ions. The generation of OH^- ion at a platinum cathode within the solution provides the most convenient method. Potentiometric or indicator end point can be used for these titrations.

Coulometric titration of strong and weak bases can be performed with H^+ ion generation at a platinum anode.

$$H_2O \rightleftharpoons 2H^+ + \tfrac{1}{2} O_2 + 2e^-$$

The generation may be carried out internally as well as externally.

A real advantage to the coulometric method in neutralisation titrations is that the carbonate problem is far less serious; it is necessary to eliminate carbondioxide from the solution to be analysed, by aeration with a carbondioxide free gas, before beginning for analysis.

2. *Precipitation and Complexometric titrations:*

Reilley and Porterfield have studied coulometric titration of several cations by means of EDTA ion (HY^{3-}) generated at a mercury cathode. Excess of Hg(II) complex of EDTA is introduced into ammonical solution of sample and then reduction of Hg(II) takes place with liberation of EDTA anion, which then reacts with cation under test.

$$Hg\ NH_3Y^{2-} + NH_4^+ + 2e^- \longrightarrow Hg + 2NH_3 + HY^{3-}$$

HY^{3-} then reacts with cation under investigation. Let it be Ca^{2+} in this reaction.

$$Ca^{2+} + HY^{3-} \longrightarrow CaY^{2-} + NH_4^+$$

Some typical applications of coulometric titrations in case of neutralization, precipitation and complex formation reactions are as follows.

Species Determined	Generator Electrode Reaction	Secondary Analytical Reaction
Acids	$2H_2O + 2e^- \rightleftharpoons 2OH^- + H_2$	$OH^- + H^+ \rightleftharpoons H_2O$
Bases	$H_2O \rightleftharpoons 2H^+ + ½O_2 + 2e^-$	$H^+ + OH^- \rightleftharpoons H_2O$
Cl^-, Br^-, I^-	$Ag \rightleftharpoons Ag^+ + e^-$	$Ag + Cl^- \rightleftharpoons AgCl$
Zn^{+2}	$[Fe(CN)_6]^{3-} + e^- \rightleftharpoons [Fe(CN)_6]^{4-}$	$3Zn^{+2} + 2K^+ + 2[Fe(CN)_6^{4-}] \rightleftharpoons K_2Zn_3[Fe(CN)_6]_2$

3. Redox titrations:

Electro generated bromine was proved to be particularly useful among the oxidizing agents and the development of a host of interesting methods has been based upon this substance. The titration of arsenic(III), antimony(III) and H_2S can be carried out by electrolytically generated bromine or iodine.

$2Br^- \rightarrow Br_2 + 2e^-$ (anode) $\quad 2H_2O + 2e^- \rightarrow 2OH^- + H_2$ (cathode)

$AsO_3^{3-} + Br2 + 2OH- \rightarrow AsO_4^{3-} + 2Br^- + H_2O$

Some applications of the coulometric titrations involving redox reactions are summarized below:

Reagent	Generator Electrode Reaction	Substance Determined
Br_2	$2Br^- \rightleftharpoons Br_2 + 2e^-$	As(III), Sb(III), U(IV) Tl(1), I^-, SCN^-, NH_3, N_2H_4, NH_4OH, C_6H_5OH, $C_6H_5NH_2$
Cl_2	$2Cl^- \rightleftharpoons Cl_2 + 2e^-$	As(III), I^-
I_2	$2I \rightleftharpoons I_2 + 2e^-$	As(III), Sb(III), $S_2O_3^{2-}$, H_2S
Ce^{4+}	$Ce^{3+} \rightleftharpoons Ce^{4+} + e^-$	Fe(II), Ti(III) ,U(IV) As(III), I^- , $Fe(CN)_6^{4+}$
U^{4+}	$UO_2^{2+} + 4H^+ + 2e^- \rightleftharpoons U^{4+} + 2H_2O$	Cr(IV), Ce(IV)
Ag^{2+}	$Ag^+ \rightleftharpoons Ag^{2+} + e^-$	Ce(III), V(IV), $H_2C_2O_4$, As(III)
Mn^{3+}	$Mn^{2+} \rightleftharpoons Mn^{3+} + e^-$	$H_2C_2O_4$, Fe(II), As(III)

CONTROLLED POTENTIAL COULOMETRY:

Controlled potential coulmetry was first originated by Hickling, who used platinum electrode in the estimation of copper by cathode deposition and iodine by anodic oxidation. Lingane used mercury cathode, because the control potential of mercury electrode can be pre-assessed from polaorographic data. But mercury is not good as an anode.

In controlled potential coulometry the potential of the generating electrode is held constant and the current decreases exponentially with time.

$i = i_o .e^{-k t}$

where i is the current at time 't', i_o is the current at time zero, k is a constant

Since the current is proportional to the concentration of the ion at any given time the fraction of the ion which is unreduced at any time may be calculated. Current may not fall to zero except when the reaction is ideal with 100% efficiency. The number of coulombs 'Q' may be obtained experimentally from sets of current- time data. The plotting of the corrected points will define a straight line of the form

$k_t = \log i - \log i_o$

$-k_t = \log i - i_o$

From the plot of log'i' verses 't' on semi log paper the slope 'k' may be evaluated. The 'y' intercept will be i_o and it can be shown that

$$Q = \frac{i_o}{k(2.303)}$$

Advantages of coulometric methods:

1. Standard solutions are not required.
2. The titrant is produced itself during the reaction.
3. Very small quantities of reagent may be determined.
4. Reagents that are difficult to be stored and standardised may be used
5. Titrations are extremely precise.

UNIT 4

SOLVENT EXTRACTION

Lesson 1

Objectives of the lesson:

This lesson deals with the application of solvent extraction technique as a separation tool describing the theory, apparatus, techniques and applications.

INTRODUCTION:

Recent advances in analytical chemistry are characterized by great progress towards more powerful tools of separation, equaling in significance with the great forward strides made in instrumental methods of determination. Problems of chemical analysis generally involve two steps: (i) Separation of the desired constituent and (ii) measurement of the amount or concentration of this constituent.

Solvent extraction occupies an unique position among the separation techniques because of its ease, simplicity, speed and wide scope. It needs a simple apparatus i.e., a separatory funnel, requiring at most several minutes to perform. The method is applicable both to trace and macro levels of metals. Extraction procedures offer much to the analytical chemists. Since it does not involve co-precipitation which is an undesirable feature of separations based on precipitation, it frequently appears to be the ideal method for separating trace constituents from large amounts of other substances. The liquid –liquid extraction of metal chelates plays an important role in the purification of chemical reagents and semi conductor materials. This method is also used frequently in separation of various radio isotopes and the reprocessing of nuclear fuels. This technique is being fully exploited for the separation and quantitative determination of a number of elements of considerable industrial and especially toxilogical importance.

The formation of an uncharged species is a prerequisite for extraction into organic solvents which generally have low dielectric constants. Such species may be formed by metal containing ions through coordination involving chemical rather than physical bonds. A charged species may also be achieved through the neutralization of charge attending the association of ions on the basis of purely electrostatic extraction. It is relevant to point out that there is a smooth transition between true coordination complexes and ion association complexes.

However, as far as the extraction of metal complexes is concerned it is convenient to classify the extraction systems broadly into chelate extraction systems and ion association systems. The most important terms that are used in solvent extraction are 1.Distribution ratio 2.Separation factor 3.Percent extraction and 4.synergism

PRINCIPLES OF SOLVENT EXTRACTION:

Separation techniques, such as chromatography and ion exchange, homogenous precipitation, as well as solvent extraction, brilliantly highlight the usefulness of phase distribution as a separation principle; in each of these methods movements of matter across phase boundaries is involved.

1. Phase rule:

For all phase distributions, the classical phase rule of Gibbs can be considered

$$P+V = C+2$$

P = number of phases
V = number of degrees of freedom,
C = number of components.

In particular case of solvent extraction which deals basically with two essentially immiscible solvents and one solute distributed between them, so that P= 2, C=1. At constant temperature and pressure, the rule predicts a variance of unity. Thus when we choose the concentration of the solute in one phase, the solute concentration in the other phase is fixed. There will be a definite relation between the solute concentrations in each of the solvent phases. This relation is quantitatively described in the distribution law.

2. Distribution law:

Although the phase rule predicts that a system composed of two immiscible solvents and one distributing solute has one degree of freedom, the distribution law reveals greater restraint. The ratio of solute concentration is shown to be invariant i.e., independent of total concentration.

The distribution law states that a solute will distribute between two essentially immiscible solvents in such a manner that, at equilibrium, the ratio of the concentrations of the solute in the two phases at a particular temperature will be a constant, provided the solute has the same molecular weight in each phase.

For a solute 'C' distributing between two solvents 1 and 2, we have

$$C_1 \rightleftharpoons C_2$$

$$K_D = \frac{\text{Concentration of solute in solvent 1}}{\text{Concentration of solute in solvent 2}} \frac{[\overline{C_1}]}{[C_2]} (or) \frac{[C_1]_{organic}}{[C_2]_{aqueous}}$$

Where K_D is the distribution coefficient, a constant independent of total solute concentration, and the square brackets denote concentration.

Although the above expression is a useful approximation it has two shortcomings.

1. The law as stated is not thermodynamically rigorous.
2. The second is encountered when the distributing species is involved in chemical reaction such as dissociation or association in either phase.

3. Thermodynamic derivation of distribution law

For a closed system at equilibrium and at constant temperature and pressure the chemical potential of the third component that is solute is constant. (or)

Equilibrium is attained at constant temperature and pressure when the chemical potentials, (μ or partial molar free energies), of the solute in each phase are equal. Thus

$$\mu_1 = \mu_2 \qquad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

where the subscripts 1 and 2 refer the respective solvent phases.

Substituting suitable expression for μ, we have

$$\mu_1 = \mu_1^0 + RT \ln a_1 + RT \ln r_1$$

$$\mu_2 = \mu_2^0 + RT \ln a_2 + RT \ln r_2$$

$$\mu_1^0 + RT \ln a_1 + RT \ln r_1 = \mu_2^0 + RT \ln a_2 + RT \ln r_2 \qquad \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

where μ_0 represents the chemical potential of solution in a hypothetical ideal 1 Molal solution.

a = the solute concentration in molality,

r = the molal activity coefficient.

$$\therefore \text{Molal distribution coefficient, } K_D = \frac{a_1}{a_2} = \frac{r_1}{r_2} e^{-(\mu_2^0 - \mu_{1)}^0)/RT} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(3)$$

4. Distribution ratio:

This is a stoichiometric ratio including all species of the same component in the respective phases.

$$q \text{ or } D = \frac{\text{Total concentration in organic phase}}{\text{Total concentration in aqueous phase}}$$

(or) $$D \text{ or } q = \frac{[C]_{organic}}{[C]_{aqueous}} = \frac{[C]_o}{[C]_w}$$

5. Percent extraction:

The ultimate practical interest of describing extractions is the use of the term percent extraction. This quantity is related to the distribution ratio 'D' by the equation.

$$\%E = \frac{100D}{\left(D + \frac{V_\omega}{Vo}\right)}$$

Where D = Distribution ratio

V_ω and V_0 are volumes in aqueous and organic phases where both the volumes are equal , the denominator simplifies to the form D + 1.

That is if $V_W = V_O$ the above equation reduces to the form

$$\%E = \frac{100D}{D+1}$$

A problem often encountered in practice is to identify the most efficient method for removing a substance quantitatively from solution. It can be shown that if V ml. of say, an aqueous solution

containing x_0 g. of a solute be extracted n times with v-ml. portions of a given solvent, and then the weight of solute x_n remaining in the water layer is given by the expression:

$$x_n = x_0\left(\frac{DV}{DV+v}\right)^n$$

Where D is the distribution ratio between water and the given solvent. Thus the best method of extraction with a given volume of extracting liquid is to employ several fractions of the liquid rather than to utilize the whole quantity in a single extraction.

For example: Let us suppose that 50ml of water containing 0.1g of iodine is equilibrated with 25ml of carbon tetrachloride. The distribution coefficient of iodine between water and carbon tetrachloride at room temperature is 1/85, i.e., at equilibrium the iodine concentration in aqueous layer is $1/85^{th}$ of that in the carbon tetrachloride layer. Let us compute the weight of iodine remaining in the aqueous layer after one extraction with 25ml and also after 3 extractions with 8.33ml of solvent by application of the above formula. In case of former if x_1 g of iodine remains in the 50ml of water its concentration is $x_1/50$ g per ml.; The concentration in the carbon tetrachloride layer will be $(0.1 - x_1) / 25$ g/ml. Hence :

$$\frac{x_1/50}{(0.1-x_1)/25} = \frac{1}{85}, \text{ or } x_1 = 0.00230 \text{ g.}$$

The concentration in the aqueous layer after three extractions with 8.33ml of carbon tetrachloride is given by:

$$x_3 = 0.1\left(\frac{(1/85)\times 50}{(50/85)+8.33}\right)^3 = 0.0000145 \text{ g}$$

The extraction may therefore be regarded as virtually complete in the case where three extractions with 8.33 ml of solvents were done.

FACTORS EFFECTING SOLVENT EXTRACTION

1. Separation Factor:

To get simple separation, it is essential that the distribution ratios of the material of interest and that of the interfering substance be sufficiently different.The effectiveness of separation is generally expressed by means of the separation factor β, which is related to the individual distribution ratio.

$$\beta = \frac{[C_1]_o/[C_2]_o}{[C_1]_\omega/[C_2]_\omega} = \frac{[C_1]_o/[C_1]_\omega}{[C_2]_o/[C_2]_\omega} = \frac{D_1}{D_2}$$

$[C_1]_0$ and $[C_1]_\omega$ are concentration of component '1' in organic and aqueous phase.

$[C_2]_0$ and $[C_2]_\omega$ are concentration of component '2' in organic and aqueous phases.

If distribution ratio of one component is small and the other is relatively large, clean separations can be achieved quickly and easily.

∴ Separation factor (β) is the ratio of distribution ratios.

$$\beta = \frac{D_1}{D_2}$$

Example:

If A and B are two chelates with same chelating agent (same chemical environment). That is if A and B are in mixture of water and CCl_4, so both have different partition coefficients and so different 'D' values.

$D_A \neq D_B$ (or)

$q_A \neq q_B$

When we considered separation of a species between a pair of solvents it should have more 'q' or 'D' value than the other from which the desired one is to be isolated.

$$\beta = \frac{[A]_0 / [B]_0}{[A]_{aq} / [B]_{aq}}$$

$$= \frac{[A]_0 / [A]_{aq}}{[B]_0 / [B]_{aq}} = \frac{q_A}{q_B} \text{ or } \frac{D_A}{D_B}$$

If $D_A = D_B$ implies no Separation

$D_A \neq D_B$ implies separation

D_A or $D_B = 1$ implies maximum separation possible.

2. Kinetic factors in extraction:

Both quantitative and qualitative descriptions of extraction are based upon the assumption that two phases are in equilibrium. The rate of achievement of equilibrium, the point at which the net rate of matter across the boundary between the two liquid phases is zero, depends on two factors.

(1) The rate of formation of the extractable species and

(2) The rate of transfer of the species from one phase to another.

(i) Rate of Transfer:

The transfer of any solute from one phase to another involves more than one process. The solute molecules must first move by a diffusion process (eddy diffusion) from the bulk of the solution, which is in more or less violent motion through a relatively thin, stationary layer or film of the solvent on each side of the boundary. The thickness of this film depends on the relative velocity of the liquid in the bulk phase but it never vanishes altogether. The rate of diffusion of the solute through this layer will depend on the size and shape of the solute as well as on the viscosity of the solvent. The rate of passage through the phase boundary is rapid where there is interfacial turbulence. Once though, the solute molecule must diffuse through another stationary level of the second solvent before it reaches the bulk phase where mixing by agitation will adjust the concentration gradient.

There is a practical limit to the degree of agitation, which can be advantageously employed in equilibrating an extraction mixture. Although shaking is desirable in reducing the thickness of the stationary films on either side of the phase boundary, it is important to remember that it is the velocity of one phase relative to that of the other which determines the film thickness. Too violent agitation serves no purpose besides resulting in an emulsion, which is undesirable. *Craig* has shown that simple repeated

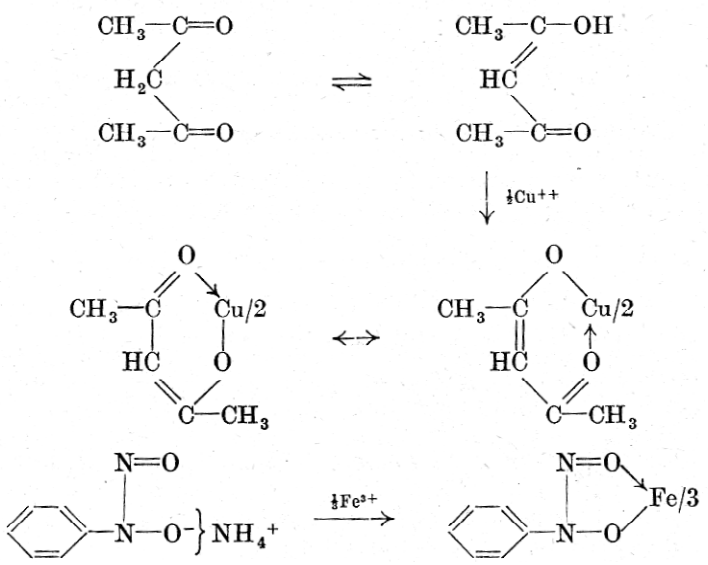
inversion of a tube containing the two phases imparted sufficient relative velocity to the phases to give equilibrium in a relatively few inversions. Even high molecular weight solutes such as *pencillins* need a maximum of 50 inversions to attain equilibrium.

Unless the liquids employed are quite viscous, one may reasonably conclude that as far as the rate of transfer of material from one phase to the other is concerned, equilibrium can be affected with a shaking time of several minutes.

2. Rate of Complex Formation:

Uncharged complexes derived from metal ions are usually soluble in organic solvents. These may be formed by the complexation of metal ions either by co-ordination (leading generally to chelation complexes) or by ion association.

In chelation complexes (some times called inner complexes when uncharged) the central metal ion coordinates with a poly functional organic base to form a stable ring compound, e.g., cupric "acetyl acetonate" or ferric "cupferrate" ;



In ion-association complexes the inorganic ion associates with oppositely charged ions to form a neutral extractable species. Particularly in the organic solvents such complexes may form clusters larger than just simple pairs with increasing concentrations. Two types of ion association complexes may be recognized (1) ion pairs from a reagent having a large organic ion such as tetra phenyl arsonium ion or tribenzyl ammonium ion; (2) ion pair solvent molecules which are directly involved in its formation.

Explanation: In the first type these reagents combined with a suitable metal containing ion (e.g., the per-rhenate ion ReO_4^-) to give large ion aggregates or clusters. Thus in the extraction of uranyl nitrate with *iso* butyl alcohol the extractable complex is probably $[UO_2(Bu^iOH)_6](NO_3)_2$, in which the coordinated

solvent molecules contribute both to the size of the cation and the resemblance of the complex to the solvent. By and large the solvents like ethers, ketones, alcohols which participates directly in the formation of ion association complexes contain oxygen atoms; the later form coordinate linkages to the metal atoms.

FACTORS AFFECTING CHELATE FORMATIONS:

(*i*) *The basic strength of the chelating group:* a relationship exists between the basicity of a chelate group as measured by pK_a values and stability of the chelate it forms.

(ii) *The electronegativity of the donor atoms of the basic group in the chelating agent:* Atoms of lower electronegativity tend to form stronger bonds, e.g., nitrogen and sulphur are better than oxygen, thus dithizone (diphenyl thiocarbazone) forms more stable chelates than its oxygen analog diphenyl carbozone.

(iii) *Ring size:* five or six membered rings are more stable since they have minimum strain. Chelate stability increases with the number of rings that are formed since the water molecules are displaced from the metal coordination sphere.

(iv) *The metal ion characteristics such as charge / ionic radius ratio (ionic potential) or charge^2 / ionic radius ratio:* As the ratio increases the stability of metal complex rises.

(v) *Resonance and steric effects:* The stability of chelate structures is enhanced by contributions of resonance structures of the chelating ring; thus copper acetyl acetonate has greater stability than the copper chelate of salicylaldoxime.

GENERAL TECHNIQUES:

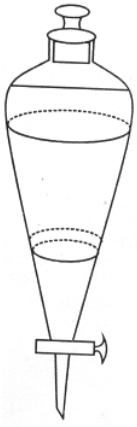
A. METHODS OF EXTRACTION:

In practice the following types of extractions are considered.

1. Batch extraction.
2. Continuous extraction.
3. Extraction of solids.
4. Counter current distribution.

1. Batch extraction:

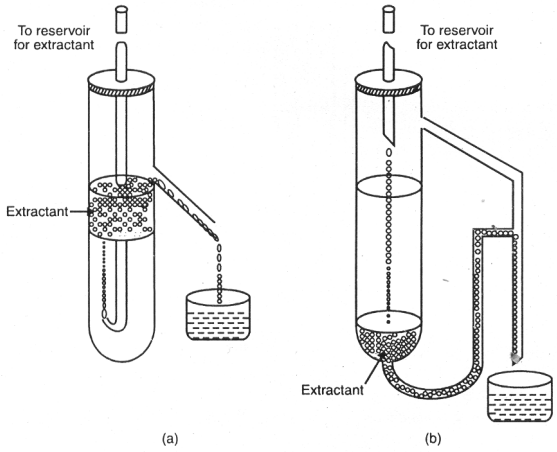
In this method the given volume of solution is brought in contact with a given volume of solvent until equilibrium is attained and the two layers are then separated.



The usual apparatus for batch extraction is separatory funnel. Batch extractions may be used to the advantage when the distribution ratio is large since in such cases a few extractions will effect quantitative separation. In this method after agitation for sufficient length of time the layers are allowed to separate. If the organic layer is present in upper layer, the aqueous layer is transferred to a second separating funnel and another fresh portion of organic liquid is added. The process is repeated as many times as required to ensure satisfactory separation.

2. Continuous extraction:

For satisfactory separation generally a large number of multiple batch extractions can be considered which are made possible by the use of continuous extraction procedure. Extraction equipment have been devised for continuous extraction using organic solvents which are lighter than water or heavier than water, such equipment are shown in the figure.



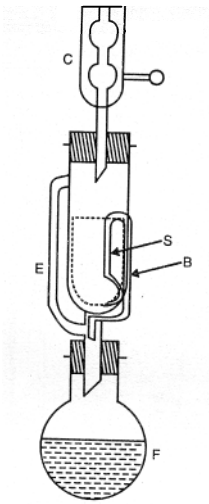
The apparatus (a) is used when the organic solvent is lighter than the solution to be extracted while (b) is used when the organic liquid is heavier than the solution to be extracted. The usual practice is to agitate the solutions during extractions. However in case of systems having tendency to produce emulsions, the agitation should be minimal.

3. Counter current extraction:

In a true counter current extraction the two immiscible solvents contact each other as they flow through one another in opposite directions. These extraction procedures have been found to be very difficult because fresh extraction is brought in contact with the solute depleted phase or when the solute enriched extractant is brought into contact with fresh aqueous solution. The amount of solute in either phase after any number of contact steps can be calculated from a binomial expansion. Various devices have been suggested for carrying out counter current extractions.

4. Extraction of solids:

The separation of solutes by extraction is best performed by liquid-liquid distribution procedures; however, there may be some situations where it is more convenient to extract a particular material present in a solid sample. Then the solute cannot be easily modified to enhance or suppress extraction, and removal is dependent chiefly on the solubility of the substance in a particular solvent. Solid-liquid extractions find their chief application in problems involving biological or natural samples, although a number of inorganic salts may be separated in this fashion.



Soxhelt extractor C = condenser, E = extractor, S = Slphon, B = boiling vapours and F = flask

Most continuous extraction procedures for solids utilize the Soxhlet extractor shown in the figure where in extraction may be allowed to run unobserved for long time and hence save the analyst's time.

B. TECHNIQUES AND EXTRACTION:

The basic considerations for the application of solvent extraction are

1. Choice of solvent
2. Stripping
3. Back washing
4. Treatment of emulsions
5. Variation of oxidation state
6. Use of masking agents.
7. Use of salting out agents.

1. **Choice of solvent:**

The most important consideration for extraction of a particular component in solvent extraction is choice of a solvent.

Generally it should have the following properties

i) Low solubility in aqueous phase.
ii) A high distribution ratio of the solute (ready separation) and low distribution ratio for the undesirable impurities.
iii) The degree of miscibility of two phases their relative specific gravity, viscosity, surface density and tendency to form emulsions are of considerable importance in solvent extraction.
iv) Low toxicity and low inflammability for organic solvent.
v) Easy recovery of the solute from the solvent phase, thus the boiling point of solvent, ease of stripping by the chemical reagents contribute to the selection of solvent when the possibility of the choice exist.
vi) Sometimes by using mixture of solvent desirable characteristics can be achieved
Ex1: Using alcohol and ether solvent mixture in the thiocyanate extraction of elements such as Co, Bi, Fe, etc
Ex2: Dibutoxy tetra ethyl glycol and ether are used in extraction of thorium from nitrate solutions.
vii) Organic diluents are also used to get varying compositions of solvent systems. Hydrocarbons and kerosene are the organic diluents used in dilution of tributyl phosphate for extraction purposes.

2. Stripping:

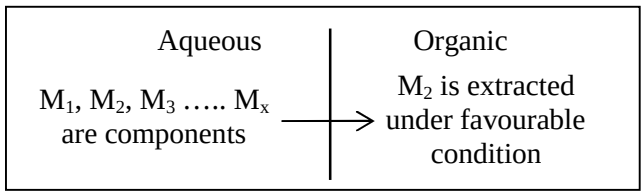
Stripping is the removal of the extracted solute from the organic phase for further purification and analytical determination. When other conventional methods of estimation are to be employed, or where further separation steps are required, it is necessary to remove the solute from the organic phase to a more suitable medium.

Depending on the volatility of the organic solvent, the simplest procedure is to add a small volume of water to the extract to hold the solute and to evaporate the volatile solvent on a steam bath. This is particularly useful when performing ether extractions. Care should be taken to avoid loss of volatile solute during evaporation. Some times adjustment of acidity of the solution, change in the valence state, etc., may be employed to avoid loss of the solute. The addition of acid to the water before evaporation of volatile solvents in which chelate complexes are dissolved helps to break the complex, there by causing metal ions to enter the water solution.

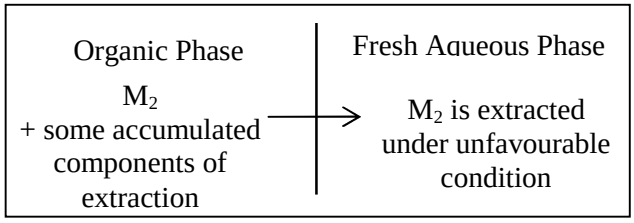
When the extracting solvent is non-volatile, it is necessary to strip the solute from the solvent by chemical means; the usual procedure is to shake the organic phase with a volume of water containing acids or other reagents under conditions where by the extractable complex is destroyed. The metal ions are then quantitatively back-extracted into the stripping aqueous phase.

Example:

If only M_2 is the component that is being extracted into the organic phase, and extraction is favourable in acidic medium.



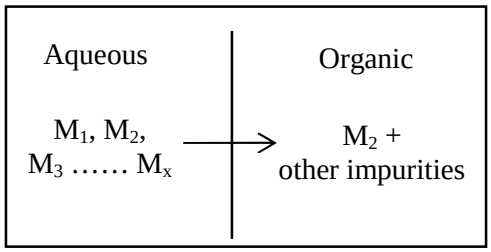
For further determination creating unfavourable conditions of acidic medium and shaking with fresh aqueous phase M_2 can be extracted into the aqueous phase from the organic phase. This is called *stripping*. This eliminates some impurities that are extracted along with M_2 in the first step.

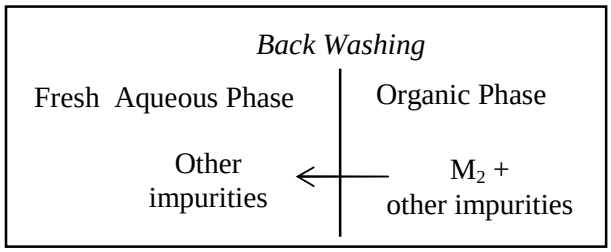


3. Back washing:

An auxiliary technique used with batch extractions to effect quantitative separation of elements is *back washing*. The combined organic phases from several extractions of the original aqueous phase contain practically all the element desired and possibly some of the impurities that have been extracted to a much smaller extent, depending on their relative distribution ratios. This combined organic phase, when equilibrated with one or more small portions of a fresh aqueous phase containing the optimum reagent concentration, salting out agent, etc., will result in redistribution of the impurities as well as of the major component between the two phases.

Under optimum conditions most of the element desired will remain in the organic layer, since its distribution ratio is high. The bulk of impurities however will be back-extracted to the fresh aqueous phase since their distribution ratios are much smaller.





4. Treatment of emulsions:

By mixing or agitating certain combinations of immiscible liquids, an emulsion may result where by one liquid is dispersed in a continuum of the other. A method for reducing the tendency of formation of emulsion is the addition of neutral salts, which possibly increases the surface tension or the density. Mixed organic solvents can also be employed, whose combined properties are less favourable for the formation of emulsions yet favour extraction of the solute of interest.

5. Variation of oxidation state:

The selectivity of extraction can be increased by modification of the oxidation states of some of the ions present in solution in order to prevent the formation of a metal complex necessary for extraction.
Ex: Extraction of iron from chloride solution can be prevented by reduction to iron (II) which does not extract.

6. Use of masking agents (sequestering agents):

Masking agents are themselves metal- complexing agents which serve to prevent particular metals from taking part in their 'usual' reactions and thus remove their interference without the necessity of an actual separation. Since the "masked" metal must remain in the solution, the complex obviously must be water soluble.

In solvent extraction, masking agents are used to prevent certain metals from forming extractable complexes and thus increases greatly to the selectivity of the extraction methods in which masking is employed.

The masking agents include cyanide, tartrate, citrate, fluoride. EDTA is restricted largely to metal chelate extraction systems.

Cation masking agents:

Ex: Separation of Nickel and Cobalt:

On addition of cyanide to Co^{2+} and Ni^{2+} mixture we get $[Co(CN)_6]^{3-}$ and $[Ni(CN)_4]^{2-}$ Nickel can be extracted with dimethyl glyoxime in the presence of cobalt if cyanide is first used to mask the cobalt. The $[Ni(CN)_4]^{2-}$ is destroyed by hydrogen peroxide or formaldehyde but the $[Co(CN)_6]^{3-}$ is very stable. So nickel forms complex with DMG and can be separated.

Anion masking agents:

Interfering anions can be masked by using masking cations. Thus if F^- interfere with a UO_2^{+2} extraction, an excess of aluminium or boran can be added to mask fluoride as a result of formation of aluminium tri fluoride or boran tri fluoride.

7. Use of salting out agents:

The addition of inorganic salt to the aqueous phase increases the distribution ratio of many metal complexes in favour of the extracting phase. The salting out effect may be explained in part by the pronounced effect of the salt that is added on the activity of the distributing species, as well as the strong ability of these ions to bind water around them, there by depleting the aqueous phase of water molecule for use as a solvent. The magnitude of enhancement of extraction by the added salt depends on the charge as well as the ionic size of the added cation for a given anion. Thus, polyvalent cations provide better salting-out agents, and for a given charge, the smaller the cation size, the greater the effect on extraction.

Aluminium or ferric salts are strong salting out agents, where as ammonium salts are much weaker but analytically more convenient.

QUANTITATIVE TREATMENT OF SOLVENT EXTRACTION EQUILIBRIUM:

Quantitative treatment of solvent extraction equilibria can be discussed under two systems.

1. Chelate extraction systems
2. Ion Association extraction systems.

1. Chelate Extraction Systems:

As discussed earlier formation of uncharged species (chelate compounds) is the prime requisite in chelate extraction system. In this case there are several stages that are expected before actually achieving the goal of chelate extraction.

Let us assume HR to be a chelating agent. In order to form a metal chelate, chelating agent must undergo ionization.

Ionization of Chelating agent:

$$HR \rightleftharpoons H^+ + R^-$$

$$K_i = \frac{[H^+][R^-]}{[HR]} \qquad \text{.....(1)}$$

Formation of Chelate:

$$M^{n+} + R^- \xrightarrow{k_1} M R^{n-1}$$

$$\therefore K_1 = \frac{[MR^{n-1}]}{[M^{n+}][R^-]} \text{ and finally}$$

$$MR_{n-1}{}^+ + R^- \xrightarrow{k_n} MR_n$$

$$K_n = \frac{[MR_n]}{[MR_n]^+[R^-]} \qquad \text{.......(2)}$$

Over all formation $K_f = k_1 k_2 \ldots . k_n$

Competing reactions of metal ion with hydroxides and with metal anion-coordinates.

$$M^{n+} + OH^- \longrightarrow M(OH)^{n-1} \qquad \text{.....(3)}$$

$$M^{n+} + X^- \longrightarrow MX^{n-1}$$

Where $X = Cl^-, SO_4^{2-}, NO_3^-$

Finally the distribution of chelating agent and chelate between the two phases is as follows:

Distribution of Chelating agent:

$$K_{DR} = \frac{[HR]_o}{[HR]} \qquad \text{.....(4)}$$

Distribution of Chelate:

$$K_{Dx} = \frac{[MR_n]_0}{[MR_n]} \qquad \text{...……..(5)}$$

The equilibrium expression may be used to derive an expression for D, (the ratio of stoichiometric metal concentration between the two phases). It is assumed that only the metal bearing species in the organic phase is MR_n.

$$D = \frac{[M]_o}{[M]} =$$

$$\frac{\text{Total analytically determinable concentration of a species (metal) in the organic phase}}{\text{Total analytically determinable concentration of a species (metal) in the aqueous phase}}$$

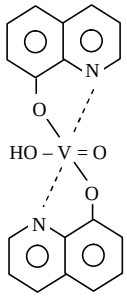
Indeed where the metal hydroxide formation assumes importance, dependence of pH decreases although the effect of the reagent concentration remains unchanged.

There are several chelating agents having functional groups like –OH, -SH from which the proton is replaced by a metal ion in order to neutralize the charge. However, there are chelating agents having coordination groups such as =N, =O which are capable of forming coordinate linkage through electron donation. Thus water molecules in the coordination sphere of the metal ion are replaced partially or fully forming chelate complexes with hydrophobic, organophilic nature.

The following may be taken as examples of the chelating agents which have been applied extensively.

8-hydroxy quinoline(oxine) and its derivatives, Morin, diketones, oximes and dioximes, cupferron, dithizone, dithio carbomates and xanthates.

Let us now consider , a typical chelate extraction system with 8-hydroxy quinoline which forms neutral , water insoluble and soluble complexes in non polar organic solvents(like chloroform and benzene) with number of metal ions.



Ex: Vanadium(V) extracts into non polar organic solvents like benzene and chloroform in the presence of oxine giving a species having vanadium and oxine in the ratio 1:2. At moderately higher pHs say 3-4 vanadium(V) species exists in the extracted species which can be represented by $VO(OH)(R)_2$

2. Ion- association extraction systems:

The problem of reducing the behaviour of ion association extraction systems to analytical expressions that quantitatively describe the relation between the extent of extraction and the experimental parameters is far more difficult for many systems than it is for chelate-extractions. However, the source of the difficulty is inherent in the nature of the forces responsible for the formation of ion association complexes.

Examples: Extraction of tetra phenyl arsonium perrhenate and extraction of Fe(III) chloride.

a. Extraction of Tetra Phenyl Arsonium Perrhenate:

Any anion, which is preferentially associated with cation will be extracted into organic phase selectively. Tetra phenyl arsonium chloride is water- soluble salt used to form chloroform - perrhenate extractable complexes with permanganate, and pertechnetate anions. Thus for perrhenate, the following equations apply.

Dissociation of the Reagent (R_4As^+, Cl^-):

$$(R_4As^+,Cl^-) \rightleftharpoons R_4As^+ Cl^-$$

$$K_i = \frac{[R_4As^+][Cl^-]}{[(R_4As^+, Cl^-)]} \qquad \text{...}\ldots\ldots\ldots\ldots(1)$$

Where R = C_6H_5

The value of K_i is probably very large.

Formation of the Ion Association Complex:

$$R_4As^+ + ReO_4^- \rightleftharpoons (R_4As^+, ReO_4^-\_)$$

$$K_f = \frac{[(R_4As^+, ReO_4^-)]}{[R_4As^+][ReO_4^-]} \qquad \ldots\ldots\ldots\ldots\ldots(2)$$

The value of K_f is probably very small

Distribution of Reagent:

$$K_{DR} = \frac{[(R_4As^+, Cl^-]_0}{[R_4As^+][Cl^-]} \qquad \ldots\ldots\ldots\ldots\ldots(3)$$

Distribution of complex:

$$K_{DX} = \frac{[(R_4As^+, ReO_4^-)]_0}{[R_4As^+][ReO_4^-]} \qquad \ldots\ldots\ldots\ldots\ldots(4)$$

Reactions of the Organic Phase:

Dimerisation of ion pairs occurs at low concentrations.

$$2\,(R_4As^+,Cl^-) \rightleftharpoons (R_4As^+,Cl^-)_2$$

and $$2(R_4As^+,ReO_4^-) \rightleftharpoons (R_4As^+,ReO_4^-)_2$$

$$\text{Hence } D = \frac{[(R_4As^+, ReO_4^-)]_0}{[ReO_4]} = K_{DX}\, K_f\, [R_4As^+] \qquad \ldots\ldots\ldots\ldots\ldots(5)$$

Thus equation (5) concludes that the distribution ratio of the perrhenate complex is solely a function of the equilibrium concentration of the reagent cation.

In the study of distribution of tetraphenyl arsonium chloride between $CHCl_3$ and H_2O. *Tribalat* found that dimerization of reagent occurs in the organic phase when initial aqueous reagent concentration is around 10^{-2}M.

SYNERGISM: (ENHANCEMENT)

Synergism is a phenomenon in which there is enhancement of extraction of metal chelates in the presence of uncharged reagents. This was first observed by Cunnigham, Scargil and Wills (1954) in the extraction of praseodemium (Pr) and neodymium (Nd) by the mixture of TTA (Theonyl tri fluoro acetate) and TBP (Tri butyl phosphate). The term synergism was first coined by Blake et.al., (1958). The properties of mixed complex ML_1L_2 are strikingly different from those of the possible binary compounds M L_1 and M L_2 (where M is the metal ion, L_1 and L_2 are the ligands). Such type of mixed ligand complexes formation particularly in the solvent extraction of metals has facilitated in several instances.

(a) Rapid establishment of equilibrium
(b) Increased absorptivity and
(c) Synergistic enhancement.

Synergism Systems:

The most thoroughly studied synergic systems are

(1) Chelating agent such as TTA (or) 1PT (β-isoproponyl tropolone) and others such as TBP(tri butyl phosphate) , M1BK(methyl isobutyl ketone), DBSO (Dibutyl sulphoxide)

(2) A dialkyl phosphoric acid and a neutral organo phosphorus ester.

Explanaiton:

$M + L_1 \longrightarrow$ 30% extraction

$M + L_2 \longrightarrow$ 10% extraction

$M + L_1 + L_2 \longrightarrow$ 99% (Enhancement in extraction that is synergism)

Thus the extraction in presence of single ligand either L_1 or L_2 is less when compared to the extraction in mixture (or) combination of two ligands.

Synergistic Coefficient (SC):

$$SC = \log \left[\frac{\text{'q' values in presencee of synergism}}{\text{Additive 'q' values in absence of synergism}} \right]$$

Explanation: (Based on example: 1)

$$SC = \log \left[\frac{\frac{99}{1}}{\frac{30}{70} + \frac{10}{90}} \right] = 2.26$$

$\therefore$ If the synergistic coefficient is more, then synergism is more.

Comparison of syngergistic coefficient values with types of ligands emphasises on the number of ligands suitable to make the extraction more effective.

Example:2

Extraction of vanadium

The extraction of vanadium (iv) in presence of individual ligands CNS- and o- phenanthroline is very less i.e., 70% and 13.3% respectively. However , in case of ,mixed ligand complexes where in both SCN- and o-phenonthroline are acting as ligands, the extraction was found to be 98% showing a marked enhancement in extractions(synergism).

Ligand	Percent Recovery	
	MIBK	n-butanol
Nil	–	13.3%
CNS^-	30%	70.0%
O-phenanthroline	–	13.3%
CNS^- + O- phenanthroline	98%	98.0%

Experimental Conditions:

pH: 1 – 3

Reagents : CH_3COONa and HCl

Solvent : Methyl iso butyl ketone(MIBK)

Synergistic Coefficient (SC):

$$SC_{MIBK} = \log\left[\frac{98/2}{30/70}\right] = \log 114 = 2.06$$

$$SC_{n\text{-butanol}} = \log\left[\frac{\frac{98}{2}}{\frac{70}{30}+\frac{13.3}{86.7}+\frac{13.3}{86.7}}\right] = \log 18 = 1.26$$

The reverse of synergism that is Anti synergism, which is generally known as antogonism was noted by Blake and Peppard in the alkyl phosphoric acid – phosphorous ester - system (HX-S) and by Healy in TTA-TBP (HX-S) on addition of excess solvent.

In first case the excess of donar solvent(s) reduces the concentration of free chelating agent by increasing interaction between HX and S through hydrogen bonding thus extraction coefficient becomes smaller.

In second case the anti-synergism is related to the water content of the organic phase and the distribution of anhydrous synergic species $M(TTA)_xS_y$.

UNIT 4

ION EXCHANGE

Lesson 2

Objectives of the lesson:

This lesson deals with introduction, details of ion exchange resins and applications.

INTRODUCTION:

Thomson and Way the two British agricultural chemists proved that ammonium and potassium salts from water were exchanged by soils with a release of equivalent amount of calcium salt. This has become the point for invention of the new separation technique namely **ion exchange.** The term ion exchange is generally understood to mean exchange of ions of like sign between a solution and a solid highly insoluble body in contact with it. The solid (ion exchanger) must contain ions of its own, and must have open permeable molecular structure so that ions and solvent molecules move freely in and out. The exchange involves equal quantities of ions and differs from true physical adsorption. A number of common clays, soils, minerals particularly zeolite and synthetic zeolites are known to exhibit ion exchange characteristics.

Definition:

The term ion exchange generally means the exchange of ions of like sign between a solution and a solid. Many substances both natural and artificial have ion exchanging properties. All ion exchangers have several properties in common

1. They are almost insoluble in water and in organic solvents
2. The ion exchangers are complex, porous and polymeric in nature
3. The crystalline lattice has a core either anionic or cationic in nature with a loosely bound cation or anion (counter ion or active ion).
   $(\text{Core Cation})^+ \ Cl^-$ or $(\text{Anionic Core})^- \ Na^+$
4. These active or counter ions will exchange reversibly with other ions in a surrounding solution with out any appreciable physical change in the material.
5. The polymer carries an electric charge that is exactly neutralised by the charges on the counter ions. (These active ions are cations in cation exchanger and anions in anion exchanger)

Thus a cation exchanger consists of a polymeric anion and active cation while an anion exchanger consists of a polymeric cation and active anion.

A cation - exchanger resin is defined as a high molecular weight cross linked polymer containing sulphonic, carboxylic, phenolic etc., as groups as an integral part of the resin and an equivalent amount of cations (active ions).

1. Sulphonic acid is a strong acid cation exchange resin

$$(\text{Resin})\ SO_3H^+ + Na^+ \rightarrow (\text{Resin})\ SO_3Na^+ + H^+$$

Anionic exchange resin is a polymer containing amine groups as integral parts of the polymer lattice and an equivalent amount of anions such as chloride, hydroxyl or sulphate ions as active ions.

The basic requirements for a resin to be used are:

(1) The resin must be sufficiently cross linked so as to have solubility negligible.

(2) The resin should be sufficiently hydrophilic so as to permit the diffusion of ions through its structure at a finite and usable rate.

(3) The resin must contain a sufficient number of accessible ionic exchange groups and must be chemically stable.

(4) In swollen condition resin must be denser than water.

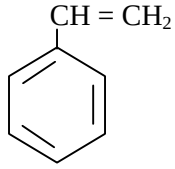
Examples:

1. Strong base anion exchange resin:

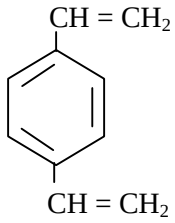
A cross linked polystyrene containing quaternary ammonium groups are largely ionised in both the hydroxide and salt forms.

$$2(Res.N\,Me_3^+)Cl^- + SO_4^- \rightarrow 2(Res.N\,Me_3^+)SO_4^- + 2Cl^-$$

$$2(Res.N\,Me_3^+)OH^- + H^+Cl^- \rightarrow 2(Res.N\,Me_3^+)Cl^- + H_2O$$



Styrene



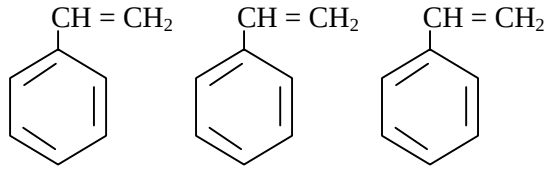
Divinylbenzene

Synthetic Resins:

Synthetic anion exchange resins are essential for removal of industrial wastes.

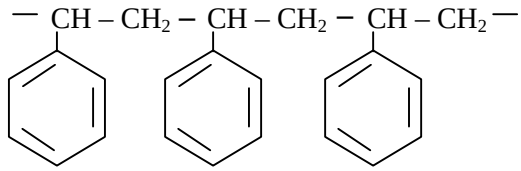
The most commonly used resins are

Styrene

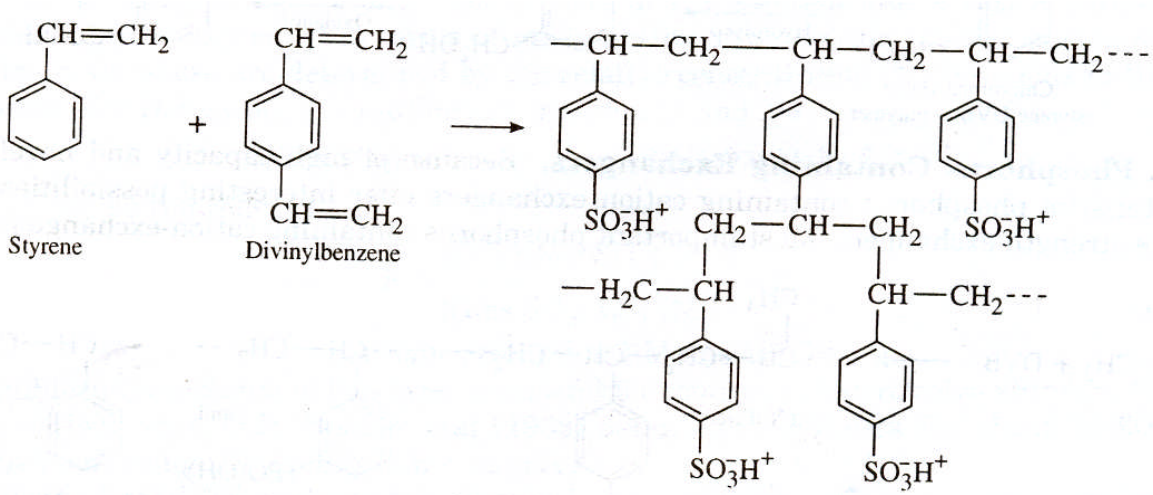


When polymerisation occurs, the double bonds disappear and single bond formation takes place between monomers.

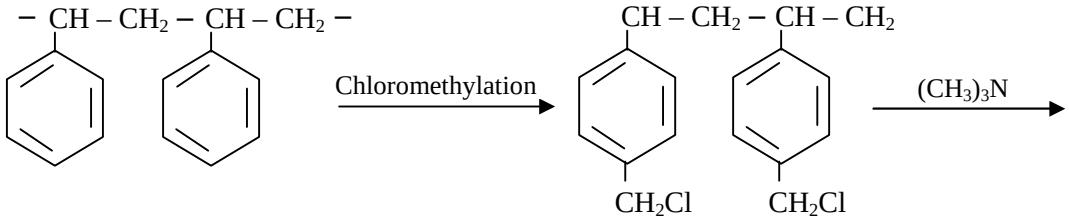
Polystyrene

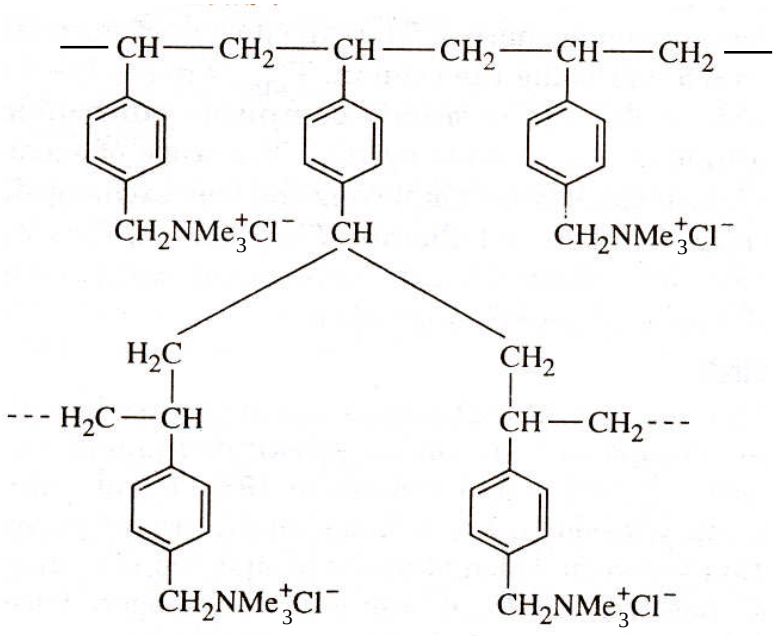


The polystyrene when cross linked with another organic molecule such as Divinyl benzene (DVB), a widely used **cation exchanger resin** is obtained by co-polymerisation of styrene and a small portion of DVB followed by sulphonation.



A widely used anion exchange resin is prepared by co-polymerisation of styrene and a little of DVB followed by interaction by chloromethylation and interaction with base such as trimethyl amine $(CH_3)_3N$.





Cation of Ion -Exchange resins:

Cation exchange resins contain free cations which can be exchanged for cations in solution.

$$(\text{Resin } A^-)\, B^+ + C^+ \text{ (solution)} \rightarrow (\text{Resin } A^-)C^+ + B^+ \text{(solution)} \quad \text{-------- (1)}$$

Under suitable experimental conditions, the C^+ ions are completely fixed on the cation exchanger by replacing the B^+ ions.

If the solution contains several ions (C^+, D^+ and E^+) the exchanger may show different affinities thus making the separations possible. A typical example is the displacement of sodium ions in a sulphate resin by calcium ions.

$$2(\text{Resin } SO^-_3)Na^+ + Ca^{++} \text{ (solution)} \rightarrow (\text{Resin } SO_3^-)_2Ca^{++} + 2Na^+ \text{(solution)} \quad \text{----------(2)}$$

The reaction is reversible. By passing solution containing sodium ions through the product, the calcium ions may be removed from the resin and the original sodium form restored. Similarly by passing a solution of a neutral salt through the hydrogen form of a sulphonic resin, an equivalent quantity of the corresponding acid is produced by following reaction.

$$2(\text{Resin } SO^-_3)H^+ + Na^+ Cl^- \text{ (solution)} \rightarrow (\text{Resin } SO^-_3)Na^+ + H^+ Cl^- \text{ (solution)} \quad \text{--------- (3)}$$

For strongly acidic cation exchange resins, such as cross linked polystyrene sulphonic acid resins, the exchange capacity is independent of the pH of the solution. For weak acid cation exchangers, such as these containing carboxylic groups, ionisation occurs to an appreciable extent only in alkaline solution that is in their salt form.

Ex: $(\text{Resin } COO^-)H^+ + Na^+ OH^- \text{ (solution)} \rightarrow (\text{Resin } SO^-_3)Na^+ + H_2O$ --------- (4)

For strongly basic anion exchange resins Ex: A cross linked polystyrene containing quaternary ammonium groups are largely ionised in both the hydroxide and the salt forms.

$$2(\text{Resin } NMe^+_3)\, Cl^- + SO^-_4 \text{(solution)} \rightarrow (\text{Resin } NMe^+_3)OH^- + 2Cl^- \text{ (solution)} \quad \text{---------(5)}$$

$$(\text{Resin } NMe^+_3)OH^- + 2Cl^- \text{ (solution)} \rightarrow (\text{Resin } NMe^+_3)\, Cl^- + H_2O \quad \text{-------- (6)}$$

These resins are similar to the sulphonate cation exchange resins in their activity and their action largely independent of pH .

Weakly basic ion-exchange resin contain little of the hydroxide form in basic solution

$$(\text{Resin } NMe_2)^+ + H_2O \rightarrow (\text{Resin } NHMe_2)^+ OH^- \quad \text{-------- (7)}$$

In acidic solutions they behave like the strong basic ion exchange resins, yielding highly ionised salt form.

$$(\text{Resin } NMe_2) + H^+ Cl^- \rightarrow (\text{Resin } NHMe_2^+)Cl^- \quad \text{--------- (8)}$$

They can be used in acid solutions for the exchange of ions.

$$(\text{Resin } NHMe_2^+)Cl^- + NO^{3-} \rightarrow (\text{Resin } NHMe_2^+)NO^{3-} + H^+ Cl^- \text{ (solution)} \quad \text{---------(9)}$$

Ion exchange equilibria:

The ion exchange process involve in the replacement of exchangeable ions A_R in the resin by ions of like charge B_s from a solution, may be written as

$$A_R + B_s \rightleftharpoons B_R + A_s$$

The process is a reversible one. The factors that determine the distribution of ions between an ion-exchange resin and a solute include

(i) Nature of exchanging ions: The extent of exchange increases with increase in valency of exchanging ion and with decrease in size of hydrated cation.

(ii) Nature of ion-exchange resins: The absorption of ions will depend upon the nature of functional groups in the resin and upon the degree of cross-linking.

Ion exchange capacity:

The total ion exchange capacity of a resin is dependent upon the total number of ion active groups per unit weight of the material. Hence the greater the number of ions the greater will be the capacity.

The total ion exchange capacity is generally expressed as milli equivalents per gram of exchanger. The exchange capacity of a cation exchange resin may be measured in the laboratory by determining the number of milligram equivalents of sodium ion which are absorbed by one gram of the dry resin in the hydrogen form.

Similarly the exchange capacity of a strongly basic anion exchange resin is evaluated by measuring the amount of chloride ion taken up by one gram of dry resin in the hydroxide form.

Column operation: Principle:

Ion exchange is reversible but the exchange reaction can be driven to completion in either direction by passing the solution through a column of the exchange resin. Let us suppose that we wish to replace the calcium ions in a solution by hydrogen ions. The solution is passed through the hydrogen form of a cation exchanger. As the solution passes down the column it continually meets fresh hydrogen exchanger and the reaction is displaced to the right.

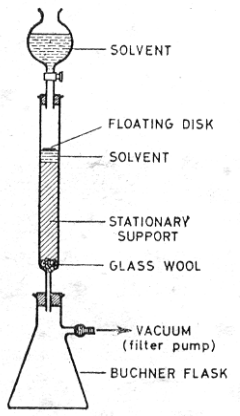
$$2\,[\,Res.SO_3^-\,]\,H^+ + Ca^{++} \rightleftharpoons [Res.SO_3^-]_2\,Ca^{++} + 2H^+$$

Experimental Techniques:

The simplest apparatus for ion-exchange work in analysis consists of a burette provided with a glass wool plug or sintered glass disk whose porosity may be zero or one at the lower end. A glass wool pad may be placed at the top of the bed of the resin in order to prevent the turbulence in resin packing. The following models will serve the purpose.

Packing of the column:

The ion exchange column is packed with resin which should be fine in order to provide large surface contact. However it should not be so fine since the flow rate will be slow. For most analytical work 50 – 100 mesh or 100 – 200 mesh materials are satisfactory. The diameter of the resin should be less than one-tenth of the height of column. It is better not to fill the column with dry resin and then run water into the column, which may lead to breaking of the column. Hence the resin should be thoroughly shaken with water in an open beaker for several minutes and then transfer to the column. The column is always backwashed with distilled water before use in order to suspend the resin granules. The resin packing should be free from air bubbles so that there is no channeling. To obtain satisfactory separations, it is essential that the solutions should pass through the column in a uniform manner.



Apparatus for column chromatography

Factors affecting the rate of exchange:

The separation of ions may be influenced by

(i) Nature of ion exchange resin.
(ii) Length of the column.
(iii) Particle size.
(iv) Rate of flow of eluent.
(v) pH.
(vi) Temperature.

APPLICATIONS:

1. Separation of zinc and magnesium on an anion exchange:

Several metal ions those of Fe, Al, Zn, Mn, etc., can be adsorbed from hydrochloric acid solutions on anion - exchange resins owing to the formation of negatively charged chloro complexes. Each metal is adsorbed over a well defined pH, and this property can be used as the basis of a method of separation. Zinc is adsorbed from 2M acid, while Mg (and Al) is not; thus by passing a mixture of zinc and magnesium through a column of anion exchange resin a separation is effected. The zinc is subsequently eluted with dilute nitric acid.

Procedure:

Prepare a column of the anion exchange about 15g of De - Acidite FF in the chloride form. Pipette out 10ml of zinc ion solution and 10ml of the magnesium ion solution into a small separatory funnel supported in the top of the ion exchange column, and mix the solutions. Allow the mixed solution to flow through the column at a rate of 5ml per minute. Wash the funnel and column with 50ml of 2M hydrochloric acid. Do not permit the level of the liquid to fall below the top of the resin column. Collect all the effluent in a conical flask; this contains all the magnesium. Now change the receiver. Elute the zinc with 30ml of water, followed by 80ml of 0.25 M nitric acid. Determine the magnesium and the zinc in the respective eluates by neutralisation with sodium hydroxide solution, followed by titration with standard EDTA solution using a buffer solution of pH = 10 and Eriochrome black-T as indicator .

2. Concentration of Electrolytes:

a) Dilute solutions of uranyl ion in sulphuric acid { $[(UO_2(SO_4)_2]^{2-}$ or $[(UO_2(SO_4)_3]^{4-}$ } can be concentrated by passing the solution through quaternary amine anion exchange resin in sulphate form at pH 1-2 and eluted with 1M perchloric acid.

b) $PtCl_6^{2-}$ can be exchanged on anion exchange in chloride form. If this is eluted with small volume of concentrated HCl, $PtCl_6^{2-}$ can be obtained in a less volume of acid. If the acid is evaporated the platinum chloride is obtained in solid form.

3. Separation of Inorganic mixtures or components:

Au, Ag, Co, Cu, Zn, Fe: Separation of this mixture through ion exchange method. By adding cyanide to the above mixture all the components are converted into complex cyanides and thus attain anionic nature. If a strong base anion exchanger is used, these get adsorbed on the exchangeable sites of the anion.

1. Elute with 0.2n HCl - Ni and Zn separated.
2. Elute with strong sodium cyanide - Fe and Cu are separated.
3. Elute with acetone and HCl - Au and Ag are separated.
4. Potassium thiocyanate - Co gets separated.

After each separation receiver should be replaced by another for collecting the components separately.

4. Removal of interfering Ions:

a) Gravimetric determination of potassium by perchlorate or chloroplatinate method:

During this process sulphate interferes and forms potassium sulphate. Sulphate can be removed by anionic exchange.

(Resin) Cl^- + K^+ and SO^-_4(solution) $\longrightarrow$ (Resin) SO^-_4 + K^+Cl^- (solution)

Hence, potassium is precipitated as potassium per chlorate or as potassium chloroplatinate.

b) Determination of sulphate

In determination of sulphate, sodium and iron are serious interferences. It is passed through hydrogen form of cation exchangers so that Na^+ and Fe^{2+} are taken up by the resin, and sulphuric acid is being collected and precipitated as $BaSO_4$ using $BaCl_2$ precipitating agent.

$$R^-)\,H^+ + Na^+ \text{ or } Fe^{2+} \text{ or } SO_4^{-2} \longrightarrow H^+\,SO_4^{-2} + (Res^-)\,Na^+ \text{ or } (Res^-)\,Fe^{2+}$$

$$H^+\,SO_4^{-2} + BaCl_2 \longrightarrow BaSO_4$$

In deducing a method for removal of interfering ions care must be taken to ensure that the system behaves as anticipated.

Ex: Phosphate and Ferric mixtures:

Ferric ion can be separated by holding it on a cation exchanger, but at times it happens that $[Fe\,HPO_4]^+$ ions also get adsorbed on the resin as cation. Therefore complete separation is not possible.

USE OF ION EXCHANGE IN WATER TREATMENT

Ion exchange has been used extensively to remove hardness, iron and manganese salts from drinking water supplies. It has also been used to selectively remove specific impurities, and to recover valuable trace metals like chromium, copper, lead, cadmium and nickel from industrial waste discharges. The process takes advantage of the ability of certain natural and synthetic materials to exchange one of their ions with another contained in the water passing through them.

In the water softening process, the hardness producing elements such as calcium and magnesium are replaced by sodium ions. A cation resin operating on the sodium cycle is normally used. The typical exchange reaction is

$$R^{-}Na_2 + \begin{Bmatrix} Mg \\ Ca \end{Bmatrix} \begin{matrix} Cl_2 \\ SO_4 \\ (HCO_3)_2 \end{matrix} \rightarrow R^{-}\begin{Bmatrix} Mg \\ Ca \end{Bmatrix} + \begin{Bmatrix} 2NaCl \\ Na_2SO_4 \\ 2NaHCO_3 \end{Bmatrix}$$

where R represents the solid phase of the exchange resin. The product water thus has high sodium content which is not likely to be trouble some unless the original water is very hard. When the exchanger is saturated it has to be regenerated to allow reuse of the expensive resin. Regeneration can be achieved using sodium chloride solution which removes the calcium and magnesium ions in the form of their soluble chlorides and restores the original condition.

$$R^{-}\begin{Bmatrix} Mg \\ Ca \end{Bmatrix} + 2NaCl \rightarrow R^{-}Na_2 + \begin{Bmatrix} Mg \\ Ca \end{Bmatrix} Cl_2$$

Demineralisation of waste water is achieved in two steps (the cation and anion exchange resins).

The positive ions such as Ca, Na, or Mg are removed in the cation exchanger using a hydrogen cycle. A typical exchange reaction is

$$R^{-}H_2 + \begin{matrix} Ca \\ Mg \\ 2\,Na \end{matrix} \Bigg\} \begin{matrix} Cl_2 \\ SO_4 \\ CO_3 \end{matrix} \rightarrow R^{-}\begin{Bmatrix} Ca \\ Mg \\ 2\,Na \end{Bmatrix} + \begin{Bmatrix} 2\,HCl \\ H_2SO_4 \\ H_2CO_3 \end{Bmatrix}$$

In anion exchange step the negative ions such as Cl^{-}, SO_4^{-2}, or CO_3^{-2} are removed and demineralised water is produced.

$$R^{+}OH + \begin{matrix} HCl \\ H_2SO_4 \\ H_2CO_3 \end{matrix} \Bigg\} \rightarrow R^{+}\begin{Bmatrix} Cl \\ SO_4 + H_2O \\ CO_3 \end{Bmatrix}$$

The regeneration or activation of the resin is done by treating the cation exchanger with a strong acid and the anion exchangers with caustic soda. The steps are

$$R^{-}\begin{cases}Ca\\Mg\\2\,Na\end{cases} + 2\,HCl \rightarrow R^{-}H_2 + \begin{cases}CaCl_2\\MgCl_2\\2\,NaCl\end{cases}$$

$$R^{+}\begin{cases}Cl\\SO_4\\CO_3\end{cases} + NaOH \rightarrow R^{+}OH + Na\begin{cases}Cl\\SO_4\\CO_3\end{cases}$$

Suspended solids in waste waters can clog the exchangers and cause operational problems. Hence, the feed water to the exchange should be free of suspended matter. Another serious problem is the resin binding caused by residual organic matter in the feed water. Although the ion exchange process is very effective and produces high quality effluents, the cost of this treatment is fairly high.

It has been successfully applied for the recovery of chromate from the waste water in the pigment manufacturing. Resins are also available for particular applications and one natural Zeolite, Clinoptilolite, seems to adsorb both phosphate and ammonium ions and may prove to be of great value in waste water treatment.

The method is also useful in case of the following:

i. Separation of lanthanides
ii. Separation of actinides
iii. Separation of sugars
iv. Separation of aminoacids

UNIT 4

CHROMATOGRAPHY: PART A

Lesson 3

Objectives of the lesson:

This lesson deals with the study of chromatographic techniques like column chromatography, absorption chromatography, partition chromatography, paper chromatography and thin layer chromatography.

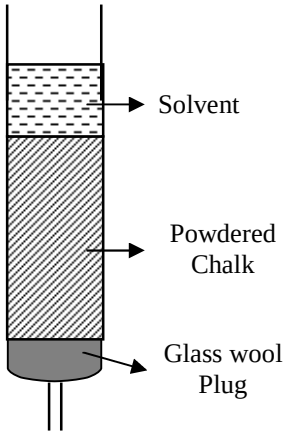
INTRODUCTION:

The use of separation techniques, such as chromatography and electrophoresis is possibly the most important aspect of modern methods of analysis. It used to be much different for analyzing one element in the presence of others that reacted similarly or which interface with the test employed. Thus for example in the gravimetric analysis of nickel by dimethyl glyoxine (DMG), it was extremely difficult to perform a satisfactory determination in the presence of cobalt. How ever, because of the simple and elegant methods that are available for separating mixtures into their individual components, it becomes simply a matter of devising a quite non-specific mode of analysis in order to determine each of the separated species.

Chromatography is a technique for separating a mixture into its individual components. The term was first given by Russian Botanist Michael Tswett, (1903) which implies Chroma means colour and graphy means writing, thus the name Chromatography arose from the Greek, means colour writing.

As a matter of fact, the technique is now used also for the separation of colourless compounds, and so the term Chromatography is really inappropriate though still retained.

Tswett's original procedure depended on applying a continuous separation based on differential adsorption. He extracted the green colour chlorophyll from leaves as a solution in petroleum ether, and showed that much of the colour could be adsorbed on to powdered chalk. As an extension of this single stage adsorption, he passed the green solution down on a vertical glass tube packed with powdered chalk and observed that the pigment was held at the top of the column. When more petroleum ether was passed down the column, the green pigment gradually separated into four bands or zones.



At this point the semi-shift column of chalk could be pushed out, or extruded, from the enclosing tube, and the individual bands of different pigments could be cutout and dissolved in a suitable solvent.

The original mode of separation now known as Adsorption Chromatography, and desorption of compounds on a stationary support. Thus these compounds that are adsorbed more weakly will be displaced from top of the column by the more firmly bound compounds, and in as much as adsorption is a reversible process, the continuous percolation of solvent down the column will gradually move each band down the column. This type of use of a physical property in a continuous process is analogous to fractional distillation in which good equilibrium between liquid and vapour is an important criterion for efficient separation.

In view of the fact, various physical properties can be used for a continuous process of separation, it has become necessary to adopt a more comprehensive definition of chromatography. Thus chromatography may be defined as " a method of separating the components of a mixture on a stationary support, such separation being effected by means of a mobile fluid phase that carries the components at different rates along the support".

The various physical principles involved in the separation techniques have given rise to the following subdivisions of chromatography. The nature of stationary support gives rise to a different scheme of subdivisions.

Chromatography

Column Chromatography	*Paper Chromatography*	*Thin layer Chromatography*
1. Adsorption	(i) Single dimension	
2. Partition	(a) Ascending	
3. Ion Exchange	(b) Descending	
4. Gas chromatograpy	(ii) Two dimensional	

Although gas chromatography is really a specific branch of column chromatography it became so important so as to warrant an extra subdivision.

For a theoretical treatment of chromatography, especially from the point of the view of equilibria and mass transfer, it has been suggested that the following classification, depending on the nature of the mobile and stationary phase, might be preferable; Liquid - Solid Chromatography, Liquid-Liquid Chromatography, Gas-Liquid Chromatography and Gas - Solid Chromatography.

GENERAL INTRODUCTION:

All methods of Chromatography basically aim at separating two or more substances. Chromatographic separations can be carried out by the distribution of components in a mixture between a fixed and moving phase. The fixed phase is known as "stationary phase," while the moving phase is known as "mobile phase". Separations between two substances begins to take place when one is held more strongly by the stationary phase than the other, which tends to move on faster in the mobile phase. Quantitative chromatography separations can be carried out by the following three important distinctive techniques.

1. Elution Development: (Tswett, 1903)

This technique may be described by taking a mixture of two components. The mixture is introduced at the top of the column of adsorbent and the components are separated into zones by the passage of one or more solvents through the column. The mobile solvent phase is adsorbed either weakly or not at all by the stationary solid phase. However, this idea of elution development is not always easy to achieve in practice.

2. Frontal Analysis: (Developed by Tiselius –1940)

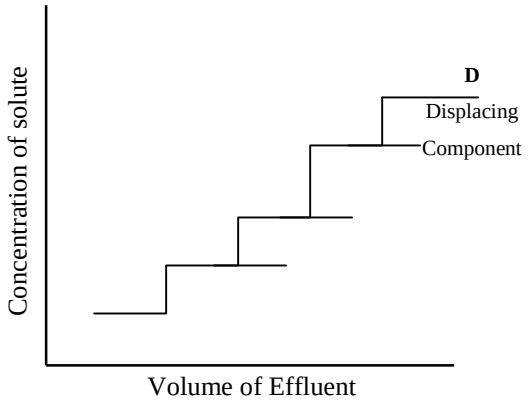
In this technique no solvent is used for irrigation. Solution it self is added continuously. As soon as the solution touches the column, the components say X and Y get fixed. The pure solvent moves ahead followed by the less adsorbed component say X. 'X' will be moved further away when more and more solution is added. This is due to the fact that adsorption of solute X is weaker than that of Y. Consequently the first event will be pure solvent to the extent the whole of the retention volume flows out and the first fractions will contain only the less strongly adsorbed material but later a mixture of both substances appears.

This type of analysis is clearly a preparative technique and has the disadvantage compared with other two techniques that a great amount of mixture is required since it has to be applied continuously to the column.

3. Displacement Analysis: (Tiselius – 1943)

In this technique on passing the solution containing mixture of ions through the column packed with the suitable resin, all the ions are adsorbed on the column. On elution, most strongly adsorbed ions displace less strongly adsorbed ions. Thus a separation is affected and the volume of effluent in each step is collected and measured. If the volume of the effluent is plotted against the concentration, a step wise graph is obtained and such steps represent the individual pure components.

This method of displacement analysis is quite useful for isolation of organic substances and structural studies. Here over lapping may be possible since zones are not distinctly separated.



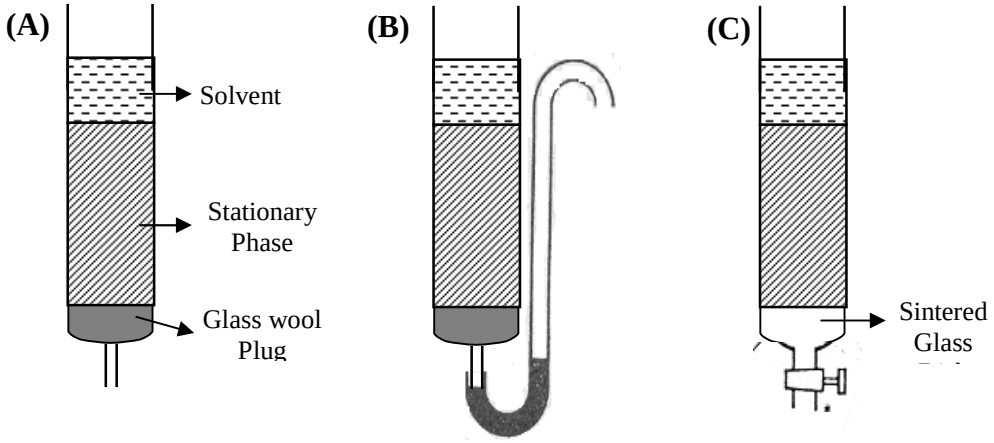
(Each step represents one component)

COLUMN CHROMATOGRAPHY

Although different physical principles may be involved in the mode of separation, column methods of chromatography may be grouped together from the point of view of practical purposes. So adsorption and partition chromatography will be considered primarily.

Chromatography Columns:

The basic equipment usually consists of a long vertical glass tube, restricted (constricted) at the lower end, in which column the packing material is contained as the Stationary Phase. It is important that the stationary phase consists of uniform particles, packed uniformly, air bubbles must be absent and the packing must never be allowed to become dry, that is solvent must always be present above the level of the stationary support.



Column (A) is the simplest form, in which stationary phase is kept in position by a non-absorbant and porous plug, usually glass-wool. The flow of liquid from a column should be fairly slow of the order of a drop every 2-seconds and the nature of the packing frequently allows this rate of percolation of solvent. If the drop rate is too fast, however, a tap (or tubing and clip) can be fitted at the end to control the flow, and similarly, if the rate is too slow, suction may be applied at the lower end or positive pressure applied from above (the later is preferred because it does not disturb the packing so much)

Columns (B) and (C) are simply modified models of the basic equipment. The side arm in (B) is very easily fitted, and has the function of maintaining a constant level of solvent. It acts as a siphon so that the column never runs dry. Similarly it serves to control the drop rate, which will now depend on the rate at which solvent is added to the column. In practice, the side - arm is a glass tube of narrow bore, connected to the base of the column by flexible tubing. It can therefore be adjusted to the required height and held in position by means of a rubber band or adhesive tube.

Now-a-days many firms are producing glass columns specially designed for chromatography, as in C. This consists of glass tube fitted with a porous sintered glass disk as a support for the packing material. A tap is fitted at the exit to the column in order to control the flow rate. Frequently a ground glass socket is incorporated at the top in order to insert separating funnel fitted with a ground glass cone. This type of column is obviously convenient, but much more expensive than the first two described.

Packing the column:

The inert packing that is to form the stationary support of the column should consist of uniform particles, and these are usually graded by sieving or less frequently, by decantation of fine particles from a slurry. Fortunately, such materials are commercially available in a given range of particle size 100-200 mesh, 200-300 mesh etc.

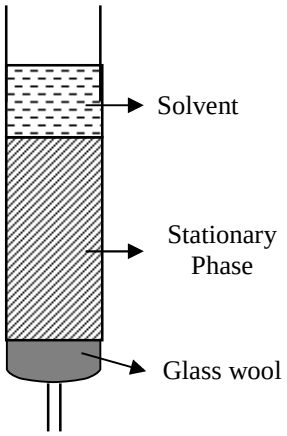
In general the most suitable particle is chosen by a balance between two factors. Thus the smaller the particle size, the better will be the separation of components, but the larger the particles, the better flow rate. Packing of 100-200mesh will normally be quite suitable for simple separation.

It is occasionally possible to pack the column with stationary phase in dry form, and then to add the solvent, but this is liable to the introduction of air bubbles which cannot be removed.

The most favoured method of packing a column is to prepare slurry with the dry packing in the minimum amount of solvent that allows a free running mixture. The slurry is poured in one movement into the chromatographic column, and therefore settles uniformly. Small amounts of solvent may then be added to rinse the sides of the tube, which is tapped occasionally to aid sedimentation, and the liberation of air bubbles.

Final preparation of column:

The technique of column chromatography involves the application of a mixture at the top of the column in as compact a form as possible, followed by a separation of components brought about by a solvent percolating down the stationary support. In the simplest case, it is convenient to add the solvent from a tap funnel that is connected to the top of the column by an airtight joint. This may be simply a rubber bung, or perhaps a ground glass joint. In view of the disturbance of the packing that would normally occur from the drip of the solvent, it is usual to float a disk on top of solvent column. The disk may be a cork, though polythene is more inert. Alternatively another plug of glass wool may be inserted above the packing to protect it from disturbance. It has been already stated that positive or negative pressure may be applied to the column in order to boast the flow rate and that positive pressure is to be preferred. On the other hand, it is more convenient to apply suction to the base of the column, and this may be affected by connecting to the Buchner Flask.



Chromatographic Technique and Nomenclature:

The requirement is that the mixture to be separated should be dissolved in the minimum quantity of solvent before applying it to the column. In general, this solvent is the same as that used in preparing the column.

The solvent in the tube is allowed to drain almost to the level of packing and a solution of the mixture to be separated is added in one portion. This solution is now allowed to percolate through similarly and when it has fallen nearly to the top of the stationary phase the top funnel is attached to the top of the column and solvent allowed to drip through.

The nature of the chromatographic separation is independent of whether the components of the mixture are coloured or not but it is more convenient to describe the process of separation for the case of coloured components. The mixture after application to the column will appear as a single coloured band at the top of the stationary support. Gradually as the solvent percolates down, a process of development takes place, in which the components separate out into bands or zones. The whole column including all the constituents (such as the stationary support, solvent and bands of separated mixture) during the process of chromatographic separation is referred to as the Chromatogram.

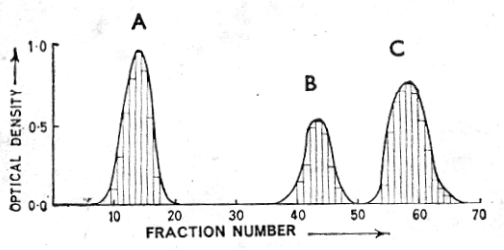
In some simple chromatograms, the process of development may be sufficient for a complete separation of components. In early methods, the column was drained and the moist packing pushed out or extruded, by means of a rod pushed through the exit tube. The bands could then be cut out and dissolved off the inert support by means of appropriate solvents.

Usually the initial development is not efficient enough for complete separation and change of solvent may be necessary to carry components at different rates down the column. If such solvents are suitably chosen, an individual band can be carried down the support and dissolved off, or eluted, from the base of the column, when the band is collected in a receiving vessel. The solvent performing such elution is termed as the eluent, whilst the solution of the component thus eluted is the eluate. When solvent percolates through the base of the column without any dissolved components of the mixture it may be referred to as filtrate from the column.

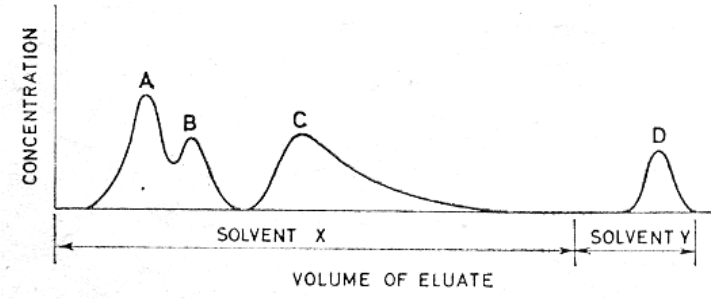
It is quite common practice to charge the eluent during a chromatographic separation and this may be performed continuously by means of gradient elution.

Gradient Elution:

From the elution diagram-1 components A, B and C show clean efficient separation. But frequently it happens during initial attempts of chromatographic separation an unsatisfactory diagram is obtained as shown in elution diagram-2.



Elution Diagram - 1

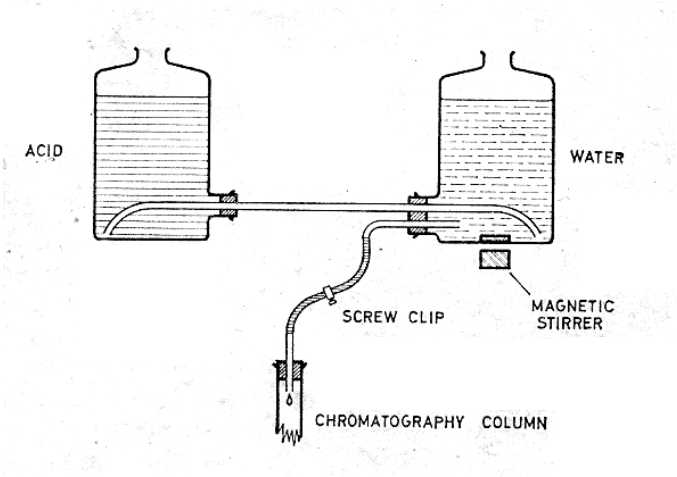


Elution Diagram -2

Incomplete separation may be due to similar properties of A and B or due to "tailing" of A, which is evident for 'C'. Tailing may be due to adsorption isotherm not being linear, the front of the band is then eluted quite sharply while the rear portion of band comes off the column gradually, thus resulting unsymmetrical peak for elution of 'C'.

The tailing effect can be removed by improving the "eluting power" of eluent. Eg: concentration, Ionic strength, pH, polarity etc., depending upon the physical property involved in separation. This is called Gradient Elution.

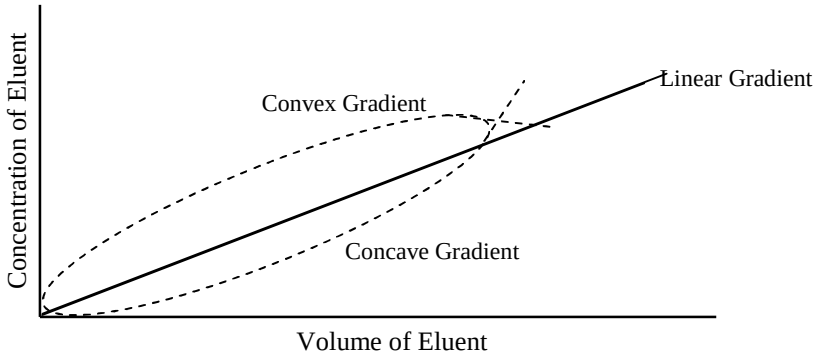
Apparatus:



Two aspirators, one with water and another with acid are joined through the outlets. The aspirator containing water also has an outlet into chromatographic column. Magnetic stirrer is used for thorough stirring.

At the start of the elution, water alone flows from the stirred aspirator. As soon as the level of liquid begins to fall however, the level of acid in other aspirator must fall to a similar extent, since the two vessels are linked. This results in acid flowing into the mixing vessel and gradually fed to the column. When diameters of the two aspirators are identical Linear gradient of acid concentration is produced.

If acid aspirators has a smaller diameter, the acid of element will increase initially more slowly than in case of linear gradient - Concave Gradient. While acid aspirator diameter is greater, the acid increases initially at faster rate and decrease with time giving Convex Gradient.



Column Chromatography: It can be broadly divided into two types

(1) Adsorption
(2) Partition.

ADSORPTION CHROMATOGRAPHY:

The technique in which the stationary phase is solid (ex: alumina or silica gel) and the mobile phase is either a gas or a liquid is known as Adsorption chromatography. Since adsorption is a surface phenomenon, the degree of separation depends upon the surface area of the adsorbent.

Principle:

The basic principle is adsorption, and can be fairly specific so that one solute may be adsorbed selectively from a mixture. Separation of components depends upon differences both in their degree of adsorption by the adsorbent and solubility in the solvent and these two are in turn governed by molecular structure of compound.

Adsorbent:

Many adsorbents are available, and commonly used materials are given below.
(1) Aluminium oxides (acidic, basic and neutral grades) (2) Bentonite (3) Calcium carbonate,
(4) Calcium hydroxide, (5) Calcium phosphate (6) Charcoal (7) Florisil (a synthetic material based on magnesia and silica gel) (8) Fuller's earth (9) Kieselguhr (10) $MgCO_3$ etc:

Adsorbents Activity:

Adsorbents have been classified into grades of activity as weak, medium or strong depending on their power of adsorption. It is also possible to activate or deactivate the adsorbent. Some materials are activated by heating or pretreatment with acid or bases (as with alumina) or organic solvent (ex: charcoal).

Deactivation of alumina has been effected by the addition of water and the different grades of alumina thus produced are standardized according to *Brockmann Activity* which is based on the adsorption capacity of various dyes.

Solvent: (Mobile Phase)

It is also termed as eluting agent. Solvents are used either to transfer the mixture of the column or for bringing about the process of desorption which results in the separation of the components into bands and finally their elutions. Solvent may be the same through out or it may be different at different stages and for different components of the mixture.

In choosing eluting agent two considerations are taken into account.
(1) Solvent should satisfy the practical factors such as viscosity, stability, comparability with detection, solubility with respect to the sample, suitable purity etc.
(2) Solvent should provide maximum resolution for the separation of sample in reasonable time.

In general it is suggested that adsorption effects are strongest in non-polar media. It is therefore a usual practice to apply the mixture to be separated as a solution in a non-polar solvent such as petroleum ether, benzene etc.

For the development of the chromatogram, a slightly more polar solvent may be used, so that the more weakly held components are displaced and moved down the column.

As a rough guide to the sequence of solvents used in elution of lipophilic materials, an *'Eluotropic series'* has been suggested. The order is as follows: petroleum ether, cyclohexan, benzene, chloroform, acetone, ethyl acetate, ethanol, methanol, water.

APPLICATIONS: The technique is useful
1. in separation of Methyl Blue and Fluoresce in (sodium salt)
2. in separation of 2,4 Dinitrophenyl hydrozones.
3. separation of plasma cortisol
4. in separation of mixture containing sterioisomers or related compounds.
5. separation of the ordinary 17- keto-steroids.

Separation of Methylene Blue and Fluorescein:
Material required:
Chromatographic tube (25 cm long, 1.7cm bore)
Alumina (neutral)
Ethanol (rectified spirit)
Fluorescein
Methylene Blue.

a) A small glass plug is placed in the end of the column and slurry of 25g of alumina in ethanol is poured. The column is tapped to remove the air bubbles. A thin section of cork or a polythene disk should be added as a float to prevent subsequent disturbance of the column.
b) A solution of mixed dyes is prepared by weighing 5g of each of methylene blue and fluorescein into a test tube and dissolving in 5ml of alcohol. When the float has fallen nearly to the top of the adsorbent, the dye solution is added quickly from a tap funnel; the funnel is rinsed and filled with alcohol. As soon as the level of the solution reaches with in 1-2 mm of the top of the column, the funnel is attached to the Chromatographic tube by means of a rubber bung, and allowed the alcohol to drip on to the float.

The blue colour of the methylene blue soon starts to percolate down the column whilst the fluorescein is held in a tight band at the top. Alcohol is allowed to drip from the tap funnel until all the methylene blue has passed into the receiving flask and the filtrate is colourless. Now the alcohol is replaced with water and the elution is continued. Fluorescin band widens and passes down the column, which is collected in a fresh receiver.

c) The experiment is repeated by preparing the dye and the adsorbent column in water instead of alcohol. The first elution is performed with water and then changed to alcohol after elution of first component. Under these conditions Fluorescein is eluted first, with methyl blue being at the top of the column.

PARTITION CHROMATOGRAPHY

When a solute is shaken with two immiscible solvents it will distribute itself unevenly between the two phases and at equilibrium, the ratio of concentration of the compound in two solvents is constant and is known as partition coefficient.

$$K = \frac{\text{Concentration of 'X' in solvent(1)}}{\textit{Concentration of 'X' in solvent(2)}}$$

K is the partition coefficient, and will be constant for a given temperature.

The principle of partition has been used in number of applications such as continuous solvent extraction, and in the case of separation by the use of counter current distribution. A big advance was made in 1941, however when Martin and Synge, suggested a form of chromatography based on this principle.

In partition chromatography, one of the two solvents is held on a column as the stationary phase. Silica gel is probably the most useful material for making up the column since it can bind upto about 5% of its own weight of water without becoming physically wet. This means that a free-running powder can be packed in a chromatography tube into a column in which the silica gel functions simply as an inert support for the stationary phase of water.

When performing a chromatographic separation of a mixture by this technique, the principle of the method depends on the partition of components of the mixture between water held on the column and non-polar solvent percolating down the column. Thus the more hydrophilic components, having a marked affinity for water, will be held at the top of the column, whilst the more hydrophobic (or Lipophilic) materials, being soluble in non-polar medium, will move down the column and will therefore be eluted first.

A stationary phase of water is quite suitable when the compounds to be separated have sufficient of a hydrophilic character; but highly non-polar compounds have too little affinity for such a column to allow proper separation. In order to overcome this difficulty, a method of Reversed – phase Chromatography was introduced later, to provide a hydrophobic phase. Hydrophobic materials can also be used on column to separate hydrophobic compounds. So it is called *Reverse Phase Partition Chromatography*. Ex: Dimethyl dichloro silane.

APPLICATIONS:

1. Partition Chromatography has become a powerful tool for the separation of closely related substances such as numerous amino acids formed in the hydrolysis of protein, separations and analysis of closely related aliphatic alcohols and separation of sugar derivatives.
2. Partition Chromatography is useful in the separation of organic dibasic acids as described hereunder.

Materials required:

1. Chromatography tube
2. Silicic acid (silica gel chromatographic grade is suitable).
3. m- cresol purple (0.1% aqueous solution)
4. Chloroform
5. n-Butanol
6. Succinic acid
7. Glutaric acid
8. Adipic acid
9. "Trial Mixture" of dibasic acid.

0.35g adipic acid, 0.1g glutaric acid and 0.1g succinic acid are weighed accurately into a 100ml beaker. The mixture is dissolved in about 50ml of warm water, cooled, and the solution is transferred quantitatively into a 100ml graduated flask and made up to the mark with distilled water.

Preparation of silicic acid column:

To 15g silicic acid, 2ml of water and 3ml of 0.1% aqueous solution of m-cresol purple are added with mixing. Chloroform is then added with stirring, until homogenous slurry is obtained. The slurry of silicic acid is poured, preferably in one portion so as to obtain a uniform packing.

Chromatographic separation:

10ml aliquot of the "trial mixture" is pipitted into a 20ml beaker and evaporated to dryness on the steam bath for about 1 - 2hours. This solution was mixed with 1g of dry silicic acid. The mixture is made into a slurry with about 10ml of chloroform, and the whole is transferred to the prepared column.

The screw clip is opened so as to allow the chloroform to drip through. When the level of liquid has fallen nearly to the top of the column, start development of the chromatogram with 65ml of 10% (v/v) solution of n-butanol in chloroform, followed with 45ml of 20% (v/v) solution of n-butanol in chloroform, and finally with 25ml of n-butanol.

The acids separate into bands and these are rendered visible by the indicator. As each front approaches to with in 1cm of the bottom of the column, the receiving flask is changed. Adipic acid is eluted first from the column, followed by glutaric acid and then succinic acid.

The acid content of each fraction is determined by titration with alcoholic NaOH solution.

PAPER CHROMATOGRAPHY

Introduction:

It is an extension of the application of partition chromatography. In paper chromatography, a coarse paper serves in lieu of a packed column and therefore, the silica gel as the solid support for the polar solvent is replaced by a filter paper. An organic solvent, partially miscible with water (Eg: Butanol or Collidine) is most suitable in paper chromatography.

Paper chromatography is defined as the technique in which the analysis of an unknown substance is carried out mainly by the flow of solvent on specially designed filter paper. The separation is effected by the differential migration of the mixture of substances. This takes place as a result of difference in partition coefficients.

Principle:

A drop of the solution containing the sample is introduced at some point on the paper. Migration then occurs as a result of flow of mobile phase, called the developer and whose movement is caused by capillary force. When the movement of mobile phase is in upward direction, the development is called Ascending Development and when it is in down ward direction, the development is known as Descending Development.

Migration Parameters:

The positions of migrated spots on the chromatograms are indicated by different terms such as R_F, R_x R_M and R_C. These parameters are also qualitative and quantitative parameters, characteristic of a substance.

$$R_F = \frac{\text{Distance travelled by a substance from the original line}}{\text{Distance travelled by a standard substance 'x' from the original line}}$$

R_F defines the movement of substance relative to the solvent front in a given chromatographic system. 'R' is a function of the partition coefficient and it is a constant for a given substance. The conditions of chromatographic system are kept constant with respect to temperature, type of paper, duration, direction of development, and the amount of liquid in the reservoir, humidity etc:

The R_F value of a substance depend upon a number of factors such as

1. Solvent employed
2. The medium used for separation that is, the quality of paper in case of paper chromatography.
3. The nature of mixture
4. The temperature
5. The size of vessel in which operation is carried out.

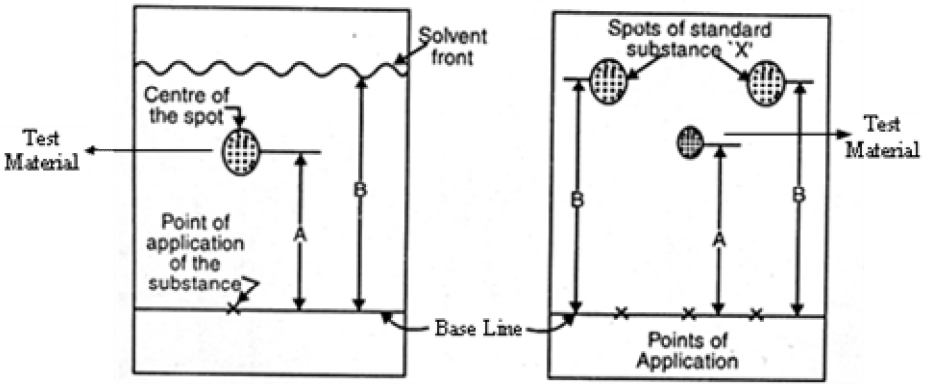
R_x: In some cases, the solvent front runs off the end of filter paper, the movement of a substance in such case is expressed as R_x but not R_F.

$$Rx = \frac{\text{Distance travelled by the substance from the original line}}{\text{Distance travelled by the standard substance from the original line}}$$

R_M: The R_F values of chemically related compounds are very close. The influence of individual functional groups is presumed to be added to a rough approximation. According to Bate - Smith and Westall, R_M is defined as

$$R_M = \log\left(\frac{1}{R_F} - 1\right)$$

Diagrammatic Representation of R_F and R_x :



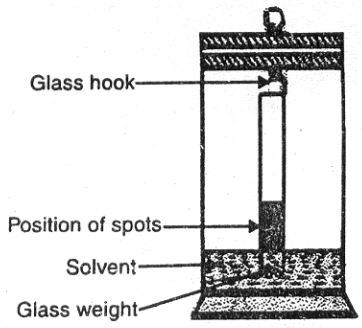
TYPES OF PAPER CHROMATOGRAPHY:

(a) Descending Chromatography:

When the development of the paper is done by allowing the solvent to travel down the paper, it is known as descending technique.

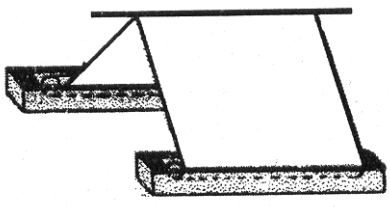
(b) Ascending Chromatography:

When the development of the paper is done by allowing the solvent to travel up the paper, it is known as ascending technique.



(c) Ascending – Descending Chromatography:

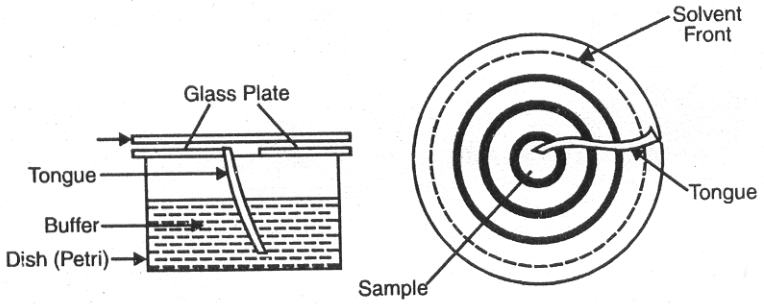
The upper part of the ascending chromatography can be folded over a glass rod allowing the ascending development to change over into the descending after crossing the glass rod.



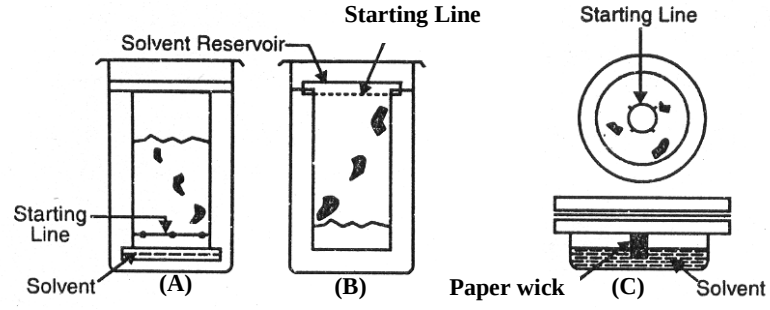
d. Radial paper Chromatography:

This is also known as circular paper chromatography. This makes use of radial development. A circular filter paper is generally employed. The various materials to be analyzed are placed at its center.

After drying the spots, the paper is fixed horizontally on the petri dish possessing the solvent so that the tongue or wick of the paper dips into the solvent. Cover the paper by means of petri dish covers. The solvent rises through the tongue or the wick, the components gets separated in the form of concentric zones.



Chromatograms obtained by ascending (A) descending (B) and circular paper (C) chromatography.



Procedure:

The method of paper chromatography may be one dimensional or two dimensional depending upon the type of complexity involved in the analysis.

A strip of filter paper usually 15 to 30cm in length and one to several centimeters in width is first laid flat. A minute drop of the sample solution is placed in the center an inch from one end of the paper and its position is marked by a pencil. The original solvent is allowed to evaporate in order to make the spot of the sample dry. The portion of the paper nearest the sample spot is then brought in contact with a suitable solvent, called developer. Both paper and developer are sealed in container. After some time (~ 6hrs) the liquid rises up the strip by capillary action, carrying the constituents of the sample along with it at various speeds, according to their partition coefficients. After the liquid has traversed the length of the strip, the paper is removed and dried. The position of the solvent front is marked with a pencil at the two edges of the paper and the so called chromatogram is then dried by keeping in an oven or over a hot plate for a few minutes. Drying is best carried out by means of a fan or hairdryer.

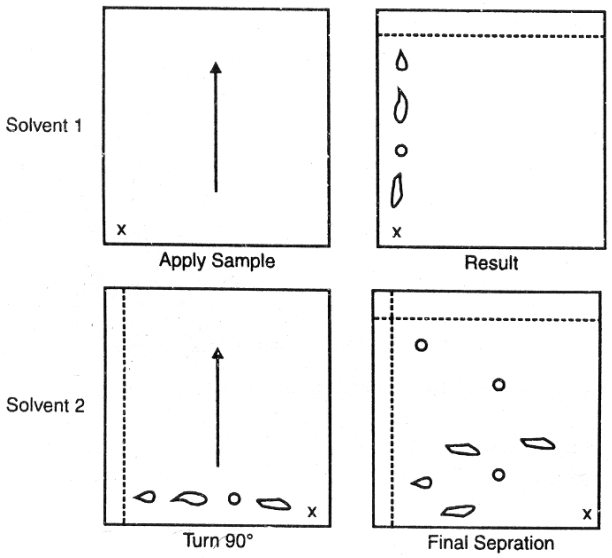
The finished dried paper thus obtained is called paper chromatogram. If the substances are coloured no difficulty arises, but in case of colourless substance a number of physical and chemical methods are employed for locating the spots.

The method given above is ‘<u>One Dimensional Chromatography</u>’.

Two Dimensional Chromatography:

In this method the sample is placed on one corner of a square sheet of paper. Development along axis is then performed as described above. After the evaporation of the solvent the paper is rotated through 90^0 so that the edge having the series of spots is now at bottom and is again developed but with different solvent.

Two dimensional chromatography is especially suitable for those substances which cannot be separated by one-dimensional chromatography. This happens when the R_F values are very close and nearly the same.



Choice of Filter Papers:

Various types of Whatman chromatographic papers are available. The choice of paper depends upon the type of separation. Generally coarser and faster papers, Whatman 31ET, are used when the substances to be separated have wide - apart R_F values.

Whatman filter paper commonly used for chromatographic purpose has been found to contain 99% α cellulose and the rest is mineral content.

Suitable solvent systems for paper Chromatography:

Stationary Phase	***Mobile phase***
Water	Phenol saturated with water
Water	n-butanol - acetic acid - water (4: 1: 5)
Formamide	$CHCl_3$
Formamide	Benzene
Kerosene	70% Iso propanol
Phenoxy Ethanol	Heptane.

THIN LAYER CHROMATOGRAPHY (TLC):

TLC as a procedure for analytical chromatography was first introduced by Stahl (1958). He was mainly responsible for bringing out standard equipment for preparing thin layers. TLC is often named by other names such as drop, strip, spread layer, surface chromatography or open column chromatography.

Experimental Techniques:

Coating Material:

A large number of coating materials are known which are commercially produced for use as thin layer adsorbent.

Coating Materials Used in TLC

Adsorbent	Acidic/Basic	Activity	Separating Mechanism	Components to be separated
Silica gel	acidic	active	Adsorption/ partition	Acidic & neutral substances
Alumina	basic	active	Adsorption / partition	Basic& neutral substances
Kieselguhr	neutral	inactive	partition	Strongly hydrophilic substances
Cellulose	neutral	none	partition	Water soluble compounds

Other materials are calcium phosphate, magnesium trisilicate, acetylated cellulose, polyamide, silica gel-aluminium (1:1), ferric oxide hydrate etc. It is interesting to note that the adsorbent do not adhere satisfactorily to the plate thus some binders like gypsum ($CaSO_4$), starch, hydrated silicon oxide etc are added to adsorbent. Generally names of various absorbents are written as silica-G, alumina-G where letter 'G' indicates gypsum added as a fixative.

Preparation of thin layers:

A large number of applicators are commercially available which are used for coating the glass plates with different adsorbents layers of uniform thickness. Most of these methods use the coating materials in the form of suspension or slurry in some liquid. The various methods of preparing layers are as follows

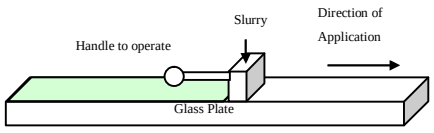
1. Pouring 2. Dipping
3. Spraying 4. Spreading.

1. Pouring: In this method amount of the slurry is put on a given size plate which is kept on a level surface. The plate is then tipped back and forth to spread the slurry uniformly over the surface.

2. Dipping: This method is developed by Piefer (1962). Plates are prepared by dipping them two at a time back to back in chloroform or chloroform-methanol slurries of the absorbent.

3. Spraying:
A small point sprayer is used for distribution of slurry on a glass plate.

4. Spreading: The slurry is placed in an applicator. This is either moved over the stationary plate or it is held stationary and the plate is pushed or pulled.



5. Activation of Absorbent:

After making thin layers on plates the next job is to remove as completely as possible the liquid associated with the thin layer. This is done by drying the thin layer plate for 30minutes in air and then in a oven at 110^o C for another 30 minutes. This drying makes the adsorbent layer active. In order to obtain very active layers silica gel and alumina plates can be heated to 150^o C for about 4 hours.

6. Purification of Silica Gel –G layers:

Silica gel 'G' contains iron impurity which causes considerable distortion of the chromatographs. Iron free layers can be obtained by giving the coated and air dried plates a preliminary development with methanol and concentrated hydro chloric acid (9:1 v/v). The iron gets migrated with the solvent front to the upper edge of the plate. The plates are again dried and activated at 110^o C .

6. Sample Application:

Agla micro syringe is generally used for transferring the sample solution to the thin layer for quantitative work. Solvents used for sample solution should be volatile and as non polar as possible.

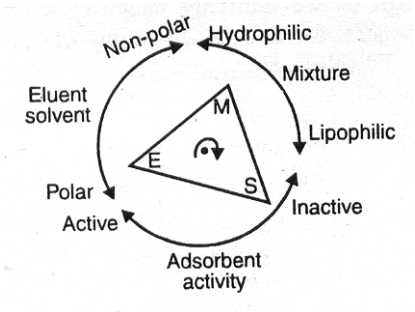
7. Development Tank:

Ascending chromatography is the most common technique in TLC. In TLC, the plate is placed in a development chamber at an angle of 45^o C. The bottom of the sides of the tank is lined with solvent impregnated paper while top is covered tightly with the lid. It is important in TLC that the development chamber is perfectly saturated with solvent vapour. As solvent ascends through the layer by capillary action, the sample is reduced into fractions. The plate is carefully with drawn after the solvent front has migration of 75% of the length of the plate.

The plate is then dried and sprayed with the reagents for determination of components or it is commonly exposed to iodine vapours. Solute positions are identified by brown spots.

8. Solvent System:

If one knows the chemical nature of the solute to be separated it is possible to know a suitable solvent by using the Original Stahl's triangle.



When the triangle is rotated so that M- points to the type of mixture to be separated, this specifies necessary activity of absorbent and the optimum polarity of the eluent at corners S and E respectively.

Suppose a mixture to be separated consists of hydro carbons and ketones, then from Stahl's triangle it is found that an active adsorbent is required together with non- polar solvent.

Solvents used in TLC:

Benzene-ethanol (9:1), Chloroform, Benzene, Cyclohexane, High boiling Paraffins, Ethyl acetate, Ethyl acetate - methanol (99:1), Benzene- methanol (95:5) are used as solvents in TLC.

Detectors:

Most of the methods used for detection of separated solutes in case of paper chromatographic technique are also applicable for TLC. The coloured substances can be easily located. However the colourless compounds can be detected either by U.V.light or with a reagent which gives a colour. Corrosive reagents like chromic acid and sulphuric acid which cannot be used in case of paper chromatography can be used in TLC.

Applications of TLC:

TLC is highly useful in checking the separation procedures and purification process. It finds applications in organic chemistry for separations, checking of purity of samples, as a purification process, examination of reactions and for identifying organic compounds like acids, alcohols, glycols, alkaloids, amines and antibiotics. It is equally useful in case of separation of inorganic ions. It finds application in quantitative analysis also.

Limitations:

The main limitation in case of TLC is it is useful only for small scale preparation work.

UNIT 4

CHROMATOGRAPHY: PART B

Lesson 4

Objectives of the lesson:

This lesson deals with the study of latest techniques in chromatography like gas – liquid chromatography (GLC), high performance liquid chromatography (HPLC).

Gas chromatography

Introduction:

The separation depends upon the partition (or distribution) of the components between a moving phase (the carrier gas) and the stationary phase (a non-volatile liquid adsorbed on an inert support such as kieslguhr). As the moving phase flows through the column packed with stationary phase, the sample also travels along and is separated into its components by virtue of differences in the solubilities of these components in the stationary phase and due to volatility.

The emergence of the separated components in the carrier gas stream is observed and the concentration measured by a detector: the output of the detector is generally recorded as a function of time by a pen- recorder.

Gas Liquid Chromatography (GLC):

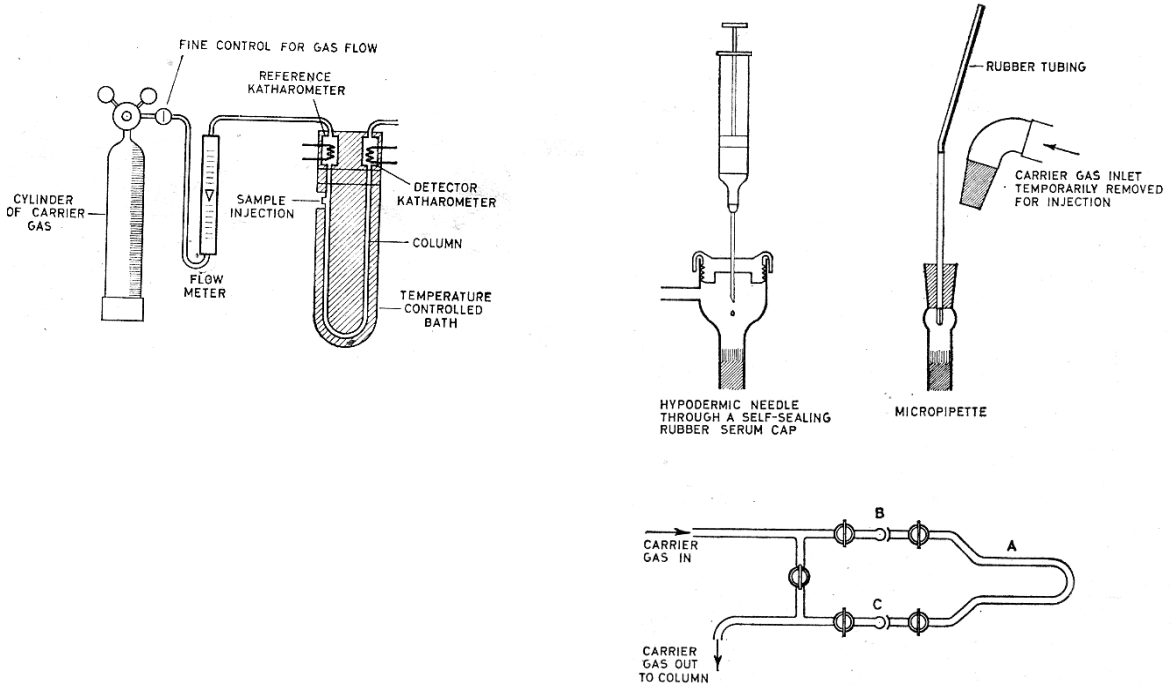
Gas Liquid Chromatography consists of a mobile gas phase and a stationary liquid phase that is coated on to either a solid matrix (ex: diatomaceous earth) or the wall of a capillary tube. Typically the stationary phase has a sufficiently low vapour pressure (mm) at the column temperature so that it can be considered as non-volatile. The sample mixture in gaseous form is run through the column with a carrier gas. Separation can be achieved by the differences in the distribution ratios of the components of the sample between the mobile (gaseous) and stationary (liquid) phases causing them to move through the column at different rates and with different retention times. After elution, the sample components can be detected by a suitable detector at the exit.

Apparatus or Equipment:

The apparatus consists of

1. Supply of carrier gas with its associated flow controls,
2. The column packed with stationary phase adsorbed on an inert support.
3. The Detector and Pen-recorder.

A schematic diagram of the apparatus for gas chromatography is as follows.



At entry to the column, there will be some means for introducing the sample for analysis.

The carrier gas:

The most commonly employed are hydrogen, helium, nitrogen, CO_2 and argon. It is preferable to use gases of low diffusivity. The choice of carrier gas depends principally upon the type of detector used and the nature of the sample.

Sample Introduction:

For good separations the sample is rapidly and reproducibly introduced into the carrier gas stream, and vaporized if it is liquid at once. Liquid samples are injected by a micropipette or by hypodermic needle through a rubber self sealing serum cap or through micro syringe.

The column:

Generally column is of 6mm in internal diameter and 2 meters long. It is packed with an inert support upon which the stationary phase is adsorbed. Usual supports are kiesulguhr and crushed fire brick carefully graded in size to about 80 mesh. The stationary phase must possess a very low vapour pressure at the temperature of operation; otherwise it will gradually be bled (bleed) off the support.

For analysis of non-polar substances such as hydrocarbons, squalene or apiezon may be used, where as for more polar molecules, liquids such as polyethylene glycol (Mol.Wt-400) have been employed. For general purpose stationary phase of moderate polarity dinonyl phthalate is used $C_6H_4(COOC_9H_{19})_2$.

The amount of stationary phase used is generally between 5 and 25% by weight, and it is uniformly dispersed over the graded support by making slurry of the appropriate amounts of the solid and the stationary phase dissolved in a volatile solvent, ex: ether. The solvent is then removed by heating and the solid carefully packed into the column ensuring that there are no voids (gaps).

Detectors:

A very large number of devices have been used as detectors.

(1) The Katharometer (or) Thermal conductivity gauge (or) Differential thermal conductivity detector:

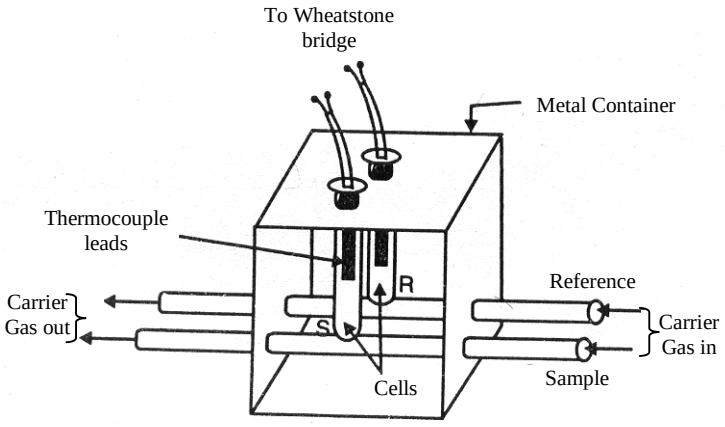
This measurement depends upon the difference between the thermal conductivity of the carrier gas and that of the merging sample. A simple gauge is used consisting of a metal or glass tube with an axial wire, normally platinum, heated by a small steady current. The temperature and hence the resistance of the wire is dependent upon the composition of the ambient gas.

The usual arrangement utilizes two identical cells, one placed in the carrier gas stream before the sample is introduced and the other placed at the column exit. These are incorporated in a Wheatstone bridge net work and the out-of balance current amplified and fed to a pen recorder. For quantitative work the detector must be calibrated and it is almost always found that the response is linear over the range of concentrations of interest in gas chromatography.

Because of the thermal conductivity of hydrogen when compared with that of most organic compounds it is preferable to use H_2, rather than N_2 as carrier gas.

(2) Thermo couple Detector:

If the carrier gas is hydrogen and if this is burnt at the exit to the column, the emergence of one of the separated substances from the column causes a considerable alternation in flame temperature. A platinum- platinum/ rhodium thermo couple in the flame thus registers a change in emf.



(3) Argon Detector:

This involves the use of argon as the carrier gas. In the detector some of the argon atoms are excited to meta stable state 11.7ev above the ground state. This is achieved by bombardment with α-radiation from radium D or with the β-emission of Sr^{90}. The energy of the excited meta stable state is sufficient on collision with an organic molecule to bring about ionization. Thus ionization current flowing between two electrodes under a potential gradient of about 750 - 1,500 v is measured which is proportional to the amount of organic material present in the detector.

However, it does not give a signal with those molecules, which require more than 11.7ev for their ionization. Thus flame ionization detector and martin gas density balance can also be used as detectors.

Theory and Evaluation:

A complete and rigorous theory of the processes taking place in gas- chromatography column is a very complex matter.

The important equation which gives **the height equivalent of a theoretical plate** (h.e.t.p) 'h' is

$$h = 2\lambda d_p + \frac{2\gamma D_{gas}}{u} + \frac{8hd_f^2 u}{\pi^2 (1+k)^2 D_{liq}}$$

Where 'u' is linear velocity of carrier gas, λ is constant characterized of the regularity of packing.
d_p – is the diameter of the particles of the packing.
γ - is constant dependent on the tortuosity of the paths in the column.
D_{gas} and D_{liq} – are the diffusion coefficients of the vapour in gas and liquid phases, k is the column partition coefficient, d_f – thickness of liquid film on packing.

Considering the individual terms in this equation, this first term represents the eddy effect in diffusion with in the irregular paths in the packing. Second term represents longitudinal diffusion of the solute in the gas phase. Final term is the contribution due to the resistance to mass transfer between the phases, i.e., the non-equilibrium effect.

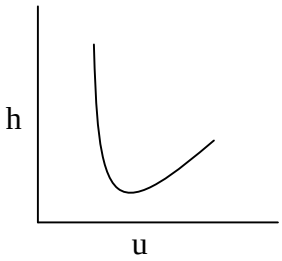
For a system the effect of gas velocity can be represented by

h = A + B/u + Cu

A- is independent of velocity and may be made small by making d_p small, although reduction below 100 mesh make packing difficult and λ tends to rise.

B- is proportional to the diffusion coefficient of the solute in the gas phase. It may be reduced by increasing the density of carrier gas.

C- may be reduced by using a low viscosity stationary phase, or by ensuring that the stationary phase is present as a thin film.

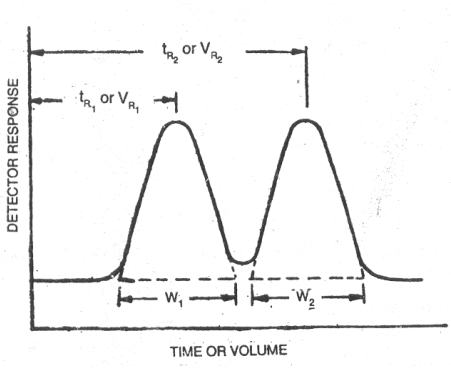


The effect of gas velocity on h.e.t.p

Resolution:

The efficiency of the separation of the components of a mixture is generally expressed as separation factor of the resolution between the peaks. It is also expressed in terms of the distance of separation of the peak maximum and width of the phase using the relation.

$$R = \frac{2(V_{R_2} - V_{R_1})}{W_2 + W_1} = \frac{2(V_{R_2} - V_{R_1})}{W_2 + W_1}$$



Where V_R and t_R represent retention volume and relation time. As shown in figure W_1 and W_2 indicate width of the phases 1 and 2. The value of R which is equal to (or) greater than 1.5 indicates complete resolution.

Applications:

GLC finds applications in large number of systems.

1. Detection of steroid drugs used by athletes and other sports personnel.
2. Marketing of hazardous environmental pollutants like hydro carbons, carbon monoxide, chlorinated pesticides and other pollutants.
3. Analysis of foods and dairy products.
4. Drug analysis.
5. Synthetic materials like plastics, paints etc.

HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

Introduction:

Consequently for a number of years liquid chromatography was not widely used for separating organic compounds. This problem was solved by the advent of HPLC. In this system pressure is applied to the column, forcing the mobile phase through at much higher rate. The pressure is applied using a pumping system. The principal advantage of the system is the speed at which separations take place. Because of the decrease in time, diffusion in the column is reduced.

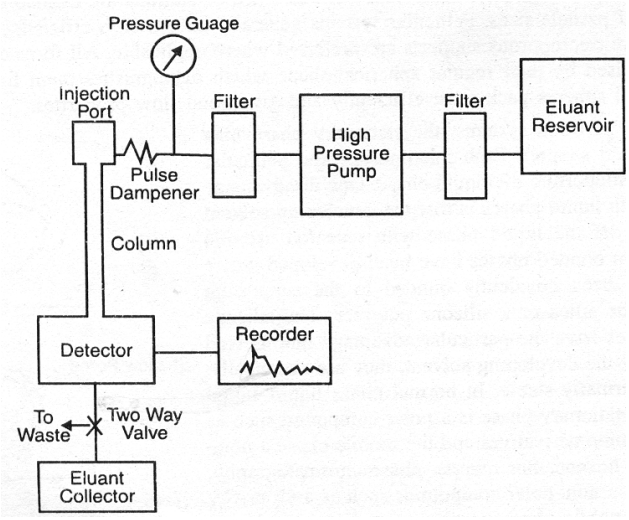
Principle:

It is known that the resolving power of a chromatographic column increases with column length and the number of theoretical plates per unit length. As number of theoretical plates is related to surface area of the stationary phase it follows that the smaller the particle size of the stationary phase, the better is the resolution. The use of faster flow rate is not possible because it creates a back pressure which is sufficient to damage the matrix structure of stationary phase. However new smaller particles size stationary phases are introduced which can withstand these pressures and of pumping systems for reliable flow rates.

Instrumentation:

The system consists of

1. A high pressure pump
2. A sample inlet pump
3. A Column
4. Detector and recording unit
5. A solvent reservoir and mixing system



The appropriate solvents (mobile liquid phase) from the reservoir are allowed to enter the mixing chamber where a homogeneous mixture is obtained. A pump capable of maintaining high pressure draws the solvents from the mixing chambers and pushes it through the column. The sample is injected through a part into the high-pressure liquid carrier stream between the pump and the column. The separation takes place on the columns which vary from 50-100cm in length and 2-3mm in diameter. Typical flow rates are 1-2ml / min with pressure upto several thousand psi.

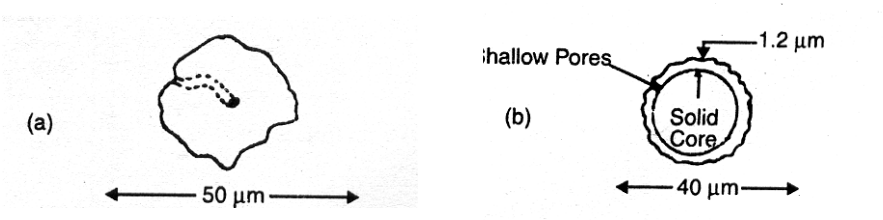
The column effluent passes through a non-destructive detector where a property such as ultra-violet absorbance, refractive index or molecular fluorescence is monitored, amplified and recorded as a typical detector response versus retention time chromatogram.

APPARATUS AND MATERIAL:

Column: Columns of HPLC are made up of stainless steel and hence withstand pressures up to 5.5 x 107 pa (8000psi)

Column Packing: Three forms of column packing materials are available

1. *Micro porous Supports:* Where micropores ramify through particles which are generally 5 to 10 μ m in diameter.
2. *Pellicular* (Superficially Porous) :
   When porous particles are coated onto an inert solid such as glass bead of about 40 μ m in diameter.
3. Bonded phases where the stationary phase is chemically bonded onto an inert support



Column Packing Procedure:

A suspension of packing is made in a solvent of equal density to the packing material. The slurry is then rapidly pumped at high pressure on to a column with a porous plug at its out let. The resulting bed of packed material is prepared for use by running the developing solvent through column, hence equilibrating the packing with developing solvent.

Chromatography Solvent: (Mobile Phase)

The choice of the mobile phase depends upon the separation to be achieved. It is also essential that all solvent are degassed before use, otherwise gassing tends to occur in most pumps.

Pumping Systems:

There is a high resistance to solvent flow due to the narrow columns packed with small particles and high pressures are therefore required to achieve satisfactory flow rates. Various pumping systems are available which operate on the principle of Constant Pressure or Constant Displacement.

1. Constant Pressure Pumps:

This produces a pulse less flow through the column. The pumps operate by introduction of high pressure gas into the pump, and the gas in turn forces the solvent from the pump chamber on to the column. The use of intermediate solvent between the gas and the eluting solvent reduces the chance of dissolved gas to enter the eluting solvent directly.

2. Constant Displacement Pump:

This maintains a constant flow rate through the column irrespective of changing conditions with in the column. In motor driven syringe type pump where a fixed volume of solvent is forced from the pump to the column by a piston driven by a motor.

Detector System:

Most commonly the detector is a variable wavelength ultra-violet visible spectrophotometer, a fluorimeter or refractive index monitor etc:

Column Efficiency and Selectivity:

The column selectivity depends upon the partition coefficient, k, where

$$k = \frac{\text{concentration of solute in stationary phase}}{\text{concentration of solute in mobile phase}}$$

The Van Deemter Equation

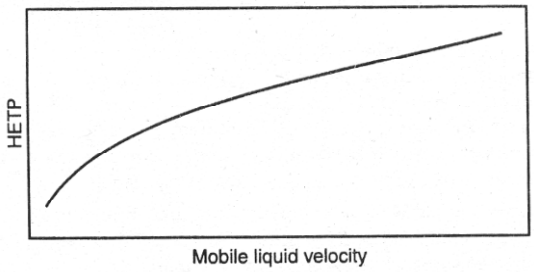
$$HETP = A + \frac{B}{u} + Cu$$

A = Eddy diffusion term

B/u = longitudinal term

Cu = non-equilibrium in the mass transfer term

In HPLC the plot of HETP against mobile phase velocity yields a curve as shown below.



Practical procedures:

There are two methods

1. *Stop Flow Injection Method:*

The sample is injected through a septum in an injection port, either directly onto the column packing or onto a small plug of inert material immediately above the column packing. This can be done when system is under pressure. When pressure was dropped to near atmospheric the injection is made and the pump switched on again.

2. *Loop Injector:*

This consists of metal loop of small volume which can be filled with the sample. By means of an appropriate valve, the eluent from the pump is channeled through the loop, the out let of which leads directly onto the column.

Applications:

1. The process has been applied for wide variety of natural products such as nucleic acids, urine, serum, carbohydrate, lipids, amino acids, bile acids and manufactured products such as pesticides, herbicides, antioxidants, surfactants.
2. Reverse Phase Partition HPLC is useful for separation of polar compounds such as drugs and their metabolites, peptides, vitamins, steroids.
3. The technique is widely used in clinical and pharmaceutical work to apply biological fluids such as serum and urine directly to column.