III YEAR - V SEMESTER
COURSE CODE: 7BCHE1A

ELECTIVE COURSE - I (A) – ANALYTICAL CHEMISTRY

Unit I **Analytical data analysis and Laboratory hygiene:**

1.1.**Need of statistical analysis:** definition for accuracy precision and error. Sources of errors and classification of errors – systematic (determinate) errors and random (indeterminate) errors. Distribution of errors. Methods of minimisation of errors.

1.2.**Data analysis:** Mean standard deviation and coefficient of variance. Significant figure.

1.3.**Reliability of results:** Q – test. Student – t – test and F-test – confidence limit and rejection of experimental data. curve fitting – methods of least squares – problems involving straight line graphs.

1.4. **Laboratory Hygiene and Safety:** Storage and handling of chemicals – carcinogenic, corrosive, explosive, toxic and poisonous chemicals – general precautions for avoiding accidents – first aid techniques for acid in eye, alkali in eye, acid burns, alkali burns, bromine burns, poisoning, inhalation of gases, cut by glasses and heat burns – methods to avoid poisoning – treatment for specific poisons.

Unit II **Separation purification and Chromatographic and Electrophoretic methods:**

2.1. **Separation and Purification Techniques:**Solvent extraction – Soxhelt extraction – Principles and applications of distillation, fractional distillation, steam distillation – crystallization and sublimation.

2.2. Basic principle of chromatography. Various types of chromatographic technique. Column chromatography, thinlayer chromatography, Paper chromatography, Gas chromatography, ion exchange chromatography and HPLC.

2.3. Basic principles of electrophoresis. Isoelectric point. Electrophoretic mobility. Electrophoretic separation of proteins.

Unit III **Colorimetry and spectrophotometry:**

1.1.**Theory of colorimetry and spectrophotometry:** Beer – Lambert's law and its limitations. Standard series method and balancing methods.

1.2.Reagents, solutions and experimental procedure for the estimation of iron, lead nickel and tin.

1.3Basic principles of spectrofluorimetry. Reagents, solutions and experimental procedure for the estimation of aluminium, cadmium, calcium and zinc.

Unit IV **Gravimetry:**

4.1. Basic principle, advantages of gravimetric analysis. Solubility product. Super saturation. Co-precipitation and post precipitation. Digestion. Precipitation from homogeneous solutions. Precipitants , specific and selective precipitant, sequestering agents.

4.2.Thermogravimetric analysis – Principle – instrumentation – characteristics of thermogravimetric curve – Applications of TGA for calcium oxalate monohydrate. Differential Thermal Analysis – Principle – instrumentation – characteristics of differential thermal curve – Applications of DTA for calcium oxalate monohydrate.

Unit V Electro-analytical techniques:

5.1. Electro- gravimetry: theory of electro-gravimetry. Faraday's laws. Ohm's law. Electrical units – ampere, volt, ohm and coulomb. Polarised and depolarised electrodes. Current density, current efficiency, decomposition potential and overpotential. Electrolytic separation of copper from nickel and copper from lead. Estimation of antimony, copper, lead and tin in alloys.

5.2. **voltammetry:** principles of voltammetry. Experimental setup for polorographic analysis. Types of polorographic methods. Determination of lead in tap water.

5.3. **Electrochemical analytical techniques:** Basic principles of voltametric analytical techniques. Potentiometric titrations and conductometric titrations. Irreversible electrode processes and overvoltage. Applications of overvoltage. Polorography and its applications.

Books for Reference:

1. R.Gopalan, P.S.Subramanian and K.Rengarajan, Elements of Analytical Chemistry, Sultan Chand & Sons, New Delhi, 1995.
2. Douglas A.Skoog and D.M.West, Principles of Instrumental Analysis, W.B.Saunders, New York, 1982.
3. Gurdeep Chatwal, Sham Anand, Instrumental Methods of Chemical Analysis, Himalaya Publishing House, Mumbai, 1998.
4. Vogel's quantitative chemical analysis – 5th edition.

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Unit - I

(1.1) Analytical data analysis Laboratory Hygiene

Need of statistical analysis :

Define for Accuracy, precision and Error.

Accuracy :

Accuracy is the difference between the true value and the value obtained.

Methods of Expressing Accuracy :

Accuracy is exposed in terms of absolute Error and relative error. The lower these values are the more will be the accuracy.

Absolute Error :

The difference between the true value (x_t) and the measured value (x_i) is known as absolute Error.

$$\text{Absolute Error} = x_i - x_b$$

Relative Error :

The absolute error exposed as a percentage of the true value is known as relative Error:

$$\text{Relative Error} : \frac{\text{Absolute Error (E)}}{\text{True value } (x_b)} \times 100$$

Precision:

Precision is defined as the degree of agreement between two or more measured values of property measured under identical condition:

Methods of Expressing precision:

The precision measurements can be expressed in terms of average deviation and standard deviation.

Average Deviation:

Average deviation is a measurement of a set is the mean of the difference of the individual measurements.

To get the Average Deviation:

The average of the given set of values is calculated

The deviation of each value from the average is calculated.

The average of all these deviation gives the average deviation.

Error:

The difference between the measured values of property and its accurate value is called Error.

Classification of Errors:

The errors that arise in a chemical analysis are classified into two types. There are.

i) Determinate error.

ii) Indeterminate Error

i) Determinate Error:

Determinate errors have a definite value and an assignable cause. These errors can be avoided, If care is taken. They are unidirectional (errors will be more (or) less then the accurate value)

Determinate error are classified into

i) Instrument Errors
ii) Method Error
iii) personal Error

Instrument Error:

Instrument Errors are introduced by defective instruments. (Eg) Defective balances, weights, pipettes, burettles etc.

The pipette is calibrated at 20°c if used at 30°c will introduse error in volume

The errors where avoided by periodic calibration of apparatus and weights and also by changing instrument

Method Errors:

These errors are introduced by define emperimental Provedimes. (Eg) In volumetric analysis using of improper Indicator leading to wrong results.

These are dibficult to identify. To avoid these

errors are must be through with the theoretical part of the experiments.

personal errors:

These errors are introduced by personal defects (or) Carelessness. (Eg) Human defects in eyes, minds, etc. Wrong calculations, Wrong placement of chemicals, nothing wrong sings etc.

Indeterminate Error:

Indeterminate errors are errors which arise in a measurement. When all known source of determinate Errors. have been identified and eliminated. These errors are also called accidental (or) random errors.

(Eg) When students measuring the boiling point of the liquid successvely reports the value as; 12.0, 119.8, 120.1°C.

These errors are caussed by

i) Instruements uncertainties

ii) Method uncertainties and

iii) personal uncertainties.

Methods of Minimisation errors:

Determinate (systematic error)

Determinate errors are assignable; to minimise these errors. we will have to use internationally

Standard accepted instruments.

Instruments must be properly maintained

proper procedure must be adopted to avoid methodic errors.

To avoid personal errors one must be careful and honest in recording the observation

Indeterminate (Random error)

Indeterminate errors are uncontrollable

To minimize these errors one must repeat experiments several times and apply statistical techniques to get maximum precision.

Blank experiments should be conducted along with regular one.

Care must be taken to avoid personal error.

While taking readings one must be very careful to note the correct readings

The experiment should not be done without getting proper and complete instruction.

When one become tired the experiment must be stopped in a convenient place and continued after taking sufficient rest.

1.8 : Data analysis :

Mean standard deviation.

The standard deviation (s) is the squares of the difference between the individual measured values

and the mean of the infinite number of measurements.

$$\text{Standard deviation} = \sqrt{\frac{\text{Sum of squares of individual deviation from their mean}}{\text{No. of measurements made.}}}$$

To get Standard deviation :

i) The average of the (x) of the measurements (x_i) is calculated.

ii) The individual deviation of each measurement from the average ($x_i - \bar{x}$)

iii) Each individual deviation is squared $(x_i - \bar{x})^2$

iv) All the individual deviation squares are added $\Sigma (x_i - \bar{x})^2$.

v) The above value is divided by no. of measurement made (N). Here we made only small number of measurements Thus $N = N-1$.

vi) The square root of the value obtained above is standard deviation (σ)

$$\text{Standard deviation} = \sqrt{\frac{\Sigma (x_i - \bar{x})^2}{N-1}}$$

Example :

Find the Standard deviation for a subset having the following four values 25.30, 25.07, 25.18 and 25.26

i) Calculate the average deviation ($\bar{x}$)

$$\bar{x} = \frac{25.32 + 25.07 + 25.18 + 25.26}{4}$$

$$\bar{x} = 25.20$$

ii) Calculate $\Sigma (x_i - \bar{x})^2$

x_i	$x_i - \bar{x}$	$(x_i - \bar{x})^2$
25.32	$25.32 - 25.20 = 0.12$	1.44×10^{-2}
25.07	$25.07 - 25.20 = 0.13$	1.69×10^{-2}
25.18	$25.18 - 25.20 = 0.02$	0.04×10^{-2}
25.26	$25.26 - 25.20 = 0.06$	0.36×10^{-2}

$$\Sigma (x_i - \bar{x})^2 = 3.53 \times 10^{-2}$$

iii) Here $N = 4$ and

$$N - 1 = 4 - 1 = 3$$

$$\frac{\Sigma (x_i - \bar{x})^2}{N-1} = \frac{3.53 \times 10^{-2}}{3}$$

$$= \frac{3.53 \times 0.01}{3} = \frac{0.0353}{3} = 0.1176$$

iv) Standard deviation (S).

$$\text{Standard deviation}(S) = \sqrt{\frac{\Sigma (x_i - \bar{x})^2}{N-1}}$$

$$= \sqrt{0.1176}$$

Standard deviation (S) = 0.1084

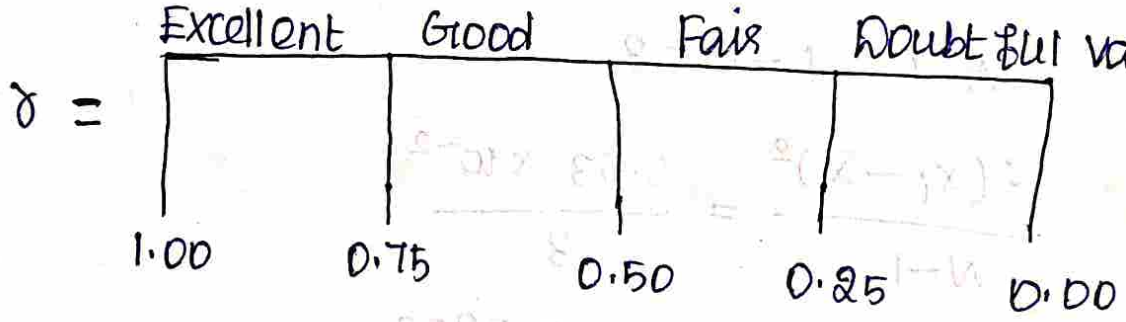
Correlation Coefficients :

It is a quantity that identi indicated the extent of a given set of data. It is denoted by (r)

$$r = \frac{N\Sigma xy - (\Sigma x)(\Sigma y)}{\{(N\Sigma x^2 - (\Sigma x)^2)(N\Sigma y^2 - (\Sigma y)^2)^{1/2}}$$

When x and y are variables : N - No of pairs of data This test helps us to find whether there linear relationship between two properties x and y from N. pairs of data.

In this method the r value is directly related in the following scale of correlation values.



If 'r' is 1.00 there is perfect linearity relationship between x and y.

If 'r' is the between 0.99 and 0.75 it means excellent.

Significant figure :

They are figures in a number which contains only digits known with certainly plus the first uncertainly one.

A measured value has a some uncertaintly about it There is a convention to give the measured value as a number such that it contains only one figure about which there is uncertainly. The practise is called significant figure convention

Importance :

Each of the following has three significant figures 583 · 0.234, 1.67, 0.00987 and 65.4

Zero is a significant figure when it is used as a number. (Eg) 0.003690. It has a four significant figure 3690

The zero used after 9 is significant figure.

Zero is not significant figure when it is used to locate decimal points in very small and very large numbers.

(Eg) 0.06870

It has a four significants figures 6870, zero before '6' is not significant figure.

Examples :

Number		Significant figure.
i) 200.06	—	5
ii) 6.030×10^{-4}	—	4 —> 0.0006030
iii) $7.80 - 10^{10}$	—	3 —> 0.00000000007 80
iv) 0.02670	—	4

(1·3) Reliability of Results.

Rejection of Data or Q Test.

Q Test is a test which has been widely used by analysis to decide. whether to retain (or) reject the suspect result.

In a set of data we come across one (or) more values that are doubtful whether to reject such a data (or) not would become difficult. In such causes we employ a test called test (Quatient test)

In this test:

The results of various observations in a given set are arranged in the decreasing order of the numerical values

The difference between the suspect value and its nearest neighbor is divided by spread of the entire set (difference between the minimum and maximum value in the entire set) to give Q_{exp}. Thus

$$Q_{exp} = \frac{\text{(suspicious value - Its nearest neighbor)}}{\text{The spread of the entire set}}$$

The ratio Q_{exp} is than compared with critical values of the rejection ratios obtained statistically at appropriate confidence levels and tabulated as a function of

the number of observations. These ratios are termed as $Q_{critical}$. If $Q_{exp} - Q_{critical}$ value. The suspects value is rejected

Example:

Consider the experimentally determined percentage of CaO in a calcite sample are 55.95, 56.00, 56.04, 56.08, 56.23. Now we suspect that the least value and so we have to decide whether to reject it (or) not. The $Q_{critical}$ value at 90% confidence level is 0.64.

Decreasing order of experimental value 56.23, 56.08, 56.04, 56.08, 56.98, 95.

Suspicious value = 55.95

$$\text{for this set of data } Q_{exp} = \frac{(\text{suspicious value} - \text{its nearest neighbor})}{\text{The spread of the entire set}}$$

$$= (56.00 - 55.95) \div (56.23 - 55.95)$$

$$= 0.05 \div 0.28 = 0.17$$

Now let us say we want our result should be 90% as real to be correct value than we look under 90% confidence column of the table. Since we have '5' observations we look for Q_{crit} against number of observation 5 and under 90% confidence the value of 0.64.

Since $Q_{exp} < Q_{crit}$ $(0.17 < 0.64)$ we conclude that the value is to be retained.

Student T test :

T-test is employed to determine the difference in precision between a new method and the standard method.

In this test, different samples of material and test having different concentrations are analysed by the new and the standard methods from the results the 't' value is obtained by the help of the relation.

$$t = \frac{\bar{x}}{s}\sqrt{N}$$

S - Standard deviation defined by the equation.

$$S = \sqrt{\frac{\Sigma (x_i - \bar{x})^2}{N-1}}$$

N - Number of measurement

x - Mean of the individual differences

Critical values of 't' are also obtained statistically are tabulated as function of the number (N) of measurements made. From the table, the critical value of 't' corresponding to any degree of freedom (N-1) can be readily obtained.

The experimental value of 't' as obtained from above equation is then compared with critical value of 't' for the same degree of freedom. If the experimental values is less than the critical value of 't' there is no significant difference between the two methods.

Student 'F' Test :

Student F Test is based on the measurement of standard deviation 'S'. The various steps involved in these test are as follows.

The standard deviation (s) is determined by using the following Equation.

$$S = \sqrt{\frac{\Sigma (x_i - \bar{x})^2}{N-1}}$$

When N-1 is degree of freedom. The value of 'N' is large (above 20) the deviation obtained by standard method is denoted by S_{std}.

The degree of freedom determined in newly developed method is small (below 20) is denoted by S_n

Determination of F-value with the help of the expression.

$$F = \frac{S^2_{std}}{S^2_n}$$

The square of standard deviation is also known as variance.

Comparing the value of 'F' obtained from the above equation with critical value (Table value corresponding 'N' as infinity)

If the value of F < Critical value, there is no significant difference in the precision of the new method and the standard method.

Confidence limit :

In cause of standard deviation we have a large number of data is required to get reliable and accurate experimental results.

In an ideal case measure mean ($\bar{x}$) should be equal to true mean (μ). By using statistical theory we can find out the range with in which the true value might fall.

Thus the confidence limit is a limit set about the measure mean ($\bar{x}$) with in which the true mean is expected to fall with certain expected to fall with certain experimental values. These limits are called confidence limits. The internal between the confidence limits is known as confidence internal.

For example : the boiling point of external falls between 77.9°c and 78.4°c these two temperatures are representing the confidence limits.

Expression for confidence limit.

The confidence limit expressed as

$$\text{Confidence limits} = \bar{x} \pm \left[\frac{ts}{\sqrt{N}}\right]$$

Where.

t - Statistical factor that depends on the number of degrees of freedom (N) and confidence limit.

S - Standard deviation

N - Number of degrees of freedom.

Thus we find by applying statistical methods we can fix the confidence limit.

Examples:

A sample of soda ash is analysed by titrating with standard HCl. The analysis of performing in triplicate gave 93.50, 93.68, 93.43 % Sodium Carbonate. Find out the confidence limit with in the range 95%. The Standard deviation is found to be 0.075. The confidence level is 4.303%.

Solution:

The mean for analytical value is = 93.50%

The Standard deviation 'S' is = 0.075

The confidence level is = 4.303%

$$\text{Confidence limit} = \bar{x} \pm \frac{tS}{\sqrt{N}}$$

$$93.50 \pm \frac{4.303 \times 0.075}{\sqrt{3}} = 93.50 + 0.19$$

Thus the mean values fall between 93.31 - 93.69%

Curve fittings methods of least squares problems involving straight into graphs.

If we want to present a mend (or) relationship we draw a graph. A graph is obtained by plotting two variables x (independent variable in horizontal axis) and y (dependent variable in vertical axis)

The graph gives the relationship between x and y

usually for the data obtained. in experiments linearity will not be as good. In such uses have to draw a best fit line This is called curve fitting.

The curve fitting was done by following

i) Σx, Σy, Σxy, and Σx^2 are calculated

ii) The above values are substituted in the following simultaneous equations.

$$\Sigma y = aN + b\Sigma x$$

$$\Sigma xy = a\Sigma x + b\Sigma x^2$$

Here N = The no. of pairs of data

iii) Now for the given values x, y values are calculated using the equation.

$$y_{cal} = a + bx$$

iv) By using calculated y values the graph is drawn we gets the best fit line for out data.

Example.

Consider the following data.

x	y
1	1.5
2	1.8
3	2.7
4	4.0

The drawn the best fit line for the above data the following steps are followed.

Σx, Σy, Σxy and Σx^2 are calculated.

(Eg) $\Sigma x = 10$; $\Sigma y = 10$; $\Sigma xy = 29.8$ and $\Sigma x^2 = 30$

The above values are substituted in the following simultaneous equation.

$$\Sigma y = aN + b\Sigma x$$

$$\Sigma xy = a\Sigma x + b\Sigma x^2$$

N = The No. of pairs of data

By substituting above values in the equation we get

$$10 = a \times 4 = b \times 10 \longrightarrow (1)$$

$$29.8 = 9 \times 10 + b \times 30 \longrightarrow (2)$$

Multiplying (1) by 3 we get

$$30 = 12a + 30b \longrightarrow (3)$$

Substracting (2) from the (3) we have.

$$0.8 = 2a$$

$$\therefore a = 0.4 \longrightarrow (4)$$

Substituting (4) in (i) we get

$$10 = 0.4 \times 4 + b \times 10$$

$$10 = 1.6 + 10b$$

$$10 - 1.6 = 10b$$

$$8.4 = 10b$$

$$\frac{8.4}{10} = b$$

$$b = 0.84 \longrightarrow (5)$$

iii) Now for the given values of x, y values are calculated using the equation.

$$Y_{cal} = a + bx$$

The calculated y values for value of x from our data are calculated.

x	$Y_{cal} = 10.4 + 0.81x$
1	1.2
2	2.4
3	3.6
4	4.8

iv) By using calculated y values the graph is drawn we get the best fit for our data.

(1.4) Laboratory Hygiene and safety:

A chemistry laboratory is place where a students has to store and Handle Chemicals. There are several Chemicals which are Corresive Flammable, Explosive, Foxic, Carcinogenic and Poisonous. So as Students should known how to store and handle that substance carefully. By known certain conditions and practices students does not spoil their health while doing experiments.

Storage and handing Chemicals.

carcinogenic Chemicals.

Chemicals which cause cancer are called carcinogenic Chemicals: (Eg) Napthyl amine and their salts, fluorene derivatives, methyl iodide benzene (causes blood cancer) benzyl Physene, thiourea, diazomethane, dimethyl sulphate, N-nitroso compounds, thioacetamide, Aziridine etc.

Storage:

They should be stored in locked container inside fume cup-boards. warning labels showing a skull and a pair of crossed bones should be pasted on the containg

Handing:

They must be handled only with gloves on. The vapours should not be intaled. They should not be allowed to come into contact with the skin. They must be handled in fume cup-boards with the exhaust fan on.

Corrosive Chemicals:

Chemicals which corrode (or) destroy gradually skin, wood, cloth, metal etc. are called corrosive chemicals.

(Eg) Acids, Alkalis, Chlorine, bromine, phenols etc.

Storage:

They should be stored in corrosion resistant chambers (or) in pits containing sand.

Handing:

Acids should not be poured directly from their containers

A funnel must be used to transfer them from their containers without spilling them on the floor, Table (or) person.

Rubber gloves and apron may be used to avoid accidental spillage of acids on the body (or) the cloth.

Sodium hydroxide pellets should not be hand picked. A pair of forceps is to be used for this purpose.

Chlorine and bromine must be handled in fume cup-boards only without allowing vapours to come, into contact with nose, eyes or skin.

Explosive Chemicals:

Chemicals which explode violently on heating, grinding (or) pressing are called explosive chemicals.

(Eg) Chlorates, perchlorates, nitrates, ethers, peroxides, polynitro compounds etc.

Storage:

They should be kept in such a way that there is no empty space above them in the container in which they are kept. They must be stored in a cool - place.

Handing:

They must be handled with all windows open and with exhaust fan on. They must be very carefully heated (or) ground.

Toxic Chemicals:

Chemicals which cause will effects create

health problems are defined as Toxic Chemicals. They are related to poisons.

Eg: Benzene, Toluene, Chloroform carbon tetrachloride naphthalene etc.

Storage:

They must be stored in well sealed bottles Chloro form is stored in dark brown / blue bottles to prevent the formation of highly poisonous phosgene.

$$CHCl_3 + \frac{1}{2}O_2 \longrightarrow \underset{\text{Phosgene}}{COCl_2} + HCl$$

Handling:

These Chemicals must be handled with all windows open and in fume cup-boards. They must not be inhaled directly. Smelling test must done by keeping the test tube Containing the toxic substance away from the nose and waving the vapours towards the nose and inhaling slowly and in small quantities. They should not be handled by naked hands. Gloves must be used while handling them.

Poisonous Chemicals:

Chemicals which when introduced into or absorbed by a living organism causes death or injury especially one that kills by rapid action even in small quantity are called Poisonous Chemicals.

(Eg) Benzene, Toluene, xylenes, naphthalene, anilines

Chloroform Carbon tetrachloride DDT, hydrazine salts of lead, Selenium Compounds cyanides, Tellurium Compounds Chromium Compounds, Vanadium compounds, arsenic compounds etc.

Storage:

They must be Stored in well Sealed tubes and labeled as poisons.

Handling:

They must be handled only with gloves on. The vapour should not be inhaled. They should not be allowed to come into contact with the skin.

General precautions For Avoiding Accidents.

i) use apron or overcoat to minimize exposure of Chemicals to skin.

ii) Wear Safety goggles to prevent eye injuries by Splashing of Chemicals.

iii) A pair of gloves must be used to handle poisonous or toxic Chemicals.

iv) To prevent fire hazard turn off, burner and electrical heaters even before opening the containers of flammable Chemicals.

v) Always use rubber bulb, When pipeting a Solution.

vi) Toxic Solutions and reagents which produce

fumes should be handled only in the fume cup-boards.

vii) Smoking, drinking, eating anything inside the laboratory should be avoided.

viii) Spillage of chemicals on the table or floor must be wiped and washed immediately with water to prevent contact with the body later.

ix) All the apparatus used should be cleaned and the hands are washed with soaps at the end of a practical class.

x) All the glass rods and tubes should be fire polished.

First Aid Techniques:

Acid in Eye:

The eye is washed with lot of water. Water is directed into the eye gently with the help of wash bottle or a tube directly from the water tap. Then the eye is washed with 5% Sodium bicarbonate solution. After washing a drop of castor oil or an eye ointment is applied. Then the person is taken to the doctor.

Alkali in Eye:

The eye is washed with a lot of wates. water is directed into the eye gently with the help of wash bottle or a tube directly from the water tap. Then the eye is washed with 5% Boric acid solution. After washing a drop of

Castor oil or an eye ointment is applied. The person is taken to the doctor.

Acid Burns:

The affected part of body is washed with a large quantity of water and then with 5% solution of Sodium bicarbonate. Burnol is applied in the victim taken to the doctor:

Alkali Burns:

The affected part of body is washed with a large quantity of water and then with 5% solution of acetic acid. Vaseline is applied and the victim is taken to the doctor.

Bromine Burns:

If bromine falls on the skin wash immediately with quantity of water and then with hypo solution. Coconut oil or vaseline is applied and the victim is taken to the doctor.

Inhalation of Gases:

If any gas is inhaled, the victim should be taken to a place where he could be breathing fresh air. If he reports headache, paracetomal tablet may be given. If chlorine or bromine is inhaled ammonia or alcohol vapour is to be inhaled carefully. If H_2S or HCN is inhaled ammonia is to be inhaled. Artifical respiration may be given if possible.

Cut by Glasses:

If the cuts are not severe, with mild bleeding, the glass pieces, dirt etc. are removed as fare as possible with cotton. The wound is treated with Spirit. Tincture iodine (3% iodine dissolved in alcohol)

Heat Burns:

Burns are caused by hot objects like naked flame, acids, alkalis, bromine, Phenol etc. Apply burnol or coconut oil for the severe burns or not. But should not do the following.

If clothes are sticking to the wound, they should not be removed by force.

Don't cover the wound with bandage.

Poisoning:

If the poison enters the mouth accidently. It must be spit immediately without panicking. The mouth is washed several times with large quantity of water. If poisonous substances enter the stomach immedialely first and must be given simultaneously informing the doctor to proceed to the spot with emergency kit to treat stomach poisoning.

When acids are swallowed milk, magnesia or lime water is to be given immediately. The first aid is repeated every ten minutes till the doctor comes. Milk or white of egg in cold water may be given.

Including of vomiting and using of Carbonates

should be avoided.

When alkalis are swallowed 5% acetic acid or vinegar and milk or white of egg are given. Here also vomiting should not be induced.

When methyl alcohol is swallowed vomiting is induced by administering tartaremetic (potassium antimony tartarate) or salt water. After vomiting milk or white of egg in cold water may be given.

When phenol is drunk 50% alcohol may be given Then vomiting induced milk or white of egg in water is given

Methods To Avoid POISoning:

Never Pipette poisonous liquids by mouth

Laboratory apparatus like beaker, Standard flask ...etc.., should never be used to keep food or drinking water

Avoid eating or drinking anything in the laboratory

Lunch boxes should not be kept inside the laboratory

Solid chemicals should be take out by Nickel spatulas and liquid chemicals by droppers

Chemicals should not be handled with bare hands

Treatment for Specific Poisons:

Universal Antidote:

2 parts of pulverized charcoal, 1 part of magnesium oxide and 1 part of tannic acid are mixed. A few grams of this mixture is added to a cup of water and then stirred well and given to the victim. This universal

antidote is administered when the specific antidote is not known.

Tartaremetic :

Tartaremetic is prepared by stirring 0.006 g of potassium antimony tartarate in 25 ml of water and given to the victim.

Uses :

1. It is used as medicine in small does to produce vomiting.
2. It is also used for the treatment of some tropical diseases.

Poisonous substance	Antidote.
Acetone	Induce vomiting. Give universal antidote
Acids	Do not induce vomiting. Give magnesium oxide, milk of magnesia or lime water immediately. Repeat the does for every fifteen or twenty minutes. Give milk or white of egg in cold water. Carbonates should not be given to patient. Give a few millilitres of mineral oil, four or five times every fifteen minutes.
Alkalis	Do not induce vomiting. Give 5% acetic acid or vinegar then give milk or white of egg
Arsenic, Barium, Mercury and Lead Compounds.	Induce vomiting. Give 4g hypo (Sodium thio sulphate) in 450 ml water 5ml milk or magnesia, 1 glass milk or white of egg.

..	Finally gives 25 ml of castor oil
Bromine and iodine solution.	Induce vomiting and give a solution of starch and 5% sodium bicarbonate followed by milk or white of egg.
Copper compounds	Induce vomiting. Give 100 ml of Sodium hydrogen phosphate solution.
Cynides Nitrobenzene.	Speedy first aid needed induce vomiting. Give 250 ml water containing 10 ml of 3%. H_2O_2 or 250 ml of freshly prepared solution containing 5% $FeSO_4$ and 5% $NaHCO_3$, amyl nitrite vapours to be inhaled by the victim Give 100 ml of 3% acetic acid solution and then large quantities of water.
Oxalic acid and oxalates	Give Induce vomiting using mustard powder in hot water (mustered emetic) Give milk or magnesium oxide paste.
permanganate.	Induce vomiting. Give milk or white of egg followed by 5ml of 3% H_2O_2 in 100 ml of water slightly acidified with acetic acid.
Phenol.	Give 50% pure ethanol and induce vomiting. Then give milk or white egg in cold water.

UNIT-II

SEPARATION PURIFICATION AND CHROMATO-GRPHIC AND ELECTROPHORETIC METHODS.

2.1 Separation and purification Techniques.

Solvent Extraction.

It is a seperation technique adopted to seperate a solid or liquid present in a mixture by extracting it with a solvent.

Principle:-

The substance to be extracted should be soluble in a particular solvent while all the other constituent in the mixture should be insoluble after extraction the solvent should be easily seperable.

Seperation technique:-

The principle used in the solvent extraction is Nerst distribution law. According to this law, at constant temperature a solute distribute itself between two immiscible solvents only in particular ratio. The ratio of the concentrations in the solvent is called partition coefficient or distribution coefficient.

If C_A and C_B are the concentrations in liquids A and B then at constant temperature. $C_A/C_B = K$.

K is a constant. Large the value of K, more coefficient is the extraction.

Advantage of Solvent extraction method.

100% seperation is achievable in solvent extraction method.

The practical part is simple.

The small amount of solvent is enough and it is recovered and recycled.

Uses:-

Solvent extraction method is used to seperate.
Dissolved substance from their solution.
one constituent from a solid mixture.
unwanted impurities from substance.

Soxhelt extraction.

Soxhelt extractor is used to extract a substance which is soluble in particular solvent while all other impurities are insoluble. After extraction the solvent should be easily seperable.

Procedure:-

A solid to be extracted is powdered and it is kept in a porous thimble (spongy cover) and the extracting solvent is taken in round bottom flask. A water condenser is attached at the top. A porous Thimble is placed at the bottom of the water condenser

The solvent is boiled. Its vapours are raised through siphon (left side tube) The vaphour enter water condenser are condensed and falls on the phorous thimble. The solid to be extracted is dissolves while all other impurities do not. When phorous thimble become full. The solution reaches the round bottom flask through (right side) tube. The extracted solid remains in the flask is distilled off, leaving behind the organic substance.

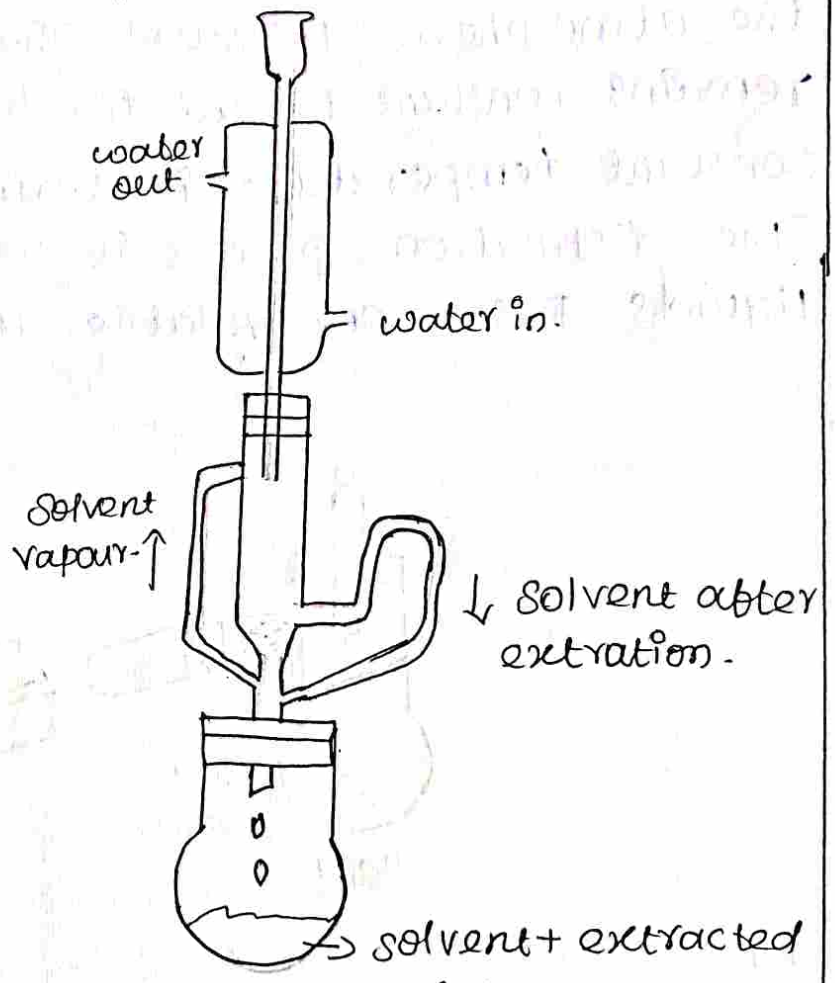
Superiority of Soxhelt extraction over other technique

In Soxhelt extraction method, small quantity of solvent is enough to extract a maximum amount of solid.

Solvent used is recycled.

This is a continuous process. So the efficiency of extraction is more in this method.

This method is used for the extraction of oil and fats from flower and seeds and alkaloids from plants.

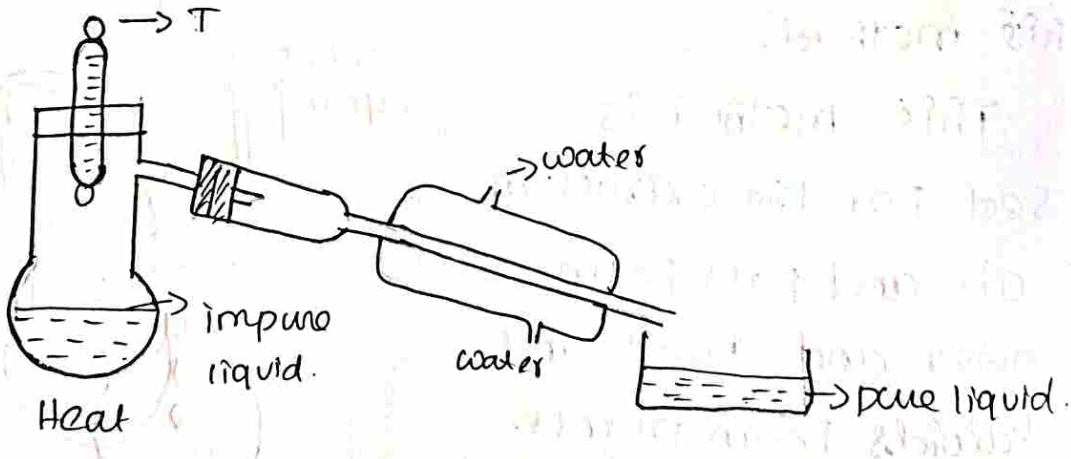


Principle and Application of Distilation

Distillation is a process employed for the purifical of liquid from non-volatile impurities. The impure liquid is boiled in a flask and the vapours formed are collected and condensed to give back the pure liquid in on another vessel. The non-volatile impurities are left behind in the flask.

Principle :-

On heating under constant pressure, say under atmospheric pressure a liquid boiles at a temperature at which its total vapour pressure become equal to the atmospheric pressure. The temperature of the liquid remains constant till all the liquid distilled over. The constant temperature is termed as the boiling point. The distillation process is used for the purification of liquids from non-volatile impurities.



Application :-

This method is used to imparity liquids which de decompose near their boiling points. For example, glycerol decomposes at its boiling point (298°C) but can be distilled at 180°c at 12 atm pressure.

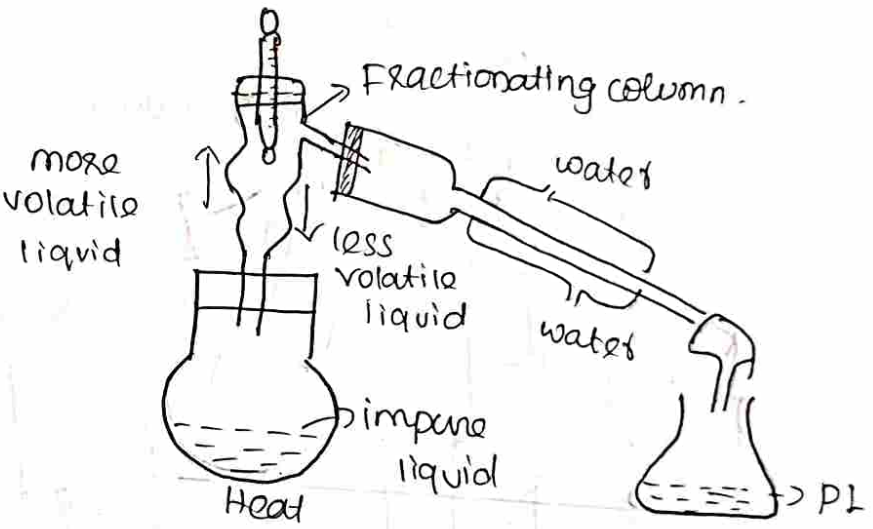
Fraction distillation.

principle:-

A mixture of two or more volatile liquid can be seperated by fractional distillation. When their boiling points differ by more than 40°c, they can be seperate by fractional distillation. The more volatile liquid passes over first and is collected in a receiver. The same procedure was followed for the further distilation. Thus the distillation is collected in fractions and the process is termed fractional distillation.

Application.

*A mixture of benzene and toluene can be seperated by this method.

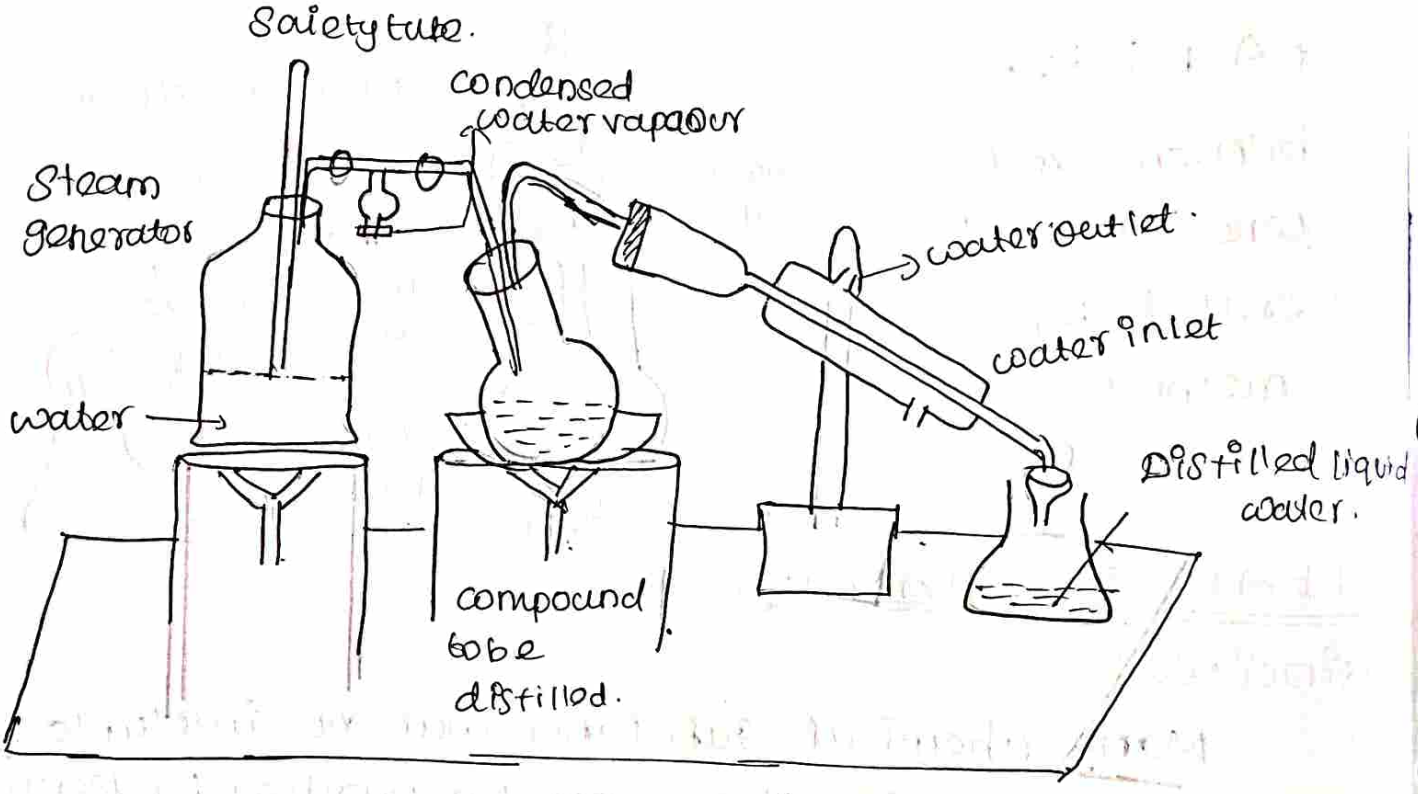


STEAM DISTILLATION.

principle:-

Many chemical substance that are insoluble in water are volatile in steam can be purified by distillation in a current of system (Steam distillation). The non-volatile impurities are left behind in the distillation flask. A liquid boiles when its vapour pressure is equal to the atmospheric pressure. In steam distillation a mixture of water and an organic liquid is heated. The mixture boils when the combined vapour pressure of water (P_1) and that of organic liquid (P_2)

is equal to the atmospheric pressure P.
ie) $P = P_1 + P_2$. Naturally, the boiling temperature of the mixture would be lower than the boiling of pure organic liquid when the vapour pressure of this liquid along would be equal to the atmospheric pressure. Thus in steam distilation, the liquid is distilled at a lower temperature then its boiling point, when it might decompose. It serves the same purpose as distillation under reduced pressure.



Application -

Steam distilation is employed in industry for the recovery of various essential oil from plants and flowers. It is also used in the manufacture of aniline and turpentine oil.

Crystallization.

Principle:-

Crystallization is commonly employed for the purification of solid compounds. The impure solid is dissolved in the minimum volume of a suitable substance pass into solution while the insoluble ones are left behind. The hot solution is then filtered and allowed to cool undisturbed till crystallization is complete. The crystals are then separated from the mother liquor by filtration and dried.

The efficiency of the process of crystallization depends on

1) Choice of solvent 2) preparation of solution
3) Filtration of the solution 4) Crystallization and
5) Separation and drying of crystals.

① Choice of Solvent

: A few mg of the substance is taken in a test tube with a few drops of solvent. If the solvent completely dissolves a solid at room temperature. It is unsuitable. If the solvent dissolves solid. on heating and give maximum solid on cooling in suitable for crystalization. The process is replaced with other solvent till the most satisfactory one is sorted out.

② Preparation of Solution.

A suitable amount of substance is taken in a conical flask. Fitted with a reflux condenser. A small volume of solvent selected in above step is also placed in the flask.

A quantity of solvent should be just enough to dissolve the whole solid on boiling according to the boiling point of the solvent.

3) Filtration of the solution.

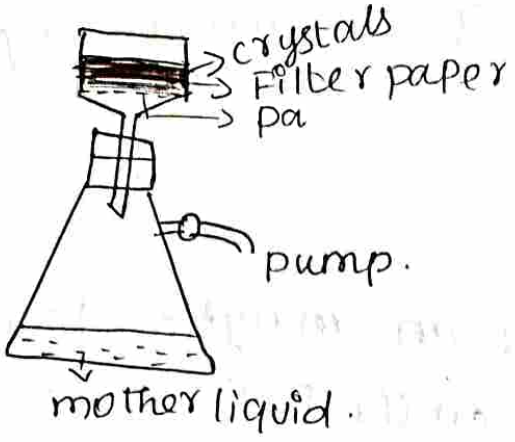
The hot solution obtained above is then filtered through the filter paper placed in a glass funnel. The crystals may form in the funnel during filtration. If the quantity of the solution is large it takes large to prevent this, a hot-water funnel may be used. The hot solution obtained in the conical flask is called filtrate solution.

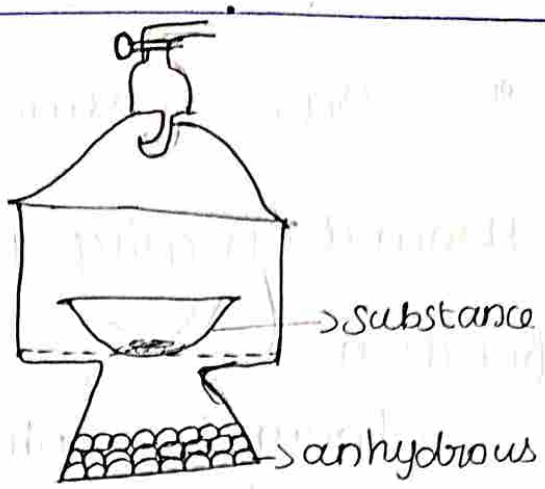
4) Crystalization:.

The hot filtrate obtained above process is then allowed to cool. undisturbed in a beaker. The pure solid substance seperate as crystals.

5) seperation and drying of crystals.

The crystal obtained from the above process is seperated from the mother liquor by filteration. The filtration is generally effected under reduced pressure. using Buchner funel. When the whole of the mother liquor has been drained into the filtration flask, the crystals are washed with small quantities of the pure cold solvent to remove other impurities if any the crystal are then dried by pressing between pads of filter paper, in an air oven, or in vaccum desicator.





Sublimation

Sublimation

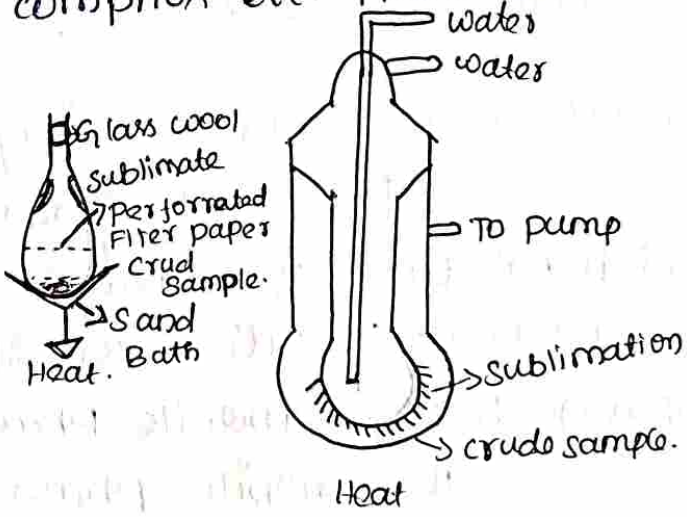
Sublimation is a process of a solid getting directly converted into its vapour on heating without becoming a liquid.

Principle:-

Sublimation is a process in which certain substance when heated pass directly from solid to vapour state without melting. The vapours when cooled give back the solid substance. This process is known as sublimation The process of sublimation is used in the purification of volatile solid like naphthalene, camphor etc. From non-volatile solid.

Applications.

This technique is used for the purification of sublimable solid like camphor, naphthalene. benzoic acid etc.



2.2. Basic principle of chromatography.

CHromatography

Defenition:-

Chromatography is an analytical technique For separating compound on the basic of the difference in their affinity For a stationary phase and a mobile phase. The affinity inrove the process of either adsorption or partition.

ADSORBTION CHROMATOGRAPHY:-

Adsorption is technique in which the binding of compounds to the surface of the solid phase (or) stationary phase. Adsorption chromatography is a technique in which small differents in the adsorption behaviour of substance in mobile phase (liquid or gas) and a stationary phase are used to separate them.

If a mobile phase is liquid and a stationary phase is solid it is called- liquid- solid chromato--graphy or adsorption column chromatography.

Partition chromatography.

Partition chromatography is a technique in which mixtures of substance are seperated by means of partition (relative solubility of a compound in two phase) between mobile phase and stationary liquid phase.

If a mobile phase is gas and a stationary phase is liquid it is called gas- liquid chromatography.

Column Chromatography.

Column chromatography is defined as the uniform Filtration of a liquid through a column of Finely divided Substances.

principle:-

It is known that the rate of absorption various with a given absorbent for different Melerial. This principle of selective adsorption is used in column chromatography.

In this method, the mixture to be separate is dissolved in a suitable solvent and allowed to pass through the tube containing the absorbed. The compound which has greater absorbing power is adsorbed in the upper part of the column. The next compound which has lesser absorbing power the first compound is absorbed in the lower partition of the column as distinct bands (chromatogram) across the column. The separation of these compound collected in seperate vessels.

working

choice of Adsorbent.

Adsorbent used in the adsorption column Chromatography should be activated. Eg Alumina or Aluminium oxide is widely used and activated by heating it about 200°C in a current of air or CO_2. other absorbent used are magnesium oxide or magnesia.

Magnesium carbonate, calcium carbonate, calcium Sulphate, Barium carbonate, Charcoal, Sucrose, talc Starch, Cellulose and Fuller's earth.

Adsorbent used in the partition column chromatography should be inert. Eg cellulose Starch, Silica gel, calcite, kieselguhr etc.

Choice of Solvent.

In a chromatographic separation, different solvents may be used for placing the solute on the column, developing the chromatogram and eluting the adsorbed material. The solvents must be pure. Non-polar solvents effect better separation hence prepared for solution mixtures. Development and elution were carried out with polar solar some commonly used solvent in the increasing order of polarity.

Petroleum ether < CCl_4 < Cyclohexane < CS_2 < ether < acetone < Chloroform < alcohol < H_2O < Pyridine < Organic acid.

Preparation of column.

Pyrex glass long tube is used as column. one end of the tube is either drawn out it is closed with rubber stopper. A small wad of cotton is pressed down on to the stopper. Thus powdered adsorbent is retained and liquid passes through

The column is packing the colum with Adsorbent by wet packing. In wet paking the column is placed in a vertical position, thick slurry of the adsorbent in a suitable medium is poured

through the open.

the tap at the lower end is then opened to allow the liquid to run out until it covers of the top.

The efficiency of column depends on.

The particle size of the solid absorbent. It should be uniform.

It should have high specific area. This is because the solution attains equilibrium between stationary and mobile phase.

There should be no air gaps. Air gabs leads to mixing of separated zones and allow the solution of the mixture to pass through with effecting separation of the mixture.

Experimental Technique.

A solution of the mixture to be separated is prepared in a relatively non-polar solvent.

The stopcolek at the bottom is opened slightly to allow the solvent to rount until a small amount of the solution remains in the column covering the top of the packed meterial.

When all the solution has been poured, it is allowed to flow steadily through the column.

Various zones of component are separated by passing suitable solvent throughout the well developed chromatogram the solvents used for this purpose are called Eluent

Various substance are separated in the column this process is known as development. The

Well- developed column is called Chromatogram.

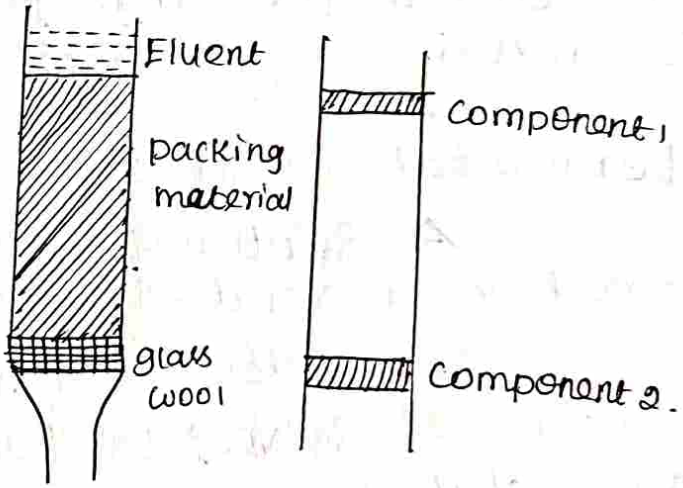
If the components are coloured, different colour zone are got in the column.

The eluent should be less polar than the components of the mixture so that it is not more strongly absorbed than the components of the mixture.

It should dissolve the components not absorbent.

The different eluents are passed through the column to collect the different zone in different vessels.

Elution is carried out till the separation is completed.



Application:-

Column chromatography is used for

i) To seperate structural isomers such as α- carotene and β- carotene.

ii) To seperate geometrical isomers of corotenoids and carboxylic acid.

iii) To Separate keto and enol tautomers.

iv) To separate amino acid.

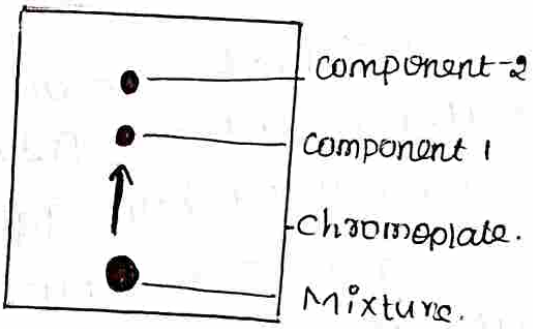
v) To separate inorganic ions such as Pb^{2+}, Ag^{2+} and Zn^{2+} ion. and mixture of Ferric aluminium and cupric sulphate.

Thin Layer chromatography. (TLC)

Principle.

TLC is based on the principle of selective adsorption of the component of a sample on the surface of the stationary phase. A Thin Layer of some solid (eg silica gel) deposits on a glass plate. called Chromatoplate. Serves as the stationary phase. When a solution containing different solutes is allowed to pass through the chromoplate, they get seperated and collected as distinct spots across the length of the Chromoplate. In the case of colourless substance the spots are located using Iodine.

working:-



Choice of Adsorbent.

Silica gel, Alumina, kieselgur, cellulose and some commercial adsorbent such as polyamide powder, Calcium Sulphate, Magnesium silicate and powdered glass are some commonly used absorbents.

A good Adsorbent should possess the Following characteristic.

It must not react with material under investigation

The Adsorbent's colour should not interfere with the colour of the chromatogram. It should be colourless.

It should be Insoluble in solvent used.

The physical and chemical properties should

not change under the experimental conditions.

Choice of solvent.

The choice of solvent depends on the nature of the substance to be separated and on the adsorbent used. This can be achived by matching polarity of solvent and substance. More polar solvents result greater migration and better separation. Combination of two solvents also give good separation than single solvent. Petroleum ether, CCl_4, benzene, pyridine, acetone, water etc.

preparation of chromatogram. (chromatoplate).

Square or rectangular glass plates, metal foils or plastic plates are used as adsorbent supports in TLC. Most widely adsorbent is silica gel.

Weighted amount of adsorbent is taken in a beaker, water is added. Beaker is stirred or shaken vigorously until we get homogenous, thick, mobile slurry.

Two chromatoplates are dipped the slurry, taken out and are held vertically for drying solvent.

After drying solvent, dry plates are separated - we get two chromato plate.

The drying plates, dray plates are kept in an oven about 100-150°c for 2-hours for removing water or other polar solvent. This is because water or polar solvents affect the development. This process is known as activation. Sample application.

Small amount of sample is dissolved in a small volume of a volatile solvent (benzene or ethanol).

For polar samples polar solvents are used. less polar samples should be dissolved in suitable non-aqueous solvent.

Base line is drawn from one edge of the plate the sample dissolved in volatile solvent is applied in small spots.

solvent is evaporated. Standared substances if any may also be applied by side of the test sample.

Development of chromatogram.

chromatogram usually developed by ascending method in a developing chamber.

The chromatoplate is placed between the glass plates and through is filled with the solvent.

The chamber is closed fixed with lid.

After certain time when solvent removed from the tank and the solvent from is carefully marked.

The solvent is evaporated.

coloured compound can be identified by visual by inspection physical or chemical methods are adopted for colourless compounds.

Hydrophobic (wate hating) compounds shows their presence as waxy

Chromatogram is inspected under UV light in a dark box compounds appear as dark spots in light background.

Chromatoplate is placed in Indine chamber. It imparts a dark brown colour to the spots.

A simple is mixed with very small amount of radioactive isotopes and applied on the plate the radioactive is measured by GM counter after development

Superiority of TLC over other techniques.

The Thin Layer Chromatography (TLC) requires simple equipment

Identification and separation by TLC can be done within 20-40 minutes.

It can be applied to a wide variety of compounds, both organic and inorganic.

The medium in TLC is a Thin Layer. The particle size is very small. So we get improved resolution and compact spot.

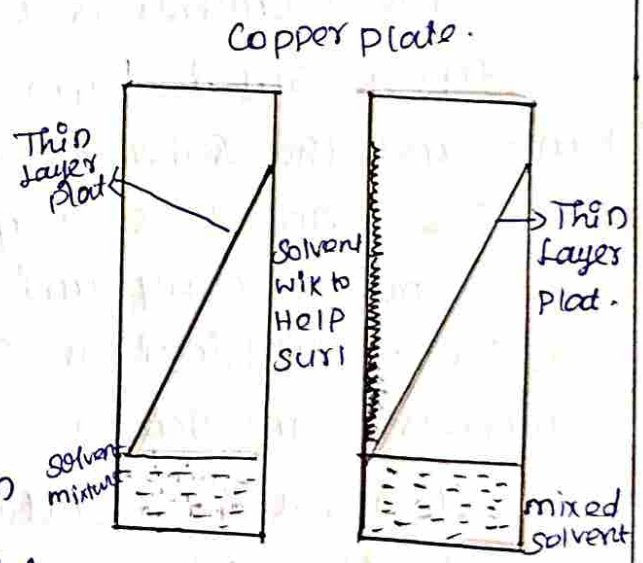
It is applicable to compounds which are decomposed by heat

TLC is sensitive and give sharpper zones.

Application:

TLC is maily used in the identification and separation of aldehyde, Ketones, alcohol, glycols and Fatty acid.

It is also used for the isolation of essential oil, amino acids, lipids steroids, bile acids and alkaloids.



TLC an ideal technique for the purification of samples prior to final crystalization in microanalysis

It is applied to detect adulterants in Food and soft drinks.

TLC is used to check the purity of samples

Impurities present even in traces can be detected

It is used to detect by-product in chemical synthesis.

paper chromatography.

Principle:-

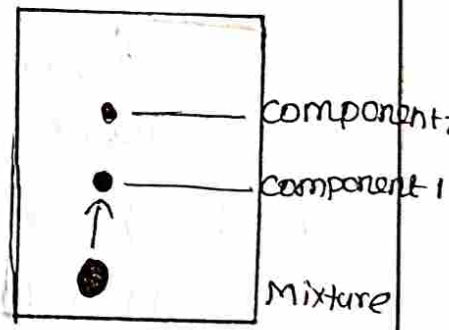
Paper chromatography is a type of partition chromatography in which the substance are distributed between two liquid mobile phase is a solvent and another one is water adsorbed on a strip of whatman Filter paper called stationary phase. The partition coefficient of compound between the two phase is given by.

$$K_D = \frac{\text{Concentration of compound in the stationary phase}}{\text{Concentration of compound in the mobile phase}}$$

The solute in a maximum mixture moves along the Filter paper at different rates depending upon their partition coefficient and get separated.

working:-

In paper chromatography a Filter paper serves as medium For partition to take place between a stationary liquid and a mobile liquid.



Choice of solvent.

Paper chromatography is based on partition of substance between two liquid, we have to use suitable solvent For stationary and mobile phase.

The Choice of solvent depend on the nature of the substance to be seperated.

Stationary phase:-

Aqueous solvent:-

water is used as the stationary phase. The Filter paper is suspended in water placed in a closed champer.

Hydrophilic solvent.

A Hydrophilic solvent can be used as stationary phase.

Ex: methanol. Formamide, Glycol, Glycerol etc.

Hydrophobic solvent.

Hydrophobic solvent can also be used

Ex. keton, Hydrocarbons, dimethyl Formamide.

Mobile phase:-

Several combination of mixture of 2,3 or more solvents solution of salt, buffer etc.

Ex: 1) Isopropyl alcohol, water and Ammonia.

2) n-butyl alcohol, water & Aceticacid.

Experimental technique

Dissolved substance are applied a small spot is formed a Filter paper.

The paper is then dipped into a vessel

containing the mobile phase.

The mixture are partitioned between the solvent held on paper (Stationary phase) and organic solvent (mobile phase)

The seperation is effected by the differential migration of the mixture of substance.

There are two forces oparate the Filter paper.

The propelling force: It drags the substance in the direction of the Flow of solvent. It is depend upon the solvent Flow and solubility of substance in solvent. The compound with higher solubility will move rapidly along the paper then the less soluable one this leads to a seperation.

The ratarting force :- It drags the substance behind towards its point of application. The retarding depends on the adsorption and partition. When a drop of solute is treated with the solvent on the strip paper. The more strongly absorbed component will move along the paper with the solvent. Cellulose of the paper contains a small amount of water. partition of the substance take place between water in the cellulose and the organic solvent (mobile phase). This also cause seperation of substance.

Development of the chromatogram.

i) Asending technique.

ii) Desending technique.

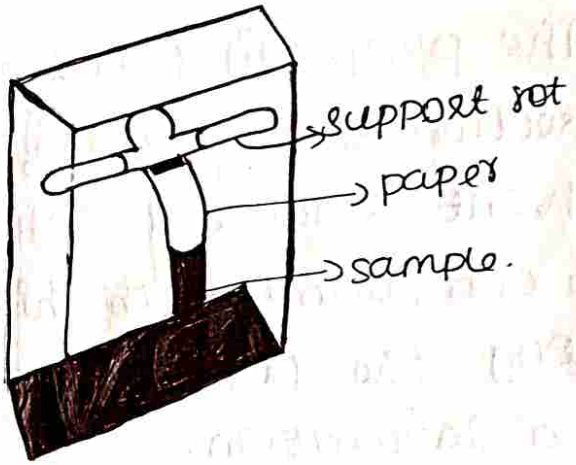
iii) Radical development.

Ascending Technique.

In this technique the solvent is placed in bottom of tank and the paper is suspended from top of with the help of clip. So that the lower end of paper containing the spot is well above the solvent The solute is partitioned between water in the Filter paper. and the solvent equilibrium is established between two phases.

Descending technique.

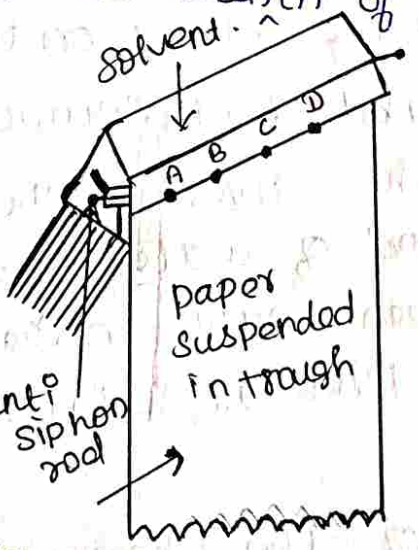
In this technique the solvent is placed at the top of the tank and the paper is hanged such that solvent flows down the paper. A small amount of solvent is placed at bottom of tank to replaced air inside the take with vapour of the solvent. The seperation is improved by increasing the length of paper.



Radical Development.

In this technique circular paper is marked with a pencil.

A wick is cut parallel to the radius from edge of the wick dipping in the liquid centre. The sample solution is applied at upper end of



the wick in the center. The paper is dried. It is placed over a petridish containing the developing solvent with the wick dipping in the liquid. The solvent flows through the wick to the sample spot and carries the solute with it. Thus the different components of a mixture are separated. This technique is also called circular chromatography.

Drying of the chromatogram.

After the solvent has moved certain distance for a certain time, the chromatogram is taken out from the tank and the position of the solvent front is marked with a pencil. The chromatogram is now dried by blowing hot air from a hair dryer or by any other suitable method.

Application.

Paper chromatography is applied for the identification and separation of Gr. I cation (Pb^{2+}, Ag^{+}...) and Gr II cation such as Bi^{3+}, Cd^{2+}

Estimation of Gr IV cation has (Ni^{2+}, Co^{2+}, Zn^{2+} and Mn^{2+}) has been carried out with this technique.

Anion like F^-, Cl^-, Br^-, I^- can be detected and separated paper chromatography.

paper chromatography is versatile technique used for the separation of amino acid

It is applied for the analysis of compound of biological origin viz. carbohydrate, lipets, steriods, alkaloids, vitamin.

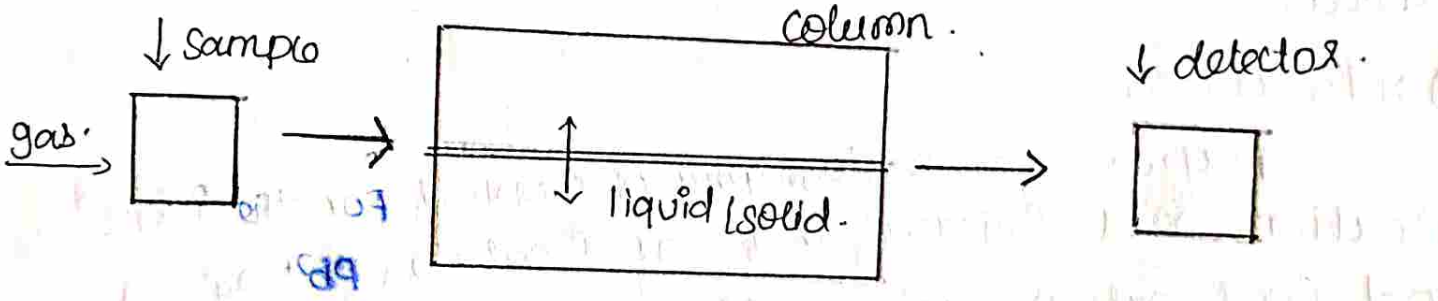
It may be used to check the purity of pharmaceutical and food products.

It may be used to detect adulterants in food and soft drinks.

Gas- Liquid chromatography (GLC).

Principle:-

Gas - liquid chromatography consists of gaseous mobile phase and liquid phase coated on the surface of an inert solid packing or on the wall of capilary tube. The sample mixture in gaseous form is run through the capilary tube with a carrier gas. seperation can be achieved by the difference in the distribution ratio of sample between mobile phase and stationary phase. After elution, the sample componets can be elected by a suitable detector at the exit.



working

There are six essential part of Laboratory gas chromatography (GC)

A gas cylinder containing a carrier gas.
A sample injection system.
The column.
The thermal compartment.
The detection system.
The recorder.

i) Carrier gas supply.

The most commonly used carrier gases are Helium, Nitrogen, Hydrogen, Argon, CO_2, the carrier gas should be pure. The flow rate of the carrier gas should be constant.

ii) Sample injection system.

A sample small amount of the sample is introduced into carrier gas with a syringe. Solid sample can be dissolved in a suitable solvent and introduced by a syringe.

iii) The column.

The columns are made from stainless steel, copper, glass or plastic. They may be coiled or bend (V or W shap) partition columns are used in GLC The partition columns are packed with an inert support like ground fire brick or glass beads. The Inert supports carry a non-volatile liquid phase. The choice of liquid phase depends upon the nature of the substance to be separated. Some liquids used are silicon oil, greases etc.

iv) Thermal compartment.

The temperature of the column can be main-tained uniformly by the use of vapour jacket contain, benzene, toluene etc.

v) Detecting system.

Detectors measure either the concentration of the solute in mole fraction in the carrier gas or the flow rate of the solute. Some of the detector

Which are commonly use are.

a) Thermal conductivity detector

b) Flame ionization detector

a) Thermal conductivity detectors.

Different gases have different Thermal Conductivities By changing the composition of the gas thermal conductivity will change, thermal conductivity detectors are based on the change in the thermal conductivity of the gas stream. An instrument used for this purpose is called Katharometer.

A current is passed through the instrument, the thermal conductivity of the surrounding gas changes with a change in the temperature of the wire. The resistance of the wire is measured from that the thermal conductivity of the gas can be calculated.

b) Flame Ionization Detector

This technique is based on the principle that organic compounds are pyrolyzed (Thermal decomposition) when introduced into hydrogen oxygen flame, ions are produced. These ion are collected and the resulting current is measured.

An oxygen flame ionization detector is used for this purpose. The column effluent gas is mixed with Hydrogen and burnt at a metal jet (cathode). A loop of cylinder acts as anode.

As the composition of the gas in the flame changes, the number of ions and electrons will also change. Thus current flow will also change with the change in

the change in composition of the gas eluted from gas chromatographic column. This is the most popular detector.

vi) Recorder.

All the detector gives rise to small and weak electrical signal. These are passed through an amplifier and fed into the recorder. The amplified signals drive the recording chart strip. we get a series of peaks on the paper.

Application:-

GLC used for quantitive determination of amount of component present in a mixture. The steroid drugs used by athletes in sports competitions are detected by GLC.

This technique is used for analyzing complex mixture of substance in industry and research.

Fatty acids, Benzene and toluene, Chloromethanes components with similar boiling point. but different polar characteristic are separated by this technique.

It is used for quantitative analysis of mixture also. peak heights, peack areas are compared with those of known substance and their quantity determined

It has been used in elemental carbon, Hydrogen and nitrogen analysis of organic compounds.

Hazardous pollutants such as Formaldehyde and CO can be monitored by GLC

GLC is used to detect aldehyde, and ketones which cause rancidity of dairy products like milk and butter and it finds application in drug analysis.

ion exchange chromatography.

principle:-

It involves exchange of ions with like signs between a solution and a solid in contact with the solution.

Types of resins:-

Ion exchange resins are granular insoluble organic compounds with giant molecules with exchange -able ions. The ion exchange resin are of two types.

They are i) cation exchange resin and
ii) anion exchange resin.

A cation exchange resin can be represented as $(ResA^-)B^+$ where Res is the basic polymer of the resin to which is attached the anion A^- and mobile cation B^+ The cation exchanger exchanges its mobile cation with the cation of the solution.

Example.

$$2(Res\,SO_3^-)\,Na^+ + Ca^{2+} \rightleftharpoons (Res SO_3)_2\,Ca^{2+} + 2Na^+$$

An anion exchange resin can be represented as $(Res\,B^+)A^-$. Anion exchanger exchanges its mobile anion with the anion of the solution.

Example:-

$$[Res\,N(CH_3)_3^+]\,OH^- + HCl \rightleftharpoons [Res\,N(CH_3)^+]\,Cl^- + H_2O.$$

i) Strongly acidic cation exchange resine.

Eg: Sulphonated polystyrene resine. They are useful in the pH range of 1-14.

These are Seperated cations, Inorganic compounds, Lanthanids, vitamins, peptides and amino acids.

ii) Weakly acidic cation exchange resine.

Eg: Carboxylic polymethacrylate resin.

They are useful in the pH range of 5-14. These are useful to seperate cations, biochemical and compounds. transition elements, amino acids, antibiotics and organic bases.

iii) Strongly basic anion exchange resins.

Eg: Quarternary ammonium polystyrene resine.

These are useful in the pH range 0-12. These are used to separate anions, halogen, alkaloids, vitamin B complex, Fatty acids etc.

iv) Weakly basic anion exchange resin.

Eg. Phenol Formaldehyde and polyamine polystyrene resin.

These are usesful in the pH range of 0-9 These are used to seperate anionic complexes of metals anions of different valencies, vitamines and amino acids.

Action of ion exchange resins:-

Ion exchange resins behave as a porous network. Carrying a surplus electric charge, which is distributed over the surface and throughout the pores.

The surplus charge is compensated by ions of opposite charge. Thus ion exchange resin comprise of static ions attached to the resin part and mobile ions. These mobile ions are exchanged with similar ions during ion exchange process. In this ion exchange process no chemical bond are formed as the available heat of exchange is low. The actual ion exchange process is taking place by diffusion occuring in two different waves.

1) Film diffusion :-

In this method diffusion of ion takes place across the liquid film which is adiacent to the resin particle. This method dominates in dilute solution and with small ions.

2) particle diffusion :-

In this method diffusion of ions take place within the poses of the resin particles. This method dominates in concentrated solution and with large ions.

Experimental techniques.

The ion exchange chromatography is carried out in a chromatographic column. The column consists of a burette provided with a sintered glass wool plug at the lower end. The column is packed with wet ion exchange resin uniformly. The top of the resin bed is covered with a glass wool pad. The column should never be allowed to drain out.

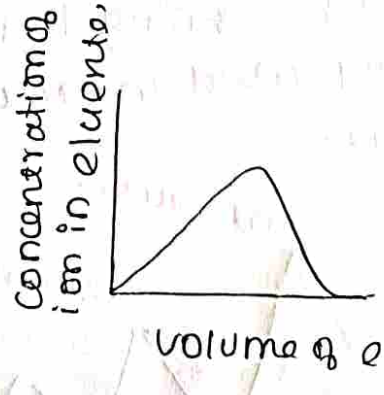
Let us suppose that we wish to replace the Cl^- ion by OH^- ions. the resin column is washed with a concentrated solution of NaOH to ensure the column

only OH ion and no other anion. The solution containing Cl ion is run through the column Cl is exchanged by OH. The effluent will contain a quantitative yield of the hydroxide compound. The same process occurs when a cation exchanger is used.

In a mixture of small quantities of two or more different cation x and y etc. is passed through an ion exchage column they get separated. If cation x is held more firmly by the exchange resin then cation y. y will flows out of the bottom of the column before x. This separation technique is called ion-exchange chromatography. The liquid entering the column is called influent. The liquid leaving the column is called the effluent. The process by which the absorbed ions are removed from the column is known as elution. The solution used for elution is eluent and the solution obtained as a result of elution is called the elute

If the solution of suitable eluent is passed through a column containing an ion x. The effluent is continuously analysed and the concentration of x is plotted against the volume of eluate, an elution curve is obtained.

(a)



(b)

If the column contains several ion of similar charge y etc. elution curve are obtained for each ion by uses of suitable eluants. If the elution curves are sufficiently far apart quantitative separation is possible. If the elution curve overlaps only incomplete seperation is possible.

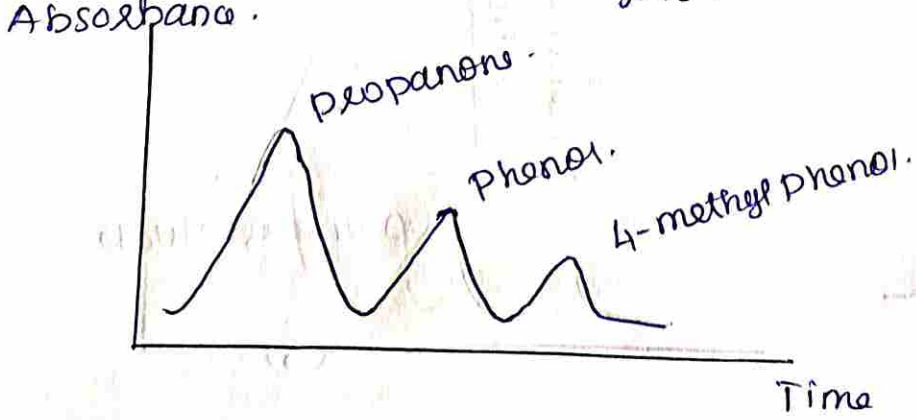
High Pressure Liquid chromatography.

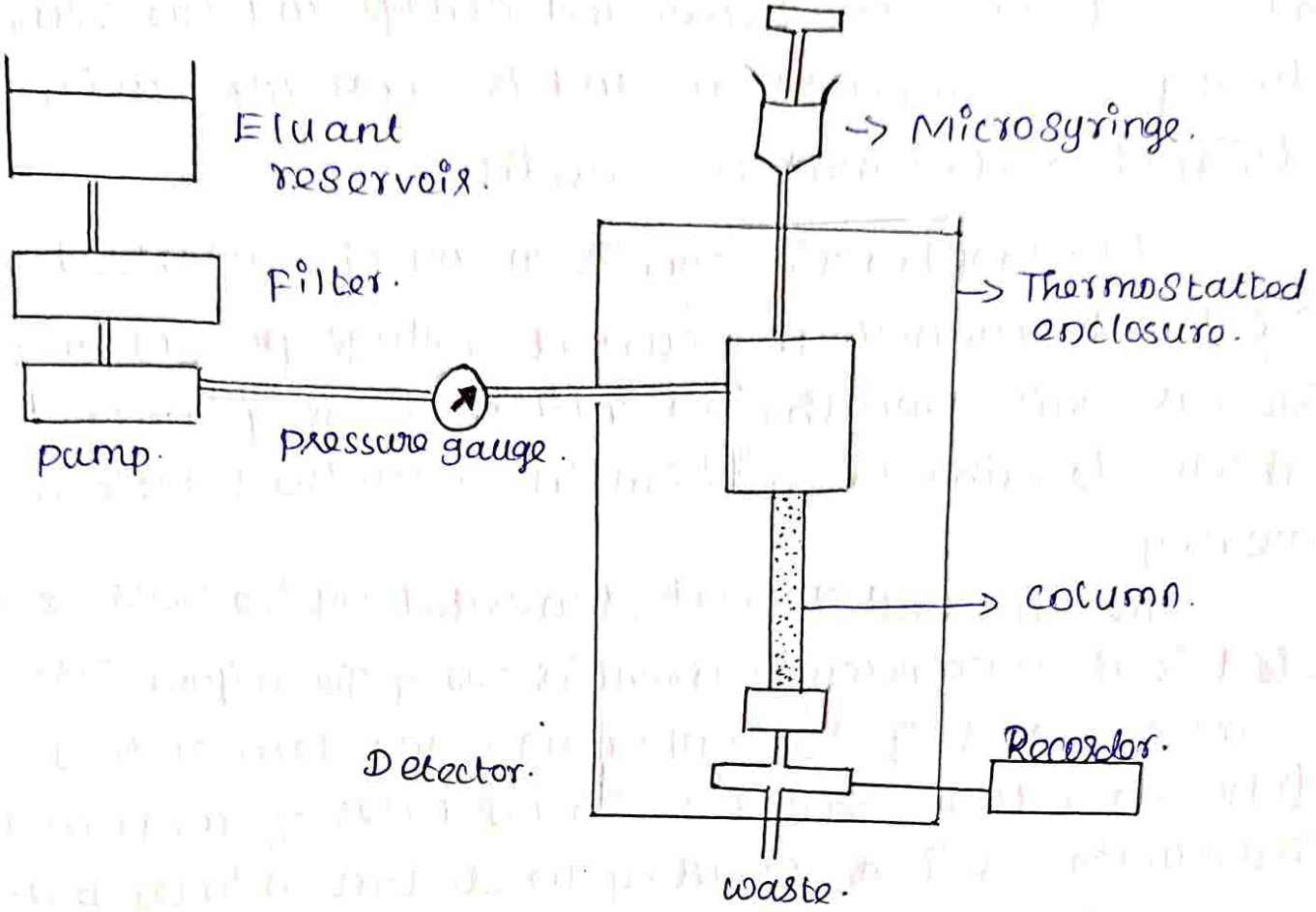
Gas Chromatography proved to be such a resounding success that a varsion that used liquid rather then gas as the eluent has been invented. The principle is much the same as in GLC.

However because liquids are more viscous than gases, the pressure used to make them pass through a column is greater then in GLC between 20 and 200atm

Such higher pressures required a strong column, which is often about 25 cm in length Fig shows you the scheme of the process.

The molecule coming off the column are detected by an ultraviolet spectrophotometer and the output appears an a series of peaks very much like the GLC charats Fig. owing to its accuracy HPLC has become very widely used in analysis.





2.2. Basic principles of Electrophoresis.

Electrophoresis.

Principles.

Electrophoresis is a general term that describes the migration and separation of charged particles (ion) under the influence of an electric Field. An electrophoresis system consists of two electrodes of opposite charge (anode, cathode) connected by a conducting medium called an electrolyte. The separation effect on the ionic particles results from differences in their velocity (v), which is the product of the particle's mobility (m) and the field strength (E)

$$1V = mE.$$

The amount of protein can be measured either by using densitometer or by cutting the spot and dissolving the protein in suitable solvents and estimating the amount of proteins by colorimetry.

Electrophoretic Mobility.

It is the observed rate of migration of a component (v) divided by electric field strength (E) in a given medium. The symbol u applies to entities B. It is also used for friction coefficient.

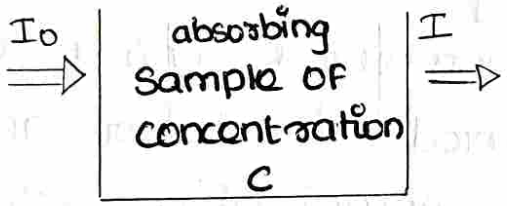
Electrophoresis is a general term that describes the migration and separation of charged particles (ion) under the influence of an electric field. An electrophoretic system consists two electrodes of opposite charge (anode, cathod) connected by a conducting Medium called an electrolyte.

UNIT - III

1) Theory of colorimetry and spectrometry

Beer - lambert's law

When a beam of monochromatic radiation of a suitable frequency passes through a solution, it is absorbed by a solution. As a result, the intensity of the light when it finally emerges from the solution is considerably reduced.



$$I = I_0 e^{-kCx}$$

where, I = Intensity of the emerging light.

I_0 = Intensity of incident radiation.

c = Concentration of the solution.

k = Constant

x = Thickness of the solution.

limitations of Beer-lambert's law

1) Beer-lambert's law is not obeyed if the radiation used is not monochromatic.

2) This law only applicable for dilute solutions.

3) The temperature of the system should not be allowed to vary to a large extent.

a) It is not applied to suspensions.

b) Deviation may occur, if the solution contains impurities.

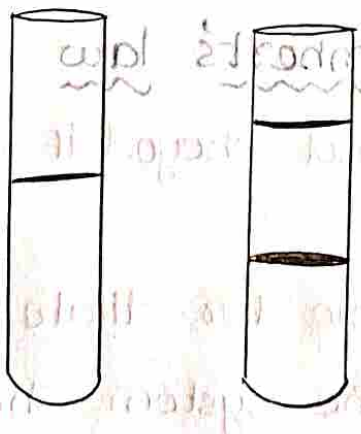
b) Deviation also occur if the solution undergoes polymerization or dissociation.

VISUALS COLORIMETER.

Standard series Method (Nessler's Method)

The unknown solution is taken out a 5ml or 100ml Nessler tube and made up to the mark. The solution is throughly mixed. The colour of the unknown solution is compared with a series of standard solution prepared with known amounts of the ion under analysis. The concentration of the unknown solution is known solution whose colour is matches exactly.

If the colour is not exactly match, further series of standard solution is prepared until an match is available.



Balancing Method

Balanced method is used for visual colour Balancing. For this method, Dubosque colorimeter is used.

The unknown solution is taken into a cylinder with a transparent base.

The standard solution is taken into a second cylinder. A transparent plunger is kept in each cylinder.

The plungers are moved up and down until the colours seen from the top of each become identical.

From the readings of the depth samples, the concentration of the unknown can be evaluated.

When the colours of unknown and standard are equal in intensity, the absorbance in each arm is same.

I_0 and I are same in both beams.

Applying the Beer's law to the two solutions,

$$A = -\log \frac{I}{I_0} = \varepsilon l_1 c_1$$

$$A = -\log \frac{I}{I_0} = \varepsilon l_2 c_2$$

$$\Rightarrow \quad \varepsilon l_1 c_1 = \varepsilon l_2 c_2$$

$$l_1 c_1 = l_2 c_2$$

In the above equation l_1 & l_2 can be measured and C_1 concentration of standard solution is also known

∴ C_2 the concentration of the coloured component in the sample can be calculated by the equation

$$C_2 = \frac{l_1 C_1}{l_2}$$

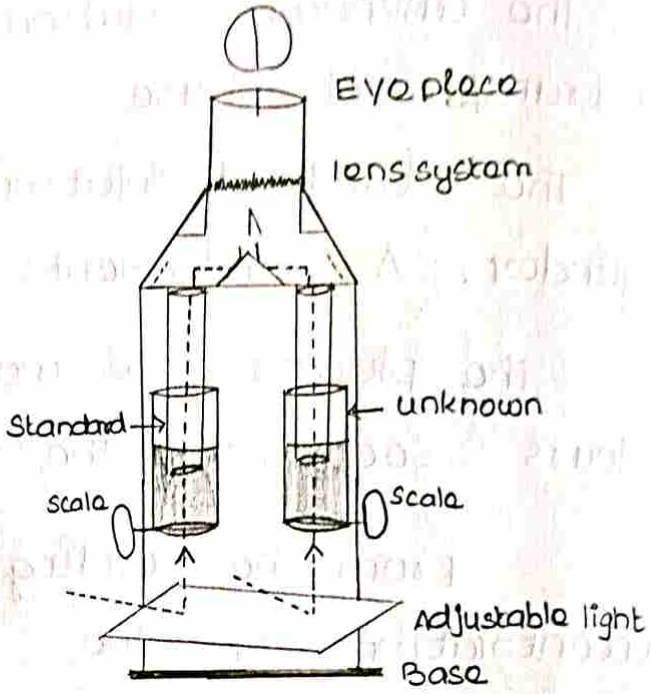


PHOTO ELECTRIC COLORIMETRIC METHOD

Estimation of IRON (Fe)

Reagents

1) Standard Iron Solution

0.865 gm of A.R. Ferric Ammonium sulphate is dissolved in water, 10 ml of con. HCl is added and the solution is diluted to 1 ltr. 1 ml of this solution contains 0.1 mg of Fe.

2) potassium thiocyanate solution

20 g of A.R. potassium thiocynate is dissolved in 100ml of water

3) con. HCl

procedure

Standard Iron solution is taken at various concentration in series of test tubes. 1ml of con. Hcl and 0.5 ml of potassium thiocynate are added to all the tubes.

The volume in all the test tubes are adjusted to 10 ml with de-ionized water. The blank is prepared by adding the same quantities of Reagents to de-ionized water.

The red coloured developed is measured at 540 nm in a photoelectric colorimeter.

A standard graph is obtained by plotting the Absorbance against the concentration.

From the standard graph, the amount of iron in the unknown solution is calculated.

Estimation of Nickel (Ni)

Reagents:-

1) Standard Nickel solution

0.673 g of pure ammonium nickel sulphates is dissolved in water & diluted to 1 Ltr.

1 ml of of this solution contains 0.1 mg of Ni.

This solution is further diluted to a basis of 0.01 mg of Ni per ml.

2) 1% dimethyl glyoxime solution

3) Saturated bromine water.

4) NH_4OH solution.

procedure

Standard nickel solution is taken at various concentration in a series of test tube.

2ml of bromine water, 2 ml of ammonium hydroxide & 1 ml of 1% dimethyl glyoxime are added to all the test tubes.

The volumes in all the test tubes are adjusted to 10ml with de-ionised water.

The colour developed is measured at 445 nm in a photoelectric colorimeter.

A standard graph is obtained by plotting the absorbance against the concentration.

The unknown solution is diluted to an definite volume in a standard Flask.

known volumes of solutions are treated in the same way as that of the standards and the absorbance measured. From the standard Graph, The amount of Ni in the unknown

Solution is Calculated.

Estimation of Tin

Reagents

Standard Tin Solution

Transfer 0.2000 g of pure tin metal into a 100 ml beaker, add 10 ml of sulfuric acid and heated to dissolve the metal completely.

Cool to temperature, transfer to a 1000ml volumetric Flask, Dilute the mark with HCl and mix.

Transfer 10 ml of this solution to a 1000ml volumetric flask again dilute to the mark with HCl and Mix.

phenyl Flurone Solution

Transfer 0.5000 g of PhenylFlurone into a 200 ml beaker.

Add 100 ml of Ethanol and 10 of HCl stir until complete dissolution. Transfer to a 500 ml Volumetric Flask, dilute to the mark with ethanol, and mix.

Hydrochloric acid - Citric acid Solution

Dissolve 10g of Citric acid in a small volume of water to which 30 ml of HCl has been added.

Transfer to a 100ml volumetric flask, dilute to the mark with water, and mix.

DTMAB Dissolve 10g of DTMAB in 500ml of water

procedure

Standard procedure follows the basis of JIS Method.

Transfer 5 ml of standard tin solution into a 50ml volumentric flask. Add potassium permanganate solution until the solution into turned slightly red.

Stand for several minutes to allow tin to be oxidized.

Add 0.1g of ascorbic acid mix to reduce the Excess potassium permanganate

Add 5 ml of HCl & citric acid solution, then a certain volume of ammonia water and then 5ml of PVA solution.

Add 10 ml of DTMAB solution. 5ml of phenyl Fluorone solution, and dilute to the mark, stand for 20 min.

Transfer a portion of this solution to a 1.0cm cell and measure the absorbance at 510nm against a reagent blank.

Vary the concentrations of Hcl - citric acid, PVA, DTMAB & phenylFluorone to find the optimal conditions

for the maximum absorbance.

Estimation of lead

Reagents:- Standard lead solution. Dissolve 0.160g of analytical grade lead nitrate in 1l of distilled water. 100ml of this solution, diluted to 250ml gives a working solution containing 4µg of Pb mL^{-1}.

Dithizone reagent Dissolve 5mg of the solid in 100 mL of Chloroform

Ammonia-cyanide-Sulphite solution prepared by diluting 35 mL of concentrated Ammonia solution and 8.0mL of 10 percent potassium cyanide solution to 100ml and adding 0.15g of sodium sulphite.

procedure:- 100 mL of the working Pb solution in a 250 ml separatory Funnel, add 75 mL of the Ammonia-cyanide-Sulphite solution and then by the addition of HCl acid adjust the pH of the solution.

This operation must be carried out slowly.

IF the pH of the solution falls even temporarily below 9.5, HCN may be liberated and use

of a fume cupboard is necessary.

Now add 7.5ml of the dithizone reagent to the seperatory funnel, followed by the further 17.5ml of chloroform.

Shake for one minute, allow the layers to seperate, then remove the chloroform layer.

Measure the absorbance of this against a blank solution, using a 1cm cell and a wavelength of 510nm

Repeat the procedure with 5.0ml, 7.5ml and 15.0ml portions of the working lead solution and then with 10ml of the test solution.

Spectrofluorimetry

Reagents, solutions and Experimental procedure for the estimation of Aluminium.

Reagents

Standard solution of aluminium. Dissolve 1.760g aluminium potassium sulphate crystals in distilled water, add 3mL concentrated sulphuric acid, and dilute to 1L in a graduated flask.

pipette 10.0mL of this solution into a little water, add 2.0 ml concentrated sulphuric acid, and

dilute to 1L with distilled water. This Solution contains 0.00100 mg aluminium per L.

Ammonium acetate Solution, 10 percent, Dissolve 25g of the pure salt in water and dilute to 250 mL.

Dilute Sulphuric acid. Add 25 mL concentrated H_2SO_4 to 200 mL water, cool and dilute to 500 mL in a graduated flask.

Eriochrome blue black Rc, 0.1 per cent, prepare a 0.1 % Solution in 90% Ethanol.

procedure

Into 100mL graduated flasks, each containing 10mL of the ammonium acetate Solution,

1 mL of the dilute H_2SO_4, and 3mL of the Orichrome blue black RC solution, run in from a burrette of the standard Aluminium Solution.

Dilute each of the above solutions with distilled water, and adjust to a PH of before making up to the 100 mL mark. Stayed Still for one hour.

measure the Fluorescence of each of the above solutions at 590nm, using the containing 0.005 mg mL Al as Standard.

The use of a primary filter will depend upon the Quality of the eriochrome blue black Rc. It can be dispensed with.

The secondary filter may be a chance for a locark instrument.

Draw a calibration curve, plotting instrument Readings against concentration of Al.

Determine the number of Mg of Al per L in an unknown solution utilising the calibration curve.

Reagents, solutions and Experimental procedure of the estimation of Cadmium

Reagents

2- Benzoxazole solution. Dissolve 1.0g of the solid reagent in 1L of 95% Ethanol.

Standard Cadmium ion solution. prepare a standard Cadmium ion solution containing 0.04mg mL^{-1} Cd using hydrated Cadmium Sulphate.

Solutions for Calibration curve with Fluorimeter

prepare the Cadmium Complex of the reagent by precipitating it from a solution of

pure cd salt as follows.

Introduce a large excess of sodium tartrate, warm to 60°c, adjust the pH by the addition of 0.5 M sodium hydroxide, add a slight excess of Reagent and digest at 60°c for 15 mints.

Filter on a sintered - glass crucible wash with 50% Ethanol to remove excess of the Reagent, and dry at 130 - 140°c for 1-2 hours.

weigh out 0.2371 g of the complex & dissolve it in 1L of glacial acetic acid.

Remove volumes of the acetic acid solution equivalent to cd and dilute each to exactly 50mL with glacial acetic acid.

procedure

Aqueous solution of the sample containing from 2 mg of cd and about 0.1g of ammonium titrate.

Add an equal volume of 95% Ethanol warm to 60°c, treat with a slight excess of the reagent solution.

wash 80-85% Ethanol containing a trace

of ammonia, and dry the precipitate at 130°C for 45 minutes.

Dissolve the ppt in 50.0ml of glacial acetic acid, and measure the fluorescence of the solution as in the calibration procedure. Evaluate the cd content from the calibration curve.

Reagents, solutions and Experimental procedure of the estimation of Calcium.

Reagents

Standard Calcium Solution

prepare a standard solution containing 40 mg calcium by dissolving the calculated quantity of calcium carbonate in the minimum amount of HCl acid diluting to 1L in a graduated flask.

Calcein solution Dissolve sufficient calcein, or its disodium salt, in the minimum amount of 0.40M potassium hydroxide solution and dilute with water to give concentration of 60 mgL^{-1} in a graduated flask.

A small amount of EDTA solution may be needed in the calcein solution to achieve balancing of the blank on the Fluorimeter.

This is only necessary in those cases in which the Potassium hydroxied used is found to

contain a small amount of Ca impurity.

Aqueous solution of Calcein are not stable for longer than 24 h and should be kept in the dark as much as possible.

potassium hydroxide solution. prepare 0.04M KOH solution by dissolving solid KOH in de-ionised water and make up to 1L in a graduated flask.

procedure

prepare a series of calcium ion solutions covering the concentration by adding sufficient of the 40mg calcium standard to 25mL graduated flask each containing 5.0mL of 0.4M KOH solution and 1mL of Calcein solution.

Dilute each to 25mL using de-ionised water.

Determine the fluroscance for each solution at 540nm with excitation at either 330nm or 480nm, and plot a calibration curve.

prepare the sample solution in a similar manner to give a fluroscance value falling within the range of the caliboration curve, & hence obtain the original concentration in the sample.

Reagents, Solutions and Experimental procedure for the estimation of zinc.

Reagents

Standard zinc Solution dissolve 4g aqurate zn shot in 35 ml concentrated Hcl, and dilute with distilled water to 1L in a graduated flask.

pipette 10 ml of the solution into a 1 ltr graduated flask and dilute to the mark with distilled water.

8 - Hydroxy Quinoline solution: 5%. dissdve 5g oxine in 12g glacial acetic acid and dilute to 100ml with water.

Standard dichlorofluroscein Solution:

Add a 0.1% ethanolic solution of dichlorofluorescein dropwise to 1L of distilled greater than that produced by the most concentrated zinc solution to be investigated. About 1.0ml of dichlorofluorecein solution is required.

Gum Arabic Solution 2%. Grind finely 2g arabic in a glass mortar, dissdve it in water and dilute to 100ml. Filter if necessary.

Ammonium acetate solution, ca 2M Dissolve 15.5g crystalised ammonium acetate in water and dilute to 100mL.

paccedure

Calibrated burette of 25 ml of the standard zinc solution into separate 100mL graduated Flask.

To each Flask add 10ml of the ammonium acetate solution, 4mL of the gum arabic solution, dilute to about 45mL with distilled water.

Now add exactly 40mL of the solution dilute to the mark with distilled water, shake Gently, and transfer immediately to the cell of a Fluorimeter for measurement.

Employ the dichlorofluorescin solution as standaerd.

Use a chance 082 as primary Filter and 0y2 as the Secondary Flask.

commence measurement with the most concentered zinc Solution. It is important that the Fluorescence of the zinc.

use the calibration crave for the determining the zinc content OF test Solutions containing 0.5mg zinc L".

Unit-IV Gravimetry

4.1

Basic principle

Gravimetric analysis is an analytical technique by which one estimates the amount of a substance present in a given sample by determining the weight of precipitate obtained from that sample.

For example, to determine the amount of Lead present in a given solution it is treated with enough potassium chromate (reagent) solution to precipitate the Lead as Lead chromate completely. The precipitate is filtered off, dried and weighed. From the weight Lead chromate precipitate, amount of Lead present in the whole of the given solution is calculated.

Advantages of Gravimetric analysis :

I. Gravimetric analysis was used to determine the atomic masses of many elements to six figure accuracy.

II. It is accurate and precise when using modern analytical balance.

III. Possible sources of error are readily checked since filtrates can be tested for completeness of precipitation and precipitates may be examined for the presence of impurities.

IV. It is an absolute method ; it involves direct measurement without any form of calibration being required.

V. Gravimetry provides very little room for instrumental error and does not require a series of standards for calculation of an unknown.

Solubility product :

The solubility product of a sparingly soluble salt is the product of the concentration of its ion in the saturated solution. It is a constant at a given temperature. It is denoted as K_{sp}

Explanation

When a slightly soluble ionic solid such as silver chloride is placed in water. Ag^+ ions and Cl^- ion from the solid phase pass into solution till the solution become saturated, Now their exist an equilibrium between the ion presence in the saturated solution and the solid phase. Thus,

$$\underset{(\text{solid})}{AgCl} \rightleftharpoons \underset{(\text{in solution})}{Ag^+ + Cl^-}$$

Applying the law of chemical equilibrium the value of equilibrium the value of equilibrium constant.

$$K = \frac{a_{Ag^+} + a_{Cl^-}}{a_{AgCl}}$$

Since, the activity of a solid is taken as unity the above expression may be written as,

$$Ka_{AgCl} = a_{Ag^+} + a_{Cl^-} \quad (\text{or})$$

$$K_{sp} = a_{Ag^+} + a_{Cl^-}$$

K_{sp} is called solubility product.

Saturated and Super Saturated solution :

If to given amount of a solvent at a fixed temperature, we go on gradually adding a solute and stir the solution after each addition a stage will come when the added solute will not dissolve any

more but settle down at the bottom of the container. This solution is known as a saturated solution.

If 100 g of solvent is taken the amount in gram of solute has dissolved will be called the solubility of the substance in that particular solvent at given temperature. In a saturated solution. The dissolved substance is in equilibrium with the undissolved substance present at the bottom of the vessel. Sometime a solution contain greater amount of dissolved substance as compared to that present in a saturated solution such a solution is referred it as a super saturated solution. This state of super saturation is generally unstable and exists only for a short period of time.

Co-precipitation

The process of impurity precipitates getting precipitated with the precipitate being separated is called co-precipitation.

Eg. In the estimation of Barium ions by precipitating as Barium Sulphate, other Barium salts such as Barium nitrate and Barium chloride are occlude and precipitated along with Barium sulphate. Such process in known as co-precipitation.

Mechanism of Co-precipitation :

There are three forms of co-precipitation.

(i) Inclusion (ii) Occlusion (iii) Isomorphous replacement.

Inclusion :

It is a process of impurities being randomly distributed in the form of individual ions or molecules throughout the crystal.

Occlusion

* It is a non-homogeneous distribution of impurities, numerous ionic or molecular impurities present within the imperfect crystal lattice of the precipitate.
* This will occurs when whole droplets of solutions containing impurities are trapped by a rapidly growth crystal.
* Contaminants are located within the crystal and therefore washing will not remove these impurities from the precipitate.
* This can be studied by lower precipitation rate, when precipitation is slow the impurities will have sufficient time to escape form precipitate before they become entrapped.
* The contamination by occlusion can be eliminated by keeping several hours of digestion.

Isomorphous replacement

An ion in a crystal of the precipitate may be replaced by an impurity ion of similar size and shape. This phenomenon is called as **Isomorphous replacement.**

This impurity is permanently incorporated in the crystal lattice and cannot be removed by washing. Removal of this ion takes part by isomorphous replacement or to dissolve the precipitate and reform it under favourable conditions.

For example, $BaSO_4$ will get contaminated with alkali metal ions. The Isomorphous replacement can be achieved by K^+ ion.

Methods to minimize co-precipitation:

✓ The solution from which precipitation is carried out should be diluted.

✓ The precipitant is added in small quantity with constant stirring, so that the precipitation takes place as slowly as possible.

✓ precipitation should carry out in hot condition. So that, solubility increased. formation of colloidal particles would be decreased and the attraction between the precipitate and impurity would also be decreased.

✓ Occlusion can be controlled by drying precipitate at high temperature and by slowing the crystal growth.

Post Precipitation

Post precipitation is "the precipitation of an impurity from its supersaturated solution sometime after the appearance of the substance to be estimated as precipitate".

Eg. When calcium is determined as calcium oxalate, if the solution contains magnesium ions, magnesium oxalate will be precipitated slowly on calcium oxalate. This post-precipitation is greater when precipitate is kept in contact with the mother liquor. It occurs with sparingly soluble substances which forms supersaturated solutions. These substances usually have an ion in common with the primary precipitate.

Differences between Co-precipitation and Post-precipitation

Co-precipitation	post- precipitation
It decreases, when precipitate is kept in contact with the mother liquor.	It increases, when precipitate is kept in contact with the mother liquor.
It decreases, when the solution is stirred or heated.	It increases, when the solution is stirred or heated.
The amount of the substance co-precipitated is fare less.	The amount of the substance post-precipitated is much more.

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Digestion of Precipitate

Digestion is carried out by allowing the precipitate to stand for several hours (sometimes even for a day) at room temperature or at higher temperatures in contact with the solution from it was formed.

Effect of Digestion:

- ✓ Digestion promotes complete precipitation in a form which can readily be filtered.
- ✓ During digestion small particles tend to pass into solution and then redeposit on the large particles.
- ✓ It promotes the formation of regular crystal shape with lesser surface area. Hence co-precipitation by adsorption would be less.
- ✓ During digestion the impurities trapped in some pockets may also escape from these places, making precipitate less impure.

Precipitation From Homogeneous Solution

This is a technique that the precipitant is not added, but it is slowly generated by a homogeneous reaction within the solution.

Eg. Barium can be precipitated as Barium Sulphate from a homogenous medium using sulphonic acid. Sulphamic acid slowly generate sulphate ion (SO_4^{2-}) on hydrolysis.

$$\underset{\text{Sulphamic acid}}{NH_2SO_3H} + H_2O \longrightarrow NH_4^+ + H^+ + SO_4^{2-}$$

Sulphamic acid added a solution containing Ba^{2+} ions is slowly hydrolyzed and precipitates $BaSO_4$ gradually.

Advantages / superiority

* The precipitate obtained in this technique is dense and easily filterable.
* Minimum co-precipitation is obtained; this can be minimized by varying rate of reaction. The slower is the reaction, the larger are the crystals formed.
* Precipitation obtained from homogenous solution is an excellent way of enhancing the purity of a precipitate.

Precipitants (or) Characteristic of precipitating agent :

A reagent added to a solution of a substance to be estimated, so as to precipitate that substance is called a precipitating agent or precipitant.

For example, to estimate of Barium in a solution of Barium chloride we use potassium chromate solution. Thus potassium chromate solution is the precipitant.

An ideal precipitating agent or precipitant should react specifically with ion or substance to be estimated gravimetrically and give following precipitate,

✓ Precipitate has sufficiently low solubility so that losses due to solubility of the solid are negligible.

✓ It will becomes readily filtered and washed free of contaminants.

✓ It should unreactive and of known composition after drying or ignition.

Choice of Precipitants :

A precipitant is a reagent added to a solution containing the constituent being determined to form precipitate with that constituent.

Eg. Nickel precipitated as Ni-DMG : here

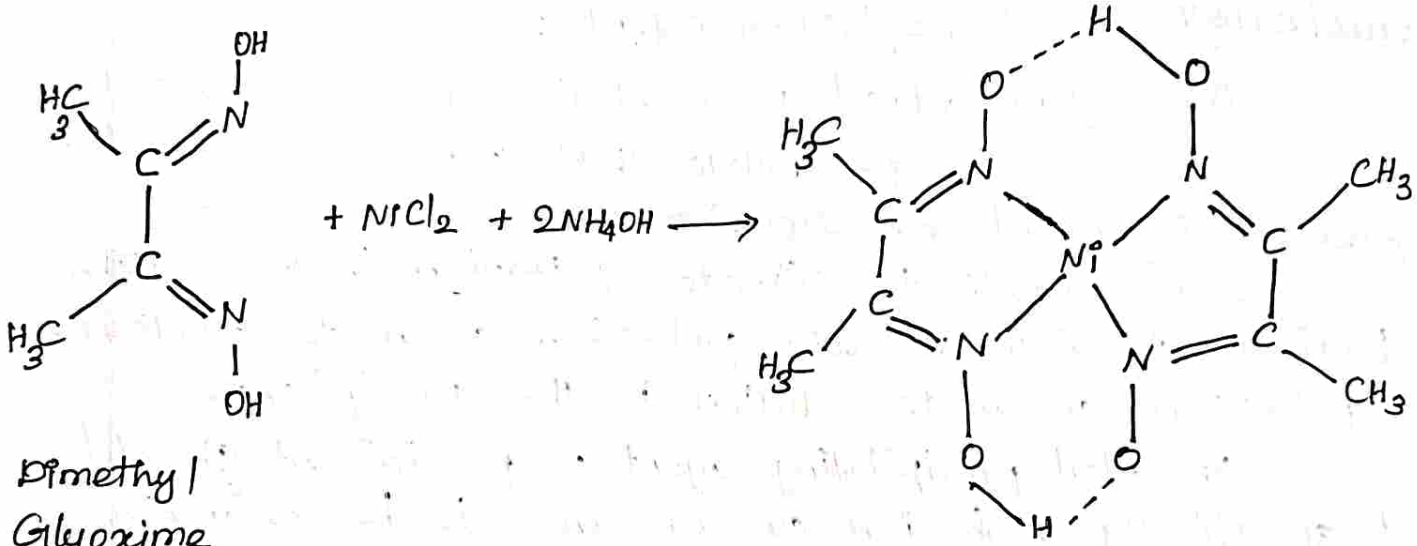
Dimethyl Glyoxime (DMG) is a precipitant.

Specific precipitants :

Specific precipitants are used to separate a particular metal ion or a substance form a mixture of a solution. This is an ideal case and no specific precipitants in reality. However, some precipitants may use nearly specific.

1) Dimethyl Glyoxime (DMG)

It is specific precipitants for estimating nickel (in alkaline medium) and Palladium (in acid solution).

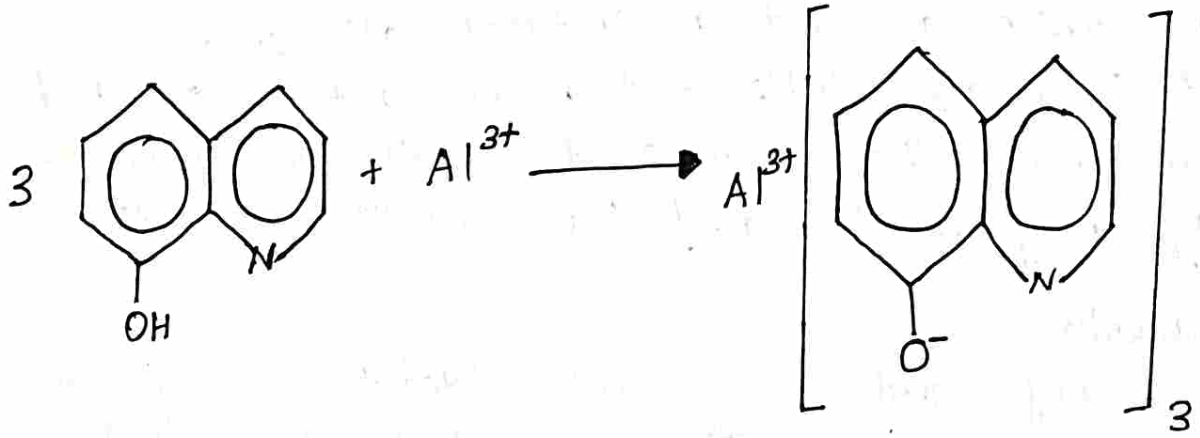


Dimethyl Glyoxime (DMG)

Nickeldimethyl glyoxime (Bright red precipitate)

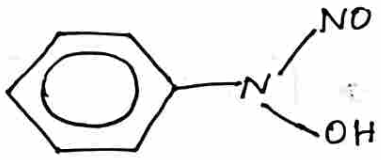
2) Oxine (8-Hydroxyquinoline)

It is used to estimate aluminium from a solution with p^H around 3. About 24 cations give precipitates with oxine. Mg, Cu and Zn are some other metals that precipitated by oxine. The solubilities of metals oxinates vary from cation to cation and are pH dependent. By controlling a p^H degree of selectivity can be achieved.



3) Cupferron :

N-nitroso-N-phenylhydroxylamine is known as Cupferron. It is used to estimate Cu(II) and Fe(II) ion in cold aqueous acid medium.



4) Salicylaldehyde oxime :

It is used to estimate Cu(II) in presence of acetic acid at pH 2.6.

5) Nioxime :

It is cyclohexane-1,2-dioxime used to estimate Palladium.

6) Ethylene Diamine :

It is 1,2-Diaminoethane used to estimate Cu(III), Hg(II) and Cd(II) ions.

Selective Precipitant

Selective precipitants precipitate a small group of ions from solutions containing several ions. Most of the gravimetric precipitants are only selective.

Example,

OH^- precipitates a few metal ions as their

hydroxides from a solution containing several metal ions. The metal ions which are not precipitated also from hydroxides but they are soluble and so are not precipitated S^{2-}, CO_3^{2-} are some other examples of selective precipitants. The selectivity may be increased by controlling conditions.

Sequestering agents

Sequestering agents are reagents added to eliminate the interference by a substance in estimation. They are also called Masking agents.

If we want to estimate Mg^{2+} ions gravimetrically in presence of Cu^{2+} using oxine, then we have to eliminate Cu^{2+}. For this we use CN^- which forms a soluble complex with Cu^{2+} as shown below.

$$Cu^{2+} + 4CN^- \longrightarrow [Cu(CN)_4]^{2-}$$

Thus Cu^{2+} is prevented from reacting with oxine. Now CN^- is the sequestering or masking agent.

The process of eliminating an ion or substance using a chemical agent so that it does not interfere in the elimination of another ion or substance is called sequestration.

Uses :

1. Mg^{2+} can be estimated gravimetrically with oxine in presence of Cu^{2+} using CN^- as the sequestering agent.
2. Ca^{2+} can be estimated with suitable reagent in presence of Cu^{2+} using cyanide ion as sequestering agent.
3. In the presence of EDTA, beryllium may be precipitated with ammonia in presence of chromium, cobalt, cadmium, iron, copper, lead, manganese, zinc, aluminium, bismuth etc.
4. Uranium can be separated from numerous other ions by precipitation with oxine from an EDTA

solution at pH 5·3.

5. Copper has been masked with EDTA in the polarographic determination of antimony in alloys.

6. Precipitate of soaps as their calcium and magnesium salts by hard water can be checked by transforming these metals into soluble complexes of EDTA.

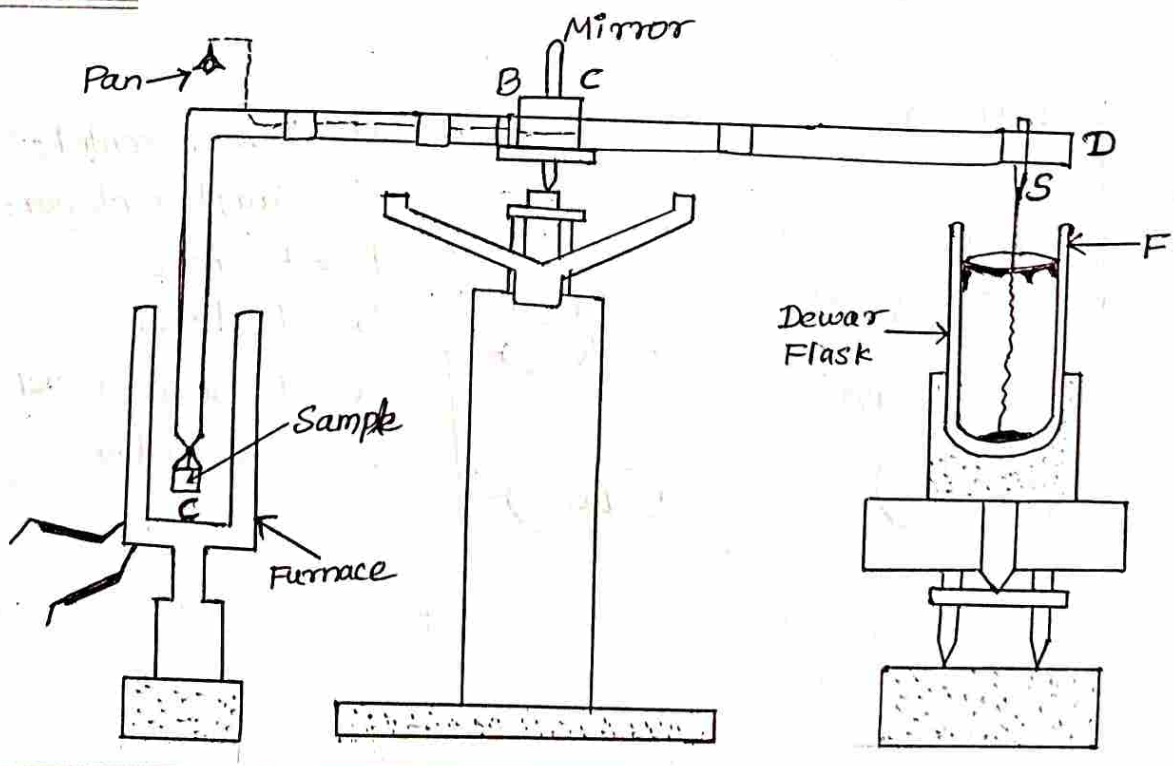
4.2 THERMOGRAVIMETRIC ANALYSIS (TGA)

Principle

Thermogravimetric Analysis (TGA) technique is based on the principle that, increasing a temperature at a constant rate for a known initial weight of the substance and changes in weight are accurately recorded at different times.

Resulted weights are plotted against temperature a curve characteristic of the substance studied is obtained. This curve is called Thermogravimetric curve (TG curve) or a thermogram.

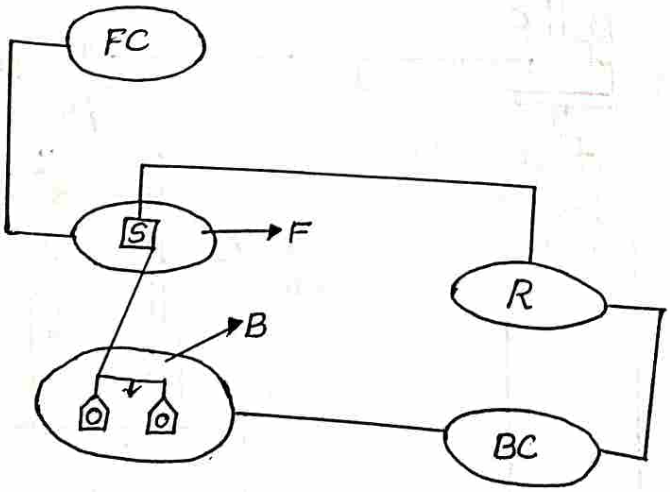
Instrumentation



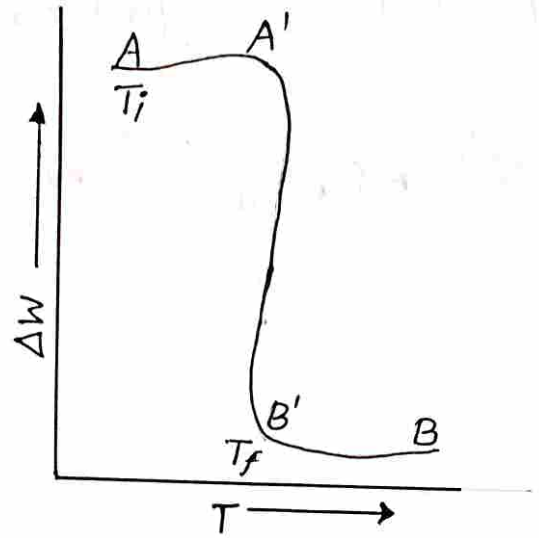
TGA thermo balance consists of i) a furnace ii) a precision thermo balance and iii) a recorder.

AB and CD are two arms of the balance beam. The platinum crucible (C) suspended with platinum wires from A. The spiral (S), attached to D and the bottom of a Dewar flask (F) prevents oscillation of the beam during heating. This arrangement acts as a damper. The sample temperature is measured by platinum thermo couple. Changes in weights are found out by finding the beam deflection on adding a known weight to the pan.

The sample is kept in a crucible C which is inside a furnace. The furnace temperature is raised at a slow and steady state. A platinum thermo couple is used to measure sample temperature. It regulates the furnace temperature continuously and sends signals to the recorder. A recorder is a device with a pen and graph sheet. It records weight change in the y-axis and signals from thermocouple on the x-axis. We get a thermogram.



FC = Furnace control;
S = Sample container;
F = Furnace;
B = Balance
BC = Balance control
R = Recorder



ΔW - Weight change

Precautions needed in the use of Thermobalance

1. The hot zone of the furnace should be uniform to within 15°C and for reasonable length.
2. The crucible must always be located within the hot zone.
3. Conducting and magnetic samples must not interfere with the furnace electrical winding.
4. The heating rate should be linear and reproducible.
5. Radiation and convection currents from the furnace must not affect the weighing unit.

Characteristic of TGA curves :

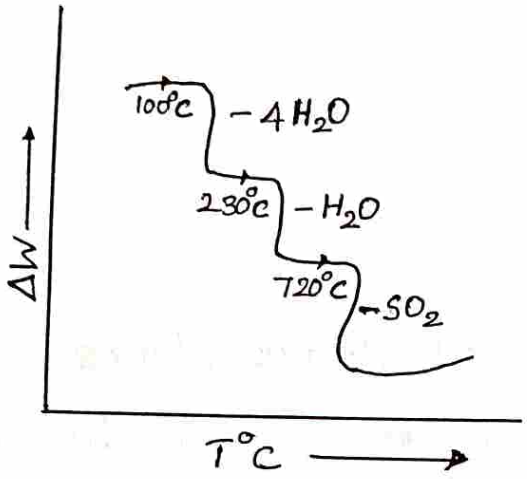
The TGA curves are characterized by breaks (A'B') and plateaus (A, A' and B', B). Each break corresponds to some loss in weight due to evolution of H_2O, CO, CO_2 etc. and plateaus corresponds to the formation of stable compounds.

For, example, the TGA curve of $CuSO_4 \cdot 5H_2O$ at above 100°C it loses four molecules of water and become pale blue monohydrate $CuSO_4 H_2O$. At about

230°c it becomes white anhydrous $CuSO_4$. Anhydrous $CuSO_4$ decomposes at about 720°C to give CuO and SO_2.

$$CuSO_4 5H_2O \xrightarrow{100^\circ C} CuSO_4 H_2O \xrightarrow{230^\circ C} CuSO_4 \xrightarrow{720^\circ C} CuO + SO_2$$

Blue — pale Blue



ΔW = Weight change T = Temperature

Applications of TG Curve :

i) The TG curve is quantitative, so stoichiometric calculations can be done at any given temperatures.

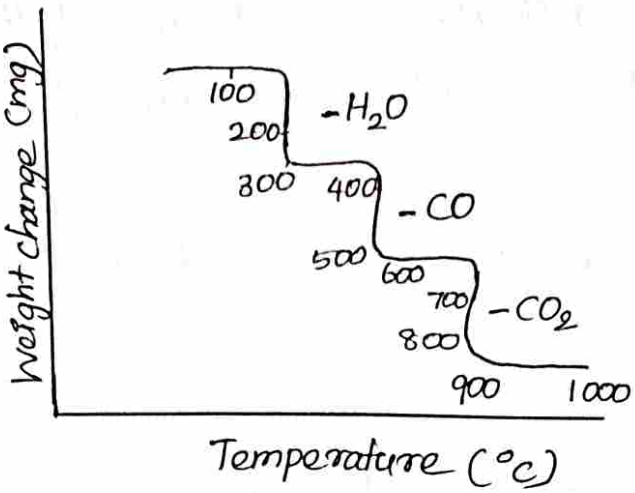
ii) To correct drying temperature of precipitates in gravimetric analysis can be determined.

iii) TGA is used to find out suitable analytical standard substances such as EDTA, NaF etc.

iv) Thermobalance is used to determine the purity of various substances.

Application of TGA for Calcium Oxalate Monohydrate

The thermogram for the compound Calcium Oxalate Monohydrate shows, water is evolved at about 100°C plateaus, anhydrous salt is formed at about 250°C. Calcium carbonate is present between 500°C to 600°C. Calcium carbonate is present at above 870°C.



$$CaC_2O_4 \cdot H_2O \xrightarrow{100^\circ C} CaC_2O_4 + H_2O$$

Calcium Oxalate Monohydrate → Calcium Oxalate + water

$$CaC_2O_4 \xrightarrow{500-600^\circ C} CaCO_3 + CO\uparrow$$

Calcium Oxalate → Anhydrous Calcium Carbonate salt + CO↑

$$CaCO_3 \xrightarrow{\text{above } 878^\circ C} CaO + CO_2\uparrow$$

Calcium Carbonate → Calcium Oxide. + CO_2↑

DIFFERENTIAL THERMAL ANALYSIS (DTA)

Principle

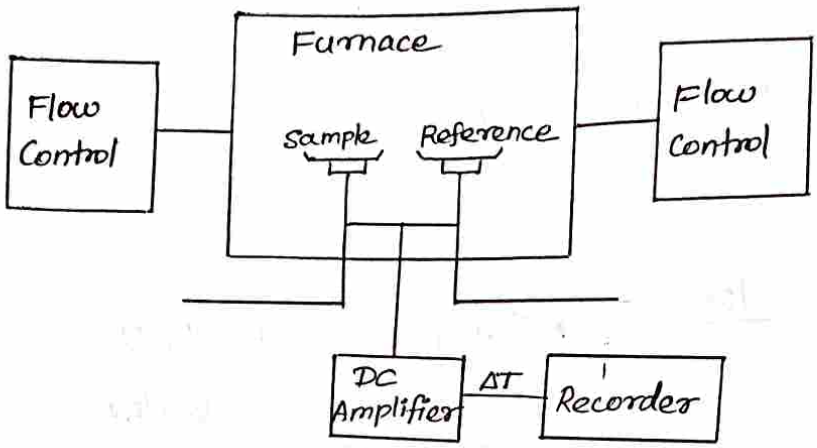
The substance to be analysed and an inert reference (like α-alumina) are heated or cooled in a suitable environment and a controlled rate.

If the temperature of the substance will be lower than that of the reference it may undergo endothermic change like when it melts or dehydrated. If the temperature of the substance will be higher than that of the reference it may undergo exothermic change. If the substance does not undergo any heat change, there will be no difference between substance to be analysed and the reference

material. These temperature difference (ΔT_s) are plotted against temperature or time, we get DTA curve.

Instrumentation

The DTA instrument consists of the following components



(i) Sample or reference holders with thermocouple assembly

These are used to hold the sample to be analyzed and an inert reference. The thermocouple assemblies are inserted separately.

ii) A furnace assembly

This set up is used to heat the sample to be analyzed and reference.

iii) A furnace power programmer and controller

This can be used to increase the furnace level and substance block temperature at a linear rate (5-12° C/min). This is done either by increasing voltage through the heater or by a thermocouple.

iv) Flow controller system:

Flow controllers continuously control the difference in temperature between the sample and the reference.

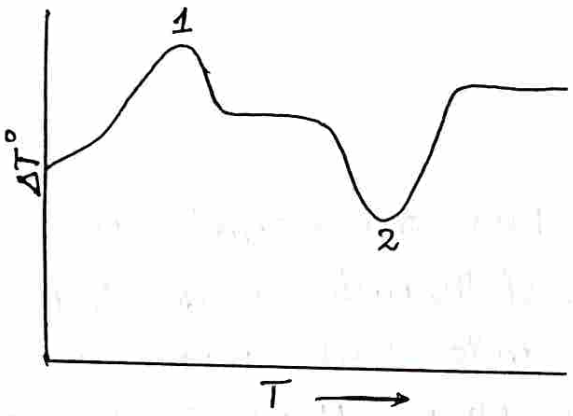
v) DC amplifier and recorder

The signals got from the thermocouple are

amplified by about 1000 times and the difference signal is recorded on the Y-axis of millivolt recorder. The temperature of the furnace is measured by a separate thermocouple and is recorded on the X-axis.

Characteristics of DTA curves

In DTA, a plot is made between ΔT and Temperature or time. A typical DTA curve is shown in figure. From the shape and size of the peaks we can get information about the nature of the test sample.

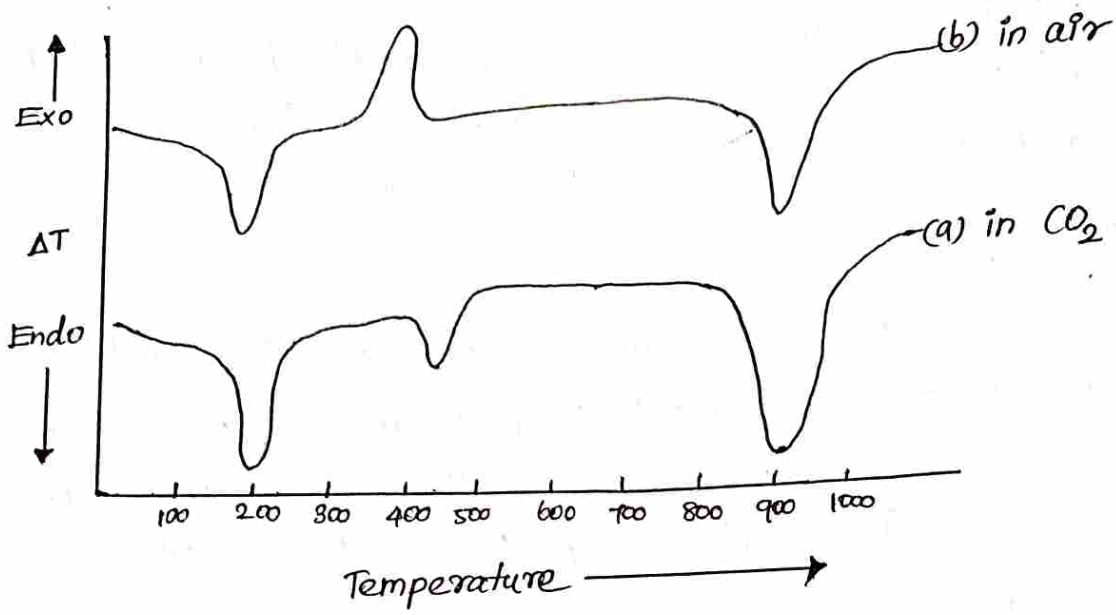


(1) Exothermic peak
(2) Endothermic peak

* The sharp endothermic peaks show the changes in crystallinity or fusion processes.
* The Broad endothermic peaks indicate the dehydration reaction.
* The endothermic curves results physical changes in the sample.
* Chemical reactions like oxidation are exothermic.

DTA curve for Calcium Oxalate Monohydrate

The DTA of Calcium Oxalate Monohydrate in two different atmospheres i.e. air and CO_2 is shown in figure.



In air

we get three peaks : Two endothermic peaks and one exothermic. The first endothermic peak indicates elimination of H_2O. The exothermic peak corresponds to the endothermic peak in CO_2 atmosphere. Here CO is eliminated and this is oxidized to CO_2 which is exothermic. The second endothermic peak corresponds to elimination of CO_2.

In CO_2

Here we also get three endothermic peaks. These correspond to the successive elimination of H_2O, CO and CO_2 respectively. These reactions require energy to break the bonds and thus are endothermic

Applications of DTA

1. DTA is very useful in the identification of dyes and melting point of substance.
2. It is used for the quality control of a

large number of substances like cement, glass, textiles, explosives etc.

3. This technique is used to study the thermal stability of inorganic compounds and complexes.

4. It is used to assign heating range of precipitates in gravimetric analysis.

UNIT - V

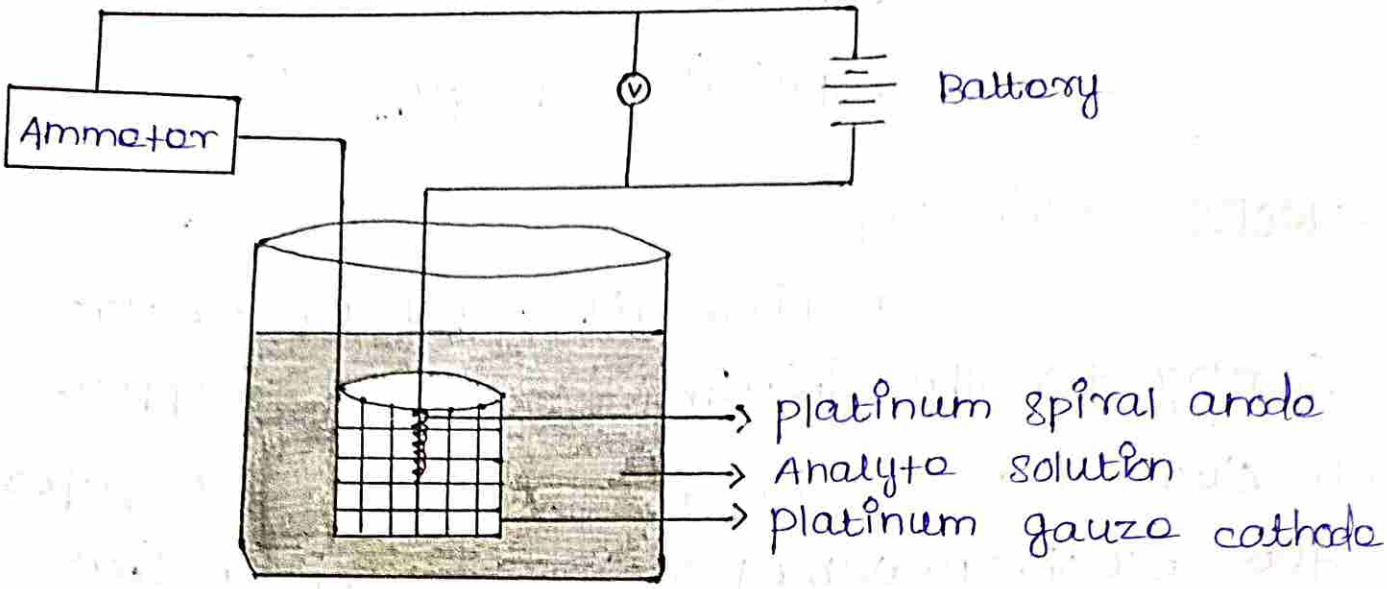
Electro - analytical techniques

5.1. Electro - gravimetry :-

Luckow first discovered the electro gravimetry for the determination of the copper. Then Alexander classon first published the paper on the electrogravimetry in 1881. After that, Gibb's was the first founder of the electro gravimetry for the deposition of the metals on the mercury cathode. Electrogravimetry is a method for the separation of the metal ions by using the electrodes. the deposition takes place on the one electrode. the weight of this electrode is determind before and after deposition. this gives the amount of the metal present in the given sample solution.

Principle :-

The main principle involved in this method is the deposition of the solid on an electrode from the analyte solution.



The material is deposited by means of potential application. the electrons are transported to electrode by the following mechanism:

- Diffusion
- Migration
- convection

Theory of Electro-gravimetry:

A metal is electrolytically deposited on the electrode by increasing the mass of the electrode.

$$M^{+2} + 2e^- \longrightarrow M(s)$$

therefore,

$$E_{electrolysis} = E_{cathode} - E_{anode}$$

The electrons deposition is governed by ohm's and Faraday's laws of electrolysis which states that the amount of the electrons deposited on the electrode is directly proportional to the amount of the current passed through the solution and the amount of different substance deposited is directly proportional to the molar masses divided by the number of electrons involved in the electrolysis process.

That is the current (I) is directly proportional to the electromotive force (E) and is indirectly proportional to the resistance (R).

$$E = IR$$

From the above equation, we get the following:

$$E_{electrolysis} = E_{cell} - IR$$

$$E_{cell} = E_{cathode} - E_{anode}$$

where

Therefore,

$$E_{applied} = E_{cathode} - E_{anode} - IR$$

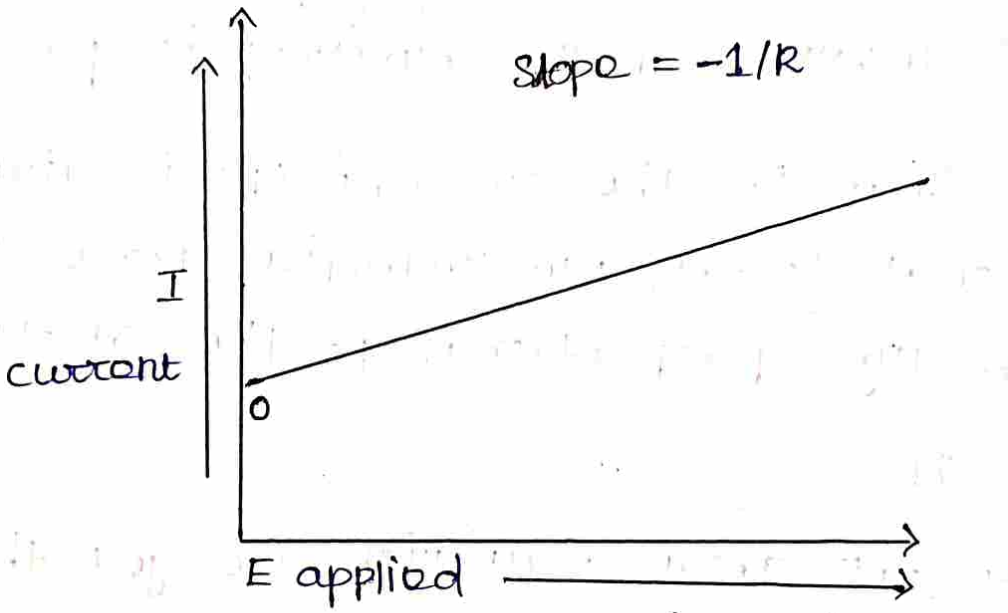
$$I = (-E_{applied}/R) + 1/R\,(E_{cathode} - E_{anode})$$

$$I = (E_{cell} - E_{applied}/R)$$

$$I = (-E_{applied}/R) + K$$

where K is the constant.

A plot of the current of the applied potential in an electrolytic cell should be straight line with a slope equal to negative reciprocal of the resistance.



Electrogravimetric plot

Applications of Electro-gravimetry:

- used in the successive deposition of the metals.
- Example: Cu, Bi, Pb, Cd, Zn and Sn.
- Used in the simultaneous deposition of the metals.
- Used in the electro synthesis.
- Used in the purification process by removing the trace metals from the samples.

Faraday's Law:

Faraday's law of electromagnetic induction (referred to as faraday's law) is a basic law of electromagnetism predicting how a magnetic field will interact with an electric circuit to produce an electromotive force (EMF). this phenomenon is known as electro magnetic induction.

Faraday's First Law:

Any change in the magnetic field of a coil of wire will cause an emf to be induced in the coil. this emf induced is called induced emf if the conductor circuit is closed, the current will also circulate through the circuit and this current is called induced current.

Method to change the magnetic field:

1. By moving a magnet towards or away the coil.
2. By moving the coil into or out of the magnetic field.
3. By changing the area of a coil placed in the magnetic field.
4. By rotating the coil relative to the magnet.

Faraday's second Law

It states that the magnitude of emf induced in the coil is equal to the rate of change of flux that linkages with the coil. The flux linkage of the coil is the product of the number of turns in the coil and flux associated with the coil.

$$\mathcal{E} = -N \frac{\Delta \phi}{\Delta t}$$

where,

$\mathcal{E}$ = electromotive force

ϕ = magnetic flux

N = number of turns

The negative sign indicates that the direction of the induced emf and change in the direction of magnetic fields have opposite signs.

Additionally, there is another key law known as Lenz's law that describes electro magnetic induction as well.

Applications of Faraday's Law:

1. Electrical equipment like transformers works on the basis of Faraday's law.

2. Induction cooker works on the basis of mutual induction which is the principle of Faraday's law.

3. By inducing an electromotive force into an electromagnetic flowmeter, the velocity of the fluids is recorded.

4. Electric guitar and electric violin are the musical instruments that find an application of Faraday's law.

5. Maxwell's equation is based on the converse of Faraday's laws which states that change in the magnetic field brings a change in the electric field.

Ohm's Law :-

ohm's law states that the current through a conductor between two points is directly proportional to the potential difference across the two points, and inversely proportional to the resistance between them.

Ohm's Law gives a relationship between the voltage (V), current (I), and resistance (R) as follows:

$$V = IR$$

Electrical units

Ampere (A):

Ampere is the electrical unit of electric current. it measures the amount of electrical charge that flows in an electrical circuit per 1 second.

$$1A = 1C/1s$$

volt (V):

one volt is the energy of 1 joule that is consumed when electric charge of 1 coulomb flows in the circuit.

volt is the electrical unit of voltage.

$$1V = 1J/1C$$

ohm (Ω):

ohm is the electrical unit of resistance.

$$1\Omega = 1V/1A$$

Coulomb (C):

coulomb is the unit of electric charge.

$$1C = 6.238792 \times 10^{18} \text{ electron charge}$$

polarized electrode and depolarized electrode

polarized electrode:

If the electrode potential has great changes when infinite small current flow through the electrode, such electrode is referred to as polarized electrode.

Example: Dropping mercury electrode (DME).

Depolarized electrodes:

If the electrode potential does not change with current, such electrode is called ideal depolarized electrode.

Example: saturated calomel electrode (SCE).

current density:

The amount of electric current traveling per unit cross-section area is called current density. and expressed in amperes per square meter. More the current in a conductor, the higher will be the current density. However, the current density alters in different parts of an electrical conductor and the effect takes place with

alternating currents at higher frequencies.

Electric current always creates a magnetic field. stronger the current, more intense is the magnetic field. varying AC or DC creates an electromagnetic field and this is the principle based on which signal propagation takes place.

current density is a vector quantity having both a direction and a scalar magnitude. the electric current flowing through a solid having units of charge per unit time is calculated towards the direction perpendicular to the flow of direction.

current Density Formula:

The formula for current density is given as,

$$J = I/A$$

where,

I = current flowing through the conductor in Amperes.

A = cross-sectional area in m^2

current density expressed in A/m^2.

current Efficiency:

current efficiency is the ratio of the electrochemical equivalent current density for a specific reaction to the total applied current density. current efficiency describes the efficiency with which charge (electrons) is transferred in a system facilitating an electrochemical reaction. this phenomenon was originally understood through Michael Faraday's work and expressed in his laws of electrolysis.

In mathematical terms:

where,

m = Theoretical Yield (current efficiency)

M = Molar mass (weight of displaced element in grams)

I = Amperes

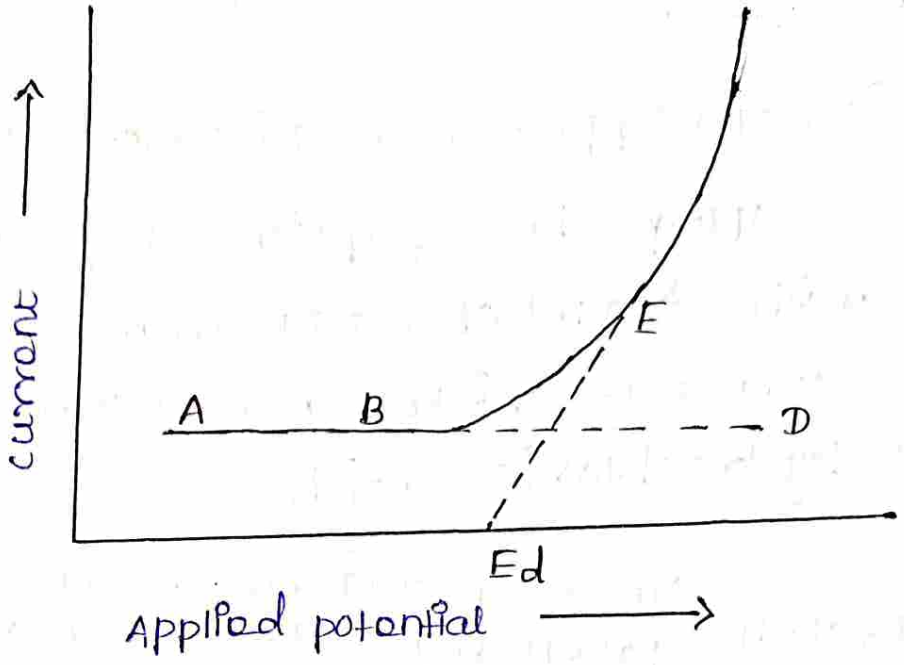
T = Time in seconds

N = oxidation state (number of displaced electrons per atom)

F = Faraday's constant (96487 coulombs).

Decomposition potential:

Electrolytic cells are devices in which chemical reactions are brought about using electrical energy. For example, acidified water is electrolyzed when an external potential is applied across the two platinum electrodes dipped in the solution. Evolution of H_2 and O_2 gases is expected to take place as soon as the external potential is applied. When the applied potential is gradually increased, the current passing through the solution should also increase. But in actual practice, the current density does not increase so rapidly as the applied voltage and so significant electrolysis has not taken place. However, electrolysis with continuous evolution of gases take place when the applied potential reaches a certain limiting value. this minimum potential required to cause continuous electrolysis is known as the decomposition potential or decomposition voltage. it is known from the current density vs. applied potential graph as shown below;



Determination of decomposition potential

over potential (or) over voltage :

In electrolysis the potential at which metal ion start depositing at cathode is very close to standard reduction potential of that metal flow over some cases usually evolution of gass the potential required for their liberation is much higher than standard reduction potential there fore the difference between the potential required for the standard reduction potential of that gas is over voltage (or) bubble over voltage.

Electrolytic separation of copper from Nickel :-

Separation of copper from Nickel :

After the sorption step, copper was eluted with 280 ml of 0.5 M ammonium acetate solution whereas nickel was eluted with 250ml of 1.2 M hydrochloric acid.

S. No	Metal taken	Amount of metal taken mg	Amount of metal found mg	percentage recovery
1.	Cu	57.60	58.00	100.7
2.	Ni	29.10	29.40	101.0
3.	Cu	29.40	29.40	100.0
4.	Ni	29.10	29.00	99.9

Electrolytic separation of copper from Lead :-

Separation of copper from Lead :

Lead is less strongly bound to the resin than copper. Hence, after sorption of these two ions. Lead is first eluted with 300ml of 0.25 M ammonium acetate solution whereas copper is subsequently eluted by the process of gradient elution with about 250 ml of 0.5 M ammonium acetate solution.

S. No	Metal taken	Amount of metal taken mg	Amount of metal found mg	percentage recovery
1.	Cu	29.40	29.30	99.6
2.	Pb	29.40	29.60	100.7
3.	Cu	29.40	29.70	101.2
4.	Pb	114.50	111.10	97.2
5.	Cu	84.00	83.10	98.9
6.	Pb	6.00	6.30	105.0

Estimation of Antimony, copper, Lead and Tin in alloys:-

The principle of electrolysis with controlled cathode potential have been discussed in section 12.6. and the details given below serve to illustrate the procedure. In this case the amounts of copper and antimony are small, and so the cathode potential can be set immediately to the limiting value, but with the higher proportion of tin it can be set intially to a value which is more positive than the limiting value so as to speed up the deposition process.

procedure:

weigh accurately 0.2 - 0.4 g of the alloy into a small beaker, dissolve the alloy by warming with a mixture of 10 ml conentrated hydrochloric acid, 10 ml water, and 1g ammonium chloride solution may be hastened

by the addition, drop by drop, of concentrated nitric acid. When all the alloy has dissolved boil off the excess of chlorine and nitrous fumes, and 5 mL concentrated hydrochloric acid, dilute to 150 mL and then add 1g of hydrazinium chloride. Stir the solution efficiently and electrolyse, limiting the cathode potential to −0.36 volts vs S.C.E copper and antimony are deposited together. After 30-45 minutes the current becomes constant (usually at about 20 mA) remove the saturated calomel electrode, stop the stirrer, withdraw and the electrode from the solution while washing them with distilled water, and then break the electrolysis circuit. After the normal procedure, weigh the dried cathode.

Separate the copper and antimony by dissolving the deposit in a mixture of 5mL concentrated nitric acid, 5 mL 40 per cent hydrofluoric acid (CARE), and 10 mL water, boil off the nitrogen oxides, dilute to 150mL and add dropwise a solution of potassium dichromate until the liquid is distinctly yellow. Deposit the copper by electrolysing the solution at room temperature and limiting the cathode vs S.C.E. potential to −0.36 volt. Evaluate the

weight of antimony by difference.

To the solution from which the copper and antimony have been separated as above, add 5ml concentrated hydrochloric acid and 1g hydrazinium chloride. Electrolyse using a weighed copper-coated cathode after adding sufficient distilled water to cover the electrode. Set the potentiostat to give a cathode potential of -0.6 volts vs the S.C.E (saturated calomel electrode). changing to -0.7 volt vs the S.C.E. over a period of 20 minutes. continue the electrolysis for a further 25 minutes to complete the deposition of lead and tin. Neutralise the electrolyte by adding dilute ammonia solution (1:1), otherwise some tin may re-dissolve during the washing of the electrodes, then remove the cathode, wash, dry and weigh to determine the weight of tin and lead.

Calculated the percentages of antimony, copper, lead and tin in the alloy. In a similar determination described by Lingane and Jones," an alloy containing copper, bismuth, lead, and tin is dissolved in hydrochloric acid as described above.

and then 100ml of sodium tratrate solution (0·1M) is added followed by sufficient sodium hydroxide solution to adjust the pH to 5·0. After the addition of hydrazinium chloride (4g) the solution is warmed to 70°C and then addition of electrolysed. copper is deposited at -0·3 volt, and then sequentially, bismuth at -0·4 volt, and lead at -0·6 volt, all cathode potentials quoted are vs the S.C.E. After deposition of the lead, the solution is acidified with hydrochloric acid and the tin then deposited at a cathode potential of -0·65 volt vs the S.C.E.

Examples of controlled cathode potential determinations:

Metal	Electrolyte	E cathode vs S.C.E (V)	Separated from
Antimony	Hydrazine / HCl	-0·3	Pb, Sn
cadmium	Acetate buffer	-0·8	Zn
copper	Tartrate / hydrazine / Cl^-	-0·3	Bi, Cd, Pb, Ni, Sn, Zn
Lead	Tartrate / hydrazine / Cl^-	-0·6	Cd, Fe, Mn, Ni, Sn, Zn
Nickel	Tartrate / NH_4OH	-1·1	Al, Fe, Zn
Silver	Acetate buffer	+0·1	Cu, heavy metal

5.2. Voltamotry:

In voltammetry we apply a time-dependent potential to an electrochemical cell and measure the resulting current as a function of that potential. We call the resulting plot of current versus applied potential a voltammogram and it is the electrochemical equivalent of a spectrum in spectroscopy. providing quantitative and qualitative information about the species involved in the oxidation. or reduction reaction. the earliest voltammetric technique is polarography developed by Jaroslav Heyrovsky in the early 1920s - an achievement for which he was awarded the Nobel prize in chemistry in 1959. Since then, many different forms of voltammetry have been developed, a few of which are highlighed. Before examining these techniques and their applications in more detail, we must first consider the basic experimental design for voltammetry and the factors influencing the shape of the resulting voltammogram.

Principle of voltammetry:-

Although early voltammetric methods used only electrons, a modern voltammeter makes use of a three-electrode potentiostat. In voltammetry we apply a time dependent

potential excitation singal to the working electrode changing its potential relative to the fixed potential of the reference and auxiliary electrode is generally a platinum wire, and the reference electrode is usually a SCE or a Ag/AgCl electrode.

Experimental setup for polarographic analysis:

Polarography is an electroanalytical technique that measures the current flowing between two electrodes in the solution to determine the concentration of solute and its nature respectively. it is a type of voltammetry where the working electrode is a dropping mercury electrode (DME) or a static mercury drop electrode (SMDE), which is useful because they have a wide cathodic range and renewable surface.

Voltammetry is a category of electro analytical methods where the information about the analyte voltammetric experiment is depicted in the form of a voltammogram which plots the current produced by the electrolyte vs. the potential of the working electrode.

Types of polorographic methods:

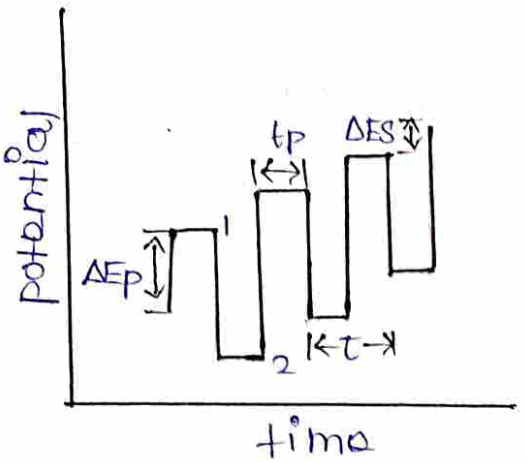
- Direct current polarography (DCP)
- Square wave polarography (SWP)
- Normal pulse polarography (NPP)
- Differential pulse polarography (DPP)

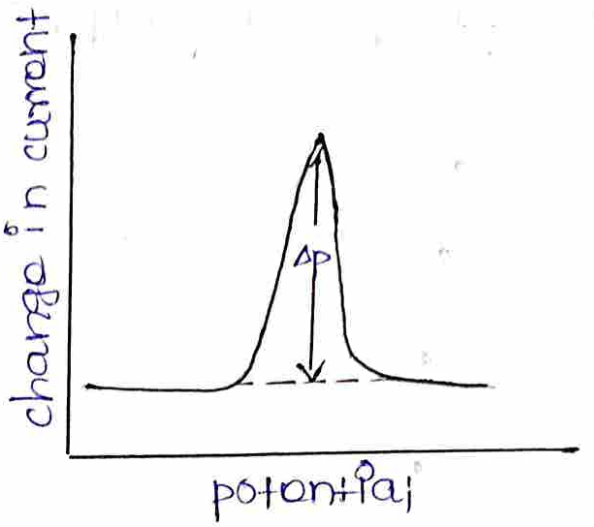
Direct current polarography (DCP):

In DCP a constant potential is applied during the entire drop-life time. A current-voltage curve is constructed by applying a series of potential steps, each as step being synchronized with the drop fall. In most instruments however, linearly changing potential is applied, with a rate slow enough that the change of potential throughout the drop-life time is about a few millivolts. the current is measured at the end of the drop life.

Square wave Polarography (SWP):

In square wave polarography, the current at a working electrode is measured while the potential between the working electrode and a reference electrode is swept linearly in time. the potential waveform can be viewed as a superposition of a regular square wave onto an underlying staircase.



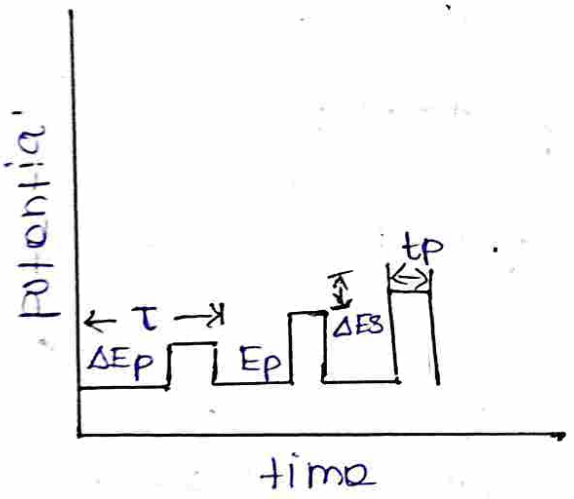


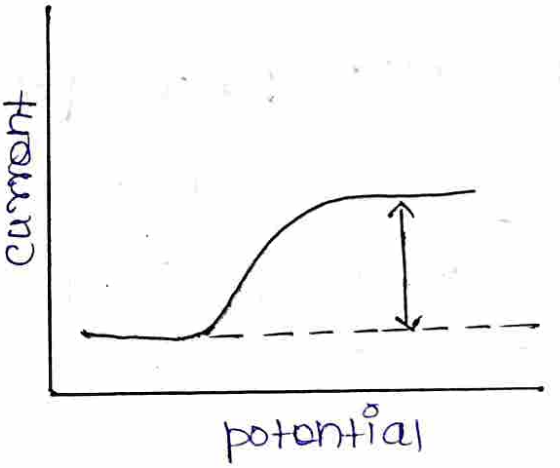
The current is sampled at two times - once at the end of the forward potential pulse (1) and again at the end of the reverse potential pulse (2). As a result of this current sampling technique, the contribution to the current signal resulting from capacitive current is minimal. When the difference between these two current values determined for a potential ramp is plotted against the particular potential, and then a peak-shaped polarogram is obtained with the peak current and potential.

Normal pulse polarography (NPP):

In normal pulse polarography (NPP) the potential is not altered by a continuously increasing height overlaid on a constant intial potential. the mercury-drop electrode is

held for most of its duration at a overlaid on a constant intial potential. the mercury-drop electrode is held for most of its duration at a constant potential En, at which no electrochemical reactanht takes place under given exporimental conditions. the potential of interest Ep is applied in the last stage of the drop life, for a length of time tp. the values of En and tp are kept constant throughout the recording of the polarogram and Ep is changed from drop to drop.



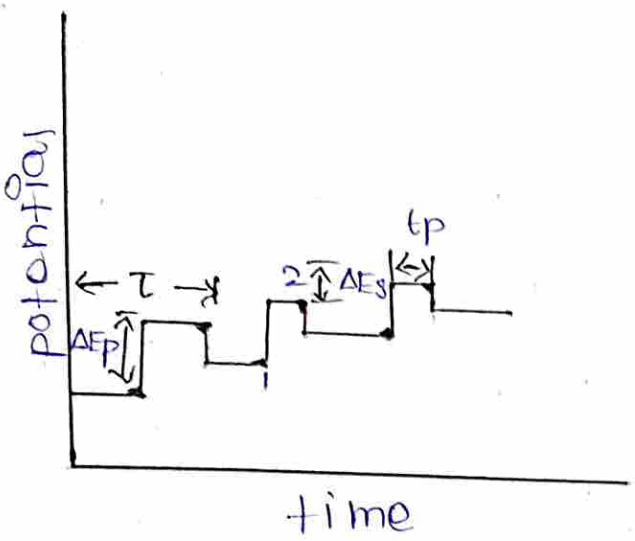


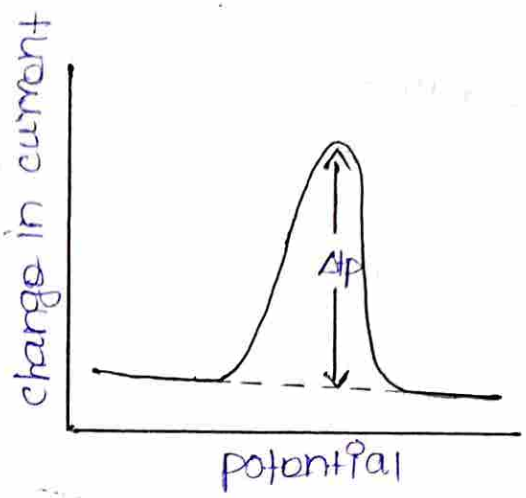
The limiting current in NPP is diffusion controlled. since tp. is of the order of milliseconds, the diffusion layer thickness is minimal compared to the radius of the mercury drop reached at the end of its life. further more, the area of the drop is virtually

constant during the application of the pulse. A potential alteration at each drop is relatively significant and the pulse time very short a large concentration gradient is produced and as a result, a sizeable faradaic current. the measured current is recorded or stored until the next measurement. if the individual current values are plotted against the potential alteration of the pulse, then step-shapped current-potential curves are obtained. The curves are peak-shaped if the current of each preceding pulse is substracted from the stored measured value of the following one.

Differential pulse polarography (DPP):

The most efficient pulse method is differential pulse polarography (DPP). in digital instruments, the excitation signal consists of a staircase-shaped increasing direct potential to which small square wave pulses with a constant potential are applied in periodic succession. the superimposition is synchronized with the drop time and takes place when the electrode surface no longer changes.





The current is measured twice at each mercury drop, before each pulse and at the end of the pulse time tp. the difference between the measurements (Δip) is plotted against the direct potential and produces peak-shaped polarograms. the formation of this difference also leads to a further reduction of the capacitive current contribution and therefore to an increase in sensitivity, even when compared with determinations by normal pulse polarography.

Determination of Lead in tap water:

In the following determination use of the S.M.D.E and of differential pulse stripping is described. All the glass apparatus used must be rigorously cleaned. vessels should be filled with pure 6M nitric and left standing overnight and then thoroughly

cleaned with re-distilled water.

procedure:

prepare (1) a standard (0.01M) lead solution by dissolving 1.65 g analytical grade lead nitrate in re-distilled water and adjusting to the mark in a 500 ml graduated flask, (2) a supporting electrolyte solution by dissolving 1.0 g of 'Aristar' in 500 ml of redistilled water. confirm that this solution does not contain significant amounts of impurities by carrying out the pre-concentration and stripping procedure described in detail below using 10ml of the solution and 10 ml of re-distilled water. If a significant lead peak is obtained, the solution must be discarded.

place 10 ml of the tap water and 10ml of the supporting electrolyte in the electrolysis vessel, add a magnetic stirring bar and mount the vessel on a magnetic stirrer. insert an S.C.E, a platinum plate auxilliary electrode. Opperate the dispensing mechanism to form a mercury drop at the end of the capillary. pass oxygen-free nitrogen through the solution for 5 minutes, and then adjust the nitrogen through to pass over the surface of the liquid.

Make the connections to the polarographic analyser and adjust the applied voltage to -0.8V, i.e. a value well in excess of the deposition potential of lead ions. Set the stirrer in motion noting the setting of the speed controller, and after 15-20 seconds, switch electrolysis to proceed for 5 minutes. On completion of the electrolysis time, turn off the stirrer, but leave the electrolysis potential applied to the cell. When the lead peak at ca 0.5V has been passed, turn off the stripping current and the recorder. A suitable scan rate for stripping is $5 mVs^{-1}$.

Clean out the electrolysis cell and charge it with 10 mL of supporting electrolyte, 10 mL of re-distilled water and 1 µL of the standard lead solution. Set up a new mercury drop, pass nitrogen for 5 minutes and then record a new stripping voltammogram by repeating the above procedure with timings and stirring rate repeated exactly. Repeat with three further solutions containing 2, 3 and 4 µL of the standard lead solution. Measure the peak heights of the five voltammograms and thus deduce the lead content of the tap water.

5.3. Electrochemical analytical techiques

Basic principles of voltamotric analytical techniques:

Voltammetry is concerned with the study of voltage - current - time relationships during electrolysis carried out in a cell. the technique commonly involves studying the influence of changes in applied voltage voltage on the current flowing in the cell, but in some circumstance, the variation of current with time may be investigated. the procedure normally involves the use of a cell with an assembly of three electrodes (1) a working electrode at which the electrolysis under investigation takes place (2) a reference electrode which the used to measure the potential of the working electrode and (3) an auxilliary electrode which, together with the working electrode, carries the electrolysis current. in some circumstances the working electrode may be a dropping mercury electrode (DME) and the auxiliary electrode is a pool of mercury at the base of the cell for this special case the technique is referred to as polarography.

potentiometric titrations:

Titrations where the end points are detected by the measurement of emf are known as potentiometric titrations.

They are of three types:

i) Acid - Base titrations

ii) oxidation - Reduction titrations

iii) precipitation titrations.

i) Acid - Base titrations:

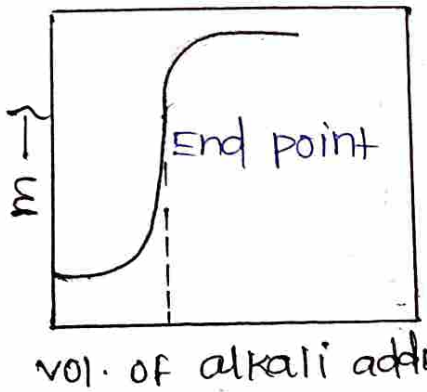
The end point of acid - base titrations may be detected by measuring the emf of a cell formed by coupling a by drogen electrode with a calomel electrode.

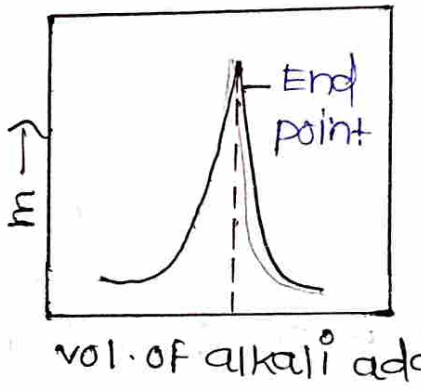
Pt, $H_{2(g)}$ | Test solution | SCE

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

With successive addition of alkali to a known volume of acid, the concentration of H^+ ion decreases and hence emf of the solution increase. it is observed that initially the emf rises gradually and then rapidly at the end point. After the eno point, the emf changes slightly.

A plot of emf (E) vs volume of a alkali added gives a curve with a steep rise at the end point. A better result is obtained from a differential curve obtained by plotting $\Delta E/\Delta V$ against volume of alkali added. A maximum would be obtained at the end point.





iii) oxidation - reduction titrations:

The oxidation - reduction titrations involve changes in the concentration of the oxidised and reduced form of the substance. consider $FeSO_3$ vs $KMnO_4$ titration. A known volume of $FeSO_4$ is taken in a beaker and a platinum wire is dipped into it. From a burette, $KMnO_4$ is added. A redox electrode Pt. Fe^{2+} | Fe^{3+} is set up. it is coupled with a calomel electrode and the emf of the cell is measured periodically.

Pt, Fe^{2+} | Fe^{3+} || Cl^- | $Hg_2Cl_{2(s)}$, Hg

$$E_{cell} = E_{SCE} - 0.0591 \log \frac{Fe^{2+}}{Fe^{3+}}$$

With successive addition of $KMnO_4$, Fe^{2+} is converted into Fe^{3+} and the ratio Fe^{2+}/Fe^{3+} decreases. It is observed that emf increases gradually at the beginning. A sudden rise in emf is noted at the end point.

(iii) precipitation titrations:

In precipitation titration, an ion of the solution is precipitated out by the addition of a titrant. For example when $AgNO_3$ is titrated against NaCl solution, AgCl is precipitated out. A reversible Ag – AgCl electrode is set up. It is coupled with a calomel electrode and the emf of the cell is recorded after successive addition of NaCl.

$$Ag \mid AgCl \mid Cl^- \parallel SCE$$

$$E_{cell} = E_{SCE} - 0.0591 \log [Ag^+]$$

The emf increase gradually due to removal of Ag^+ ion as $AgCl_{(s)}$. At the end point, there is steep rise in emf. the maximum of the curve obtained by plotting $\Delta E/\Delta V$ vs volume of NaCl corresponds to the end point.

Conductometric Titrations:

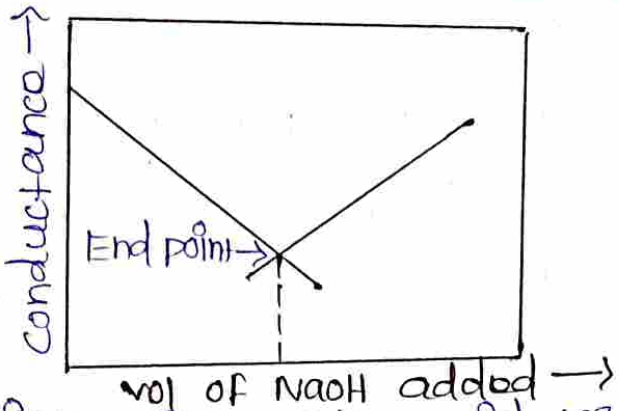
The determination of the end point of a titration by conductance measurements is known as conductometric titrations.

a) Acid - Base titrations:

When an alkali is added to an acid, the fast moving H^+ ions are replaced by slow moving Na^+ ions. Hence the conductance of the solution decrease, when all the H^+ ions are removed at the neutralization point, further addition of the alkali in an increase in conductance due to fast moving OH^- ions. the plot between conductance of solution and volume of titrant added (NaOH) is called the conductometric titration curve. the break in the curve indicates the end point.

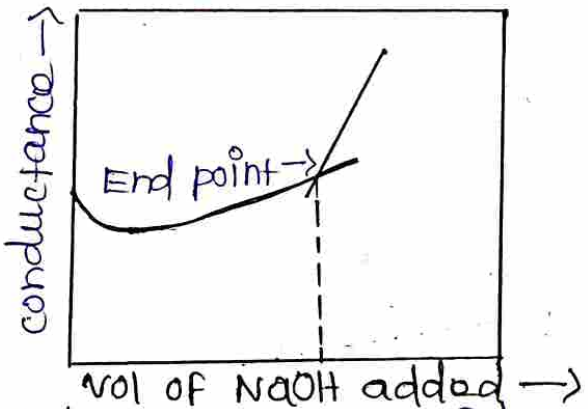
i) Titration of strong acid vs strong base (e.g. HCl vs NaOH):- when NaOH is added to HCl the fast moving H^+ ions of the acid are replaced by the slow moving Na^+ ions and the conductance decrease. After the end point the conductance increase due to Na^+ ions and fast moving OH^- ions.

$$(H^+) + Cl^- + (Na^+ + OH^-) \longrightarrow (Na^+ + Cl^-) + H_2O$$



ii) Titration of weak acid vs strong base (e.g. CH_3COOH vs NaOH):- since acetic acid is weak, the dissociation is poor to furnish free H^+ ions. when NaOH is added to the acid, the limited number of H^+ ions are replaced by Na^+ ions causing a slight decrease in conductance. soon, the conductance increase due to the CH_3COO^- and Na^+ ions of sodium acetate formed.

$$CH_3COOH + (Na^+ + OH^-) \longrightarrow (CH_3COO^- + Na^+) + H_2O$$



When the acid is completely neutralized further addition of NaOH would cause a sharp increase in conductance due to excess of Na^+ and fast moving OH^- ions.

iii) Titration of strong acid vs weak base (e.g. HCl + NH_4OH) :- When HCl is titrated against NH_4OH the conductance decreases sharply

due to the replacement of fast moving H^+ ions by slow moving NH_4^+ ions. After neutralization further addition of NH_4OH does not make much change in conductance since the base is weakly ionised.

$$(H^+ + Cl^-) + NH_4OH \longrightarrow (NH_4^+ + Cl^-) + H_2O$$

electrodes with a back e.m.f which opposes the applied potential. Now, the electrodes are said to be polarized and the phenomenon is called electrode polarization. As a result of electrode polarization and back emf continous electrolysis is prevented. However, rapid electrolysis occurs when the applied potential exceeds the back e.m.f the decomposition potential or acids and bases is found to be 1.7 volts.

Over voltage:

It has been found that the voltage required to decompose an electolyte solution is higher than that calculated from electrode potentials. this means that the observed decomposition potential is always greater than the theoretical value which is equal to the e.m.f of the cell set up with the product of electrolysis. the difference is more marked when gases are evolved

more marked when gases are evolved during electrolysis. For, example in a aqueous solution of H_2SO_4 is 1.23 volt.

over voltage observed with the decomposition of aqeous solution of acids or bases is due to polarization both the electrodes and hence can be divided into two parts, one is called hydrogen over voltage and the other oxygen over voltage.

Electrode	Hydrogen overvoltage	oxygen overvoltage
Platinized platinum	0.00V	0.25V
Palladium	0.00V	0.43V
silver	0.15V	0.41V
Load	0.64V	0.31V
zinc	0.78V	–

Applications of over voltage :-

1. The existence of high hydrogen overvoltage makes it possible for the electro-deposition of metals like zinc, cadmium and tin from an acid solution.

2. The charging of storage battery is possible because of overvoltage.

3. Overvoltage permits the production of chlorine and NaOH by the electrolysis of

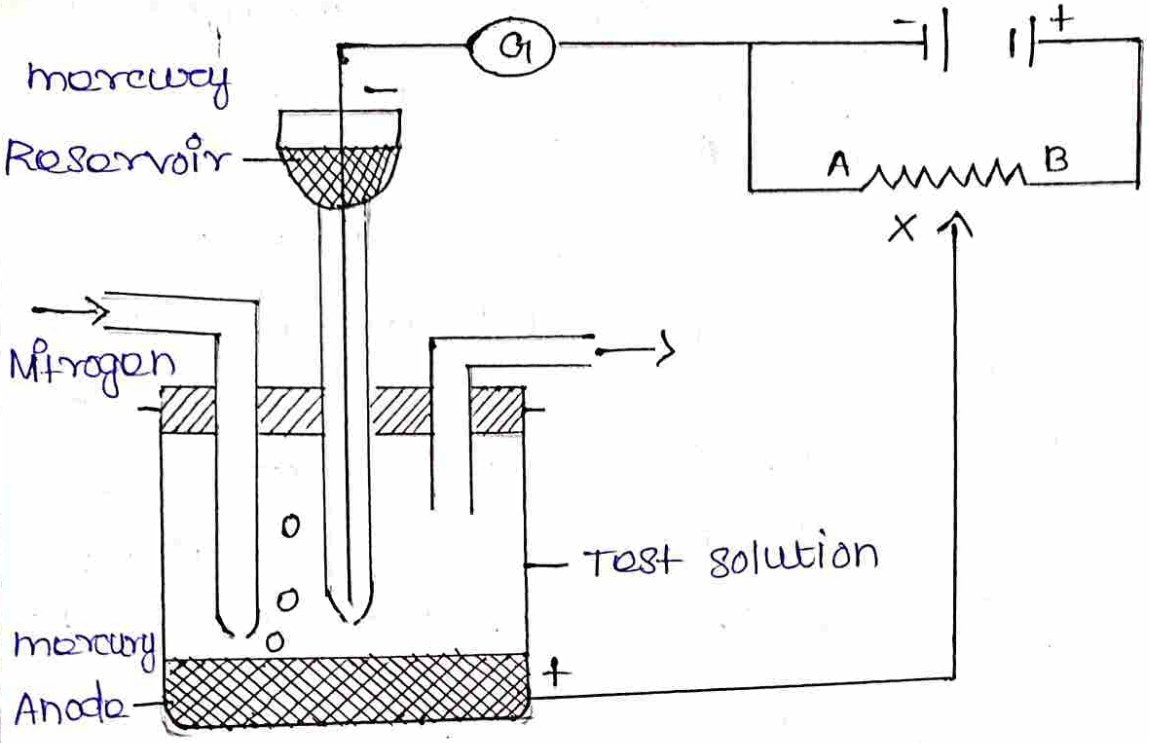
chlorine and NaOH by the electrolysis of NaCl solution.

4. Overvoltage is of great importance in electrolytic reduction of organic compounds. For example, lead with high overvoltage is used instead of platinum as electrode in the reduction of nitrobenzene.

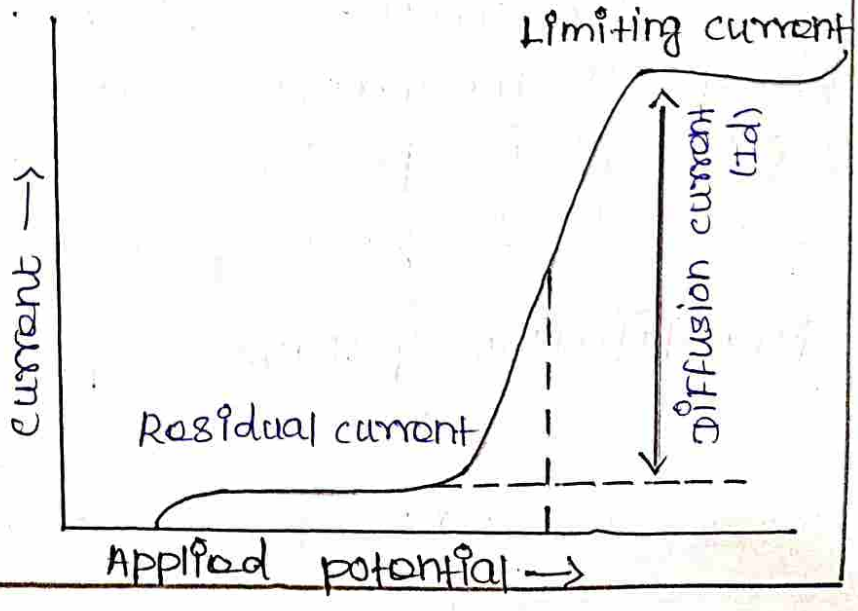
Polarography:

Theory :-

Polarography is an analytical technique used to identity and estimate electroactives substance metal ions present in a solution even in traces. the chemical analysis is carried out by electrolysis the solution using suitable electrodes. to such a small extent that the composition of the solution electrolysed micro-electrode like a dropping mercury electrode (DME) as the cathode. A large excess of an indifferent or supporting electrolyte such as KCl is added to suppress the transport of metal ions in the solution. the electrolysis is then practically diffusion controlled.



A slow stream of N_2 gas is passed through the solution to drive out the dissolved oxygen. the electrodes are connected to a source of emf and the current flowing through the solution is recorded by means of a galvanometer G. the potential applied across the cell is varied using a potentiometer and the values are plotted against the corresponding current. this gives a current - voltage (C-V) curve called polarographic wave or polarogram.



it is seen from the c-v curve that the current at the beginning remains practically constant. this is called residual current. when the potential reaches the value Eo the current rises sharply and attains an maximum limiting value. this is known as the limiting current. the difference between the limiting and residual current is termed diffusion current, it is equal to the height of the polarographic wave. the value of Id depends upon the concentration of the electrolyte and forms the basis of quantitative polarography. this is called half wave potential, $E_{1/2}$ the measurement of $E_{1/2}$ is the basis of qualitative polarography.

Application :-

The polarographic method of chemical analysis is so sensitive and accurate that it left behind order electro chemical methods. From the current, voltage curve it is possible to analysis an electrolyte quantitatively and qualitatively.

@uantitative polarography :

it is based on the measurement of the diffusion current Id.