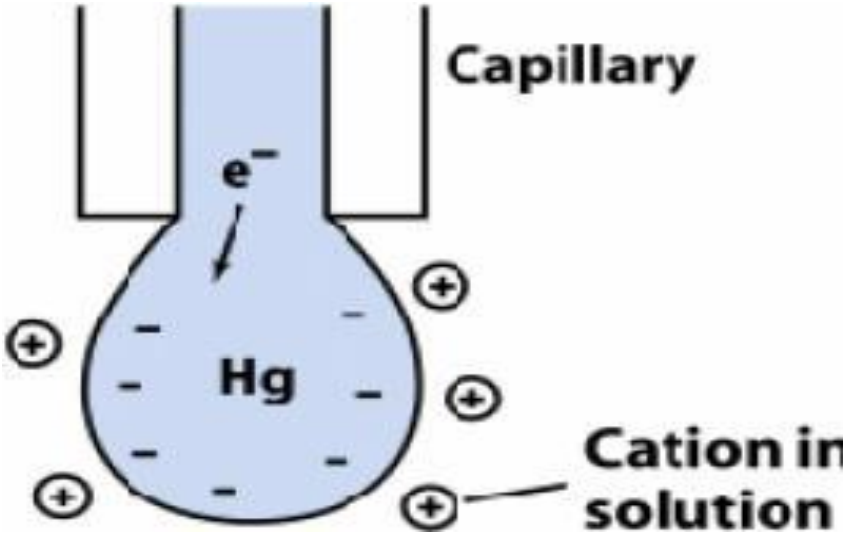
Polarography

Dropping Mercury Electrode (DME)



Polarography

- Polarography is one of the Voltametric methods of analysis;

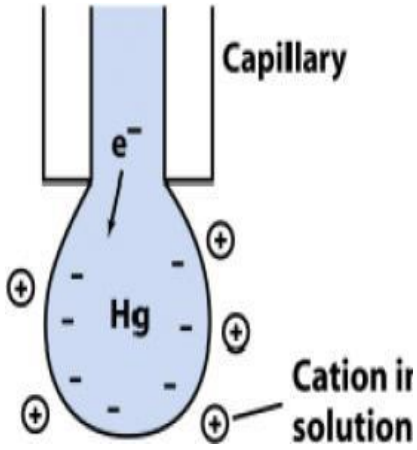
electrochemical methods where current voltage curves obtained at the
surface of microelectrodes are studied.

- In polarography the microelectrode is a dropping mercury
electrode (DME).
- The method is used for the analysis of electroreducible or oxidizable
metal, ion or organic substance (electroactive species).
-

Electroactive species is transferred into a polarographic cell
(electrolytic cell) where voltage is applied to the electrodes

- One of the electrodes is a polarizable microelectrode (DME) while the
other is reference non polarizable electrode

-DME is the cathode •
(attached to the negative •
pole of the voltage supply) •
-upon applying the voltage, •
electroactive species will •
move towards DME, •
electron transfer occurs and •
a current flows. •
-The current produced is •
proportional to •
concentration of the •
electroactive species •



Polarization:

Ohm's law : $E_{cell} = I R$

E □ I (current)

If the increase in cell potential is not accompanied by increase in current it is called Polarization.

Modes of Transport of Electroactive species to DME

1-By Convection:

by mechanical stirring or by heating, as it increases current increases . This type can be prevented by:

-avoiding stirring

-controlling the temperature.

-adding gelatin to increase viscosity of medium

2-By electrostatic attraction :

between positive species and the negative cathode; The current produced here is known by migration current, it can be minimized by:

-adding large excess of inert electrolyte (not reducible) known by supporting electrolyte (50- 100 time analyte concentration)

3-By diffusion:

-occurs due to concentration gradient of ions

-The rate of mass transport by diffusion depends on theconcentration and the diffusion coefficient (a constant

value characteristic for the analyte)

-the transport (current) will depend on concentration.

Small ion conc small inflection of curve

high ion conc large inflection of curve

in polarographic analysis the mode of mass transport should be only by diffusion.

Instrument (Polarograph):

1-electric circuit

2-polarographic cell

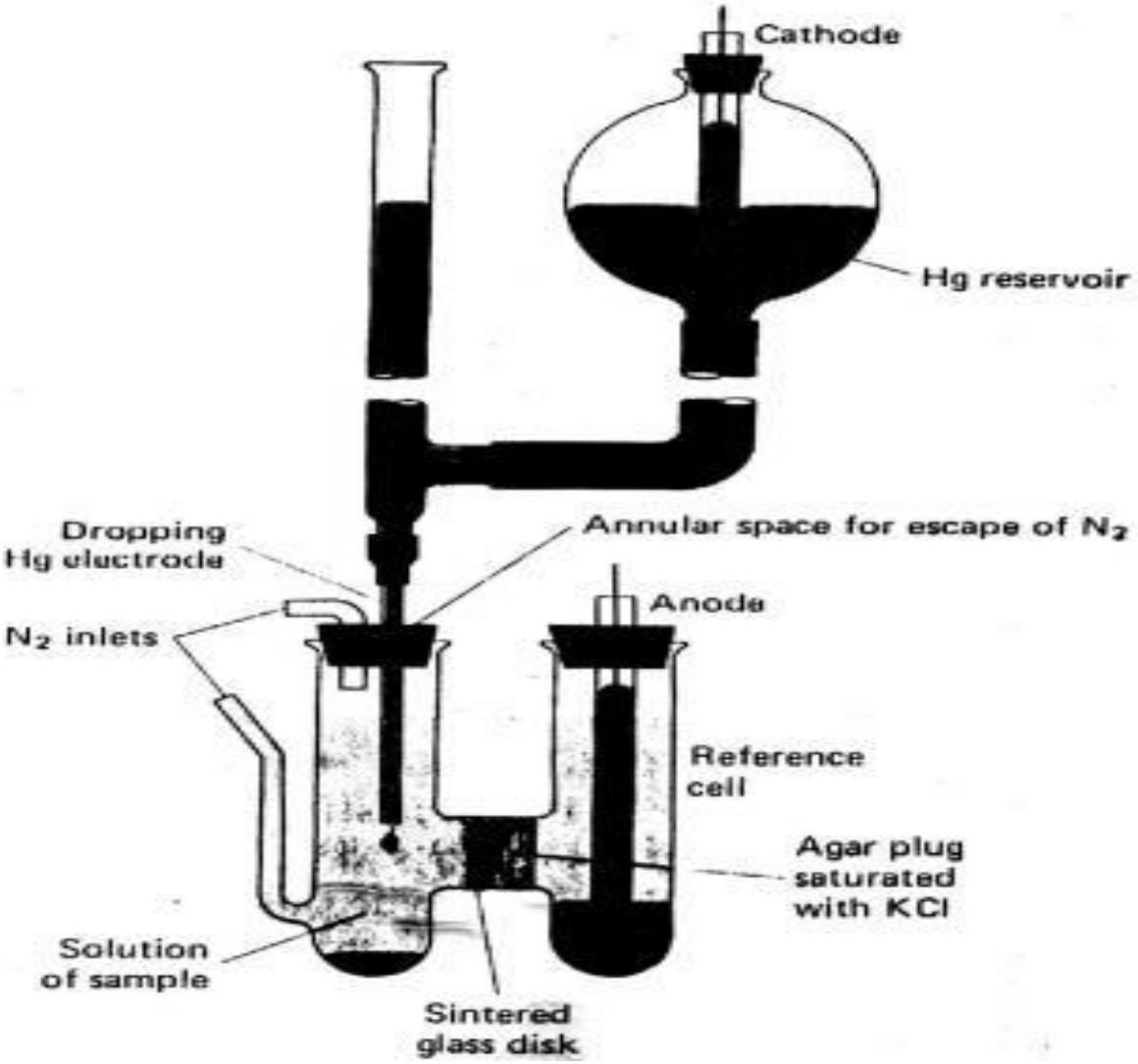
1-electric circuit

-increasingly negative potential from +0.5 to -2.5 volt at a definite rate of millivolt.

2-Polarographic cell

-lifetime of a drop from 2 to 6 seconds

- Nitrogen is bubbled through the solution for five minutes to expel oxygen. Also kept at the surface

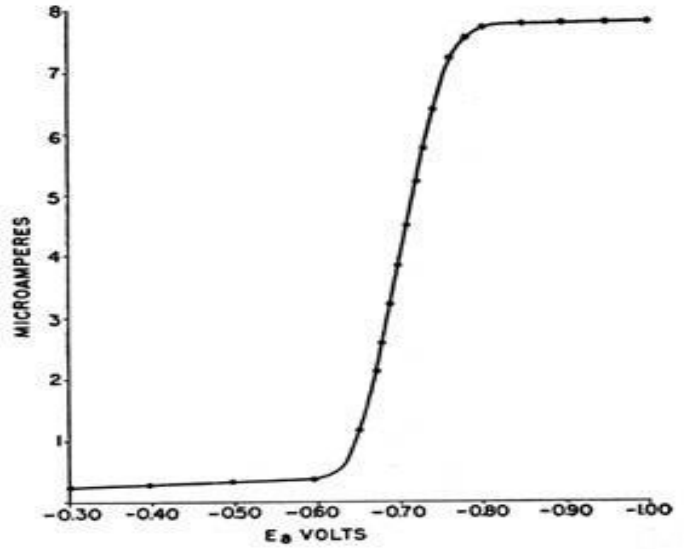

Cathode
Hg reservoir
Annular space for escape of N_2
Dropping
Hg electrode
N_2 inlets
Anode
Reference
cell
Agar plug
saturated
with KCl
Solution
of sample
Sintered
glass disk

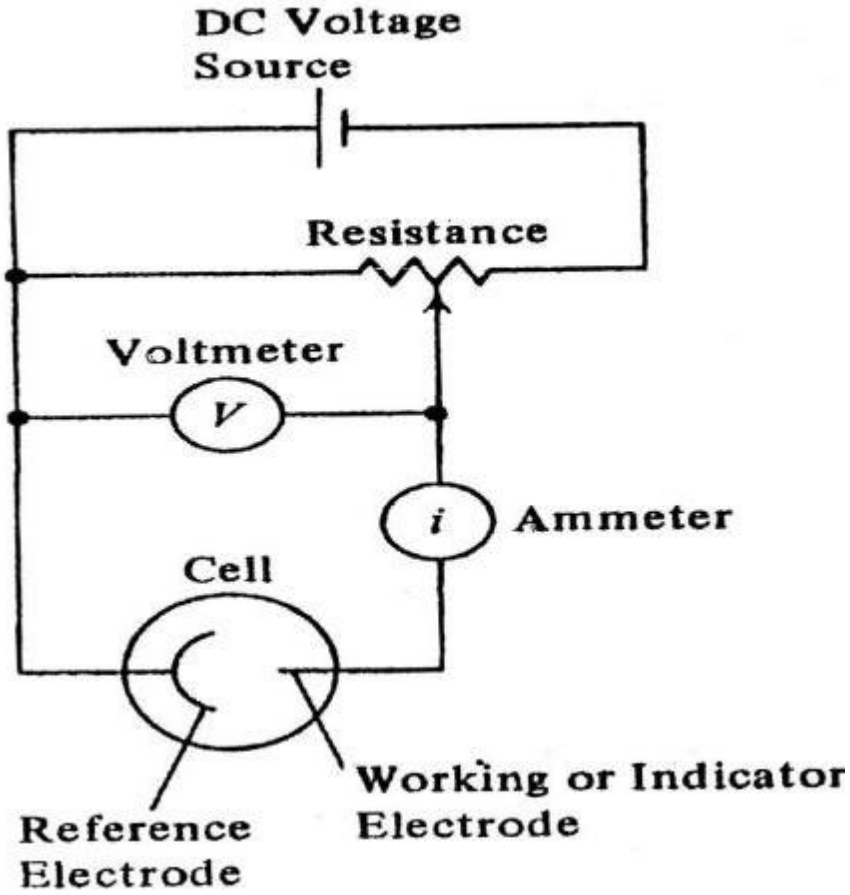
Polarogram

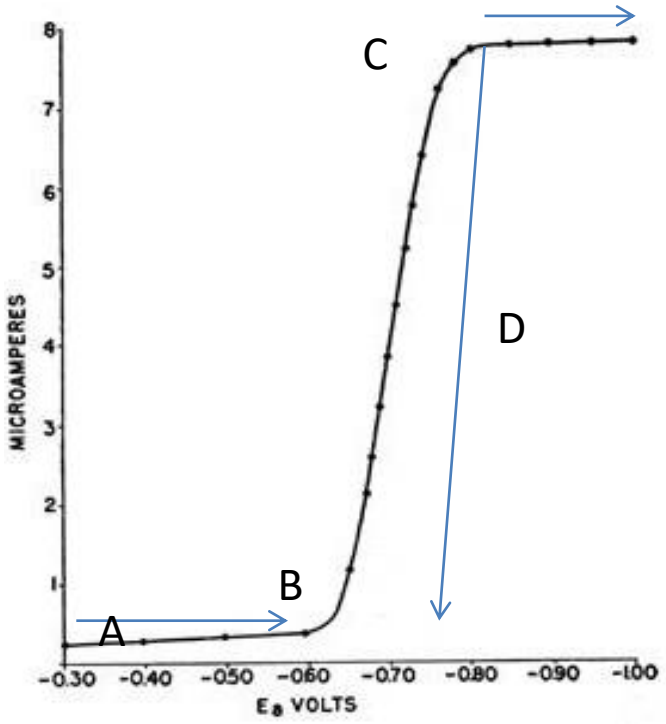
I in

-a plot of current as a function of applied potential

-The applied potential is given a negative sign as the microelectrode is connected to the negative terminal of the power supply.




DC Voltage
Source
Resistance
Voltmeter
V
i
Ammeter
Cell
Working or Indicator
Electrode
Reference
Electrode


C
D
B
A
MICROAMPERES
8
7
6
5
4
3
2
1
-0.30
-0.40
-050
-060
-0.70
-0.80
-0.90
-1.00
Ea VOLTS

A-B : Activation polarization

Increase in volt not accompanied by increase incurrent , additional potential is needed to overcome the energy Barrier. B : Decomposition potential

Potential once exceeded, reduction begins

B-C :Increase in volt is accompanied by increase in current

(diffusion current)

small current passing through the cell is known by residual current i_r

Ilkovič Equation:

Id = 607 n D1/2 C m2/3 t1/6

Id average diffusion current

n number of electron in reduction of a molecule

D diffusion coefficient

C concentration

m rate of the mercury flow in capillary

t lifetime of a drop of mercury (2 to 7 sec.).

n,D,m and t are constants

(id = k C)

m2/3 t1/6 is known by the capillary characteristics it depends on

1- the mercury column height above the capillary tube

2- the internal capillary dimensions.

A) Advantages of DME

1-The current voltage curve shows only the process

2- can be done in acidic solutions as Large overvoltage is needed for reduction of H+

3- reproducible results are obtained as Mercury electrode surface is continuously renewed, smooth surface of the mercury drop which allows reproducible rapid electron transfer. .

4- several runs can be performed using the same solution

as the surface area of the electrode is very small the

amount electrolyzed is negligible and the concentration

of the original solution nearly remains the same

5- The reduced metals at the electrode surface form

amalgum

Disadvantage of the DME:

1) potential above 0.4 V

Hg metal is oxidized with a production of a wave that interferes with the analyte.

2-The drop surface area is changeable

3-The drop surface area change by of potential change

Application of polarography

organic
Polarography

In organic
Polarography

- **Cations**
- **Anions**
- **Molecules**

1- Cations

a- No interference in E1/2:

-Mixture of Cu+, Cu2+, Cd2+ Ni2+ Zn2+ Mn2+ is determined simultaneously in 0.5 M NH4OH, O.5 M NH4Cl as each cation has its characteristic E1/2 and shows separate wave.

b- interference in E1/2:

1-Pb2+, Ti+ and Sn2+ the same E1/2 (-0.5V) in neutral and acidic medium.

Use NaOH medium:

•Pb2+ form a complex with E1/2 -0.8 V

•Sn2+ can be oxidized to Sn4+ which is reduced at -0.35 V• Ti+ is reduced at -0.49.

2- Cu2+ and Bi3+ both are reduced at -0.25 in HNO3 .Use tartarate at pH 2 - 5 the potential is altered to -0.15 for Cu2+ and - 0.37 for Bi^{3+}

Amperometry

Amperometry

Definition

Amperometry refers to the measurement of current under a constant applied voltage and under
these conditions it is the concentration of analyte which determine the magnitude of current.

In Amperometric titration the potential applied between the indicator electrode (dropping mercury electrode) and the appropriate depolarizing reference electrode (saturated calomel electrode) is kept constant and current through the electrolytic cell is then measured on the addition of each increment of titrating solution.

In these titrations the current passing through the cell between the indicator electrode and
reference electrode at a suitable constant voltage is measured as a function of the volume of the titrating reagent.

By diffusion:
-occurs due to concentration gradient of ions
-The rate of mass transport by diffusion depends on the
concentration and the diffusion coefficient (a constant
value characteristic for the analyte)
-the transport (current) will depend on concentration.
=Small ion conc. small inflection of curve
=high ion conc. large inflection of curve
in polarographic analysis the mode of mass transport should be only by diffusion.

Ilkovič Equation:

Id = 607 n D1/2 C m2/3 t1/6

Id **average diffusion current**

n: number of electron in reduction of a molecule

D: diffusion coefficient

C: concentration

m rate of the mercury flow in capillary

t lifetime of a drop of mercury (2 to 7 sec.).

n,D,m and t are constants

(id = k C)

Principle:

According to Ilkovic equation

(Id= 607 X n X D1/2 X m2/3 X t 1/6 X C) , the diffusion current

(= limiting current - residual current) is directly proportional to the concentration of the electroactive

material in the solution.

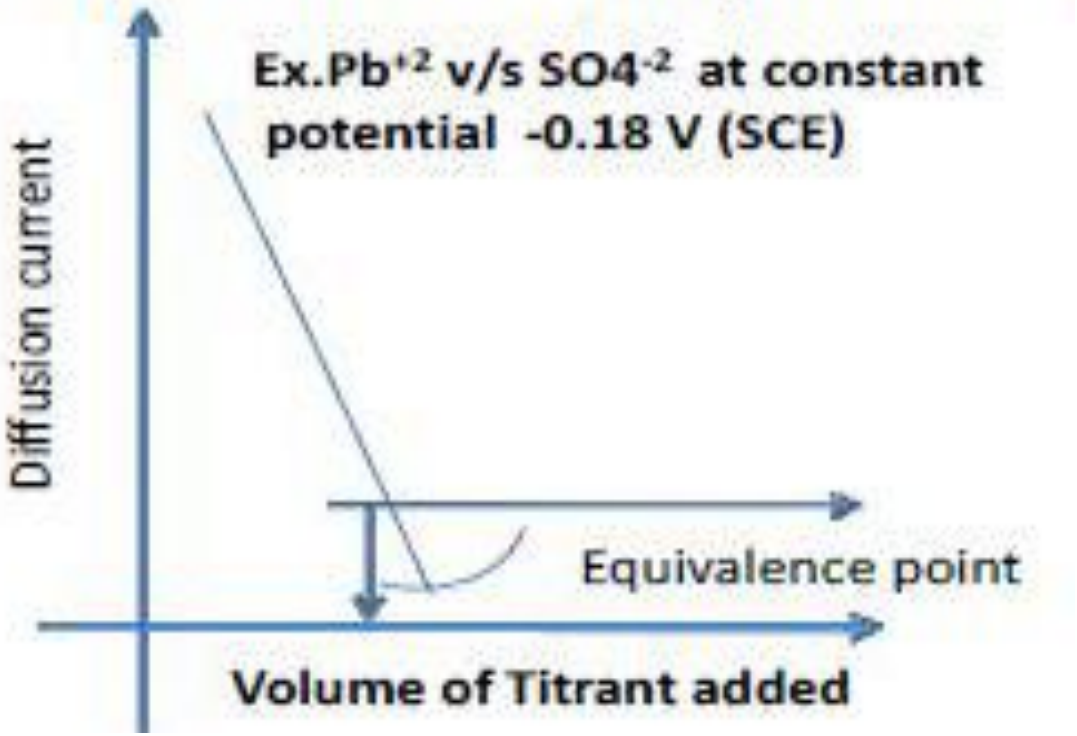
If some of the electro-active material is removed by interaction
with reagent, the diffusion current will decrease. This is the fundamental principle of
amperometric titrations. The observed diffusion current at a suitable applied voltage is measured as a function of the volume of the titrating solution: the end point is the point of intersection of
two lines giving the change of current before and after the equivalence point

Titration Curves in Amperometry:

- **Titrand + Titrant ---→ Product.**

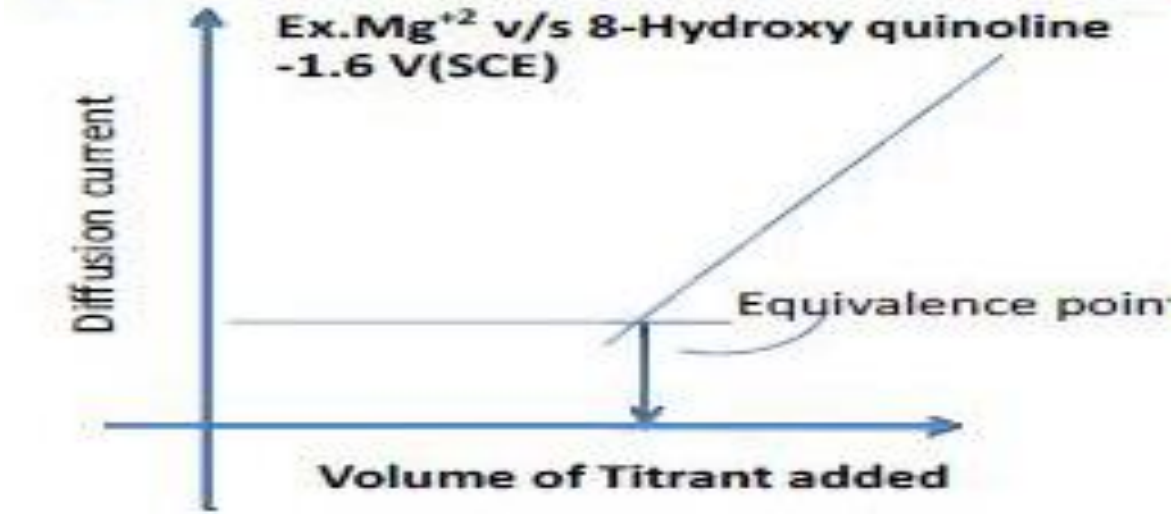
A) **Titrand is reducible but titrant and product not:** When solution containing Pb+2 ion is titrated against SO4-2 ion. A precipitate of PbSO4 is formed. The titration can be performed at fixed potential -0.8 Volt v/s saturated calomel electrode**.**

A) Ttrand is reducible but titrant and product not.



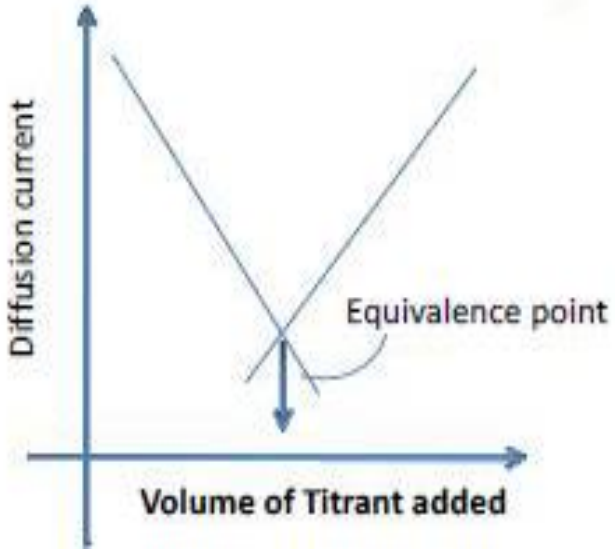
B) Titrant is reducible but titrand and product not : When solution containing Mg+2 ion is
titrated against with the reducible species such as 8- hydroxy quinoline because Mg+2 ion does
not undergoes reduction. Beyond the end point the 8- hydroxyl 4quinoline undergoes reduction.
As its concentration increases diffusion current also increases.

B) Titrant is reducible but titrand and product not



C) Titrand and titrant both are reducible but product not : When solution containing Pb+2
ion is titrated against K2Cr2O7 . The titration is performed at potential of -0.8 Volt v/s SCE . Diffusion current is decreases due to removal of Pb+2 ion. The current is minimum at the end point. On further addition of the titrant the current once again increases. V shaped curve is obtained.

C) Ttrand and titrant both are reducible but product not Ex.Pb^{+2} v/s $K_2Cr_2O_7$ at constant potential -0.8 V (SCE)



CONDUCTOMETRY

CONDUCTOMETRY

- INTRODUCTION
- PRINCIPLE
- IMPORTANT DEFINITIONS & RELATIONS
- INSTRUMENTATIONS
- MEASUREMENT OF CONDUCTIVITY
- CONDUCTOMETRIC TITRATIONS
- ADVANTAGES & DISADVANTAGES OF CONDUCTOMETRIC TITRATIONS
- APPLICATIONS OF CONDUCTOMETRY

- INTODUCTION:

  - It is an electrochemical method of analysis concerned with electrical conductance through an electrolyte solution .

    (or)

  - It is defined has as determination or measurement of the electrical conductance of an electrolyte solution by means of a conductometer .
    - electric conductivity of an electrolyte solution depends on :
      1. Type of ions (cations, anions, singly or doubly charged
      2. Concentration of ions
      3. Temperature
      4. Mobility of ions

- PRINCIPLE:
  - Based on the conductance of electrical current through electrolyte solutions similar to metallic conductors
  - The electric conductance in accordance with ohms law which states that the stength of current(i)passing through conductor is directly porportional to potential difference & inversely to resistance.

$$i = V/R$$

- Important definitions & relations
  - Conductance
  - Specific conductance
  - Molar conductance
  - Equivalent conductance
  - Resistance
  - Specific resistance

- Conductance:(G)
  - ease with which current flows per unit area of conductor per unit potential applied & is reciprocal to resistance(R)

$$G = I/R$$

- Specific conductance (K):
  - conductance of the body of uniform length(l) &uniform area cross section(A)

$$K = 1/R \times 1/A$$

- Molar conductance: (^)
  - Conductance of a solution containing 1 mole of the solute in 1000 cm of the solution which placed between two parallel electrodes which are 1 cm apart

$$^{} = 1000/C$$

- Equivalent conductance: ($\wedge_{eq}$)
  - ❖ specific conductance of the solution containing 1gm equivalent of solute in 1000cm^3 of solution.

$$\wedge_{eq} = 1000k/c_{eq}$$

- Resistance (r):
  - ❖ Is a measure of the conductors opposition to the flow of electric charge

$$R = 1/G$$

- Specific resistance:(ρ)
  - ❖ Is resistance offered by a conductor of unit length and having unit cross section

$$R \propto l/A$$

- Instrumentation

The instrument used for measurement of conductance are know as conductometers

It consists of :

1. Current source
   - Alternating current source
2. Conductivity cells
   - Wide mouthed cells
   - Cell for reactions producing precipitates
   - Dip type cells
3. Electrodes

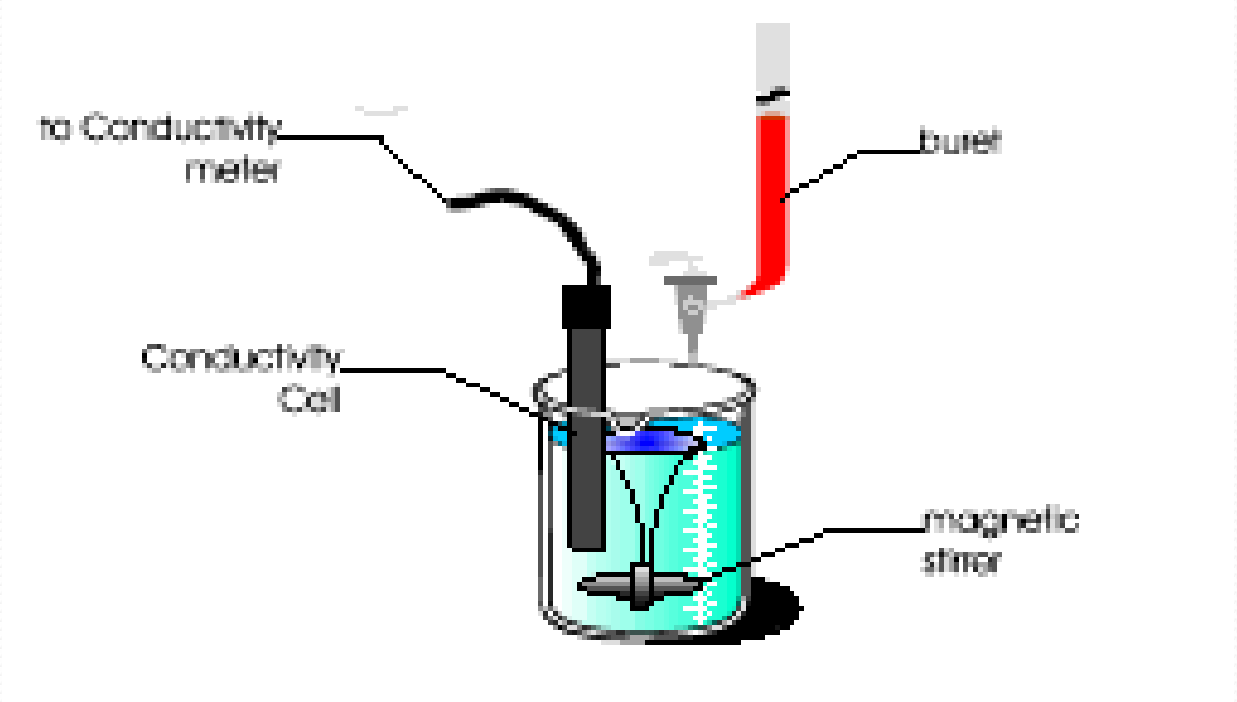
CURRENT SOURCE:-

1. Mechanical high frequency AC generator by Washburn .
2. Vreeland oscillator by Taylor and Acree.
3. Vaccum tube oscillator by Hall & Adams.
   - When electical potential is applied across electrodes two process occurs.
     - Ions accumulate near the electrodes.
     - Transfer of charge through the interface.
     - Note : DC current is not employed in conductance measurement because
       1. Electrodes becomes polarised leading to high cell resistance.

- Conductivity cells:-
  - Made of pyrex or quartz and are fitted with two platinum electrodes.
  - Should be placed in vessel containing water to maintain constant temperature
  - Types :
    1. Wide mouthed cell
    2. Cell for reactions producing precipitation
    3. Dip type cells

- Wide mouthed cell:-
  - Measurement of low conductance
  - Wide mouthed fitted with an ebonite cover which has provisions for platinum electrodes and burettes

- Cell for reactions producing ppts:
  - Mainly used for ppt reactions
  - Also wide mouthed fitted with ebonite cover which has provisions for burette ,electrode , stirrer
  - Stirrer may be mechanical or magnetic



- Electrodes:
  - Platinum sheets, each of 1 cm^2 are fixed at distance of 1 cm
  - The surface is coated with platinum black to avoid polarization effects and increase effective surface area.
  - Platinisation of electrodes is done by coating solution of 3% chlorplatinic acid and lead acetate on it to get uniform coating
  - Electrodes usage depends on conductivity and concentration
  - If conc is low then electrodes should be largely and closely packed

- Measurement:-
  - The instrument used to measure conductance is called conductance bridge or conductometer
  - Classical circuit employed for measurement is wheatstone bridge
  - All other work on this principle
  - Various types are:
    1. Kohlrausch conductance bridge
    2. Direct reading conductance bridge
    3. Phillips conductance bridge
    4. Mullard's conductance bridge
    5. Pye's conductance bridge

- Kohlrausch conductance bridge:
  - Consists of a meter bridge XY with fixed resistors r' & r" at both ends. One arm of bridge consists of resistance box 'R' & other arm with conductivity cell 'C'. Detector D is head phone while inductance coil 'J' is AC source which is operated by battery.
- Direct reading conductance bridge:-
  - In this head phone is replaced by magic eye which is electronic device

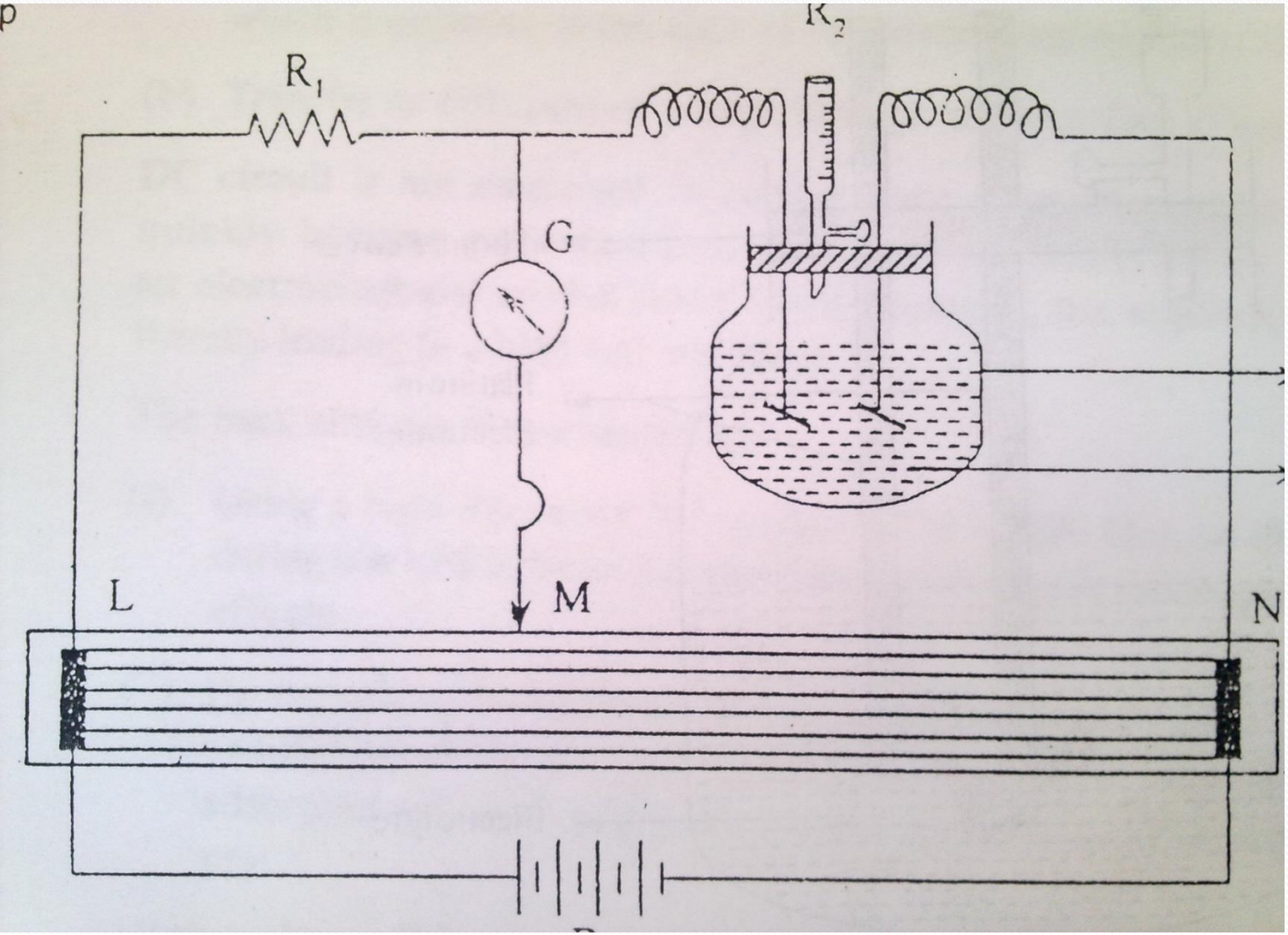
- The set up for Measurement :

  consists of meter bridge LN attached to standard resistance R1 & unknown resistance R2

  cell is connected to standard resistance to one side , meter bridge LN at other. The sliding contact with galvanometer (G) can be moved on the wire of meter bridge by means of jockey (M) so that resistance of unknown is balanced with that of standard. When galvanometer shows null deflection, the resistance of unknown is measured by following equation:

$$ML / NL = R2 / R1$$

$$R2 = ML / NL \times R1$$



Conductivity cell

Solution

Meter bridge

- Hence conductivity of unknown solution:

$$1/R2 = NL/ML \times R1$$

The measured conductivity (1/R1) is not always equal to the specific conductivity of solution , because the physical configuration of platinum electrode i.e, length and area of electrodes varies from one another . Hence conductivity of solution is obtained by calculating a factor called “cell constant”.

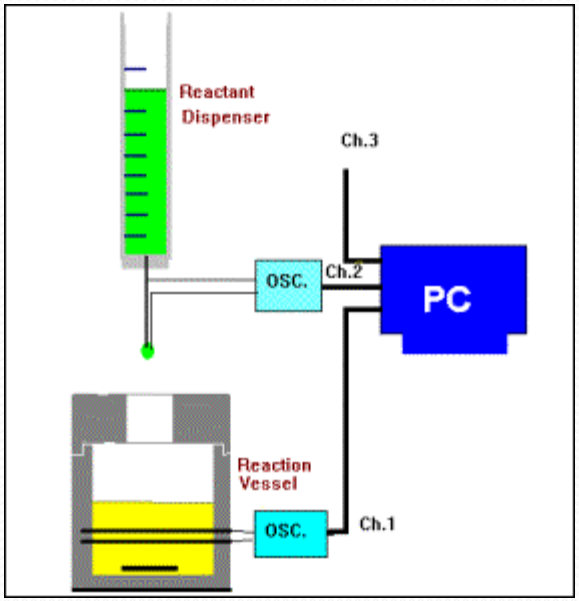
- Cell constant:

Defined as ratio of distance between the two electrodes(l) to the area of electrodes(A)

There fore,

$$\theta = 1 / A$$

- CONDUCTOMETRIC TITRATIONS:
  - INTRODUCTION:
    - Is process of qualitative chemical analysis in which conc of sample is determined.Which is done by adding areagent(titrant) of known conc in measured volumes to the sample (anylate)

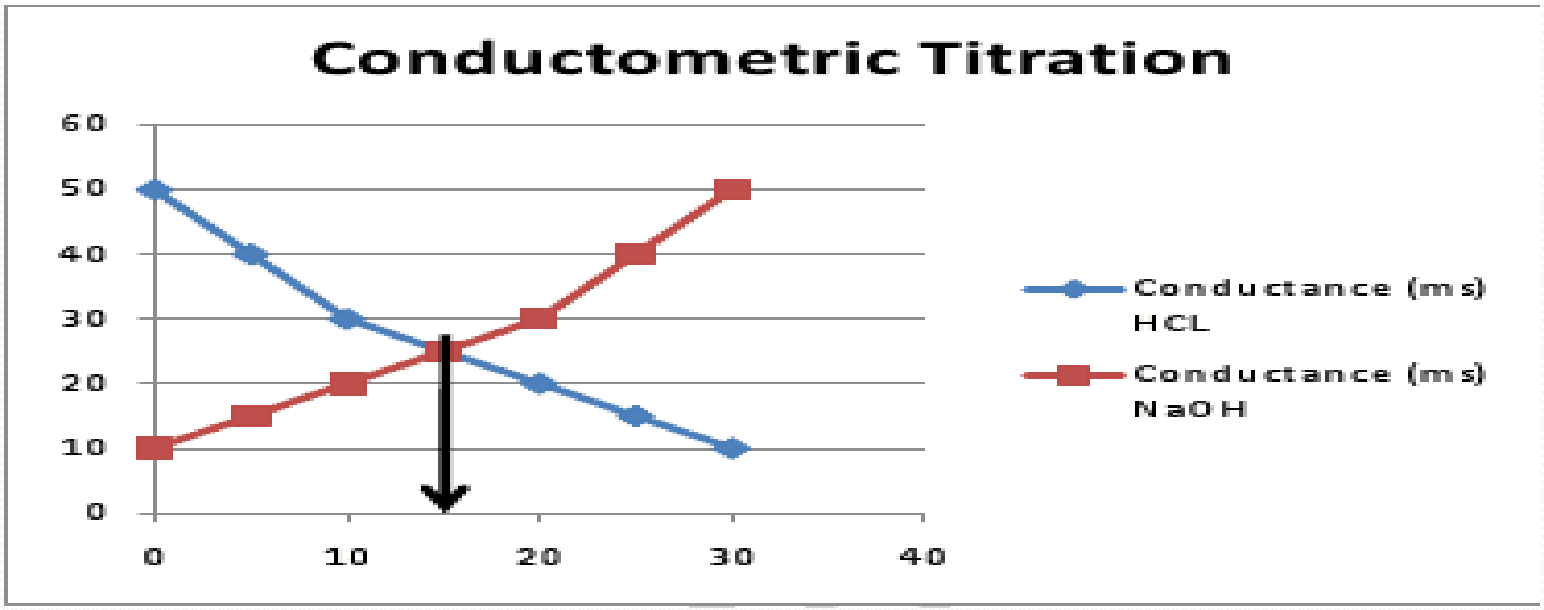


- TYRES OF CONDUCTOMETRIC TITRATIONS:
  - Acid –base or neutral titrations
  - Replacement or displacement titrations
  - Redox titrations
  - Precipitation titrations
  - Complexometric titrations
  - Non-aqueous titrations

1. ACID- BASE OR NEUTRAL TITRATIONS:
   - STRONG ACID-STRONG BASE
     - EG: HCL vs NaOH
   - STRONG ACID-WEAK BASE
     - EG: HCL vs NH_4OH
   - WEAK ACID-STRONG BASE
     - EG: CH_3COOH vs NaOH
   - WEAK ACID -WEAK BASE
     - EG: CH_3COOH vs NH_4OH

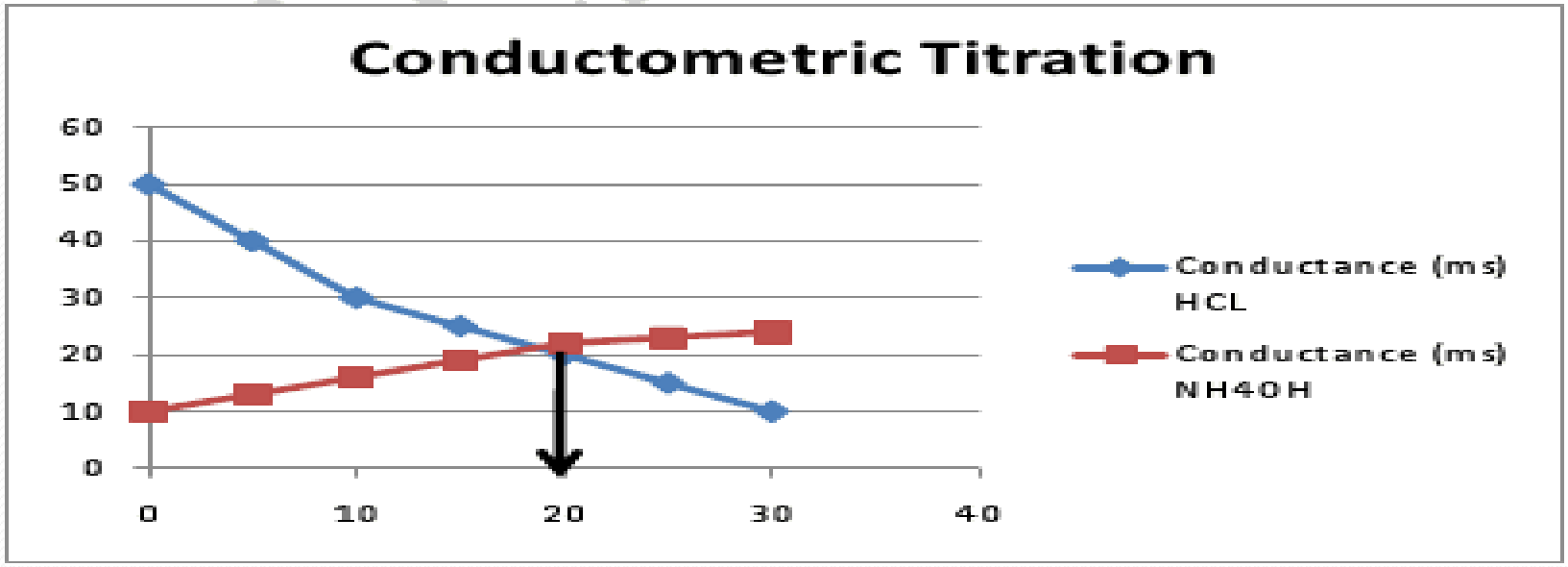
- Strong acid strong base:
  - Fall in conductance due to replacement of high conductivity Hydrogen ions by poor conductivity sodium ions
  - Rise in conductance due to increase in hydroxyl ions

Strong Acid-Strong Base

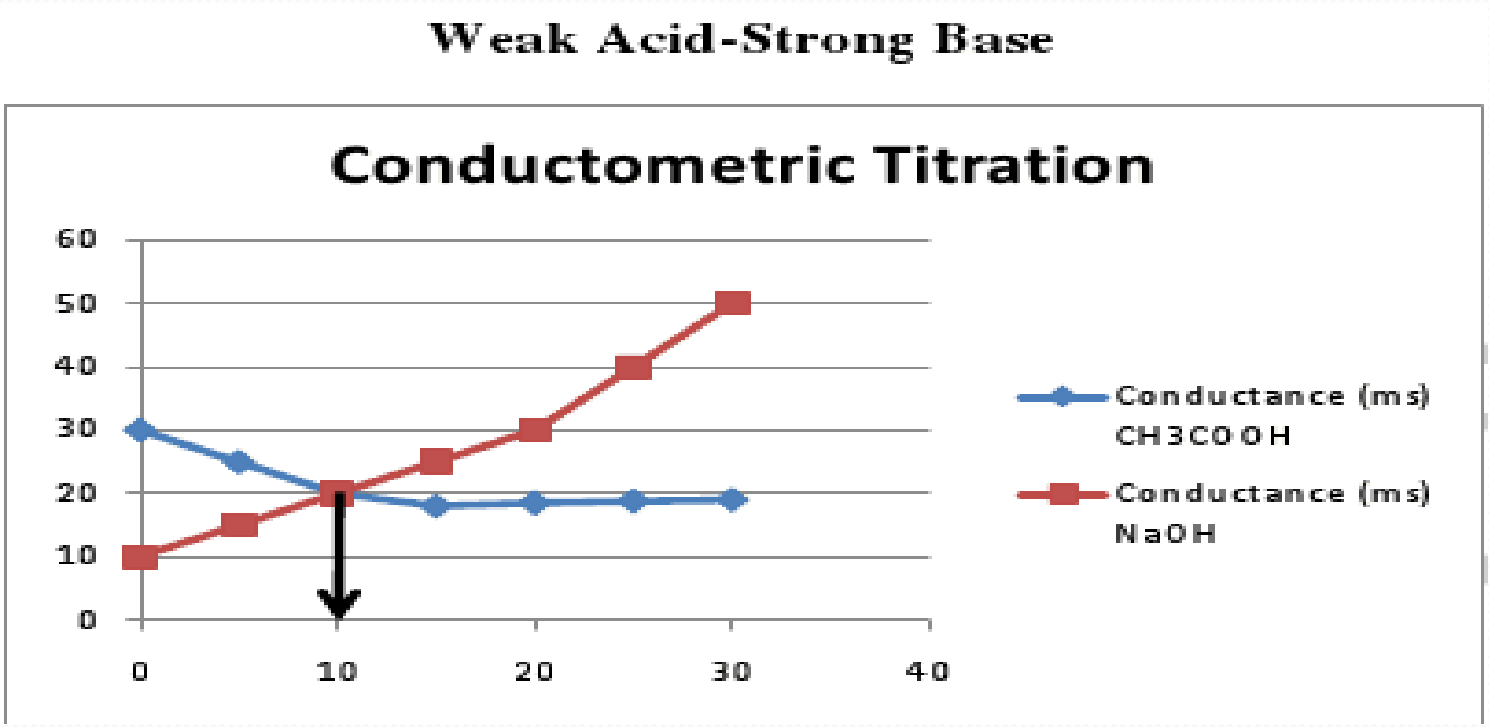


- Strong acid- weak base:
  - Fall in conductance due to replacement of hydrogen by ammonium ions
  - Conductance remain constant due to supression of NH4oH by NH4CL

Strong Acid-Weak Base

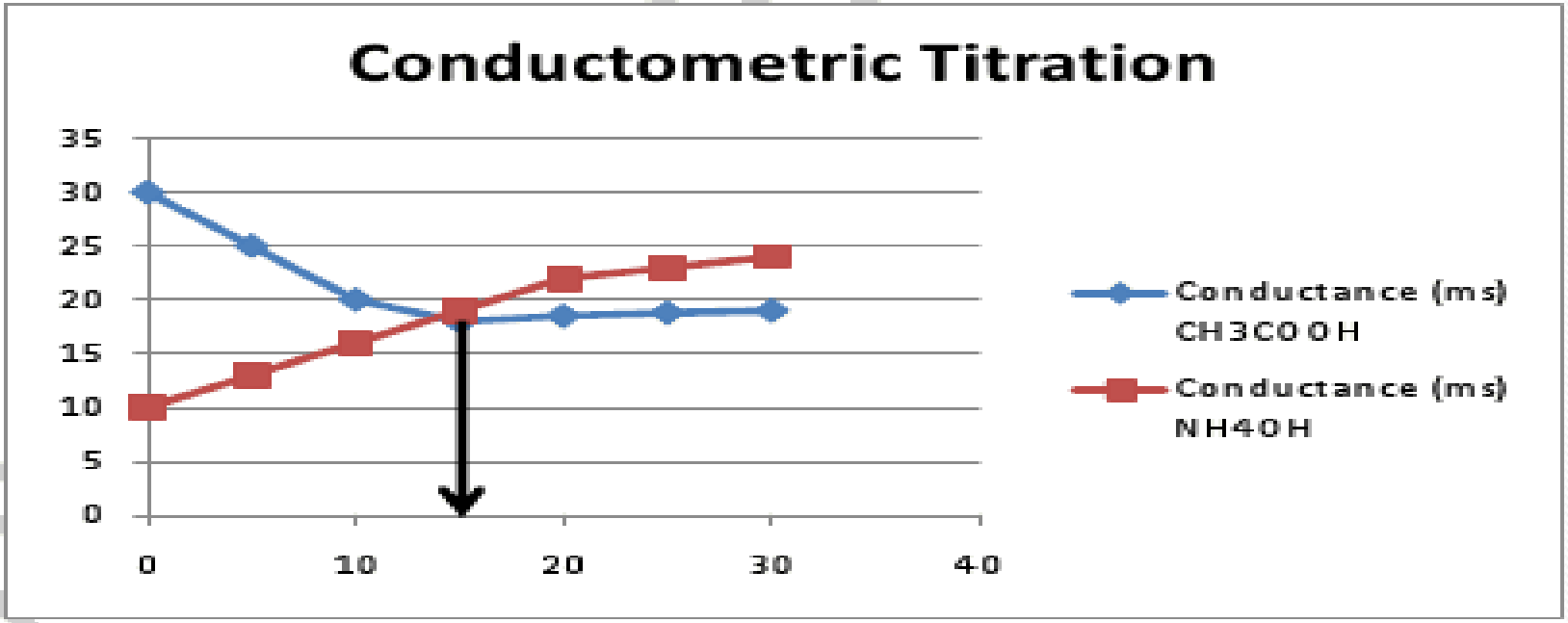


- Weak acid –Strong base:
  - Initial decrease in conductance followed by increase due to NaOH
  - Steep rise due to excess of NaOH



- Weak acid- weak base:
  - Increase in conductance due to excess of CH_3COOH
  - Constant conductance due to supression of NH_4OH by CH_3COOH

Weak Acid-Weak Base



- ADVANTAGE OF CONDUCTOMETRIC TITRATIONS:
  1. Does not require indicators since change in conductance is measured by conductometer
  2. Suitable for coloured solutions
  3. Since end point is determined by graphical means accurate results are obtained with minimum error
  4. Used for analysis of turbid suspensions, weak acids, weak bases, mix of weak & strong acids

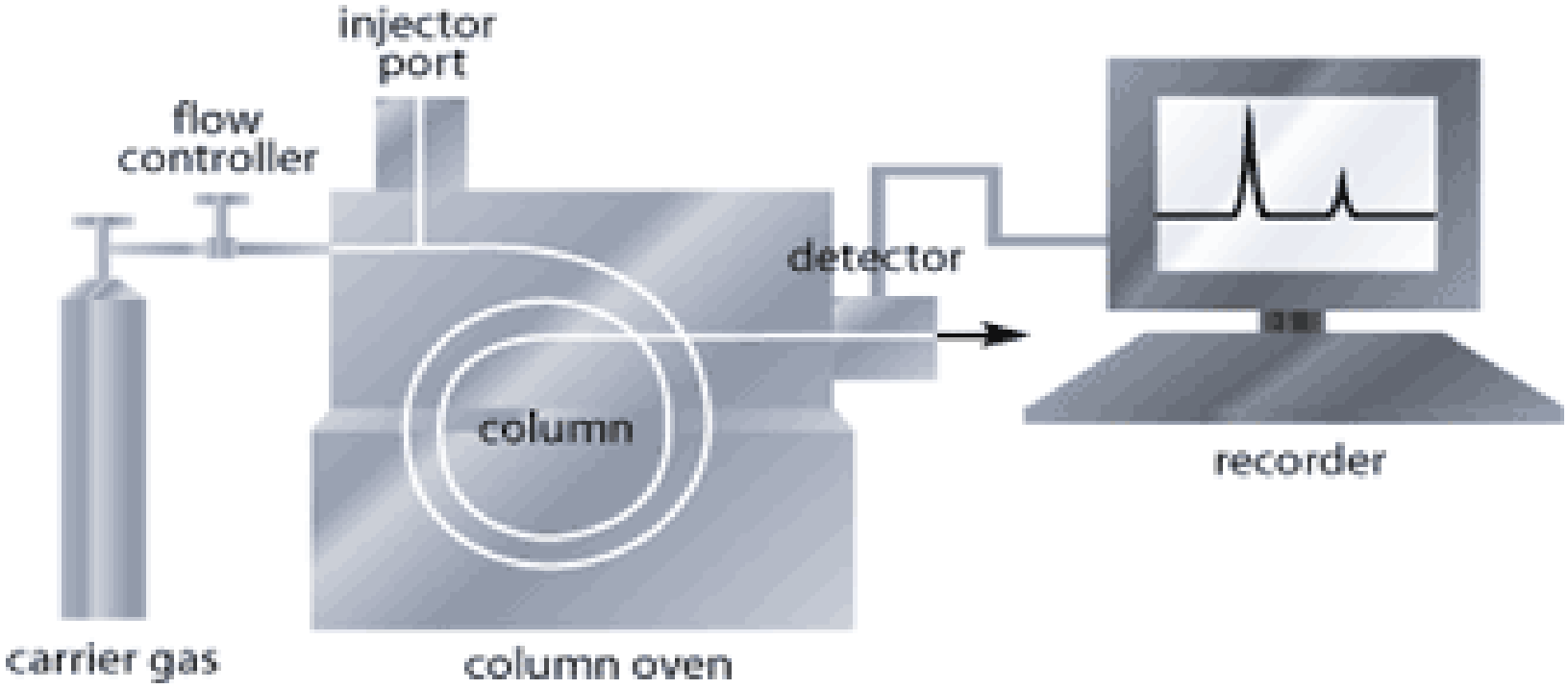
- Dis advantages of conductometric titration:
    1. Increased level of salts in solution masks the conductivity changes , in such cases it does not give accurate results
    2. Application of conductometric titrations to redox systems is limited because, high concentrations of hydronium ions in the solution tends to mask the changes in conductance

- Applications :
  1. Check water pollution in rivers and lakes
  2. Alkalinity of fresh water
  3. Salinity of sea water (oceanography)
  4. Deuterium ion concentration in water- deuterium mixture
  5. Food microbiology- for tracing micro organisms
  6. Tracing antibiotics
  7. Estimate ash content in sugar juices
  8. Purity of distilled and de - ionised water can determined
  9. Solubility of sparingly soluble salts like AgCl,BaSo4 can be detected
  10. Determination of atmospheric so_2,etimation of vanillin in vanilla flavour

References

- *Instrumental analysis* by *A. Skoog, F. James Holler and Stanly R. Crouch.*
- *Text book of pharmaceutical analysis*, third edition by *Dr.S.Ravi sankar.*

Gas Chromatography



What is Gas Chromatography?

- It is also known as…

Gas-Liquid Chromatography (GLC)

GAS CHROMATOGRAPHY

- Separation of gaseous & volatile substances
- Simple & efficient in regard to separation

GC consists of:

GSC (gas solid chromatography)

GLC (gas liquid chromatography

GSC principle is **ADSORPTION**

GLC principle is PARTITION

Sample to be separated is converted into vapour

And mixed with gaseous M.P

Component more soluble in the S.P → travels slower

Component less soluble in the S.P → travels faster

Components are separated according to their **Partition Co-efficient**

Criteria for compounds to be analyzed by G.C

1.VOLATILITY:

2.THERMOSTABILITY:

How a Gas Chromatography Machine ʕWorksʔ

– **First**, a vaporized sample is injected onto the *chromatographic column*.

– **Second**, the sample moves through the column through the flow of inert gas.

– **Third**, the components are recorded as a sequence of peaks as they leave the column.

Chromatographic Separation

– Deals with both the *stationary*
the *mobile phase*. *phase* and

- **Mobile** – inert gas used as carrier.
- **Stationary** – liquid coated on a solid

within a column. or a solid

Chromatographic Separation

Chromatographic Separation
– **In the mobile phase**, components of the sample are uniquely drawn to the stationary phase and thus, enter this phase at different times
–
The parts of the sample are separated within the column.
Compounds used at the stationary phase reach the detector at unique times and produce a series of peaks along a time sequence.

The peaks can then be read and analyzed by a forensic scientist to determine the exact components of the mixture.

– Retention time is determined by each component reaching the detector at a characteristic time.

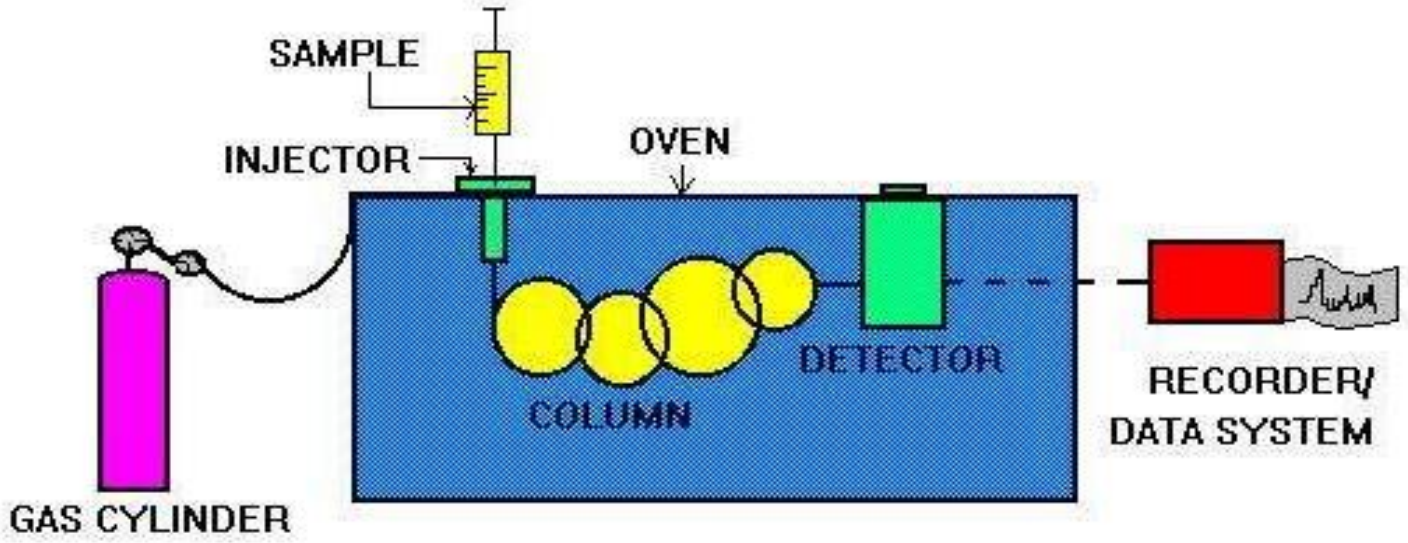
Chromatographic Analysis

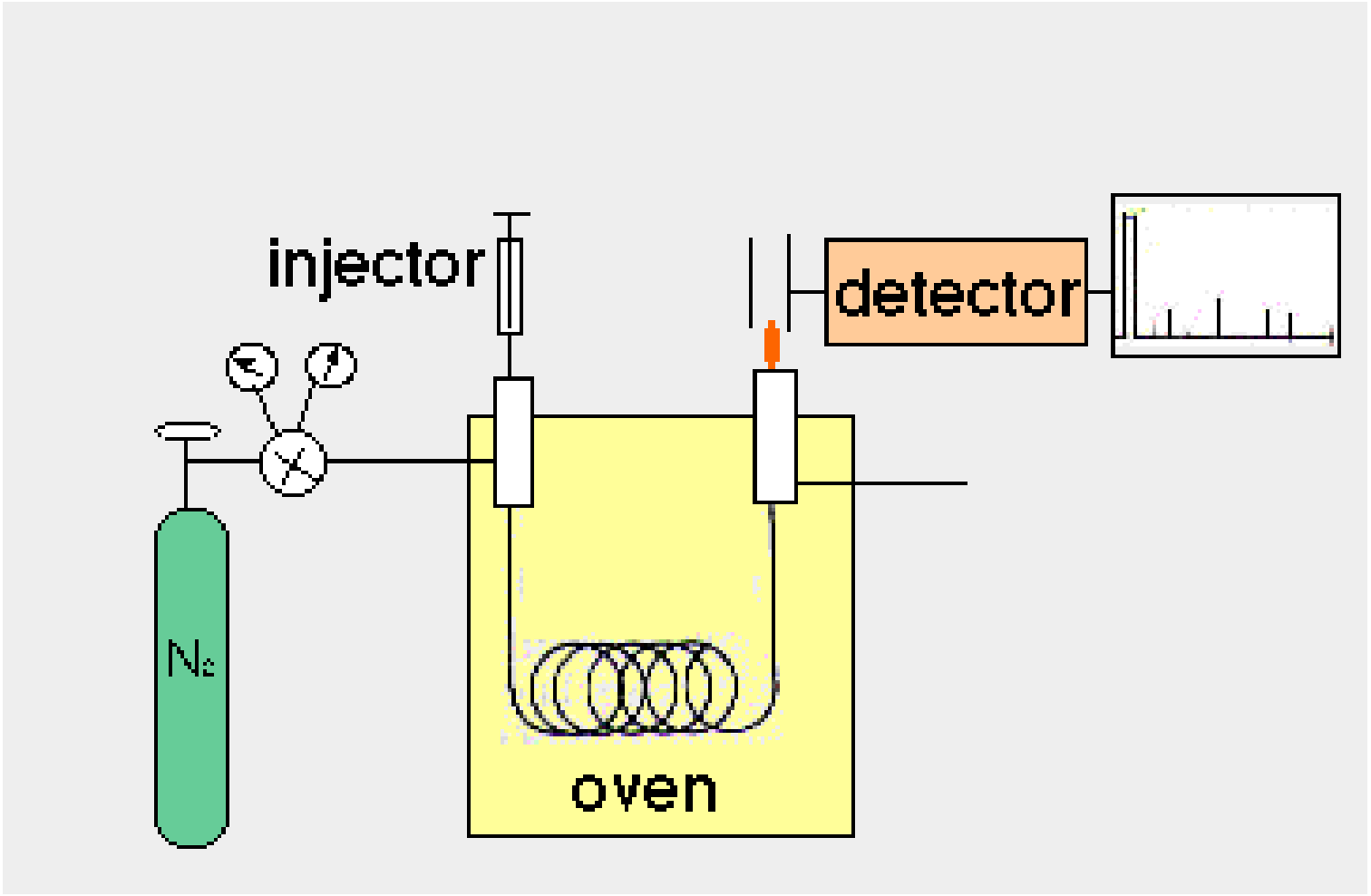
The number of components in a sample is determined by the number of peaks.

– The amount of a given component in a sample is determined by the area under the peaks.

– The identity of components can be determined by the given retention times.

GAS CHROMATOGRAPHY




injector
detector
N_2
oven

PRACTICAL REQUIREMENTS

Carrier gas

- Flow regulators & Flow meters
- **Injection devices**
- **Columns**
- **Temperature control devices**
- **Detectors**
- **Recorders & Integrators**

Requirements of a carrier gas

- Inertness
- Suitable for the detector
- High purity
- Easily available
- Cheap
- Should not cause the risk of fire
- Should give best column performance

How to select a Carrier gas

Depending on

- Availability
- Purity
- Coast
- Type of Detector
- consumption

priority

- first
- Second
- Third
- Fourth
- Fifth

Required Gases Purities

Helium For carrier gas: 99.995% high purity, with less than 1.0 ppm each of

- water, oxygen, and total hydrocarbons after purification.
- Use water, oxygen, and hydrocarbon traps.

Hydrogen For carrier or detector fuel gas: 99.995% high purity, with <

- 1.0 ppm of total hydrocarbons after purification.
- Use water, oxygen and hydrocarbon traps.

Required Gases Purities

Air For detector fuel gas: 99.995% high purity.

• Air compressors are not acceptable because they do not

• meet pressure, water, and hydrocarbon requirements.

Nitrogen For carrier or make-up gas: 99.995% high purity, with less than 1.0

• ppm of total hydrocarbons after purification.

Argon 5% Methane For ECD make-up gas: 99.995% high purity.

Carrier Gas Control

The Flow mode has four options for the carrier gas control:

- Constant flow
- Constant pressure
- Programmed flow
- Programmed pressure

Flow regulators & Flow meters

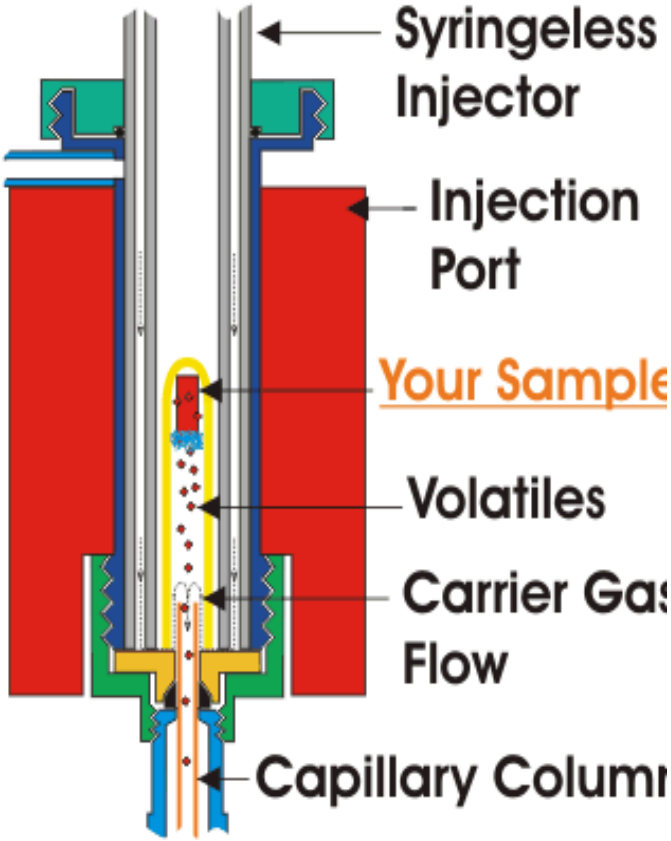
X deliver the gas with uniform pressure/flow rate

X **flow meters:-** Rota meter & Soap bubble **flow meter**

Injection Devices

Gases can be introduced into the column by valve devices

- liquids can be injected through loop or septum devices



COLUMNS

- Important part of GC
- Made up of glass or stainless steel
- Glass column- inert , highly fragile

COLUMNS can be classified

 Depending on its use

1. Analytical column

1-1.5 meters length & 3-6 mm d.m

2. Preparative column

3-6 meters length, 6-9mm d.m

Depending on its nature

1.Packed column: columns are available in a packed manner

S.P for GLC: polyethylene glycol, esters, amides, hydrocarbons, polysiloxanes…

2.Open tubular or Capillary column or Golay column

- Long capillary tubing 30-90 M in length
- Uniform & narrow d.m of 0.025 - 0.075 cm
- Made up of stainless steel & form of a coil
- Disadvantage: more sample cannot loaded

2. Column

The column

- **Is where the chromatographic separation of the sample occurs.**
- Several types of columns are available for different chromatographic applications:
- The heart of the system.
- It is coated with a stationary phase which greatly influences the separation of the compounds.

Factors Affecting Column Separations

- **Volatility of compound**: Low boiling (volatile) components will travel faster through the column than will high boiling components
- **Polarity of compounds**: Polar compounds will move more slowly, especially if the column is polar.
- **Column temperature**: Raising the column temperature speeds up All the compounds in a mixture, “Columns have lower and upper temperature limits”.

Factors Affecting Column Separations

- **Column packing polarity**: Usually, all compounds will move slower on polar columns, but polar compounds will show a larger effect.
- **Flow rate of the gas through the column**: Speeding up the carrier gas flow increases the speed with which all compounds move through the column.
- **Length of the column**: The longer the column, the longer it will take all compounds to elute. Longer columns are employed to obtain better separation.

GLC

Carrier gas

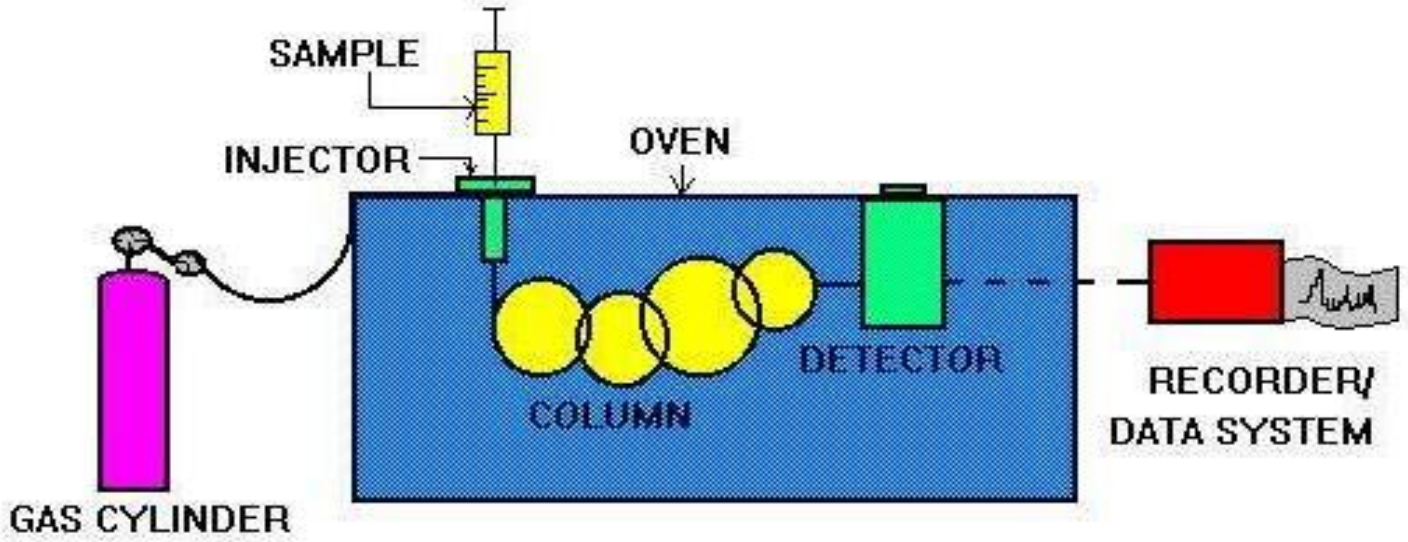
- Flow regulators & Flow meters
- **Injection devices**
- **Columns**
- **Temperature control devices**

- **Detectors**
- **Recorders & Integrators**

GC Part (2)

Gas Liquid Chromatography

GAS CHROMATOGRAPHY



GC

Carrier gas

- Flow regulators & Flow meters
- **Injection devices**
- **Columns**
- **Temperature control devices**

- **Detectors**
- **Recorders & Integrators**

Detector

- The part of a gas chromatograph
- which signals the change in
- composition of the mixture passing
- through it.

Detector types

1. Electron Capture Detector.
2. Flame ionization Detector.
3. Nitrogen Phosphors Detector.
4. Thermal Conductivity Detector.

Detector types

- 5. Flame Photometric Detector.
- 6. Photo ionization Detector.
- 7. Electrolytic Conductivity Detector.
- 8. Mass Spectrometric Detector.

1. Electron Capture Detector (ECD)

- **Mechanism:**
- • Electrons are supplied from a 63Ni foil lining the detector cell. A current is generated in the cell
- .Electronegative compounds capture electrons resulting in a reduction in the current.
- The amount of current loss is indirectly measured and a signal is generated.

ECD

- • **Selectivity**: Halogens, nitrates, conjugated carbonyls
- • **Sensitivity**: 0.1-10 pg (halogenated compounds);
- 1-100 pg (nitrates); 0.1-1 ng (carbonyls)
- Linear range: 1000-10000
- Gases: Nitrogen or argon/methane
- Temperature: 300-400°C

2. Flame ionization Detector (FID)

- **Mechanism:**
- • Compounds are burned in a hydrogen-air flame.
- • Carbon containing compounds produce ions that are attracted to the collector.
- • The No. of ions hitting the collector is measured and a signal is generated.

FID

- **Selectivity**: Compounds with C-H bonds.
- • **Sensitivity**: 0.1-10 ng
- Gases: Combustion hydrogen and air; Makeup He or N2
- Temperature: 250-300°C,and 400-450°C for high temp.

3. Nitrogen Phosphors Detector (NPD)

- **Mechanism:**
- • Compounds are burned • Nitrogen and phosphorous containing compounds
- produce ions that are attracted to the collector.
- • The number of ions hitting the collector is measured and a signal is generated.

NPD

- **Selectivity**: Nitrogen and phosphorous
- • **Sensitivity**: 1-10 pg
- Gases: Combustion - hydrogen and air; Makeup - Helium
- Temperature: 250-300°C

4. Thermal Conductivity Detector (TCD)

- **Mechanism**:
- • A detector cell contains a heated filament with an applied current.
- As carrier gas containing solutes passes through the cell, a change in the filament current occurs.
- • The current change is compared against the current in a reference cell.
- • The difference is measured and a signal is generated.

works by having two parallel tubes both containing gas and heating coils. The gases are examined by comparing the heat loss rate from the heating coils into the gas. Normally one tube holds a reference gas and the sample to be tested is passed through the other. Using this principle, a TCD senses the changes in the thermal conductivity of the column effluent and compares it to a reference flow of carrier gas. Most compounds have a thermal conductivity much less than that of the common carrier gases of hydrogen or helium.

TCD

- • **Selectivity**: All compounds except for the carrier gas
- • **Sensitivity**: 5-20 ng
- Linear range: 105 -106
- Gases: Makeup - same as the carrier gas
- Temperature: 150-250°C

5. Flame Photometric Detector (FPD)

- **Mechanism:**
- • Compounds are burned in a hydrogen-air flame.
- Sulfur and phosphorous containing compounds produce light emitting species (sulfur at 394 nm and phosphorous at 526 nm). A
- monochromatic filter allows only one of the wavelengths to pass. A photomultiplier tube is used to measure the amount of light and a signal is generated.
- A different filter is required for each detection mode.

FPD

- **Selectivity**: Sulfur or phosphorous containing compounds.
- • **Sensitivity**: 10-100 pg (sulfur); 1-10 pg (phosphorous)
- Linear range: Non-linear (sulfur); 103 -105 (phosphorous)
- Gases: Combustion - hydrogen and air; Makeup - nitrogen
- Temperature: 250-300°C

6. Photo ionization Detector (PID)

- **Mechanism:**
- • Compounds eluting into a cell are bombarded with high energy photons emitted from a lamp.
- Compounds with ionization potentials below the photon energy are ionized.
- The resulting ions are attracted to an electrode, measured, and a signal is generated.

PID

- • **Selectivity**: Depends on lamp energy. Usually used for aromatics and olefins (10 eV lamp).
- • **Sensitivity**: 25-50 pg (aromatics); 50-200 pg (olefins)
- Linear range: 105 -106
- Gases: Makeup - same as the carrier gas
- Temperature: 200°C

7. Electrolytic Conductivity Detector *(ELCD)*

- **Mechanism:**
- • Compounds are mixed with a reaction gas and passed through a high temperature reaction tube.
- Specific reaction products are created which mix with a solvent and pass through an electrolytic
- conductivity cell. The change in the electrolytic conductivity of the solvent is measured and a
- signal is generated. Reaction tube temperature and solvent determine which types of compounds are detected.

ELCD

- **Selectivity**: Halogens, sulfur or nitrogen containing compounds.
- • **Sensitivity**: 5-10 pg (halogens); 10-20 pg (S); 10-20 pg (N)
- Linear range: 105 -106 (halogens); 104 -105 (N); 103.5-104(S)
- Gases: Hydrogen (halogens and nitrogen); air (sulfur)
- Temperature: 800-1000°C (halogens), 850-925°C (N), 750-825°C (S)

8. Mass Detector (MS)

- **Mechanism:**
- • Compounds are bombarded with electrons (EI) or gas molecules (CI). then fragmented into characteristic
- charged ions or fragments. The resulting ions are focused and accelerated into a mass filter.
- mass filter selectively allows all ions of a specific mass to pass through to the electron multiplier. All of the ions of the
- specific mass are detected. The mass filter then allows the next mass to pass

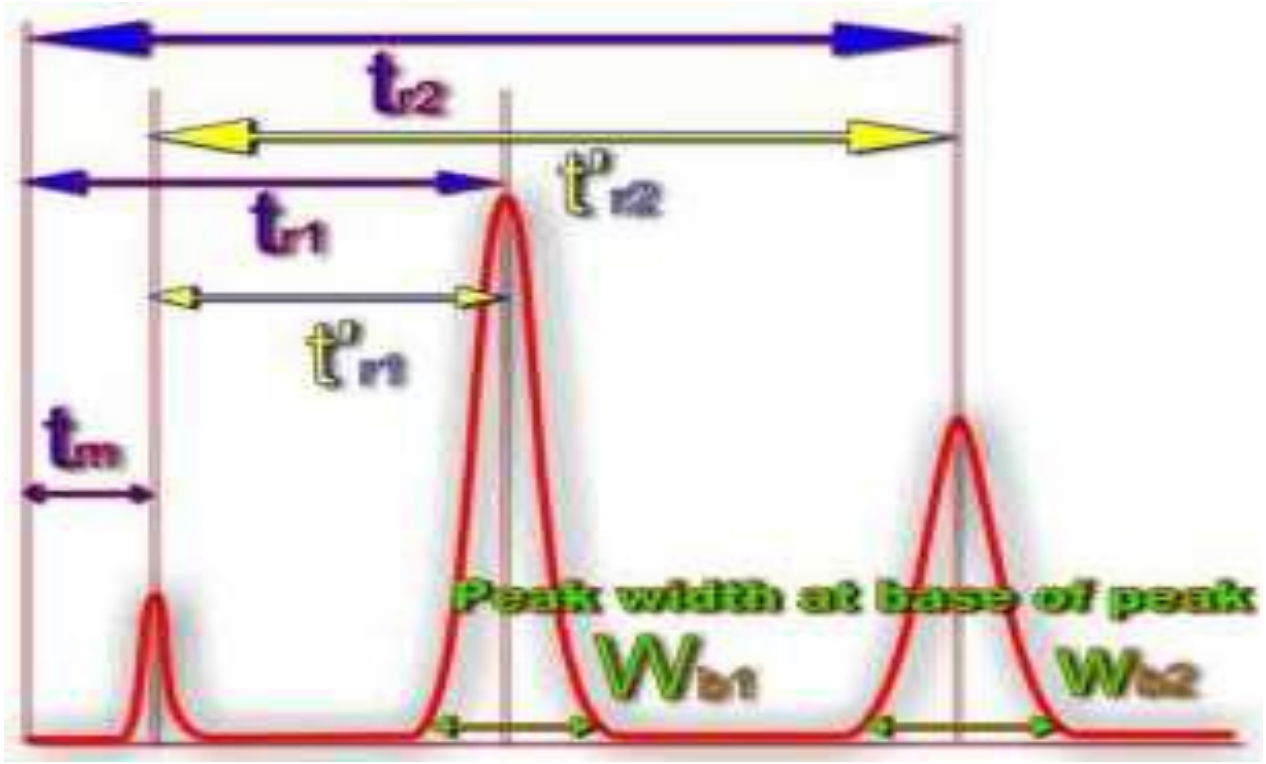
Good Detector

- 1.High sensitivity.
- 2. Rapidly respond to concentration changes.
- 3. Large linear range.
- 4. Stable with respect to noise and drift.
- 5. Low sensitivity to variation in flow,.
- 6. Possible selectivity.
- 8. Produces an easily handled signal.
- 9. A temperature range from room temperature to at least 400 C

Chromatogram

***The data recorder plots the signal from the detector over time.**

- **The retention time**, is qualitatively indicative of the type of compound.
- **The area under the peaks** or the height of the peak is indicative of the amount of each component

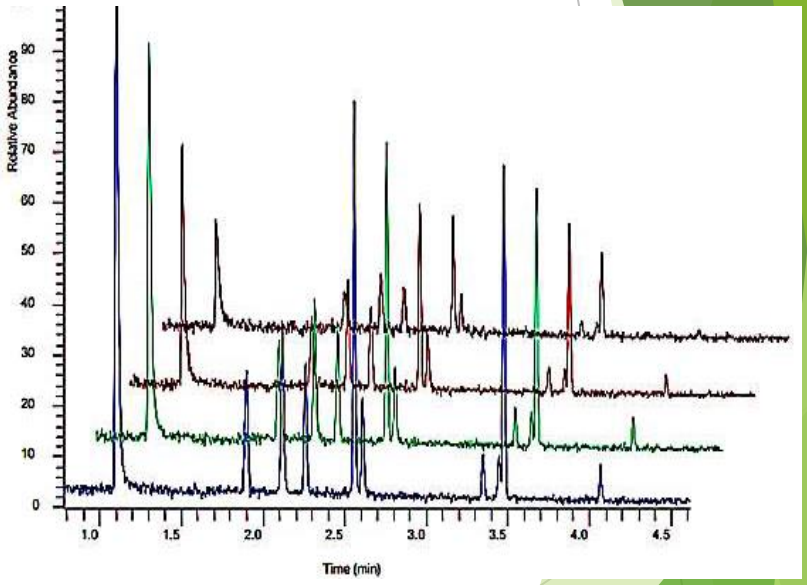

t_{r2}
t'_{r2}
t_{r1}
t'_{r1}
t_m
Peak width at base of peak
W_{b1}
W_{b2}

Retention Time (RT)

RT

Chromatogram

- **RT, is the time it takes for a compound to travel**
- **from the injection port to the detector.**
- • Thousands of chemicals may have the same
- retention time, peak shape, and detector
- response.
- • For example, under certain conditions, DDT has
- the same retention time as PCBs
- (polychlorinated biphenyls).



Applications

- the environmental
- • Testing or commercial laboratories
- • Industrial laboratories
- • Government laboratories
- • Research institutes
- **Petrochemical and Gas**
- • Refinery
- • Oil Industry
- • Gas suppliers

applications

- **Clean water analysis**
- **Pollutants in water**
- • Halocarbons
- • Acid priority pollutants: phenols,
- chlorophenols, nitrophenols
- • Pesticides
- **Other fields such as:** pharmaceutical
- foods

GC

Carrier gas

- Flow regulators & Flow meters
- **Injection devices**
- **Columns**
- **Temperature control devices**

- **Detectors**
- **Recorders & Integrators**

Instrumental Analysis

- Analytical chemistry is concerned with the chemical characterization of
- matter and the answer to two important questions: what is it ? (qualitative) and how much is it ? (quantitative).

solvent extraction

The lecture is classified to:

- 1) Introduction
- **2) Basic Principles of Solvent extraction Method**
- **3) The important of Solvent Extraction**
- 4) Classification of Extraction Systems
- **5) methods of Extraction**
- **6)** Factors Influencing the Extraction Efficiency
- 7) Analytical Applications

1-1) **Introduction To Solvent Extraction**

- Solvent extraction is a technique extensively
- utilized in both industrial applications and in
- the laboratory. It includes a variety of techniques
- such as liquid-liquid extraction (LLE),
- Liquid-solid extraction (LSE), supercritical fluid
- extraction (SFE), and other special techniques.
- **LLE is an extraction technique applied to liquids,-liquid samples, or** samples in solution, using a liquid extracting medium.

1-2) ***Introduction To Solvent Extraction***

- The quality of manufactured products often depends on proper chemical proportions, and measurement of the constituents is a necessary part of quality control [1].
- Solvent extraction technique is a part of analytical chemistry and has been
- recognized as an excellent separation method because of its ease, simplicity,

speed, and wide scope.

---

1) G. D. Christian, Analytical chemistry 6th Ed. (2004).

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2-1) *basic Principles of Solvent*

Extraction Method

- An extractant, is a substance primarily responsible for the transfer of a solute (here metal) from one phase to the other.
- The extractant is dissolved in a suitable diluent and together act as a solvent. The diluent is immiscible with other phase which is usually water.

2-2) basic Principles of Solvent Extraction Method

- The extractant reacts with the solute by
- solvation/chelation/ion pair formation etc. to extract from the aqueous phase.
- The distribution equilibrium between two phases is governed by Gibbs phase
- :rule, given by

Gibbs phase rule,

- P+V=C+2 (1)
- Where,
- P = is the number of phases,
- V = is the variance or degree of freedom and
- C = is the number of components
- And the number ***2*** corresponds Temp. and Pressure .

Gibbs phase rule,

- In solvent extraction, we have
- P = 2
- two phases namely aqueous and organic phase,
- the component C=1, viz. solute, in solvent and water phase and at constant temperature and pressure P=1, thus, we therefore have
- 2+1=1+2 i.e. P+V= C+2 …….(2)
- ,

Nernst Distribution Law

- According to Nernst distribution law,
- If [X]1 is concentration of solute in phase 1 and [X]2 is the concentration of solute in phase 2 at equilibrium:

)$K_D = [x]_1 / [x]_2$ …….. (3

- Where K_D is called as the partition coefficient or distribution coefficient

The Partition Coefficient Or Distribution Coefficient

- this partition or distribution coefficient (K_D)
- is independent of the total solute
- concentration in either of the phases

Distribution Ratio (D)

- The distribution of a solute between two immiscible solvents in contact to eac other can be described by the distribution Ratio (D)
- D = [X]**1** / [X]**2**

Where [X] represents the stoichiometric or formal concentration of a substance X

- and the subscripts 1 and 2 refer to the two phases.

Distribution Ratio (D)

- Since in most cases, two-phase
- system is of analytical interest, an organic solvent and aqueous are involved, D will be understood to be; D = [X]org / [X]aq
- The subscript org. and aq. refer to the organic and aqueous phases respectively
- Distribution ratio ‘D’ is dimensionless quantity, separation of two solutes

Separation Factor

- $D_A / D_B = \alpha$
- D_A and D_B are
- the respective distribution ratios of
- solute A and B.

Percent Extraction (%E)

- The more commonly used term for expressing the extraction efficiency by analytical chemist is the
- percent extraction “E”, which is related to “D” as
- $$\%\ Extraction\ (E) = \frac{(100D)}{D + Vaq/Vorg}$$
- Where, V represent solvent volume and the other quantities remain as previously defined.
- The percent extraction may be seen to vary with the volume ratio of the two phases as well as with D.

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3) ***Solvent Extraction May Serve***

- the following three purposes:
- i) Preconcentration of trace elements
- ii) Elimination of matrix interference
- iii) Differentiation of chemical species.

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4) Classification Of Extraction Systems

- The classification of extraction systems is based upon the process of extraction.

Thus, based upon the process of extraction,

- extraction systems can be classified into
- **four major classes**

Classification Of Extraction Systems

- a) Chelate extraction
- b) Extraction by solvation
- c) Extraction involving ion pair formation
- d) Synergic extraction

a -1)(Chelate Extraction)

- In this class, extraction proceeds by the process of formation of chelate or
- closed ring structure between the chelating agent and the metal ion to be extracted. e.g.
- **i) The extraction of Uranium with**
- **8-hydroxyquinoline in chloroform**.
- .

(a-2) Chelate Extraction

- ii) **The extraction of Iron with cupferron in carbon tetrachloride**
- the ammonium salt of ***N*-nitroso-N-phenylhydroxylamine**, is a common reagent for the complexation of metal ions. Its formula is $NH_4[C_6H_5N(O)NO]$. The anion binds to metal cations through the two oxygen atoms, forming five-membered chelate rings.
- Cupferron is prepared from phenylhydroxylamine and an NO+ source:

b) Extraction By Solvation

- **In this class,** the extraction proceeds by the process of solvation of the species which is extracted into organic phase. Oxygenated organic solvents such
- as alcohols (C-OH), ketones, ethers and esters show some basicity because of the
- lone pair of electron on the oxygen atom and can therefore directly solvate
- protons and metal ions and bring about their extraction.
- e.g. i) The extraction of Uranium with tributyl phosphate from nitric acid
- ii) The extraction of Iron(III) with diethyl ether from hydrochloric acid.

C) Extraction Involving Ion Pair Formation

- The extraction proceeds with the formation of neutral uncharged species which in turn gets extracted in to the organic phase. The best example of this is the extraction of Scandium and Uranium with trioctyl amine
- from mineral acids.

- In this case an ion pair is formed between complex of metal ion with high
- molecular weight amine and anionic species of mineral acids.

D) Synergic Extraction

- In this case, there is enhancement in the extraction on account of use of
- two extractants.
- e.g. the extraction of Uranium with tributylphosphate (TBP) as well as 2-thionyltrifluroacetone (TTA).

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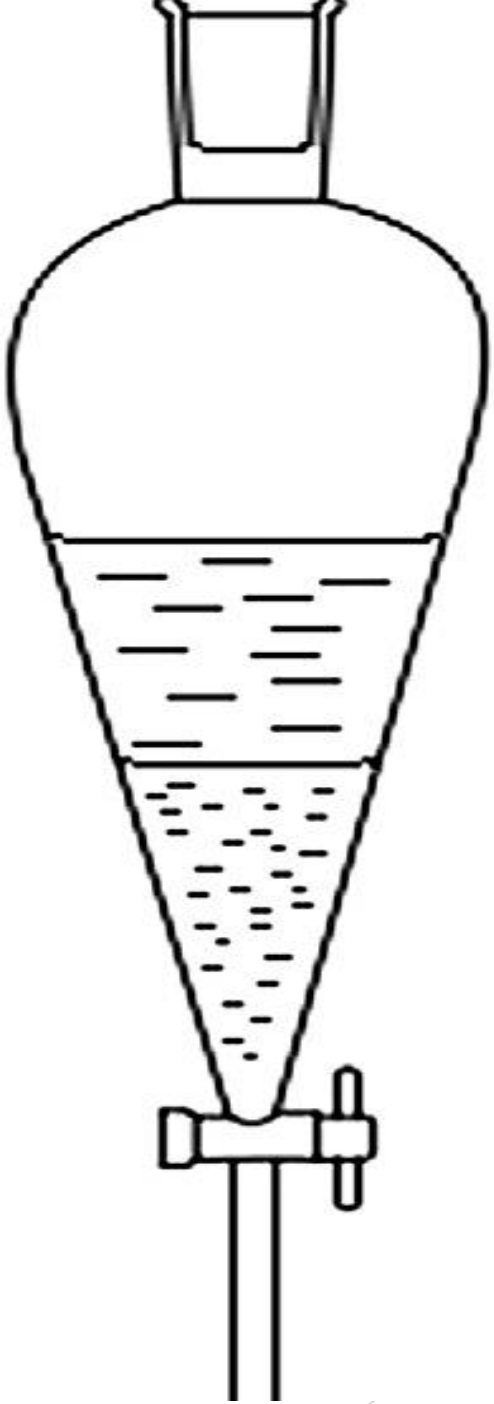
5) Methods Of Extraction

- Three basic methods of liquid-liquid extraction are generally utilized in
- the analytical laboratory.

A) Batch Extraction

- Batch extraction, the simplest and most commonly used method, consists of extracting the solute from one immiscible layer into other by shaking the two layers until equilibrium is attained, after which the layers are allowed to settle before sampling.
-
- *This is* commonly used on the small scale in chemical laboratories.
- The most commonly employed apparatus for performing a batch extraction is a *separatory funnel*.
- The batch extractions may also be used with
- *advantage when the distribution ratio is large.*



B-1) Continuous Extraction

- The second type, continuous extraction, makes use of a continuous flow of
- immiscible solvent through the solution or a continuous countercurrent flow of both phases.
- Continuous extractions are particularly applicable when the
- distribution ratio is relatively small.
- Continuous extraction device operate on the
- same general principle, which consist of distilling the extracting solvent from a boiler flask and condensing it and passing it continuously through the solution
- being extracted.

B-2) Continuous Extraction

- .The extracting liquid separates out and flows back into the receiving flask, where it is again evaporated and recycled while the extracted solute remains in the receiving flask.
- When the solvent cannot easily be distilled, a continuous supply of fresh solvent may be added from a reservoir

C) Countercurrent Extractions

- Extraction by continuous countercurrent distribution is the third general type and is used primarily for fractionation purposes.
- The separation through continuous countercurrent method is achieved by virtue of the density difference between the fluids in contact. In vertical columns, the denser phase enters at the top and flows downwards while the less dense phase enters from the bottom and flows upwards. The choice of method to be employed will depend primarily upon the value of the distribution ratio of the solute of interest, as well as on the separation factors of the interfering materials.

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6) Factors Influencing The Extraction Efficiency

- **Primary requirement of solvent extraction for**
- separation /removal purposes is
- a high distribution ratio of the solute of interest between the two liquid phases.
- It is useful to employ a number of different techniques
- for enhancing the distribution ratio.
- It depends on the nature of the species being
- extracted and extraction system.
- The attainment of selectivity in an extraction
- procedure is also very important.
- Some of the factors, which affect the
- distribution of solute of interest, are given below.

6-1) Nonchemical Factor Affecting Extraction

- factors address the nonchemical elements
- of the extraction, which include
- (1) the choice of the extraction technique,
- (2) the choice of solvent and aqueous phase volumes,
- (3) the time of extraction,
- (4) the solvent evaporation procedure, etc.

These factors are important for achieving the appropriate extraction efficiency for a successful utilization of LLE in sample preparation. The choice of the extraction procedure (batch or continuous), the number of extractions when using the batch procedure, etc.,

6-2) Factors Affecting Solvent Extraction

- A) Choice of solvent
- B) Acidity of an aqueous phase
- C) Stripping
- D) Use of masking agents
- E) Salting-out agents
- F-) Variation of oxidation state
- G) Synergic Extraction
- H) Use of organic acid media

7) Applications

- Removal of high boiling organics from wastewater
- such aniline, phenols, nitrate aromatics have
- Removal of carboxylic acid
- Essential oil extraction
- Agricultural chemical extraction
- Agricultural chemicals such as herbicides and pesticides
- Food industry applications

Solvent Extraction (part 2)

efficiency

The lecture is classified to:

1) Introduction •

2) Basic Principles of Solvent extraction •

Method

3) The important of Solvent Extraction

4) Classification of Extraction Systems •

5) methods of Extraction •

6) Factors Influencing the Extraction Efficiency •

7) Analytical Applications •

Factors Influencing the Extraction Efficiency

Primary requirement of solvent extraction for separation /removal purposes is a high distribution ratio of the solute of interest between the two liquid phases.

It is useful to employ a number of different techniques for enhancing the distribution ratio.

It depends on the nature of the species being extracted and extraction system.

The attainment of selectivity in an extraction procedure is also very important.

Some of the factors, which affect the distribution of solute of interest, are given below.

A) Choice of solvent

- safety, the toxicity and the flammability of the solvent must be considered.
- Use of a suitable solvent for effective separation is very important. Metal
- chelates and many organic molecules, being essentially covalent compounds do
- not impose many restrictions on the solvent and the general rules of solubility
- are the great use. In ion association systems and particularly in oxonium type
- ions, the role of solvents is very important. This is due to involvement of solvent
- in the formation of extractable species.

B) Acidity of an aqueous phase

The extractability of metal complexes is greatly influenced by the acidity of an aqueous phase, so it is necessary to assure optimum concentration of H^+ ions for maximum extraction. In the case of chelate extraction, the chelating reagent concentration is maintained constant; the distribution of the metal in a system is a function of pH. For this reason, curves of extractability versus pH at constant reagent concentration are of great analytical significance. Sometimes it is possible to achieve the desired characteristics of a solvent by employing a mixed solvent system.

C) Stripping

Stripping is the removal of the extracted solute from the organic phase for further processing or analysis. In many colorimetric procedures and even radioactive techniques, the concentration of solute is determined directly in the organic phase. However, where further separation steps are required, it is necessary to remove the solute from the organic layer to more stable medium.

D) Use of masking agents

- In the extraction procedures for metal pairs that are difficult to separate;
- masking or sequestering agents are introduced to improve the separation factor.

E) Salting-out agents

- The term salting-out agent is applied to those electrolytes whose addition
- greatly enhances the extractability of complexes. The function of salting-out
- agent would be primarily of providing a higher concentration of complex and
- thus improve the extraction. Water is probably bound as a shell of oriented water
- dipoles around the ion and thus becoming unavailable as “free solvent”.
- Addition of salting-out agents decreases the dielectric constant

- Addition of salting-out agents decreases the dielectric constant of the aqueous phase, which favors the formation of the ion association complexes.
- Salting-out agents have been used with great success in separation involving the halide and thiocynate systems.

F) Backwashing

- Backwashing is an auxiliary technique used with batch extractions to influence quantitative separations of This technique is analogous in many respects to the re-precipitation step in a gravimetric precipitation procedure. With the proper conditions, most of the impurities can be removed by this backwashing operation, with neglisible loss of the main component, thereby attaining a selective operation.elements.

F-) Variation of oxidation state

The selectivity of an extraction is increased by the modification of oxidation states of the interfering ions present in solution, in order to prevent the formation of their extractable metal complexes e.g. reduction of Cerium(IV) to Cerium(III) prevents extraction of this element from nitrate media, the extraction of Iron(III) from chloride solutions can be prevented by reduction to Iron(II), which is not extractable. Similarly, Antimony(V) may be reduced to the tetravalent state to suppress its extraction.

G) Synergic Extraction

- Synergism is defined as the combined action of two complexing reagents,
- which is greater than the sum of the actions of the individual reagents used
- alone. An example of the synergic extraction of Ce(III) with picrolonic acid and benzo-15-crown-5.

H) Use of organic acid media

Organic acid media are having ability of controlling the concentration of the complexing ligand, is one of the unique application, the ease of adjustment of pH and the wide difference in pH at which various metal ions form anionic complexes.

- •
- •
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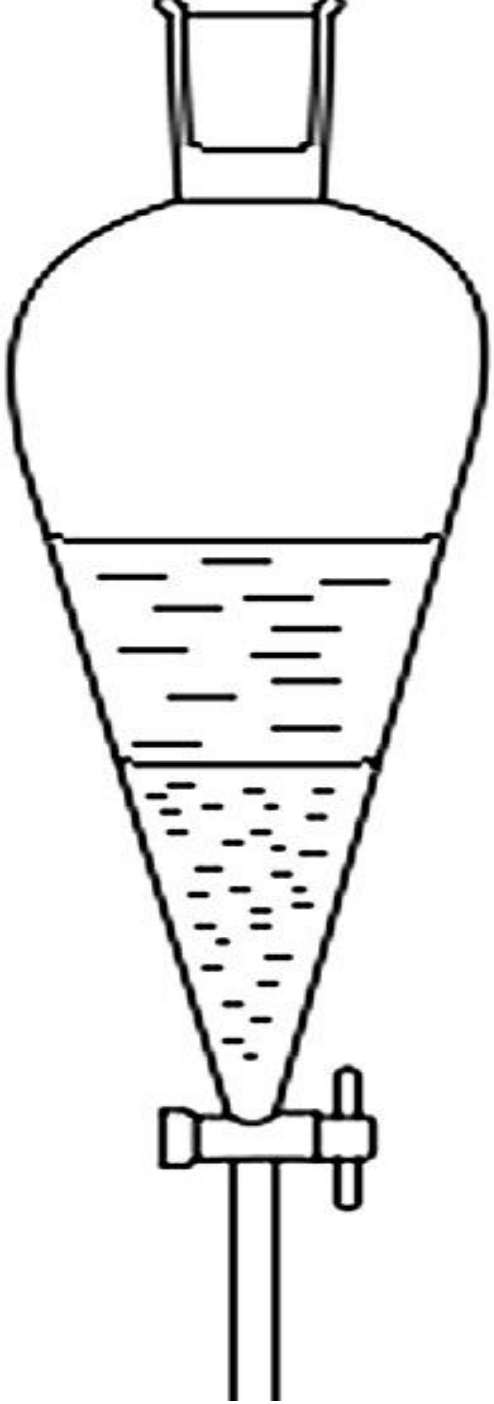

Removal of high boiling organics from wastewater

New technologies are developing day by day to reuse the water efficiently. Presence of micro pollutant such aniline, phenols, nitrate aromatics have adverse effect which renders the reuse of water. Solvent extraction method was reported as most effective method to remove and recover these chemicals from the wastewater.

Several extractants including octanol, amines, cyanex, diethyl carbonate, ionic liquid etc. has been employed to remove high boiling organics especially phenol from wastewater. [5].

Removal of carboxylic acid

Acetic acid is produced during fermentation of yeast which is an important inhibiting agents [11]. This acetic acid as well as other carboxylic acids and dicarboxylic acids
such as formic acid, succinic acid, valeric acid etc. are removed from aqueous stream using LLE process. LLE process is more economical and less energy consuming process compared to the distillation process [6].

Essential oil extraction

Bio-oil is produced from biomass pyrolysis. The end product is a complex mixture of different organic compounds. Due to high water content and high viscous property of bio-oil, LLE method is an efficient process to separate bio-oil according to their polarity and different chemical groups compared to the solid-phase extraction. The effect of extraction solvent and volume ratio is significant in case of LLE of bio-oil [8].

Agricultural chemical extraction

Agricultural chemicals such as herbicides and pesticides are extracted from the water using LLE method. Metals and mixture of organic compounds remains in the
agricultural waste are separated through the solvent extraction process [9].

Food industry applications

LLE process is commonly used in food industries. As for example, separation and
purification of a particular flavor or fragrance as well as caffeine extraction are done
by this process [12].