

UNIT-2

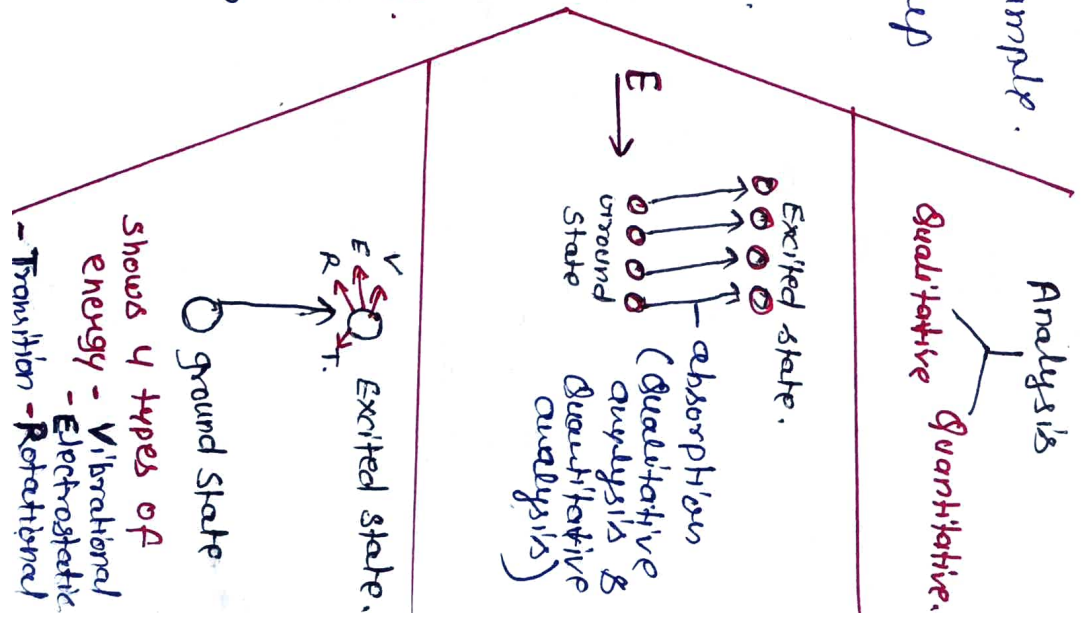
CHAPTER-1
Lecture-1

IR SPECTROSCOPY

Intro. to IR Spectroscopy

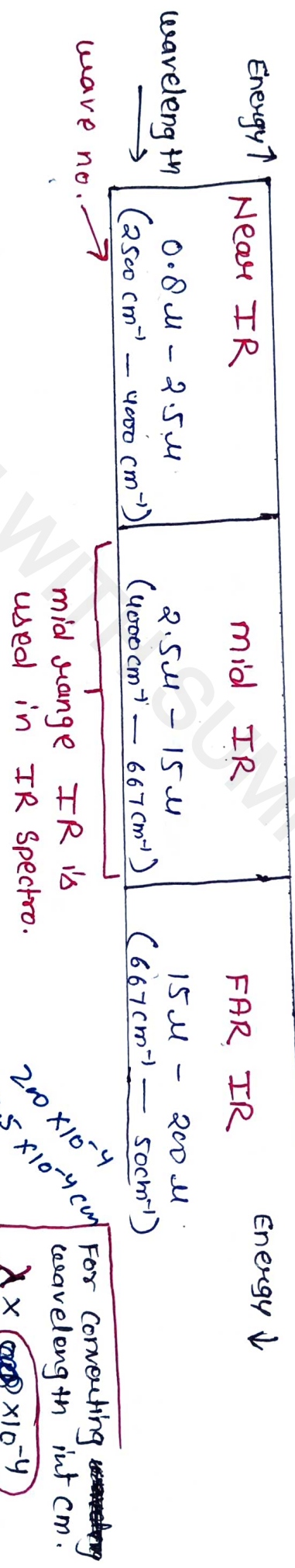
* Basic Introduction to IR-Spectroscopy and fundamentals

- it is a Qualitative analysis of unknown sample.
- it determine structure and functional group of any compound.
- it is based on absorption Spectroscopy.
- it is valid for the dipole moment compounds. [Such compounds having dipole moment value = 0 (Not valid)]
- In IR Spectroscopy only Two types of energy can be used - Vibrational, Rotational.
- If any molecules present in sample shows Vibrational and Rotational energy then we can Identify the compound by IR Spectroscopy.



- we know Energy (E) = $\frac{hc}{\lambda}$ (Energy \propto inversely proportional to wavelength λ)
 Energy \uparrow wavelength \downarrow

- IR can be measured on the basis of wavelength (λ) .
 \Rightarrow on the basis of wavelength IR can be divided into 3 regions \rightarrow



- In IR spectroscopy we can use wave number for analysis (not wavelength).

$$n = \frac{1}{\lambda}$$

n = wave number.

For converting ~~wavelength~~ wavelength into cm.
 $\lambda \times 10^{-4}$

For example ① Calc. wave number (given wavelength = 200 μ)

$$n = \frac{1}{\lambda}$$

$$\lambda = 200 \mu$$

$$n = \frac{1}{200 \times 10^{-4} \text{ cm}} = \underline{\underline{200 \times 10^{-4} \text{ cm}^{-1}}}$$

$$n = \frac{10^4}{200 \text{ cm}}$$

$$n = \frac{50}{200 \text{ cm}}$$

$$n = 50 \text{ cm}^{-1}$$

②

wave number = ?

(wavelength = 15 μ)

↓

$$n = \frac{1}{\lambda}$$

$$15 \times 10^{-4} \text{ cm}$$

$$= \frac{1}{15 \times 10^{-4} \text{ cm}}$$

$$= \frac{10000 \text{ cm}^{-1}}{15}$$

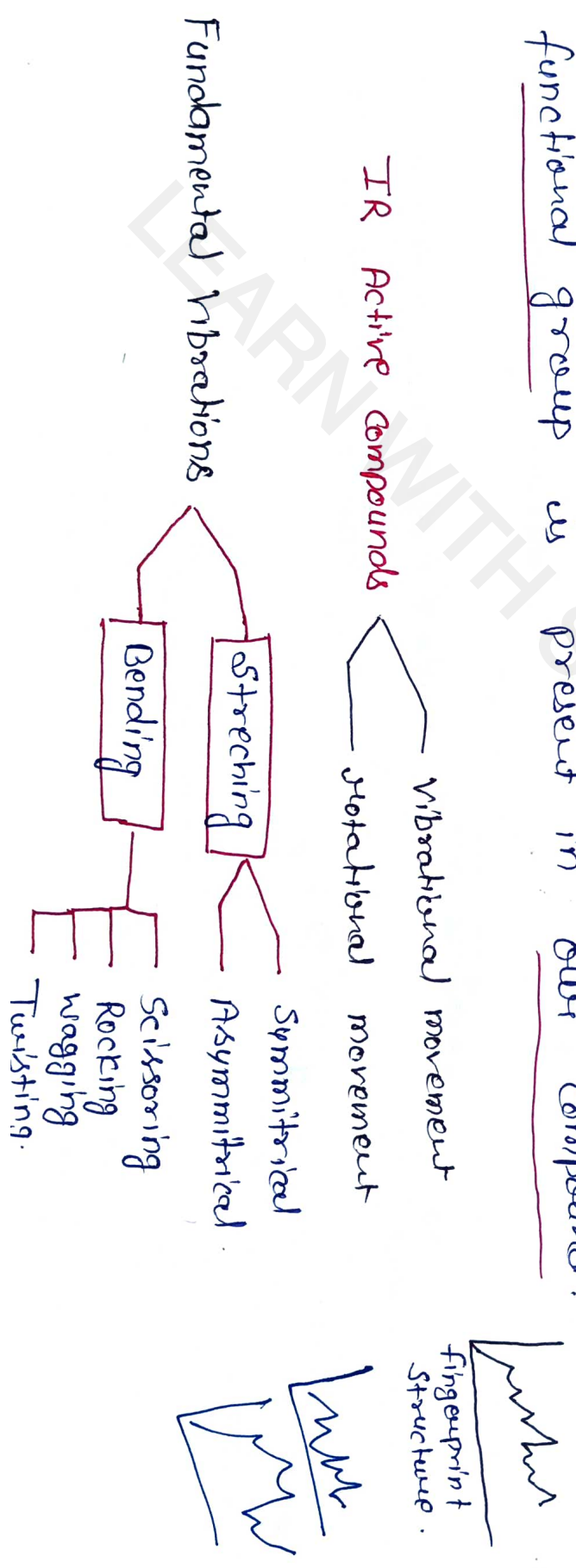
$$= 667 \text{ cm}^{-1}$$

* Fundamental modes of vibrations in poly-atomic molecules

→ The basic principle of IR - Spectroscopy is to determine the vibrational and rotational stretching and movements.

→ when any IR - active compound absorb the IR - radiation due to this movement they shows some fingerprint structure and this stretching structures for diff. diff. functional group so we can easily identify each functional group is present in our compound.

IR Active Compounds

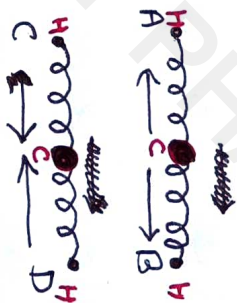


① Stretching vibrations

- In this type of vibrations, the atoms move essentially along the bond axis, so that the bond length increases or decreases periodically, at regular intervals.
- The vibration in which bond length is change.

⇒ Symmetrical vibrations

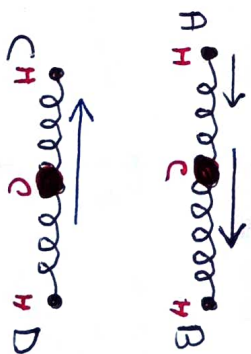
Symmetric stretching vibration of molecules AB and CD



● atoms moves away or towards the central atom.

⇒ Asymmetrical vibrations

Asymmetric stretching vibration of molecules AB and CD.



● one atom move away from central atom and one is move towards central atom.

② Bending vibration

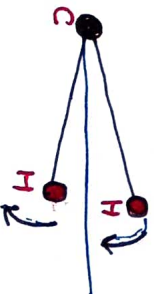
- In this type, there occurs a change in bond angles between bonds with a common atom or there occurs the movement of a group of atoms with respect to the remainder of the molecule without movement of the atoms in the group with respect to one another.
- A type of vibration in which bond angle is change.
- Bending vibrations are also called deformation vibrations.

- Scissoring vibration IN-PLANE



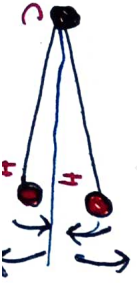
• when two bonded atoms move back and forth to each other

- Rocking vibrations



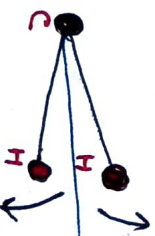
• when the same structural unit oscillate back and forth within the same plane.

- wagging vibration OUT OF PLANE



• when a non-linear three atomic structural unit oscillate back and forth out of plane

- Twisting vibration



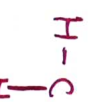
• when one atom move inside the plane and one atom move out side the plane.

* Factors Affecting Vibrations

① Vibrational Coupling

- The following four vibrations may be observed in the high resolution spectra of compounds containing both $-CH_2$ and $-CH_3$ groups.

$C-H \rightarrow$ one stretching frequency.



\rightarrow Two coupled vibrations having different frequencies.

i.e. ν_{anti} & ν_{sym} . (for Asymmetric and symmetric)



\rightarrow Equivalent couple vibrations.

② Hydrogen bonding

- The hydrogen bonding present in O-H and N-H compounds give rise to a number of effects in the IR-spectra.
- The carbonyl group or aromatic rings present in the same molecule O-H or N-H group may cause similar

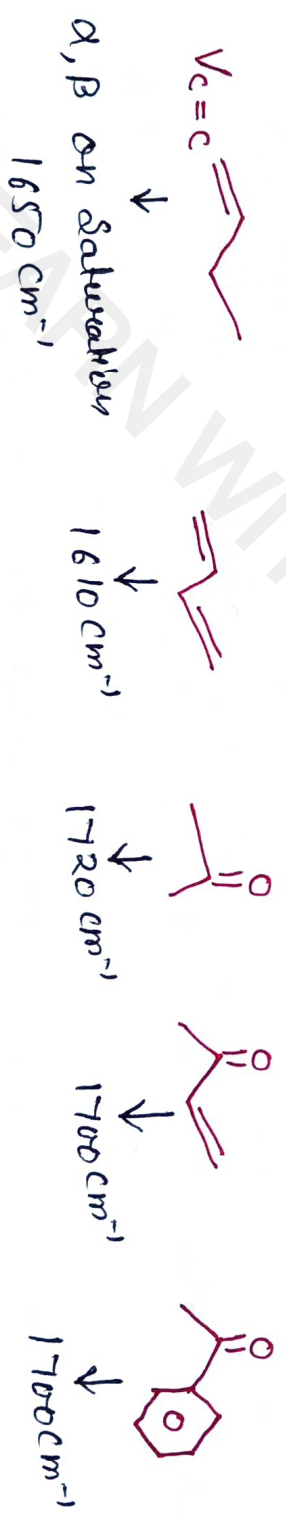
Shifts by intermolecular action.

③ Electronic effects

- Based on the theoretical principles one may explain the frequency shifts that normally take place in molecular vibrations when the substituents are altered.

① Conjugation effect

- it is observed to the lower frequency of both C=C structure and C=O str., irrespective of it is brought about by either α -B unsaturation or by an aromatic ring.



② Mesomeric effect or Resonance

- A molecule can be represented by two or more structures that differ only in the arrangement of

electrons, i.e. by structures that have the same arrangement of atomic nuclei. There is resonance.

② Inductive effect

- The inductive effect depends upon the "intrinsic" tendency of a substituent to either release or withdraw electrons i.e. its electronegativity acting either through the molecular chain or through space. This effect usually weakens steadily with increasing distance from the substituent.

④ Field effects

- These effects can be seen when two functional groups influence each other's vibrational frequencies by a through space interaction that may be either steric or electrostatic in nature.

eg- ortho-chlorobenzoic acid esters



* Sample Handling Techniques in IR Spectroscopy

- There are 4 types of sampling -

① Solid Sampling Technique

- it is done by 4 methods

② Direct Sampling method

• it is a simplest method. One sample holder is there and have to put sample on it.



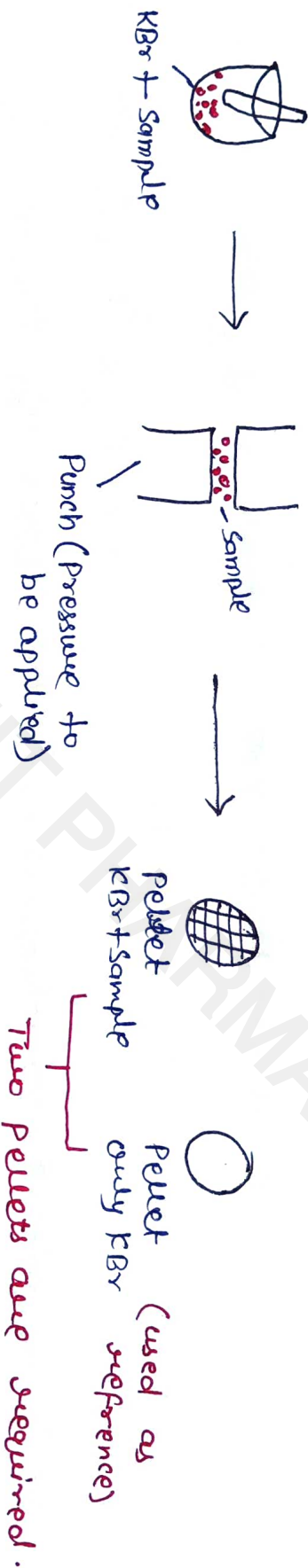
③ Pelletization technique

• we use some alkyl halides and they are able to pass IR radiation.

Eg. KBr , $NaCl$

↓
used for preparing pellet with sample.

- KBr & NaCl is used as diluents.
- Transparent for IR - radiation.



- Particle size $< 2 \mu\text{m}$,
- Sample should be 1-2% of KBr/NaCl (90%).

© millling

- Formation of paste.
- millling agent
 - NaCl
 - Hexachlorodiene,
 - Chloro fluoro carbon.



① Solid Sampling for Solution

- Sample present in volatile solvent will put in KBr/NaCl surface.
- Polymer, fats, wax material can be analyzed.

② Liquid Sampling Techniques

- Two layers of NaCl pellets (thin layer 0.1 - 0.3mm) is used.
- Liquid sample is ~~sampled~~ sandwiched b/w two layers.



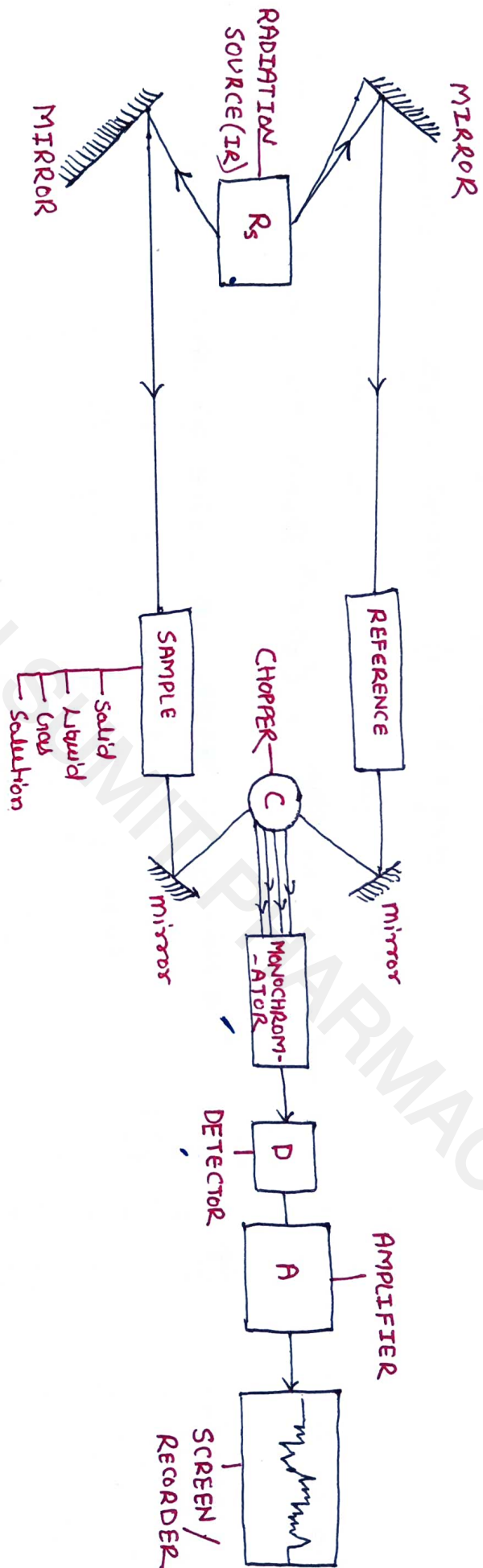
③ Gas Sampling Techniques

- Gas cells are used,
- Length of gas cells are 10cm,
- it's made up of NaCl,
- cells are put directly into the path of IR-radiation,

④ Solution Sampling Technique

- CHCl_3 (chloroform), CCl_4 (carbon tetrachloride), CS_2 (carbon disulphide)
- These solvents are used to dissolve various samples, After that sample is analyzed in the form of solution.
- **NOTE** → In all sampling techniques we have to avoid the use of water.

* INSTRUMENTATION OF IR SPECTROSCOPY



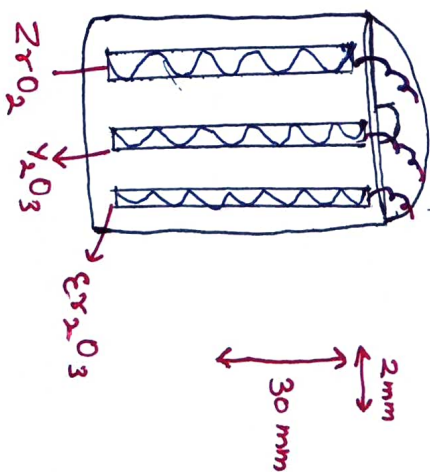
① RADIATION SOURCE

③ Incandescent Lamp

- In the near infrared instruments an ordinary incandescent lamp is generally used. However, this fails in the far infrared because it is glass enclosed and has a low spectral emissivity.

① Next glower

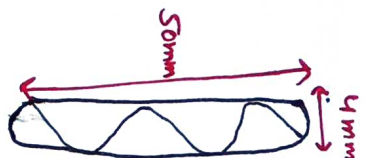
- it consists of a hollow rod which is about 2mm in diameter and 30mm in length.
- The glower is composed of rare earth oxides such as zirconia oxide (ZrO_2), yttria oxide (Y_2O_3), thoria oxides (Er_2O_3)
- it is non-conducting at room temperature and must be heated by external means to bring it to a conducting state.
- Glower is generally heated to a temperature b/w 1000 - 1800°C.
- Provide max. radiation at about 7100 cm^{-1} (1.4 μm)
- It emits the IR radiation over wide wavelength range (Far IR)



97:7:3 (Ratio)

① Cathode Source

- it is a rod of ^{sintered} Silicon Carbide which is about 50mm in length and 4mm in diameter.
- Required temperature for heating is 1300-1700°C.
- It emits max. radiation at 5200 cm⁻¹.
- it is a less intense source than the Nernst glower.



② MONOCHROMATORS

- monochromators convert polychromatic light into monochromatic light.
- These are of two types
 - Prism,
 - Grating,

① Prism

- these are made up of Alkali metal halides.



e.g → KCl, KBr, LiI, K, Rb, NaCl etc

② Grating

- this method consist many



- Series of prisms.

③ DETECTORS

① Balometry

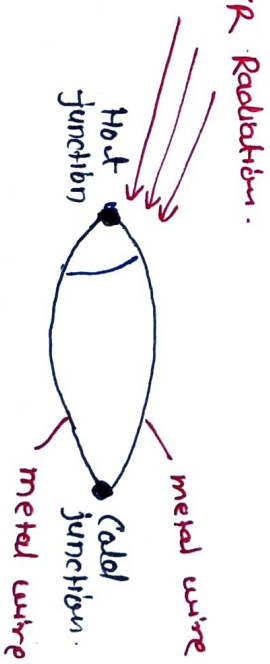
- Balometer is based on the fact that the electrical resistance of a metal increases 0.4% for every relative degree increase of temperature.

$$1^{\circ}\text{C} \uparrow \quad - \quad 0.4\% \text{ R} \uparrow$$

- Balometer is a thermo metal conductor.
- it consists of a thin metal conductor.

② Thermocouple

- it is based on the electrical IR radiation.
- ~~current~~ current flows when two dissimilar metal wires are connected together at both ends.



- A temperature differential exists b/w two ends.

- The end exposed to the infrared radiation is called the "Hot junction".
- The other connection, the cold junction, is thermally insulated and carefully screened from stray light.
- The electricity flow is directly proportional to the energy differential b/w the two connections. ✓

③ Thermistors

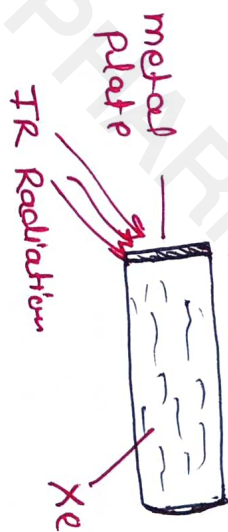
- It is made up of fused mixture of metal oxides.
- when Temp. ↑, the electrical resistance ↓

$${}^{\circ}\text{C} \text{ T} \uparrow \quad \text{---} \quad \text{R} \downarrow \text{ (5\%)} \\ \downarrow \\ \text{per } {}^{\circ}\text{C}.$$

④ Galay cell

- It contains a metal cylinder and Xenon (Xe) is filled inside.

- when IR radiation is falls on the cylinder, the gas is heated. and current is passing through it.
- when it is heated it acts like conductor.



② PhotoConductivity Cells

- This is non-thermal detector of great sensitivity.
- Consists of thin layer of lead sulphide or lead telluride supported on glass and enclosed into glass envelope.
- when IR radiation focused on lead sulphide or lead telluride, its conductance causes more current to flow.

(F)

Pyroelectric detectors

- When a dielectric placed in an electrostatic field become polarized. If the field is removed polarization disappears.
- But ferroelectric compound retain a strong residual polarization. Sometimes their residual polarization is temperature sensitive. Such materials are pyroelectric.
- A pyroelectric detector consists of a thin dielectric flake, when temp. of flake change an electrostatic charge appears, this happens upon exposure to IR radiation.
- A pyroelectric flake is cut from a single crystal and is very small (0.25 to 12 mm²)
- The most common pyroelectric is triglycine Sulphate. It response rapidly but deteriorates above 45°C, lost above 49°C. (So cooled in liquid N₂)

- New deuterated TMS detectors used at room temp
- They are detector of choice w/in Fourier transform IR.

LEARN WITH SUMIT PHARMACY

* Applications of IR - Spectroscopy

- ① Identification of Substances
- ② Determination of molecular Structure.
- ③ Studying of progress of Reactions.
- ④ Detection of Impurities.
- ⑤ Isomerism in organic Chemistry.
- ⑥ Identification of functional groups.

Miscellaneous Examples -

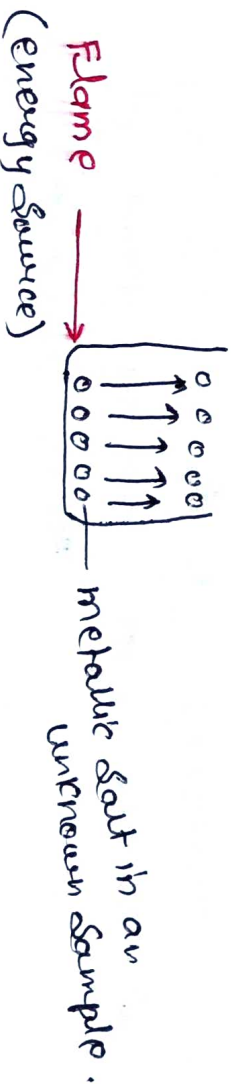
- Determination of purity.
- Shape of symmetry of a molecule.
- presence of water in sample.
- measurement of paints and varnishes.
- Examination of old paintings and Artifacts.
- In industry.

UNIT-2
CHAPTER-2

FLAME PHOTOMETRY

Introduction To FLAME PHOTOMETRY

- Flame photometry is based on the measurement of intensity of the light emitted when a metal is introduced into a flame.
- The wavelength of the colour tells us about the element is, and the colour's intensity tells us how much of the element is present.
- Flame photometry is also named as flame emission spectroscopy because of the use of a flame to provide energy of excitation to atoms introduced into the flame.



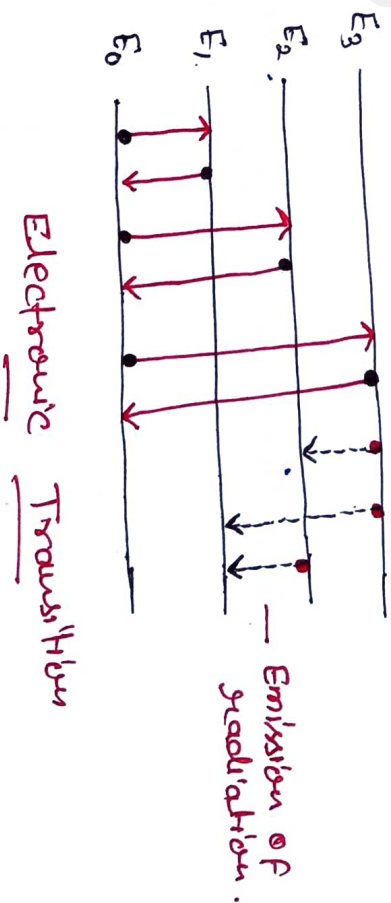
* Principle

- Flame emission spectroscopy (FES) may be explained when a liquid sample containing metallic salt solution under investigation is introduced into a flame, the following steps normally take place in quick succession, —
 - The solvent gets evaporated leaving behind the corresponding solid salt.
 - The solid salt undergoes vaporization and gets converted into its respective gaseous state.
 - All gaseous molecules give rise to free neutral atoms or radicals. (free e^-) \uparrow
 - Neutral atoms are excited by thermal energy of the flame which are fairly unstable and hence, instantly emit photons and eventually return to the ground state.

- The resulting emission spectrum caused by the emitted photons and its subsequent measurement forms the fundamental basis of FES

Example

Introduction of Sodium Salts to the flame impart a yellow colour, this is the principle of flame photometry. Larger no. of gaseous metallic atoms will remain in their ground state.



Electronic Transitions

→ In Diagram → Atoms at their lowest energy level is presented by E_0 , and E_1, E_2, E_3 represent the higher or excited energy level.

→ Bohr's equation :-

- it expresses the amount of energy absorb (ΔE) in the process -

$$\Delta E = E_1 - E_0 = h\nu = h \frac{c}{\lambda}$$

where, c = velocity of light

ν = frequency

h = Planck's constant

λ = wavelength of radiation absorb.

→ Boltzmann equation

It signifies the relationship b/w ground state and excited state atoms.

$$\frac{N_1}{N_0} = \left(\frac{g_1}{g_0} \right) \cdot e^{-\frac{\Delta E}{KT}}$$

where, N_1 = No. of atoms in excited state.
 N_0 = No. of atoms in ground state.

$\frac{g_1}{g_0}$ = Ratio of statistical weights for excited and ground state.

ΔE = Energy of excitation (hr)

K = Boltzmann constant.

T = Absolute temperature (K).

* Interferences

- In determining the amount of a particular element present, the other element can also affect the result.
- Some of commonly encountered interference processes in flame photometry are \rightarrow

① Spectral interferences

- it occurs when the emission lines of two elements can not be resolved or arises from the background of flame itself.
- They are either to close, or overlap, or occur due to high concn of salts in the sample.

②

Fewer interference :-

High temperature flame may cause ionisation of some metal atoms. e.g. Sodium



- The Na⁺ ion possesses an emission spectrum of its own with frequencies, which are diff. from those of atomic spectrum of the Na atom.

③

Cation - Anion interferences :-

- The presence of certain anions, such as oxalate, phosphate, sulphate, in a solution may affect the intensity of radiation emitted by an element.

④

Cation - Cation interferences :-

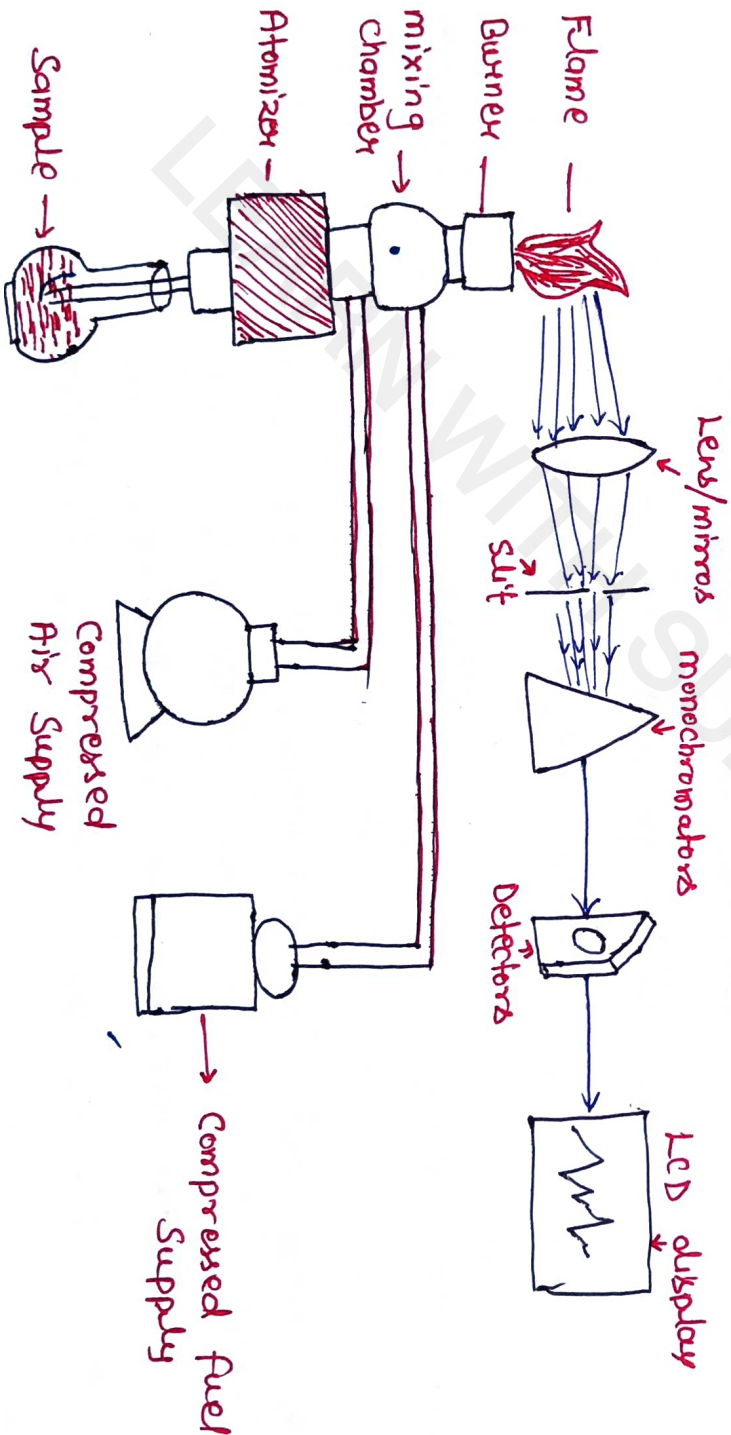
- These interference are neither spectral nor ionic in nature.

e.g. aluminium interferences with calcium and magnesium.

⑤ Oxide - formation interferences

- In this type of interferences, a large % of free metal atom usually combine with oxygen (present in flame) to form stable oxide, and thus depressed the emission intensity of free metal.

* Instrumentation of flame photometry



Parts of photometer :-

- ① Burner
- ② mirrors
- ③ monochromators
- ④ Filters
- ⑤ Detectors.

① Burner → In flame photometer, several burners and fuel-oxidant combinations have been used to produce the analytical flame.

ex. →

- ① mercer burner
- ② Total consumption burner.
- ③ Premix of laminar-flow burner.
- ④ Lindergraph burner.

② Mirrors :- The radiation from the flame is emitted in all directions in space.

- much of the radiation is lost and less of signal results in order to maximize the amount of radiation used in the analysis, a mirror is located behind

the burner to reflect the radiation back to the entrance slit of the monochromator.

- This mirror is concave and curves as wide a solid angle from the flame as possible.

③ monochromators

- Convert polychromatic light into monochromatic light.
- Prisms are most commonly made by quartz.

④ Filters

- In some elements the emission spectrum contains a few lines. In such cases wide wavelengths will be allowed to enter the detector without causing any serious error.
- In such a situation, an optical filter may be used in place of slit and monochromator system. The filter is made from such a material which is transparent over a narrow spectral range.

⑤ Detectors

- measures the intensity of radiation falling on it.
- The photomultiplier detectors are employed which produce an electric signal from the radiation falling on them.

Applications

① In Qualitative analysis - only used to detect elements of groups 1 and 2.

ex - Na, Mg, K, Ki, Sr, Br.

② In Quantitative Analysis - one of the most useful applications of flame photometry.

- Rapid, ^{Quantitative} determination of elements of group 1 & 2.

③ Simultaneous multi-element analysis :-

- This is relatively new application of flame photometry. Various methods have been used in multi elements analysis.

Unit-2

Chapter-3

ATOMIC ABSORPTION SPECTROSCOPY

⇒ Atomic absorption Spectroscopy

- Atomic absorption Spectroscopy is most powerful instrumental technique for the quantitative determination of trace ~~micro~~ metals in liquids
- Atomic absorption Spectroscopy is a method of elemental analysis. it is particularly useful for determining trace metals in liquids and is almost independent of the molecular form of the metal in the sample.

Example → we can determine the total Cadmium content of a water sample, it does not matter whether the cadmium exists as a chloride, nitrate, Sulphate or other salt.

* Principle

- AAS is the study of absorption of radiation by neutral atoms in a flame.
- Thus in atomic absorption spectroscopy, sample is first converted to atomic vapours and then absorption of atomic vapours measured at selected wavelength.
- This technique is also called as absorption flame photometry. because all the analytical applications of atomic absorption involve spraying of sample into the flame.
- In AAS, when an aerosol is delivered into a flame, the following sequence of events takes place in rapid succession :-
 - water/solvent is vaporised leaving minute particles of dry salt.

- Dry salt is vaporized at high temp. of flame.
- Then part/all the gaseous molecules are dissociated into neutral atoms.
- The neutral atoms in gaseous state absorbs radiation at a specific wavelength; ✓

* Interferences in Atomic Absorption Spectroscopy

- AAS is less affected by interferences, when compared to flame photometry.
 - This technique of AAS is free from cathodic interferences, this is because of the absorption of sharp resonance lines from hollow cathode lamp.
- Other interferences :-
- (A) Physical Interferences

① Back ground absorption

This occurs due to the sample matrix, flame itself, scattering, absorption by similar alkali halides etc.

Remedy :- use of gratings will avoid or minimize these interferences.

② Spectral line interference

- Atomic line interference, occurs due to the presence of other cations, which can emit radiation in the same region of emission by that of the element under analysis.

- This is also called cation-cation interference or molecular spectral interference.

Examples → • Aluminium interferes with emission lines of Ca and mg.

• Na and K mixture interfere with each other.

Remedy :-

- Extraction of the ions interfering with each other.

- Calibration curve of interfering material.
- Use of grating instead of prisms/filters.

③ Anionic Interference :-

Presence of certain anions in solution may affect the intensity of radiation emitted by an element and thus results in serious analytical errors.

Example Anions such as oxalate, phosphate, sulphate etc.

④ Vapourisation Interference :-

- chemical type, which occurs due to presence of some acids, by affecting the dissociation with other metals.

- physical type, due to high viscosity dextrose, sucrose overcome by following techniques :-

① Choice of flames, burners, atomisers & additives

E.g. → use of Acetylacoline/Nitrous oxide flame for thermally stable phosphates, sulphates, silicates, aluminates etc.

② Additives :- Releasing agents - Add few amount of Lanthanum/strontium as ionisation suppressant to overcome interference due to phosphate.

Chelation/masking - Add EDTA to mask Ca in presence of phosphate (cation - anion - interference)

③ Scattering effects

- This occurs due to presence of high concentrations of interfering elements.

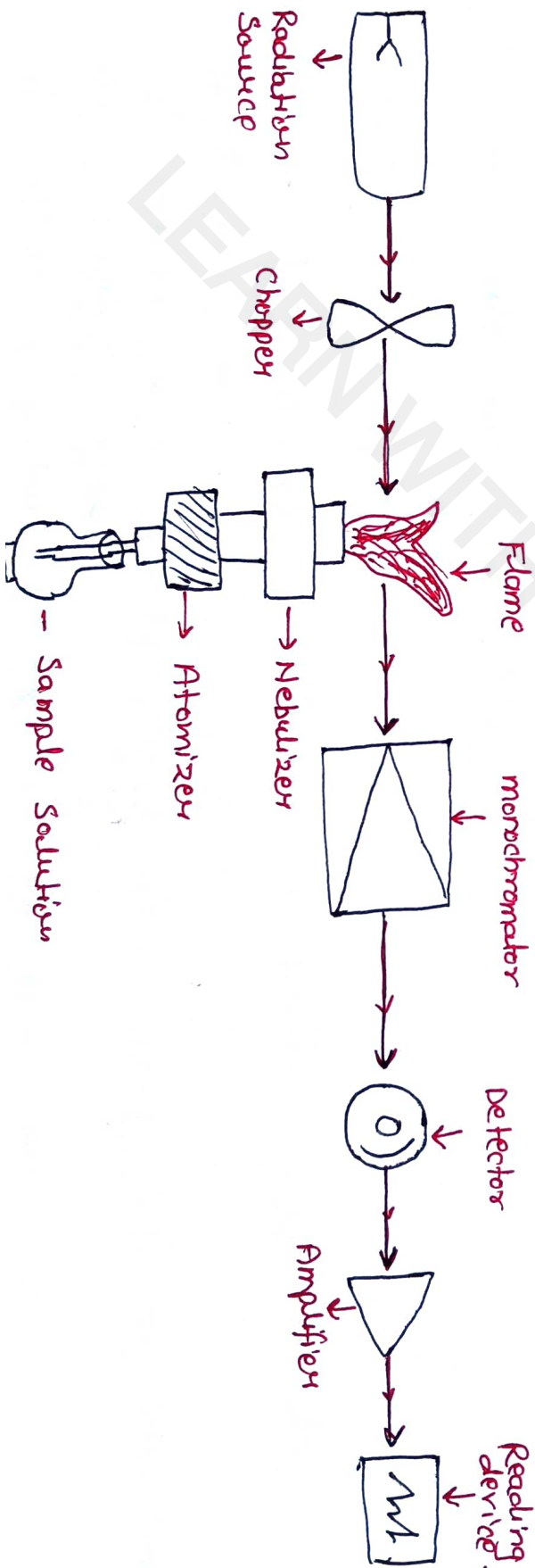
Remedy :- using continuous light source (deuterium lamp)

⑤ Ionization Interference :-

more ionization depopulates neutral atom both in ground state and excited state. Hence it decreases the sensitivity of the method.

Remedy :- Add excess of easily ionizable ions like K , Ca , $Strontium$. Hence it decreases the sensitivity of the method.

* Instrumentation



For all types of atomic absorption spectrometer, the following components are required :-

- ① Radiation Source ② Chopper ③ Atomizers ④ Nebulizer
- ⑤ Monochromators ⑥ Detectors ⑦ Amplifiers ⑧ Recorder

① Radiation Source

- The radiation source for atomic absorption should emit stable, intense radiation of the element to be determined.

- ① Hollow Cathode Lamp
- ② Electrodeless Discharge Lamp

② Chopper

- A rotating wheel is b/w the hollow cathode lamp and the flame.

- it breaks the steady light from lamp into an intermittent or pulsating light.
- it gives a pulsating current in the photocell.

③ Atomisers

- In order to achieve absorption of atoms, it becomes necessary to reduce the sample to the atomic state.

① Flame atomisers

② Non-flame atomisers

④ Nebulizer

- it converts the sample into small droplets is called nebulisation.

- A common method of nebulisation is by use of a gas moving at high velocity, called pneumatic nebulisation.

⑤ Monochromators

- In atomic absorption most commonly used monochromators are prisms, and grating.



- Converts polychromatic light in monochromatic light.

⑥ Detectors

- Photomultiplier tube is most suitable for AAS.
- it has good stability if used with a stable power supply.

⑦ Amplifier

- Amplify the electric current many times which comes from detectors.
- "Lock-in" amplifiers are preferred.

⑧ Read out device / recorder

- chart recorders are used as read out devices.

Applications

- ① In Qualitative analysis :- In AA's, a different hollow cathode lamp is to be used for each element to be tested.
- ② In Quantitative analysis :- The technique of quantitative analysis is based on the determination of the amount of radiation absorbed by the sample.
- ③ Simultaneous multi component analysis.
- ④ Determination of metallic elements in biological materials.
- ⑤ " " " in food industry.
- ⑥ Determination of Ca, Mg, Na and K in blood serum.
- ⑦ Determination of lead in petrol. ✓ ✓

* Difference b/w Atomic Absorption Spectroscopy and Flame photometry.

Atomic Absorption Spectroscopy

- Radiation absorbed by ground state.
- The thermal energy of flame is just enough to get neutral atoms. Hence it does not depend on temperature.
- wide range of elements can be analysed.

Flame photometry

- Radiation emitted by excited atoms.
- Excited atoms are obtained by thermal energy of flame. Hence, it is temperature dependent.
- Very few elements especially group 1A and 2A only can be analysed.

∩

Unit-2 Chapter-4 NEPHALOTURBIDOMETRY

Nephelometric & Turbidimetric methods

Introduction - Nephelometric and Turbidimetric methods depend on the scattering of light by particles suspended in a liquid.

- Nephelometry is the measurement of scattered light as a function of suspended particles (<100 mg/l) 90°.
- Turbidimetry is the measurement of ^{Intensity} Transmitted light as a function of concentration of suspended particles (>100 mg/l).
transmitted through the sample
180°

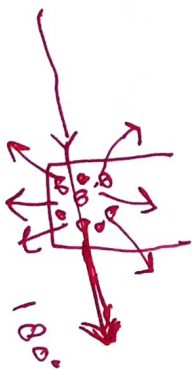
Principle

→ Nephelometry :- At low concentration of a suspended suspension, there is uniform scattering, Hence the intensity of scattered light is proportional to concentration.

The intensity of scattered light is normally measured at 90°, it can also be measured at any convenient angles like 45°, 60°, 135° etc.

→ Turbidimetry :- At high concn of a suspension, scattering is not uniform and light is scattered in all directions. Hence, it becomes difficult to measure the intensity of scattered radiation at all angles. Hence the intensity of transmitted light is measured at 180°.

- Concn ↑ Intensity of transmitted light ↓
- Concn ↓ Intensity of transmitted light ↑.



Choice of method :-

Depends upon the amount of light scattered by suspended particles present in the solution.

Turbidimetry → High concentrated suspension.

Nephelometry → Low concn suspensions. More accurate results.

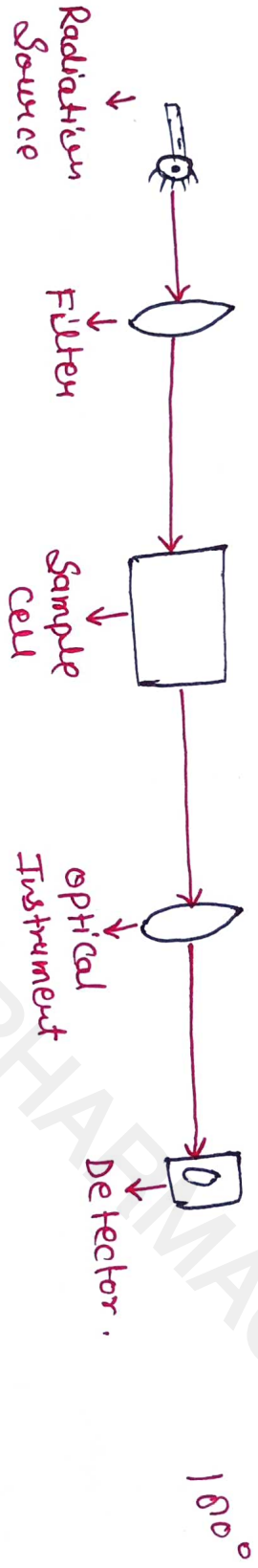
⇒ Factors Responsible for producing uniform Turbidity :-

- ① The manner, order and scale of mixing of substances.
- ② Agitation of Suspension.
- ③ Temperature.
- ④ presence/Absence of inert electrolytes, protective colloids like gelatin, acacia, dextrin.
- ⑤ Concn of Solutions mixed to get a suspension.

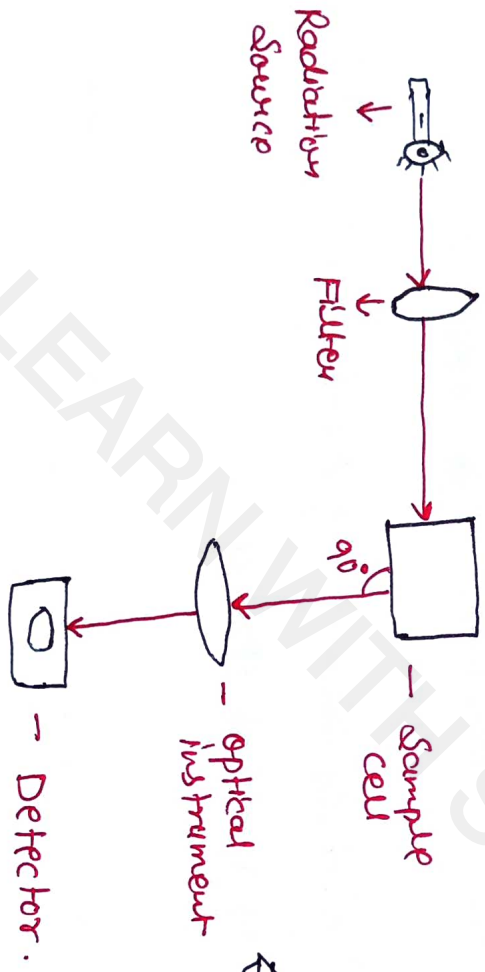
⇒ Factors Responsible for Intensity of Scattered Radiation :-

- ① No. of suspended particles.
- ② Size and shape of particles.
- ③ wavelength of radiation used.
- ④ Difference in the refractive index of particles and the medium.

Instrumentation :-



[TURBIDIMETER]



⇐ [NEPHELOMETER]

Components :-

- ① Source of light :- Tungsten lamp mercury arc lamp.
 - ② Filters & monochromators :- when a white light or polychromatic light is used, filters and monochromators are not required.
 - ③ Sample cells :- These are made up of glass, various shapes of sample cells are used in Nepheloturbidimetry.
 - ④ Detectors :- Photometric Detectors like photovoltaic, photo tubes / photomultiplier tubes are used.
- Applications :-
- ① Determination of particle size present in suspension.

- ② Determination of average molecular weight of polymer in solution.
- ③ Measurements of atmospheric pollutants.
- ④ Determining the concn of solute in a solvent made solution.
- ⑤ Growth of Bacterial cell in a liquid nutrient medium.
- ⑥ Determination of CO_2 , sugar products and clarity of Citric acid juice.
- ⑦ Determining end ^{Point} ~~point~~ of precipitation titration.

Sumit