

UNIT-II

IR SPECTROSCOPY

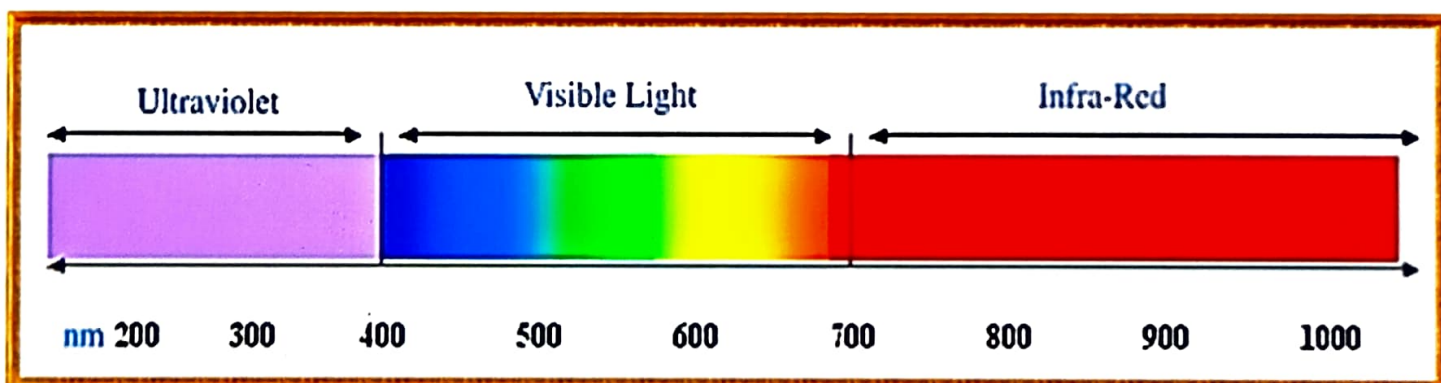
Points to be covered in this topic

- ❖ Introduction
- ❖ Fundamental modes of vibrations in polyatomic molecules
- ❖ Sample handling
- ❖ Factors affecting vibrations
- ❖ Instrumentation
 - Sources of Radiation
 - Wavelength Selectors
 - Detectors
- ❖ Applications

IR SPECTROSCOPY

❖ INTRODUCTION

- Infrared (IR) spectroscopy deals with the **infrared region** ($12800 - 10 \text{ cm}^{-1}$) of electromagnetic spectrum.
 - The term **infra means beyond**, thus **infrared means beyond red**.
 - It covers a range of techniques, the most common being a form of **absorption spectroscopy**.
 - This spectroscopic technique is used for **identifying compounds** and determining the **sample composition**.
 - **Infrared spectrophotometer** is a common laboratory instrument used for this technique.
 - The infrared region in electromagnetic spectrum is divided into the following **three regions** named for their relation with the visible spectrum :
- 1) **The far-infrared**, approximately $400 - 10 \text{ cm}^{-1}$ ($1000\text{-}30\mu\text{m}$), lies adjacent to the microwave region, has low energy and is used for **rotational spectroscopy**.
 - 2) **The mid-infrared**, approximately $4000 - 400 \text{ cm}^{-1}$ ($30\text{-}2.5\mu\text{m}$) is used to study the **fundamental vibrations** and associated rotational -vibrational structure. This region has wavelengths between 3×10^{-4} and $3 \times 10^{-3} \text{ cm}$.
 - 3) **The near- infrared**, approximately $14000\text{-}4000 \text{ cm}^{-1}$ ($2.5\text{-}0.8\mu\text{m}$) has higher energy and can **excite overtone or harmonic vibrations**.

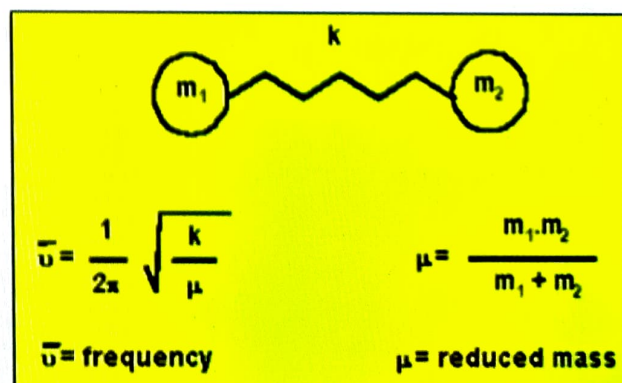


	λ (cm)	λ (μm)	λ (cm^{-1}) (Wavenumber)	Energy (E)
Near	7.8×10^{-5} to 3×10^{-4} (0.000078-0.0003)	2.5 to 0.8	14,000 to 4,000	10-37Kcal/mole
Mid	3×10^{-4} to 3×10^{-3} (0.0003-0.003)	30 to 2.5	4,000 to 400	1-10Kcal/mole
Far	3×10^{-3} to 3×10^{-2} (0.003-0.03)	1000 to 30	400 to 10	0.1-1Kcal/mole

- ✓ IR spectra are mostly reported in μm , however, $\bar{\nu}$ (nu bar or wavenumber) is another currently preferred unit.
- ✓ **Organic molecules absorb the IR radiation** and convert them into **energy of molecular vibrations**.
- ✓ In IR spectroscopy, an organic molecule is exposed to IR radiation, and **absorption occurs when the radiant energy matches a specific molecular vibration energy**.

❖ Principle

- Infrared spectroscopy works on the principle that **all molecules vibrate and absorb energy** in the infrared region.
- Most of the vibrational absorption states correspond to **2.5 – 25 μm (4000 - 400 cm^{-1}) wavelength**.
- The vibrational frequency (ν) in a **two atomic system** containing two masses (m_1 and m_2) is related to the force constant (k) and reduced mass by the following equation:
- As per the formula, **larger the force constant (k) of the bond** between two atoms, **higher is the vibrational frequency**.
- Thus, indicating that a **C =C bond** will absorb at a higher frequency than a **C —C bond**



❖ FUNDAMENTAL MODES OF VIBRATIONS IN POLYATOMIC MOLECULES

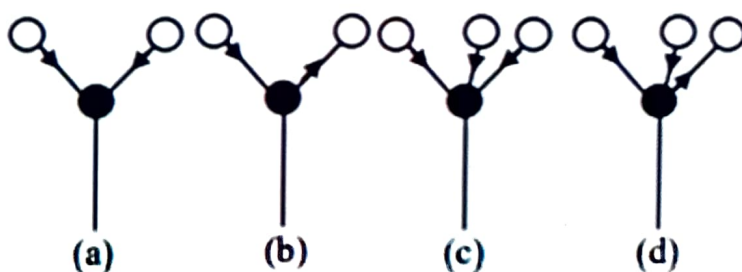
■ Fundamental vibrations are of the following two types:

- 1) Stretching Vibrations:** In this type, the **distance** between the two atoms **increases or decreases**, however, keeping the atoms in the same bond axis. Stretching vibrations are of the following two types:
 - i) Symmetric Stretching Vibrations:** In this type, the movement of atoms with respect to a **particular atom in a molecule is in the same direction**.
 - ii) Asymmetric Stretching Vibrations:** In this type, **one atom approaches and the other atom moves apart from the central atom**.
- 2) Bending or Deformation Vibrations:** In this type, the **positions of atoms change** with respect to the **original bond axis**. The stretching absorptions of a bond appear at higher frequencies (i.e., higher energy) than the bending absorptions of the same bond.

Bending vibrations are of the following four types:

- i) Scissoring:** In this type, two atoms approach each other.
- ii) Rocking:** The movement of atoms is in the same direction.
- iii) Wagging:** Two atoms move up and down the plane with respect to the central atom.
- iv) Twisting:** One atom moves up the plane and the other moves down with respect to the central atom.

- In a polyatomic molecule, the same bond can perform stretching and bending vibrations simultaneously

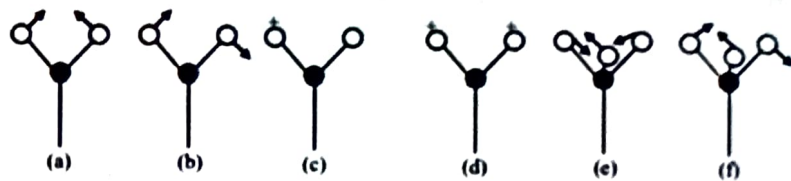


Stretching Vibrations

- (a) = Symmetric stretching vibration of AB_2 molecule
- (b) = Asymmetric stretching vibration of AB_2 molecule
- (c) = Symmetric stretching vibration of AB_3 molecule
- (d) = Asymmetric stretching vibration of AB_3 molecule

- Bending vibrations are of the following two types:

- i) **In-plane deformation vibrations,**
- ii) **Out-of-plane deformation vibrations.**



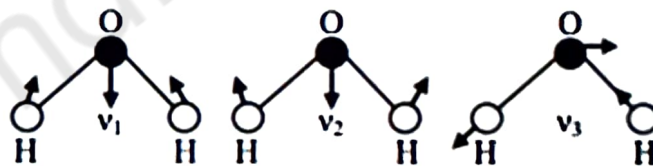
Bending or Deformation Vibrations

- Water is a triatomic non-linear molecule with $3 \times 3 - 6$ or $3(3n-6)$ normal modes of vibrations, which can be calculated by applying the following two primary forces:

- (a) **Scissoring**
- (b) **Rocking Vibrations of AB₂ Molecule; The out-of plane deformation vibrations**
- (c) **Twisting and**
- (d) **Wagging Vibrations of AB₂ Molecule;**
- (e) **Symmetric and**
- (f) **Asymmetric Vibrations of AB₃ Molecule.**

- I. The force acting against stretching or shortening of O-H bond, and
- II. The force acting against the bending of H-O-H molecule.

- These forces are applied to the water molecule and the nature of three normal modes of vibration of water is determined with the help of **Herzberg method.**



Normal modes of vibration of water

- While determining the **number of modes of vibrations** in the IR spectrum, the following experimental **limitations** are observed:
 1. Vibrations not falling in the IR region do not appear in the IR spectrum.
 2. Weak vibrational bands are not observed in the IR spectrum.
 3. The vibrational bands with same or slightly different frequencies overlap each other and are observed as a single band in the IR spectrum.
 4. Some vibrational bands may degenerate and appear at the same place in IR spectrum.
 5. No band appears in the IR spectrum of a molecule if no change occurs in its dipole moment.

❖ SAMPLE HANDLING

- Sampling Cells and Sampling of Substances.
- As infrared spectroscopy has been used for the characterization of solid, liquid or gas samples, it is evident that samples of different phases have to be handled.
- But these samples have to be treated differently. However, the only common point to the sampling of different phases is that the material containing the sample must be transparent to IR radiation.

➤ Sampling of Solids

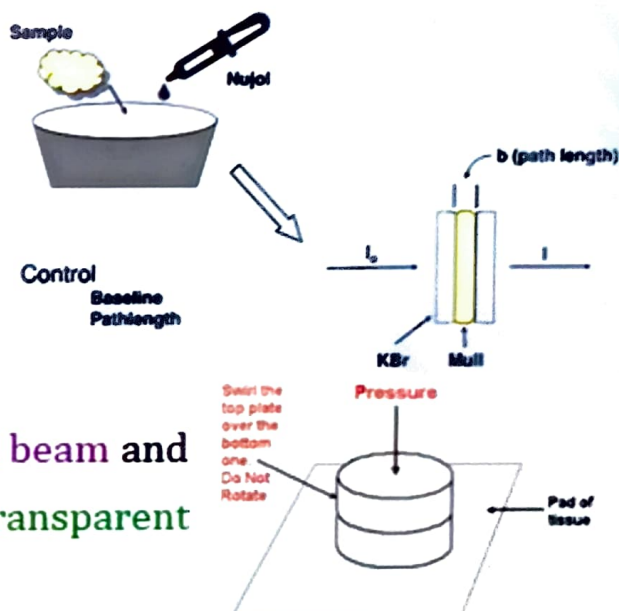
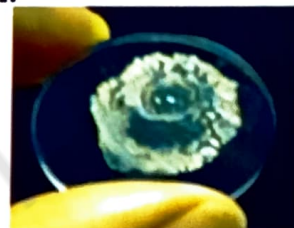
There are three techniques for recording solid spectra

1. Solid Films:

- ✓ Solid films can be deposited onto NaCl or KBr plates by allowing a solution in a volatile solvent to evaporate drop by drop on the surface of the flat.
- ✓ Polymers and waxy or fatty materials often give excellent spectra. This technique is useful for rapid qualitative analysis but becomes useless for carrying out quantitative analysis.

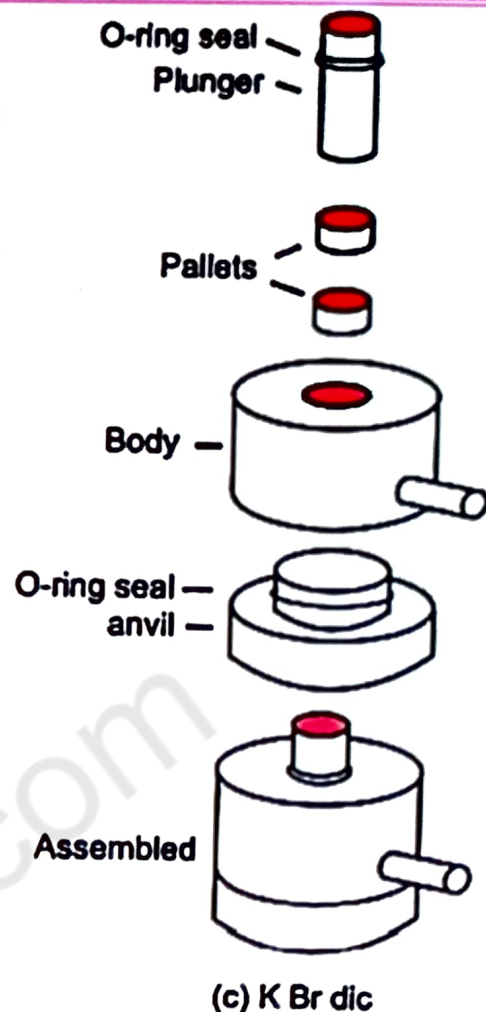
2. Mull Technique:

- ✓ In this technique, the finely ground solid sample is mixed with Nujol (mineral oil) to make a thick paste which is then made to spread between IR transmitting windows.
- ✓ This is the mounted in a path of infrared beam and the spectrum is run. Although Nujol is transparent throughout IR region.
- ✓ When IR spectrum of solid sample is taken in Nujol mull, absorption bands of the sample that happen to coincide with the absorption bands of the Nujol mull will be hidden, but others will be clearly seen in the IR spectrum.
- ✓ This method is good for qualitative analysis but not for quantitative analysis.



3. Press pellet technique:

- ✓ In this technique small amount of finely ground solid sample immediately mixed with about 100 times its weight of powdered potassium bromide.
- ✓ The finely ground mixture is then passed under very high pressure in a press (at least 25,000 p sig) to form a small pellet (about 1-2 mm thick and 1cm in diameter)
- ✓ The resulting pellet is transparent to IR radiation and is run as such 1-2 mm thick and 1cm.
- ✓ Particle size must be fine to avoid scattering is than wavelength of infrared radiation-that is, less than 2 μ m.



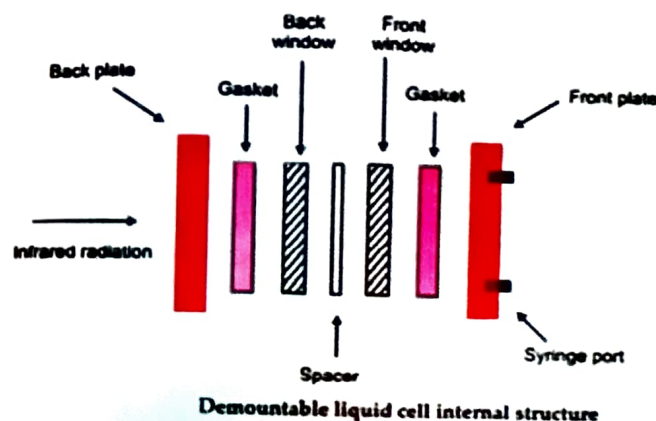
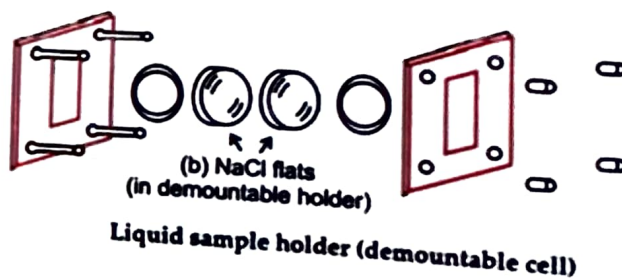
➤ Sampling of liquids

This is simplest infrared sampling technique.

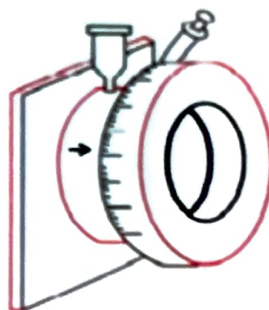
A liquid as a thin film squeezed between two infrared-transparent windows.

There are several different types of transmission solution cells available.

1. Fixed path length sealed cells are useful for volatile liquids, but cannot be taken apart for cleaning.
2. Semi-permanent cells are demountable so that the windows can be cleaned. The spacer is usually made of polytetrafluoroethylene (PTFE, known as Teflon') and is available in a variety of thicknesses, hence allowing one cell to be used for various path lengths.



3. Variable path length cells incorporate a mechanism for continuously adjusting the path length, while a vernier scale allows accurate adjustment shown



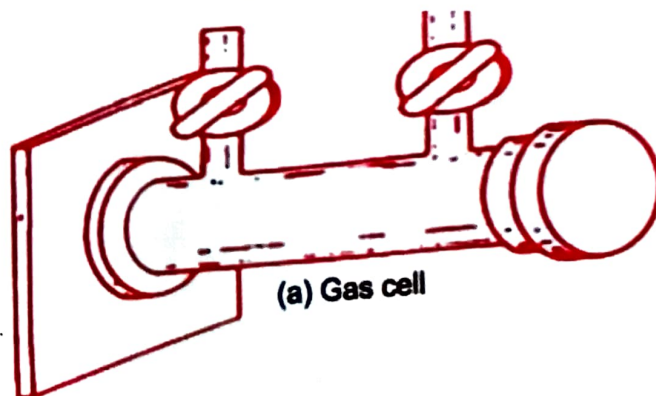
Variable path length cell

Variable pathlength cell

- All of these cell types are filled by using a syringe and the syringe ports are sealed with PTFE plugs before sampling.
- An important consideration in the choice of infrared cells is the type of window material.
- The latter must be transparent to the incident infrared radiation and alkali halides are normally used in transmission methods.
- Liquid cells made of NaCl, KBr or ThBr flats.

➤ Sampling of Gases

- ✓ The gas sample cell is similar to the cell for liquid samples.
- ✓ The gas sample cell surfaces in the light path are made of KBr. NaCl.
- ✓ To compensate for the small number of molecules of a sample that is contained in a gas, cells are larger.
- ✓ They are about 10 cm long, but may be up to 101 M long.
- ✓ Multiple reflections can be used to make the effective path length as long as 40 M. so the constituents of the gas can be determined.
- ✓ The gas must not react with the cell windows or the reflecting surfaces.
- ✓ Gas analyses are performed with IR but the method is not much used because of its lack of sensitivity. Moisture must be avoided.



(a) Gas cell

Gas sample holder

❖ FACTORS AFFECTING VIBRATIONS

- ✓ Coupled Interactions
- ✓ Hydrogen Bonding
- ✓ Fermi Resonance
- ✓ Electronic Effects

❑ Coupled Interactions

- Two bond oscillators sharing a common atom never behave as individual oscillators, except when they exhibit different oscillation frequencies. This behaviour is the result of mechanical coupling interaction between the oscillators.
- For example, CO_2 consists of two $\text{C}=\text{O}$ bonds ($\text{O}=\text{C}=\text{O}$) with a common carbon atom. Thus, CO_2 has two fundamental stretching vibrations, of which one is asymmetrical and the other is symmetrical stretching vibration.
- Labelling of symmetric or asymmetric vibrations is done with reference to the axis of symmetry about which if a molecule is rotated, an identical view is presented more than once in a complete rotation.
- The vibrational mode is labelled as symmetric if rotation about this axis does not alter the nature of vibration, while if it is altered the vibrational mode is labelled as asymmetric.
- The modes are either parallel or perpendicular depending on whether the change in dipole moment is along the axis of symmetry or perpendicular to it.
- Modes are numbered as ν_1, ν_2, ν_3 , in order of decreasing frequency within each symmetry group, starting from the symmetric mode of vibration.

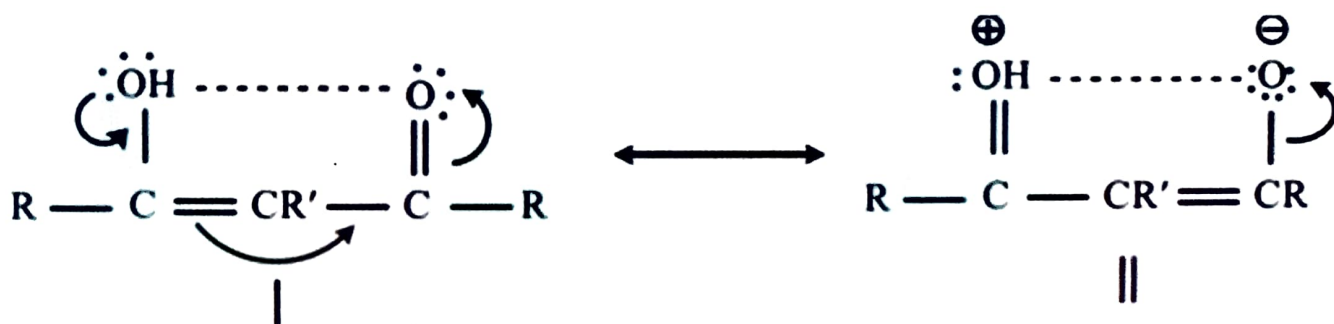
The important requirements for effective coupling interactions are:

- i) The vibrations should be of the same symmetry species for the interactions to occur.
- ii) There should be a common atom between the groups for strong coupling between stretching vibrations.

- i) Maximum interaction occurs when the coupled groups individually absorb near the same frequency.
- ii) Coupling between bending and stretching vibrations occurs when stretching bond forms one side of the changing angle.
- iii) A common bond is required for the coupling of bending vibrations.
- iv) Separation of groups by one or more carbon atoms and/or mutually perpendicular vibrations causes no coupling

❑ Hydrogen Bonding:

- This gives rise to **downward frequency shifts**.
- Stronger the hydrogen bonding, greater is the absorption shift from the normal value towards the lower wave number.
- With the help of infrared technique, the two types of hydrogen bonds can be distinguished.
- The **inter-molecular hydrogen bonds** give rise to **broad bands**, while the **intra-molecular hydrogen bonds** give rise to **sharp and well-defined bands**.
- Inter-molecular hydrogen bonds depend upon **concentration**.
- The intensities of such bands **decrease and ultimately disappear on dilution**.
- Intra -molecular hydrogen bonds do not depend on concentration.
- The **frequency difference** between free and associated molecules in intra -molecular hydrogen bonding is **smaller** than that in inter-molecular hydrogen bonding.
- The hydrogen bonding in enols and chelates is very strong and absorption due to O - H stretching occurs at very low values. As these bonds are not broken on dilution with an inert solvent.



❑ Fermi Resonance:

- Coupling of two fundamental vibrational modes give rise to two new modes of vibration having higher and lower frequencies than that observed in the absence of interaction.
- Interactions that may occur between fundamental vibrations and overtones or combination tone vibrations are known as Fermi resonance.
- For an isolated C-H bond only one C-H stretching vibration takes place.
- The C-H stretching vibrations in CH₃ groups combine together to exhibit two coupled vibrations (asymmetric and symmetric) of different frequencies.
- The vibrational frequencies of C-H coupled vibrations of CH₃ groups will be different than CH₂ groups, and thus the detection of all the four C-H stretching vibrations in the high resolution IR spectra of the compounds having CH₂ and CH₃ groups becomes easy.
- Fermi resonance commonly occurs in the IR and Raman spectra. For Fermi resonance to occur:
 - i) The vibrational levels should be of same symmetry species,
 - ii) The interacting groups should be in the molecule so that mechanical coupling can take place

❑ Electronic Effects

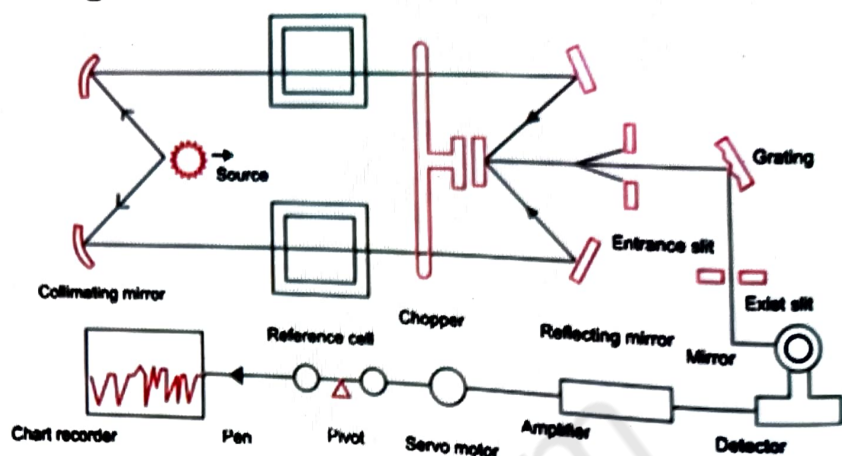
- Adding a halogen atom and an electronegative atom causes inductive effect, which either shortens or strengthens the band.
- As a result, the force constant increases along with the increase in frequency or wave number of absorption.
- On attaching an alkyl group at α -position of C=O group, a +I effect is produced and the wave number of absorption is decreased (as force constant decreases as a result of lengthening or weakening of bond).
- For example, the C=O stretching absorption of HCHO and CH₃CHO occurs at 1735cm⁻¹ and 1730cm⁻¹ region, respectively.

❖ INSTRUMENTATION

Introduction The usual optical materials (glass or quartz) absorb strongly in the IR region, and thus the apparatus for measuring IR spectra is different from that for the visible and UV regions.

The main components of an IR spectrometer are:

- 1) Sources of radiation,
- 2) Monochromators,
- 3) Sample cells, and
- 4) Detectors



Schematic diagram of double beam IR spectrophotometer

❑ Sources of Radiation

The following sources can be used as a source of IR radiation:

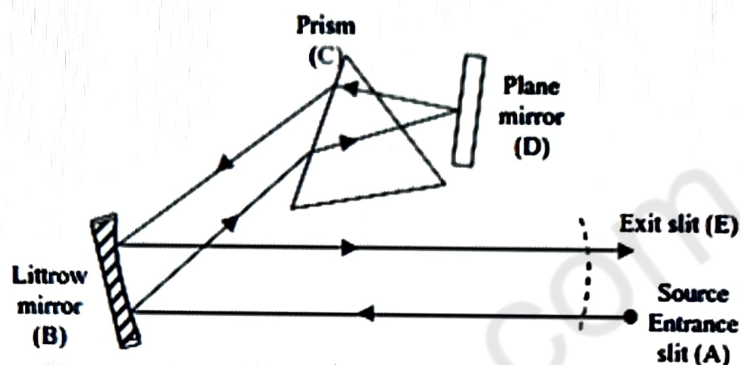
- 1) **Nernst Glower:** It consists of a rod or hollow tube (2cm long and 1mm in diameter) **made by sintering** a mixture of cerium, zirconium, thorium and yttrium oxides. It is heated between 1000-1800°C temperature. It provides maximum radiation at 7100 cm^{-1} region.
- 13 **Globar:** It is a **silicon carbide rod**, electrically heated between 1300 - 1700°C temperature.
- 3) **Nichrome Wire:** A coil of this wire is **heated by passing current** and is used when the required wavelength range and intensity are not sufficient.
- 4) **Rhodium Wire:** This wire is sealed in a **cylinder**.
- 5) **Tungsten Filament Lamp:** It is used for **near infrared region**.

❑ Monochromators (Wavelength Selectors)

- Since the sample in IR spectroscopy absorbs at **certain frequencies**, **desired frequencies from the radiation source should be selected** and the radiations of other frequencies should be rejected.
- This selection is achieved using monochromators of the following two types: 1) Prism monochromator, and 2) Grating monochromator.

➤ Prism Monochromator

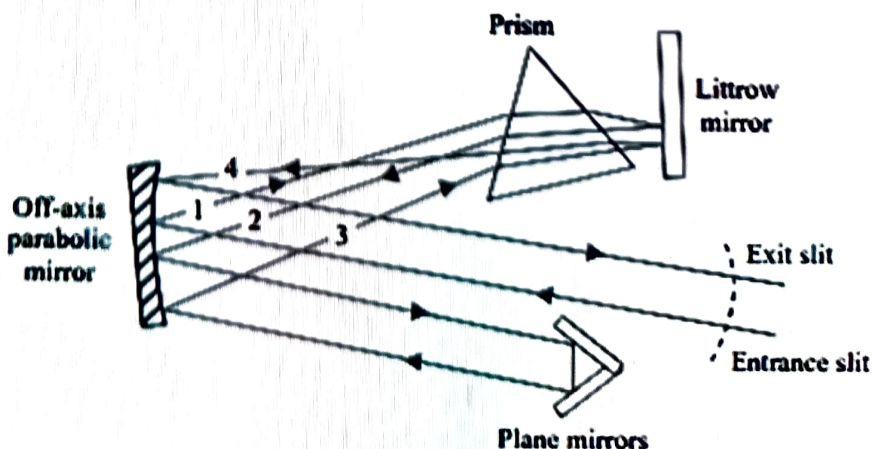
- A prism to be used as a dispersive element should be made up of materials that transmit in the infrared region (e.g., various metal halide salts).
- Sodium chloride is the most common prism salt.
- Sodium chloride is the most common prism salt due to its high dispersion in the 4 - 15 μm region (a region significantly important in the study of functional groups).



Single pass monochromator

Single pass monochromator

- The sample is placed at or near the beam focus, just before the entrance slit (A) to the monochromator.
- The radiation from the source passes through the sample and the entrance slit, and then strikes the off-axis parabolic Littrow mirror (B) which makes the radiation parallel and sends it to prism (C).
- The dispersed radiation reflects from the plane mirror (D) and returns through the prism a second time and focuses into the exit slit (E) of the monochromator.
- Through this slit, it finally passes into the detector section.



Double-pass monochromator

Double-pass monochromator

- In this monochromator, the radiation passes four times through the prism as shown (1), (2), (3) and (4) in figure.
- The double pass monochromator produces more resolution than the monochromator in the radiation, before reaching to the detector.
- In both mono - and double -pass monochromators, sodium chloride (rock-salt) prism is used for $4000 - 650\text{cm}^{-1}$ region.
- Prisms of lithium fluoride or calcium fluoride give more resolution in the region of significant stretching vibrations.

➤ Gratings monochromators:

- Same as UV radiation, the dispersion of the IR radiation can be brought about either by **transmission grating** or **reflection gratings**.
- For isolation UV-visible radiation, gratings having grooves of the order of 2000-6000 per mm of its length are used, whereas for an IR region, gratings having only 10-100 grooves per mm of its length are used.

$$n\lambda = d(\sin i \pm \sin \theta)$$

Where,

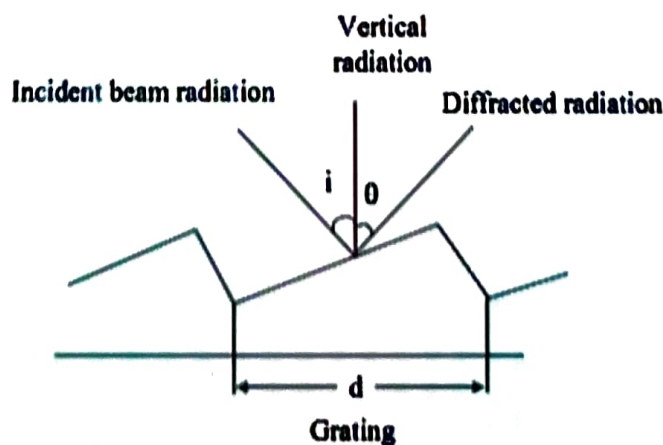
n = The order (a whole number).

λ = Wavelength of the radiation.

d = Distance between grooves.

i = Angle of incidence of IR radiation beam.

θ = Angle of dispersion of light of a particular wavelength.



Path of IR radiation diffracted by a grating monochromator

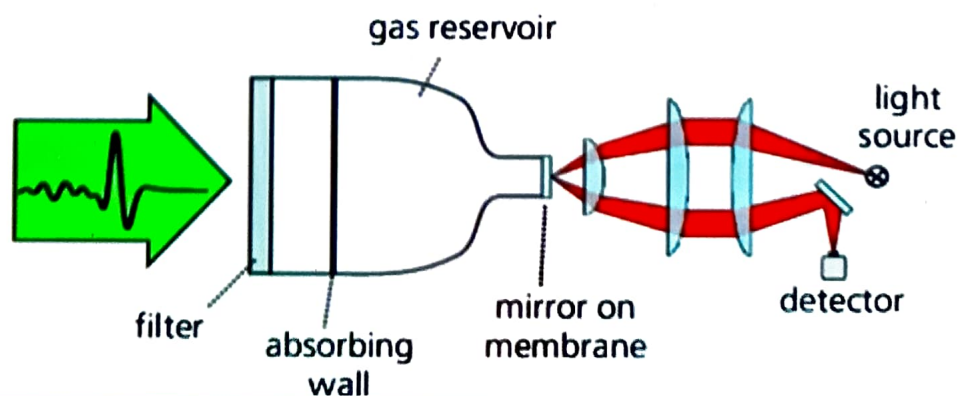
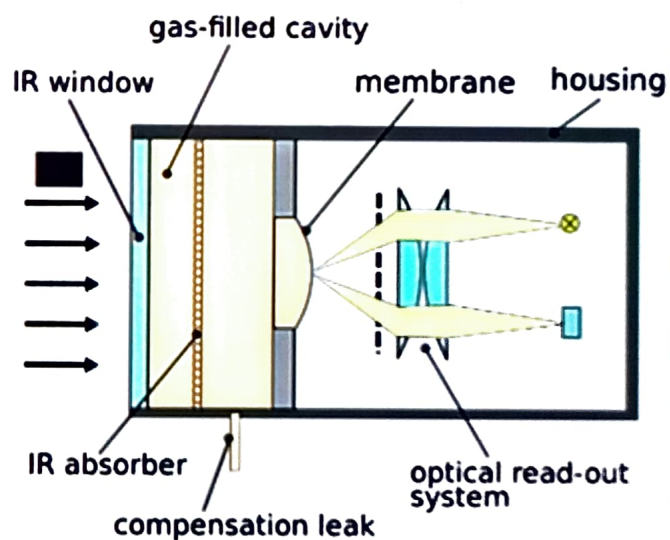
☐ Detectors

- These give responses for all frequencies.
- If the radiant power for IR region is low, detector signal will also be low.
- The various types of detectors are as follows:

- 1) Golay cell,
- 2) Bolometer,
- 3) Thermocouple,
- 4) Thermistor, and
- 5) Pyroelectric detector.

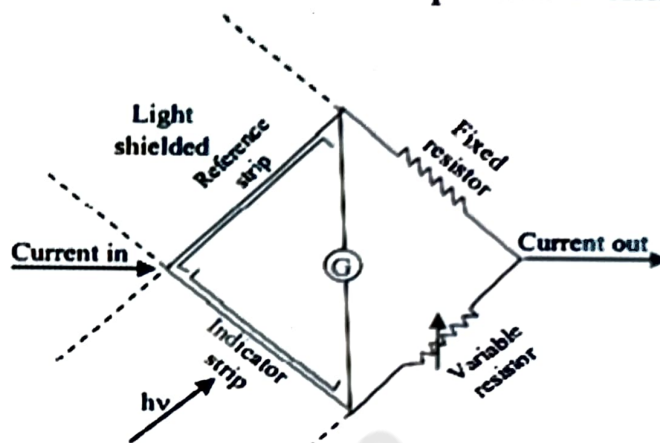
➤ Golay Cell

- ✓ It has a **small metal cylinder**, whose one end is **closed by a blackened metal plate** and the other end is **closed by a flexible metalised diaphragm**.
- ✓ The cylinder is filled with **xenon** and sealed.
- ✓ Then IR radiation is allowed to **fall on the blackened metal plate**. As a result, the gas heats up and expands.
- ✓ The resulting **pressure increases** and **deforms the metalised diaphragm** that separates into two chambers.
- ✓ A light from a lamp is allowed to fall on the diaphragm that **reflects the light on to a photcell**.
- ✓ The diaphragm motion changes the output of cell.
- ✓ The signal seen by the phototube is modulated with respect to the power of the radiant beam incident on the gas cell.



➤ Bolometer

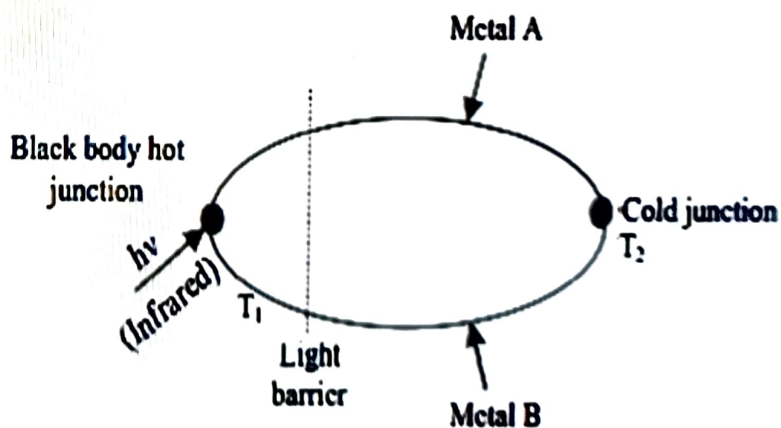
- ✓ A bolometer works on the **principle** that the **electrical resistance of a metal increases by 0.4%** for every Celsius degree increase of temperature.
- ✓ A bolometer consists of a **thin metal conductor** whose temperature changes when IR radiation falls on it.
- ✓ The resistance of this conductor also changes with temperature, and the degree of change in resistance is the measure of the amount of radiation that has fallen on the bolometer.



Schematic presentation of a bolometer

➤ Thermocouple

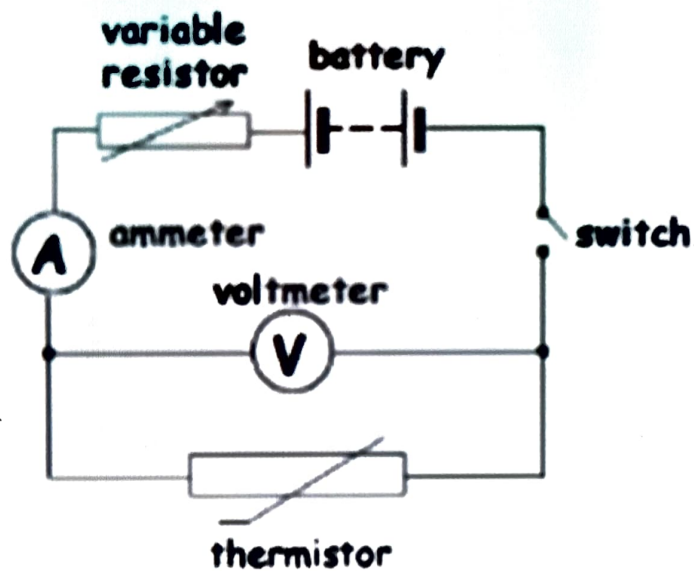
- ✓ Thermocouple detector works on the **principle** that when **two dissimilar metal wires are connected together at both ends**, a **temperature differential exists** and an electric current flow between the two ends.
- ✓ The end exposed to the IR radiation is generally a **black body** so as to increase the energy gathering efficiency, and is called the **hot junction**.
- ✓ The other end is **thermally insulated** and carefully screened from stray light and is called the **cold junction**.



Schematic presentation of a Thermocouple

➤ Thermistor

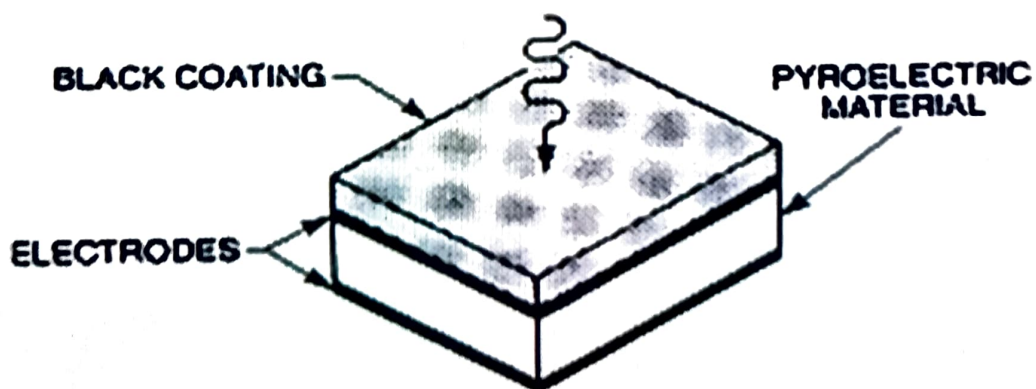
- ✓ Thermistor is made up of a **fused mixture of metal oxides**.
- ✓ The **electrical resistance of the mixture decreases with increase in temperature**.
- ✓ This relationship **between electrical resistance and temperature allows the thermistors to be used as IR detectors in the same way as bolometers**.



Schematic presentation of a Thermistor

➤ Pyroelectric Detector

- ✓ Pyroelectric detector is made up of a non-centrosymmetrical crystal, which has an internal electrical field along its polar axis.
- ✓ On applying IR radiation, a change in polarisation is observed due to an alteration of the crystal lattice.
- ✓ The pyroelectric detector acts as a capacitor if two electrodes are connected to the crystal.
- ✓ The effects of this detector depend on the rate of temperature change and not on the temperature change itself.
- ✓ Pyroelectric detector also ignores the effects of background radiation. They are usually used in FTIR spectrometers.



Schematic presentation of a Pyroelectric Detector

❖ APPLICATIONS

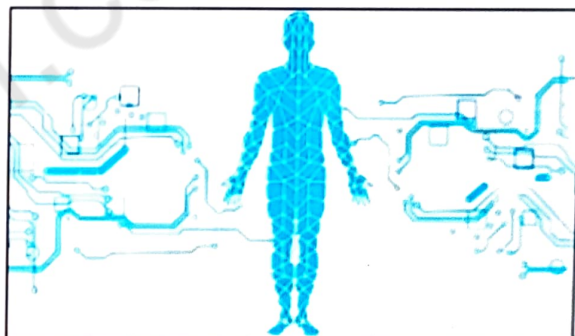
❑ **Pharmaceutical applications.**

- Infrared spectroscopy has been extensively used in **both qualitative and quantitative** pharmaceutical analysis.
- This technique is important for the **evaluation of the raw materials** used in **production the active ingredients** and the excipients.
- For the **identification of drug substances, impurities** in drug substances.
- Provide valuable additional **structural information**, such the presence of certain functional groups.
- Used to study **ratio of isomers** in a mixture of compounds.



❑ **Biological applications .**

- Biological systems, including **lipids, proteins, peptides, biomembranes, nucleic acids, animal tissues, microbial cells, plants and clinical samples**, have all been successfully studied by using infrared spectroscopy.
- A powerful tool for characterizing tissue and disease diagnosis.
- It is possible to detect **cervical cancer** arising from a **pre-malignant state** termed dysplasia.



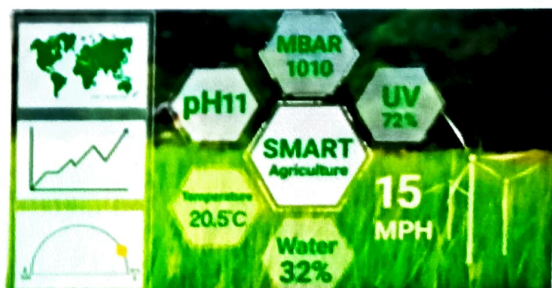
❑ **Food science.**

- **Mid-infrared and near-infrared** techniques may be used to obtain qualitative and quantitative information about food samples.



❑ **Agriculture applications.**

- The major constituents of grains are water, protein, oil, fibre, minerals and carbohydrates and it is commercially important to quantitate the composition.



❑ Pulp and paper industries.

- Infrared spectroscopy plays an important role in **quality control** in the pulp and paper industries.
- In the **mid-infrared** region, **additives**, such as **polymers** and **calcium carbonate**, may be identified in paper.
- The majority of bands in a paper spectrum are due to **cellulose**.



❑ Paint Industry.

- Infrared spectroscopy is used in the paint industry for **quality control**, **product improvement** and **failure analysis**, and for forensic identification purposes.
- May also be employed to **identify pigments in paints**, which is of particular importance in the fields of art conservation and forensic analysis.
- Colourants and dyes are commonly inorganic materials and there are collections of the infrared spectra recorded for many colourants.



❑ Environmental applications.

- Infrared spectroscopy has been applied to a broad range of environmental **sampling problems**, including **air, water and soil analysis**. Common applications include industrial **gas emissions**, emissions from fires, and astronomical applications.
- Determination of the **compositions of atmospheric gases** is important for an understanding of global climate changes.



UNIT-II

FLAME PHOTOMETRY

Points to be covered in this topic

- ❖ Introduction
- ❖ Principle
- ❖ Interferences
- ❖ Instrumentation
- ❖ Applications

FLAME PHOTOMETRY

❖ INTRODUCTION

- Flame photometry is also known as **flame emission spectroscopy** because it involves the **emission of radiation by the neutral atoms** introduced into the flames.
- **Fine droplets are produced** on spraying a solution containing metallic salt on to a flame.
- **Thermal energy of the flame** results in the **evaporation of solvent droplets**, leaving behind a solid residue in the form of neutral atoms.
- These atoms are then exposed to **thermal energy of the flame** which **converts them into excited state atoms**.
- The se excited atoms are unstable, thus, they return to **their ground state** and **emit radiation of definite wavelength**.
- This **wavelength** is characteristic of the element and is used for its **identification** (i.e., qualitative analysis).
- The emitted **radiation intensity** depends on the **concentration of the element analysed** (i.e., quantitative analysis).
- The availability of burner, fuel and oxidant combinations, and some technical reasons allow the analysis of **Group IIA (Li, Na, and K)** and **Group IA (Ca and Mg)** elements by this technique.

The steps followed in flame photometry are

Liquid sample



Formation of droplets



Fine residue



Formation of neutral atoms



λ and intensity of emitted radiation measured



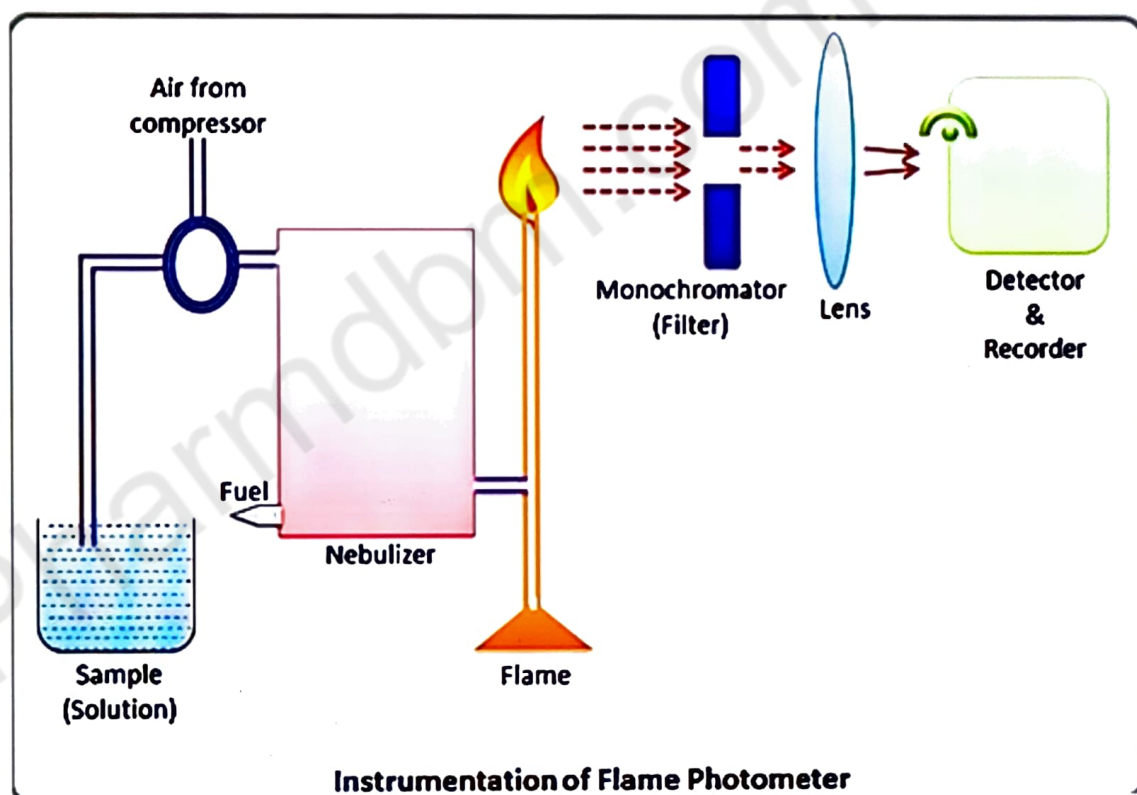
Emission of radiation of specific wavelength



Excitation of atoms by thermal energy

❖ PRINCIPLE

- flame photometry, a branch of atomic spectroscopy is used for determining the **concentration of certain metal ions** such as **sodium, potassium, lithium, calcium, Cesium**, etc.
- The basis of flame photometric working is that, the **types of metals are dissociated due to the thermal energy** provided by the flame source. Due to this thermal excitation, some of the atoms are excited to a higher energy level where they are not stable.
- The subsequent loss of energy will result in the **movement of excited atoms to the low energy ground state** with emission of some radiations as a wavelengths .The emitted wavelengths are specific for specific elements.



Whole process can be categorize as below

Flame photometer



➤ **Desolvation:**

- ✓ The **metal particles** in the flame are **dehydrated by the flame** and the process of desolvation takes place.
- ✓ Water or other solvent is vapourized leaving minute particles of dry salt.

➤ **Vapourisation:**

- ✓ **Evaporation of the solvent** occurs as the second step at the **high temperature** of the flame.

➤ **Atomization:**

- ✓ Flame heat converts a part of all of the **gaseous molecules/metal particles** to give neutral atoms.

➤ **Excitation:**

- ✓ Some of the **free metal atoms** react with other **radicals or atoms** present in the **flame gases**.
- ✓ The vapours of neutral metal atoms or molecules containing the metal atoms are **excited by the thermal energy of flame** resulting into **ionization and excitation** of neutral atoms.
- ✓ The **electrostatic force** of attraction between the **electrons and nucleus of the atom** helps them to absorb a particular amount of energy.
- ✓ The atoms then shifted to the **excited energy state**.

➤ **Emission process:**

- ✓ The excited higher energy state is **unstable** and the atoms return to the **initial stable low energy state** with the emission of energy.
- ✓ In the form of radiation of characteristic **wavelength**, which is measured by the **photo detector**.

❖ **INTERFERENCES**

- The existence of other materials in the sample may interfere with the analytical procedure.
- Some of the commonly encountered interference processes in flame photometry are:
 - ✓ Spectral interferences,
 - ✓ Ionisation interferences,
 - ✓ Cation-anion interferences,
 - ✓ Cation-cation interferences, and
 - ✓ Oxide formation interferences

❑ Spectral Interferences

Spectral interference can be categorised into three types:

- 1) The first type of spectral interference may arise due to the **partial overlapping between the spectra of two elements** (or compounds) emitting radiations at particular wavelengths.
- 2) The second type of spectral interference does not involve any spectral overlapping but occur due to the **production of much closer spectral lines of two or more elements**.
- 3) The third type of spectral interference may arise due to the **presence of higher salt concentrations in the sample**, thereby producing spectral interference between a spectral line and a continuous background.

❑ Ionisation Interferences

- Few metallic atoms (like Na) can only be ionised through an **elevated temperature flame**:



- Sodium ion produces its own characteristic emission spectrum, whose **frequencies are dissimilar to those of the atomic spectrum of sodium**.
- Therefore, the radiant power of **atomic emission decreases** with ionisation.
- This interference type can be corrected by the **addition of higher amount of potassium salts** in unknown and standard solutions.
- The potassium added undergoes ionisation but **prevents the sodium from getting ionised**.
- Consequently, the **emission spectrum** of the sodium atom is **enhanced**.

❑ Cation-Anion Interferences

- Generally, anions are **not competent to emit radiations**.
- However, some polyvalent an ions are **capable of forming less volatile salts** in the flame, thereby minimising the emission from definite cations.
- This interference can be corrected by the **addition of higher quantity of calcium precipitating agent**.

❑ Cation-Cation Interferences

- Filter instruments provide a suitable resolution for the principal lines of sodium (589 nm), potassium (767 nm), and lithium (671 nm) to facilitate an interference free analysis of different elements.
- Yet, interference may occur in the sample containing sodium and calcium having comparatively closer emission wavelengths.
- Combination of calcium with the products of combustion of the flame gases forms calcium hydroxide, which produces a broad band molecular emission at 554 nm.
- The use of an effective monochromator other than filters plays an important role in eliminating cationic interference.

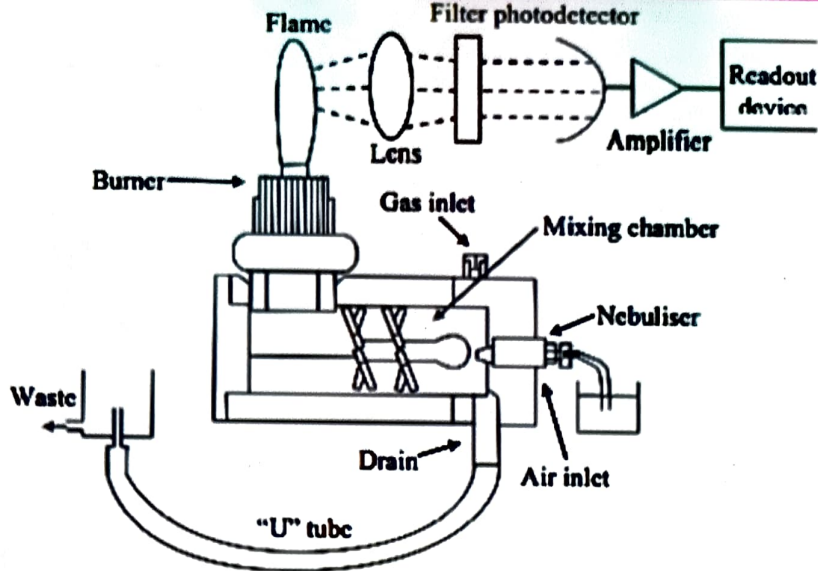
❑ Oxide Formation Interferences

- In this type of interferences, a large percentage of the free metal atoms usually combine with oxygen (present in the flame) to form stable oxides, and thus depresses the emission intensity of free metals.
- Most of the alkaline earth elements are known to form oxides and suffer this type of interference.
- This interference type can be corrected either by applying very high temperature flames. Which break the oxide-producing free atoms for their excitation or by utilising oxygen-free environment to produce excited atoms.

❖ INSTRUMENTATION

- In flame photometry, the sample is introduced into a flame where it undergoes a number of processes leading to the formation of excited atomic species that emit the radiation, which is then measured and suitably analysed. The instrument used for this purpose is called flame photometer.



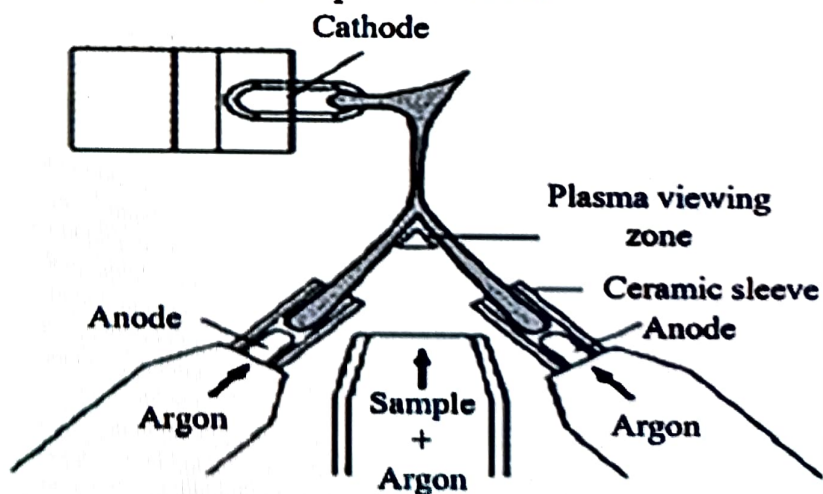


□ Atomisers

- The role of atomiser is to generate the vapours of analyte which gets excited by the thermal energy and then emits characteristic radiation that is measured.
- The flame atomiser assembly consists of two components.
- The prior is a nebuliser where the sample converted to a fine mist or an aerosol.
- It is then passed onto the second component, i.e., the burner.
- In the flame, a number of processes occur that convert the analyte to excited species.

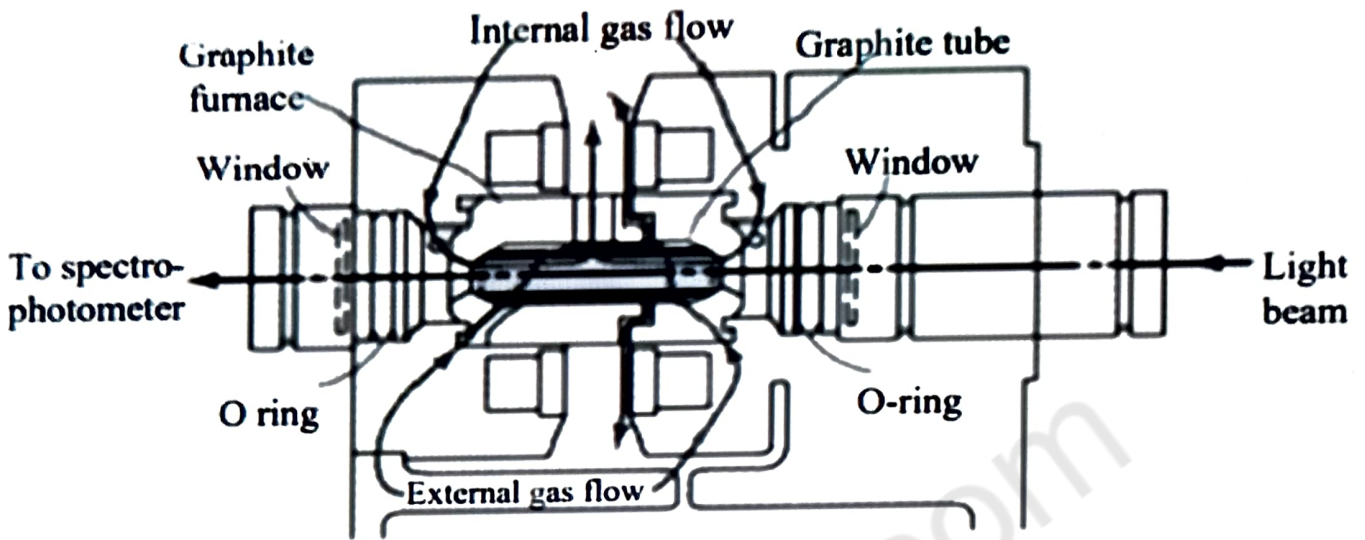
Different types of atomisers used in the atomisation process are:

- ✓ **Flame Atomisers:** These atomisers utilise a pneumatic nebuliser for converting the sample solution into mist or aerosol.



- ✓ **Non-Flame Atomisers:** Certain atomic spectrometric techniques utilise non-flame atom reservoirs. Electrothermal atomisers, like carbon rods, carbon furnaces, or tantalum ribbons, are utilised in Atomic Absorption Spectroscopy (AAS).

- 1) **Electrothermal Atomisers:** These atomisers utilise a syringe or an auto sampler for placing a small quantity (up to a few microliters) of sample in the furnace. This step is subsequently succeeded by dry ashing and atomisation steps performed through instrument programming.



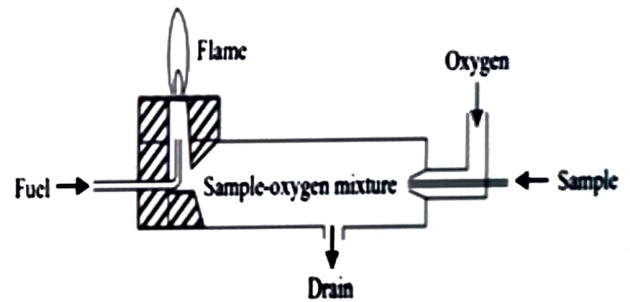
❑ Nebulisers

- It is a device used for introduction of sample into the flame.
- This process is called nebulisation, which involves thermal vaporisation and **dissociation of aerosol particles at high temperatures** producing small particle size with high residence time.

❑ Burners

Some commonly employed burners are:

- Mecker Burner
- Total Consumption Burner
- Premix or Laminar Flow Burner
- Lundergarph Burner



Lundergarph Burner

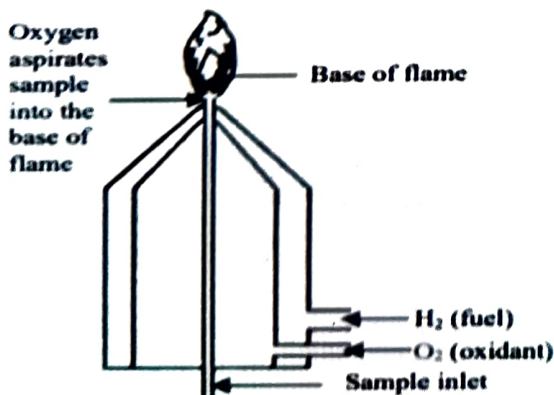


Figure 4.5: Total Consumption Burner

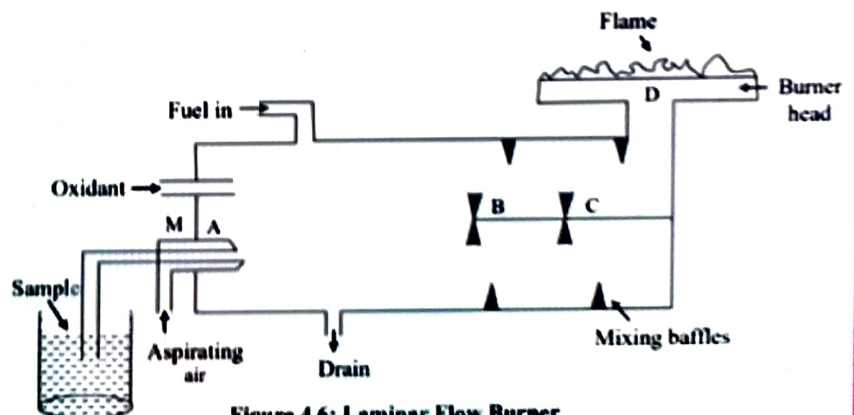


Figure 4.6: Laminar Flow Burner

Mecker Burner :

- ✓ This burner was employed in the past. It utilises natural gas and oxygen to produce a flame of low temperature and excitation energies. Thus, it is commonly employed for analysing alkali metals.

Total Consumption Burner:

- ✓ Presents a total consumption burner utilising hydrogen and oxygen gases as the fuel and oxidant, respectively. In this burner, the liquid sample is drawn directly into the flame.
- ✓ This apparatus is named as total consumption burner because the sample flowing through the capillary tube will also be driven into the flame irrespective of droplet size.

Total consumption burner has the following advantages:

- i) No loss in the fuel and oxidant,
- ii) Eliminates the errors, and
- iii) Combustible sample, e.g., petroleum, can be directly aspirated into the flame without any danger of explosion.

Premix or Laminar Flow Burner:

- ✓ Presents a premix or laminar flow burner which involves thorough mixing of aspirated sample with the fuel and oxidant before it is driven to the opening of burner and then entered into the flame.
- ✓ The gases involved flow in non-turbulent manner (laminar flow)

Lundergarph Burner:

- ✓ This burner utilises liquid samples which are aspirated into the spray chamber.
- ✓ The bigger droplets condense on the chamber sides and drain off, while the minor droplets and the evaporated sample flows into the base of the flame in the form of a mist.
- ✓ The nebulisation stage in this type of burner can be improved by utilising a number of strategies , like using the impact bead (Perkin - Elmer), ultrasonic vibrators, and thermospray heaters.

□ Mirrors

- Radiation emitted by the flame is released in all directions in space.
- Large amount of radiation is lost during this process, thus, resulting in the loss of corresponding signals.
- A mirror is placed behind the burner for reflecting the radiation back to the entrance slit of the monochromator.
- This increases the amount of radiation used in the analysis. Since the mirror used is concave, it is capable of covering a wide range of angle from the flame.
- Best results can be obtained by reflecting the hottest and steadiest part of the flame onto the entrance slit of the monochromator, which reduces the flickering of the upper part of flame (where light intensity is reduced and noise is increased).

□ Slits

- The entrance and exit slits are commonly placed prior to and after the dispersion elements of a monochromator system.
- The entrance slit prevents the access of most of the radiations, allowing only the radiations emitted by the flame and the mirrored reflection of the flame to enter the optical system.
- The exit slit on the other hand, allows only a selected wavelength range to pass through the detector.
- A narrow range of wavelength, i.e., of the order of a few nanometres is usually required for this purpose.

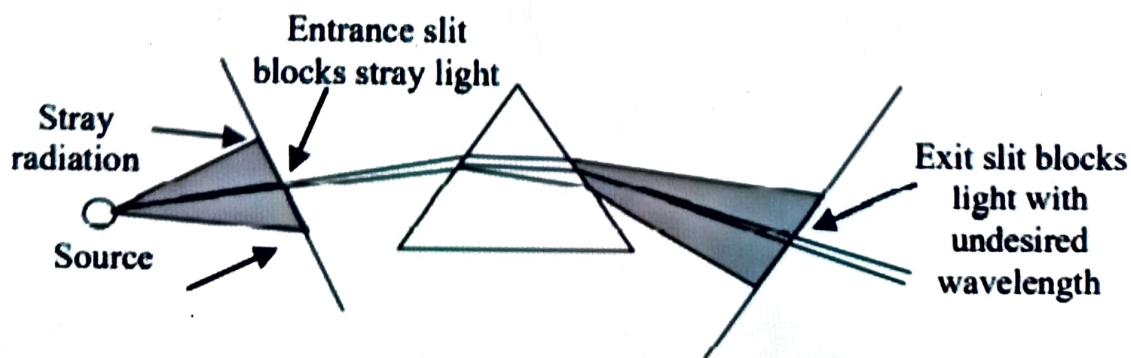


Figure 4.9: Monochromator System without Collimator Lenses for Simplification

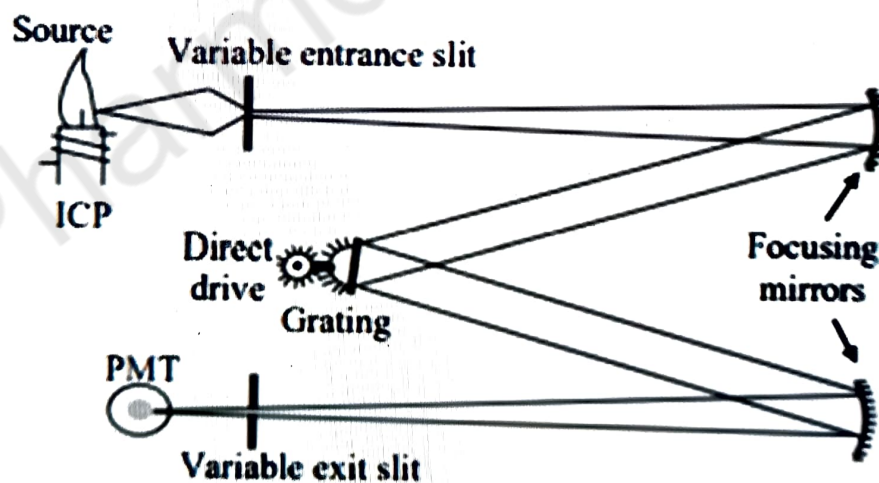
❑ Monochromators

- A monochromator is required for measuring a **single wavelength** but it can also be applied for scanning a **wide range of wavelength**.
- If a **polychromatic light** is passed through an **entrance slit** it gets dispersed by **diffraction gratings**.

Two most commonly used monochromator designs are:

1) Czerny-Turner Monochromator: In this monochromator **two mirrors** are required for reflecting and focusing the polychromatic and diffracted beams. It mostly operates on a **computer-driven rotation** of gratings in diverse ways to **select a required wavelength**. As the grating rotates, a different wavelength is focused **onto the exit slit**.

2) Echelle Monochromator: This monochromator is a **high-resolution instrument** which attains resolutions of **5ppm in comparison to 10 - 20ppm** of most traditionally used instruments. Since the spectra produced by this system may overlap each other, **these systems are very compact**.



Czerny-Turner Monochromator

❑ Detector

- The **radiation coming from the optical system** reaches the detector to **measure its intensity**.
- A detector should be capable of perceiving wide range of **emitted radiations having different wavelengths**.
- Either **vacuum phototubes** or **photomultiplier tubes** are utilised as detectors in flame photometers.

❖ APPLICATIONS

- It is extensively employed in industries associated with chemicals, pharmaceuticals, soils, agriculture, ceramics, glass, plant materials, water, oceanography, and in various biological or microbiological laboratories.
- It is employed for detecting the presence of sodium, potassium, calcium, and magnesium in biological fluids like serum, plasma, urine, etc.
- It is also employed as a standard procedure for analysing industrial and natural water for estimating the elements responsible for water hardness (e.g., calcium, magnesium, barium, etc.).
- It is commonly used for detecting the presence of sodium, potassium, calcium , and magnesium (after removing other interfering elements) in soil samples.
- It is used for determining few vital elements , e.g., aluminium, barium, calcium, cesium, chromium, copper, iron, lead, magnesium, manganese, potassium, sodium, strontium, and zinc.
- It is commonly exploited by glass industries for determining elements , e.g., sodium, potassium, boron, lithium, etc.
- It is employed by cement industries also for determining sodium (Na_2O), potassium (K_2O), calcium (CaO), magnesium (MgO), manganese (MnO_2), and lithium (Li_2O).
- It is employed in the analysis of alkali-alkaline earth metals and other metals existing in metallurgical products, catalysts, alloys, etc.
- It is a commonly used method for determining metals (like lead and manganese) in petroleum products (like gasoline), lubricating oils, and organic solvents.
- It is employed in industries for determining ash and estimating the quantity of alkali and alkaline earth metal oxides.

UNIT-II

ATOMIC ABSORPTION SPECTROSCOPY

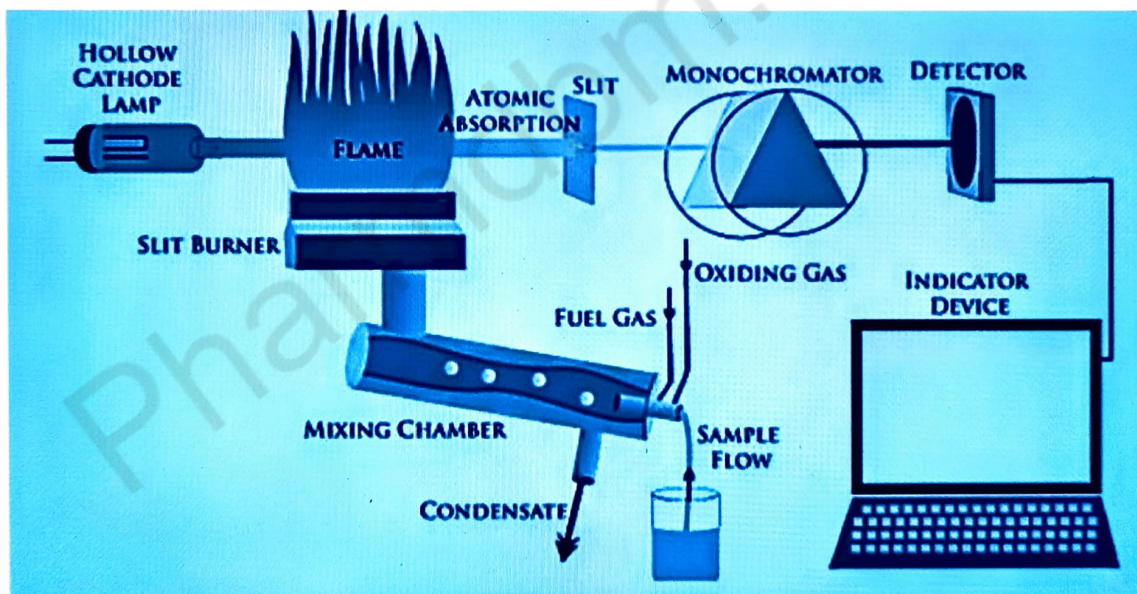
Points to be covered in this topic

- ❖ Introduction
- ❖ Principle
- ❖ Interferences
- ❖ Instrumentation
- ❖ Applications

ATOMIC ABSORPTION SPECTROSCOPY

❖ INTRODUCTION

- Atomic Absorption Spectroscopy is a very common technique for detecting metals and metalloids in samples.
- It is very reliable and simple to use.
- It also measures the concentration of metals in the sample.
- Atomic Absorption Spectroscopy is an analytical technique that measures the concentration of an element by measuring the amount of light that is absorbed at a characteristic wavelength when it passes through cloud of atoms.
- As the number of atoms in the light path increases, the amount of light absorbed increases.



❖ PRINCIPLE

- "Atomic Absorption Spectroscopy is an absorption method where radiation is absorbed by non-excited atoms in the vapour phase i.e. nebulized state."
- The principle of AAS is based on the absorption of energy by ground state atoms in the gaseous state.
- AAS uses the absorption of light to measure the concentration of gas-phase atoms.

- Since samples are usually **liquids or solids**, the analyte atoms or ions must be **vaporized in a flame or graphite furnace**.
- The atoms absorb **ultraviolet or visible light** and make transitions to higher electronic energy levels.
- The analyte concentration is determined from the **amount of absorption**.
- When a solution having metal is introduced to flame the vapour of metal is obtained.
- Then some metal atoms may get raised to **higher levels of energy to emit the radiations**.

Therefore, the total amount of light absorbed is

$$= (\pi e / mc) Nf$$

Where,

e= charge on electrons

m=mass of light

N=total no. of atoms that can absorb at frequency 'v' in light path

f= oscillar strength

c=speed of light.

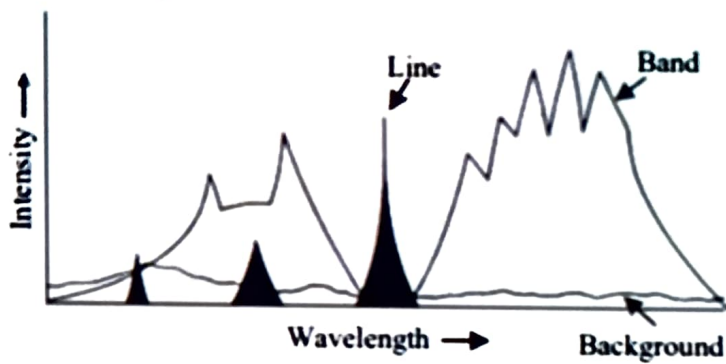
❖ INTERFERENCES

There are the following types of interferences in AAS:

- 1) Spectral interferences,
- 2) Chemical interferences,
- 3) Ionisation interferences,
- 4) Matrix or bulk interferences,
- 5) Solvent interferences, and
- 6) Dissociation of metal compounds.

❖ Spectral interferences

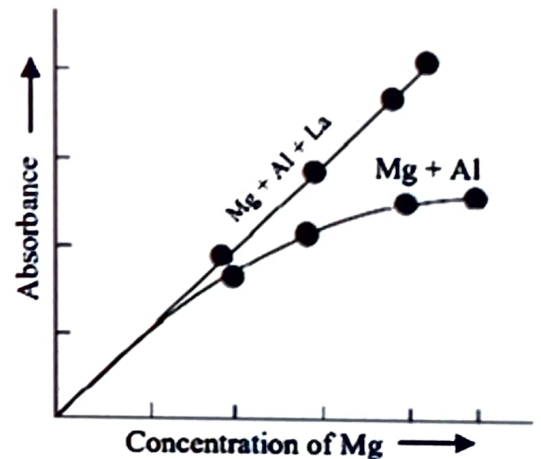
- ✓ Due to **radiation overlapping** that of the light source.
- ✓ The interference radiation may be an **emission line of another element or compound**, or general background radiation from the flame, solvent, or analytical sample.
- ✓ This usually occurs when using **organic solvents**.



Spectral interferences

❖ Chemical Interferences

- ✓ These interferences must be considered in **atomic absorption procedures**.
- ✓ If compounds or complex ions of the element being determined **incompletely dissociate** into their atoms, **low results will occur**.
- ✓ The **more concentrated the solution**, greater will be the deviation from the correct value.
- ✓ This incomplete dissociation is a chemical interference and might be removed with the use of a **higher flame temperature**.
- ✓ for example, **aluminium (Al)** and **magnesium (Mg)** form a **thermally stable mixed oxide**. Because of their thermal stability, **low results for magnesium are obtained in the presence of aluminium**. The interference may be removed by the addition of **lanthanum (La)** to the system.

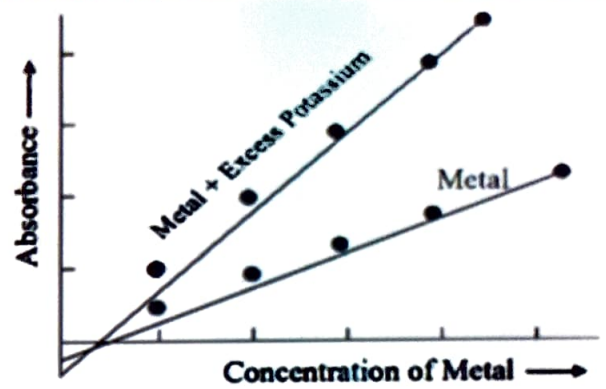


Chemical Interferences

❖ Ionisation Interferences

- ✓ These interferences arise in atomic absorption **if the flame temperature is too high**. When this occurs, a number of vaporised **atoms become ionised** by the flame.
- ✓ The resulting ions **absorb at a different wavelength** than the vaporised atoms; the new wavelength will not be selected by the monochromator, and low values result.
- ✓ For example, **ionisation interference of calcium** may be corrected by the addition of large quantities of **sodium or potassium salts** to the solution.

Since each of these elements possesses a lower ionisation potential than does calcium, their electrons will be more easily removed and calcium will remain as the vaporised metal

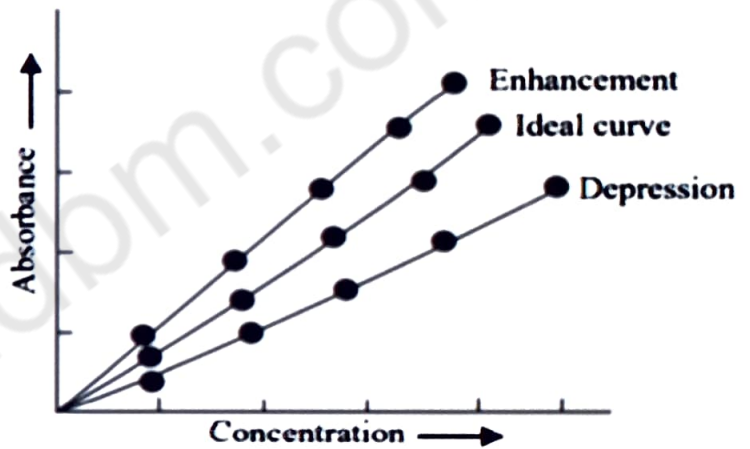


☐ Matrix or Bulk Interferences

✓ A change in the viscosity of the solution caused by either the change in a solvent or a change in concentration may result in a matrix or bulk interference.

✓ The addition of an organic solvent usually results in a decreased viscosity and a two to fourfold increase in absorbance.

✓ On the other hand, an increase in concentration results in an increase in viscosity, a slower flow through the burner, and a corresponding decrease in absorbance.



☐ Solvent Interferences

✓ Another potential source of interference is the solvent.

✓ In general, metals in aqueous solutions give lower absorbance readings than the same concentration of such metals in an organic solvent.

☐ Dissociation of Metal Compounds

✓ When metals like La, Al, and Ti are aspirated into the flame, metal atoms are not obtained but extremely stable refractory oxides are obtained.

✓ Thus, the atomic absorption studies with these elements become complicated.

✓ For such elements, nitrous oxide - acetylene flames are used which could dissociate these metal oxides to enable analysis of these elements by atomic absorption spectrometry.

Ionisation Interferences

Matrix or Bulk Interferences

❖ INSTRUMENTATION

A typical AAS has the following instrumental components in it.

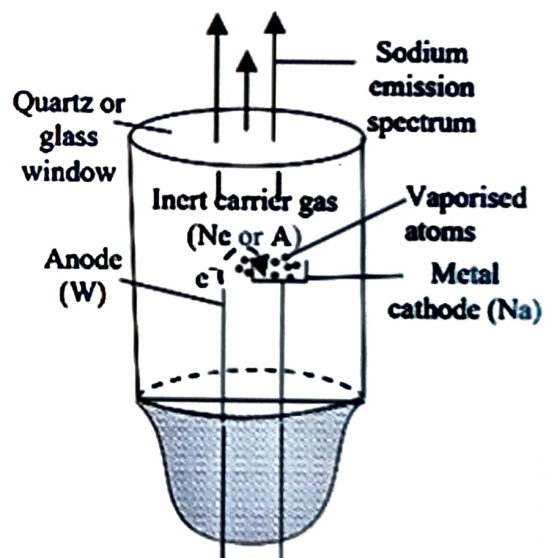
- 1) Radiation Source
- 2) Flame Neublization Unit (Atomizer)
- 3) Monochromator & Filter
- 4) Detector
- 5) Amplifier & Read out Devices

❑ Radiation Source

- An atom absorbs light at **discrete wavelengths**. In order to measure this narrow light absorption with maximum sensitivity, it is necessary to use a **line source**, which emits the **specific wavelengths** that can be absorbed by the atom.
- The two most common line sources used in atomic absorption are:

1) Hollow Cathode Lamp:

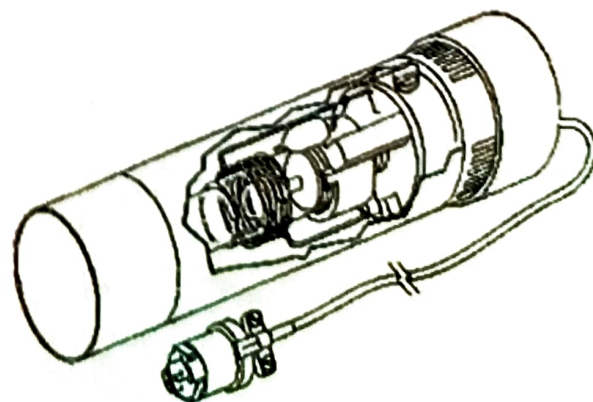
- ✓ This lamp consists of a hollow cup containing the element to be determined.
- ✓ The anode is a tungsten wire.
- ✓ The two electrodes are housed in a tube containing an inert gas.
- ✓ The lamp window is of quartz, silica, or glass.
- ✓ The exact material used depends on the wavelength to be transmitted.



Hollow Cathode Lamp

2) Electrode-less Discharge Lamp:

- ✓ In a few cases, however, the quality of analysis is impaired by limitations of the hollow cathode lamp.
- ✓ The primary cases involve the more volatile elements where low intensity and short lamp life are a problem.



Electrode-less Discharge Lamp

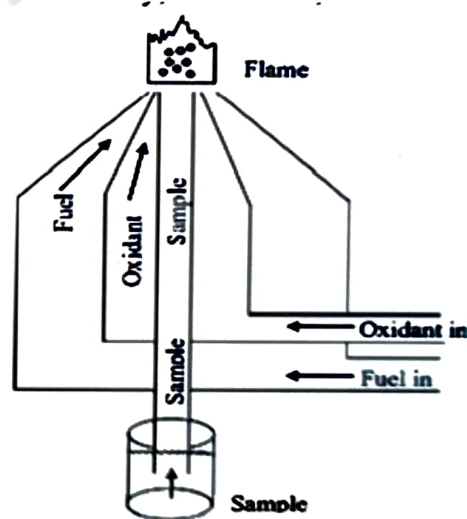
❑ Chopper

- ✓ A rotating wheel, known as chopper, is **interposed between the hollow cathode lamp and the flame.**
- ✓ This rotating wheel is interposed **to break the steady light from the lamp into an intermittent or pulsating light.**
- ✓ This gives a pulsating current in the photocell. There is also a steady current caused by light which is emitted by a flame.
- ✓ But only the **pulsating (or alternating) current is amplified and recorded** and thus, the absorption of light will be measured without interference from the light emitted by the flame itself.

❑ Flame Atomisers

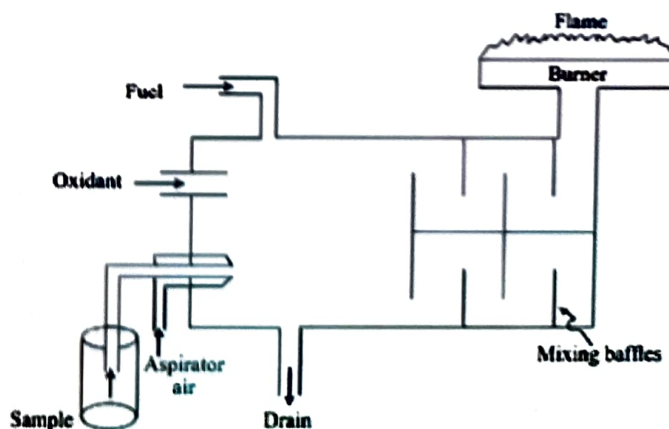
- ✓ Flame is used for **converting the liquid sample into the gaseous state** and also for converting the **molecular entities into an atomic vapour.**
- ✓ There are two types of burners in common use:

1) **Total Consumption Burner:** In this burner, the sample solution, fuel, and oxidising gases are **passed through separate passages** to meet at the opening of the flame base. This burner is however **noisy, hard to use, and its efficiency is not very good.**



Total Consumption Burner

2) **Premixed Burner:** In this burner, a **mixture of the sample (liquid) and premixed gases ($C_2H_2 + O_2$)** is allowed to enter the base. Production of atoms is initiated in **one region and is completed in another region.**



Premixed Burner

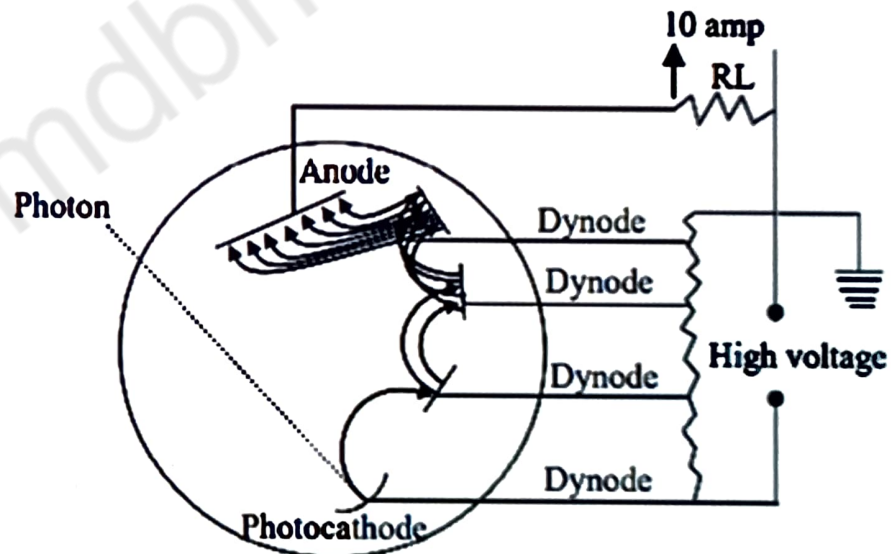
❑ Monochromators

- ✓ In atomic absorption measurements, the most common monochromators are **prisms and gratings**.
- ✓ Function of a monochromator is to **select a given absorbing line from spectral lines** emitted from the hollow cathode.
- ✓ When the cathode in hollow cathode lamp is made up of **transition metals**, the emission spectrum from the hollow cathode is so complicated that **high dispersion is essential**.
- ✓ For such cases, **large dispersion and high resolving** monochromators are advantageous for resolving spectra.

❑ Detectors

- ✓ For AAS, the **photomultiplier tube** is a most suitable detector.
- ✓ It has **good stability** if used with a stable power supply. It works satisfactorily and enables to **compare intensity** in a satisfactory manner.

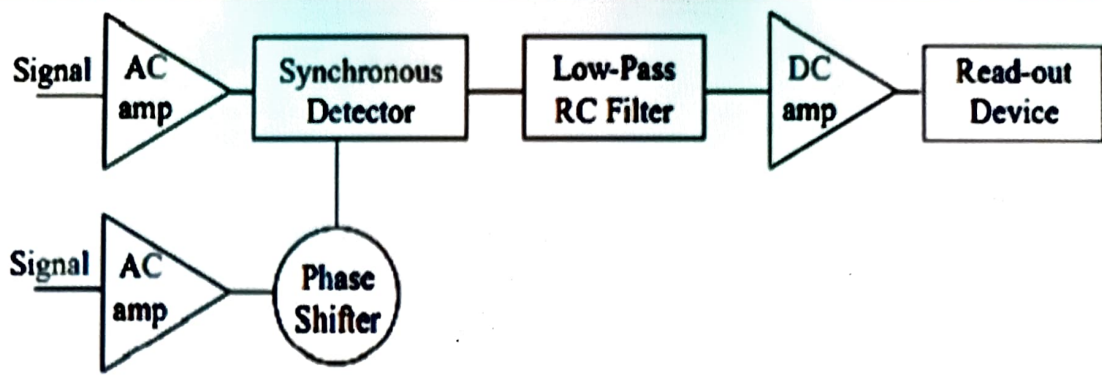
- ✓ In photomultiplier tubes, there is an evacuated envelope which contains a photocathode, a series of electrodes called **dynodes**, and an **anode**. The photocathode is fixed to the power supply terminal.



Photomultiplier tube and power supply

❑ Amplifier

- ✓ The electric current from the **photomultiplier detector** is fed to the amplifier that amplifies the electric current many times.
- ✓ Generally, **"Lock-in"** amplifiers are preferred which provide a **very narrow frequency band** pass and help to achieve an excellent **signal-to-noise ratio**.
- ✓ **Block diagram of 'lock in' amplifier**

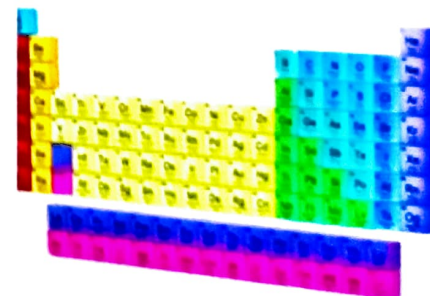


❑ Read-Out Device

- ✓ In most of the atomic absorption measurements, **chart recorders** are used as read -out devices.
- ✓ A chart recorder is a **potentiometer** using a **servomotor** to move the **recording pen**.
- ✓ The displacement is **directly proportional** to the **input voltage**.
- ✓ In some atomic absorption measurements, digital read-out devices are used.

❖ APPLICATIONS

- **Qualitative Analysis:** Due to requirement of separate hollow cathode lamp for each sample it is **rarely used** for Qualitative analysis.
- **Quantitative Analysis:** The AAS is very **sensitive and is accurate** than any other technique.
- **Simultaneous Multicomponent Analysis :** If a multi-element emission source is available ,then multi-component analysis can be carried out.
- Determination of **metallic Elements** in **Biological Materials**.
- Determination of Metallic Elements in **Food Industry:** The toxic levels of Co,Ni&Zn levels in food items are detected by AAS.
- Determination of **Calcium ,Magnesium, Sodium & Potassium** in **Blood Serum**.



- Determination of **Lead in Petrol** : Tetra ethyl & Tetra methyl lead are present in petrol or the combination is present which is checked by AAS.



- Determination of **low levels of arsenic** using Flame AAS & ultra AA Lamps.
- Extending **analysis range of Gold** using ultr AA Lamps.
- Analysis of **Iron ores**.
- Analysis of **Cement**.
- Determination of **Calcium in Saliva**.
- Application of atomic-absorption spectroscopy in physics research
- Determination of **Cobalt in Steel, Alloy Steel and Nickel**.

UNIT-II

NEPHELOTURBIDOMETRY

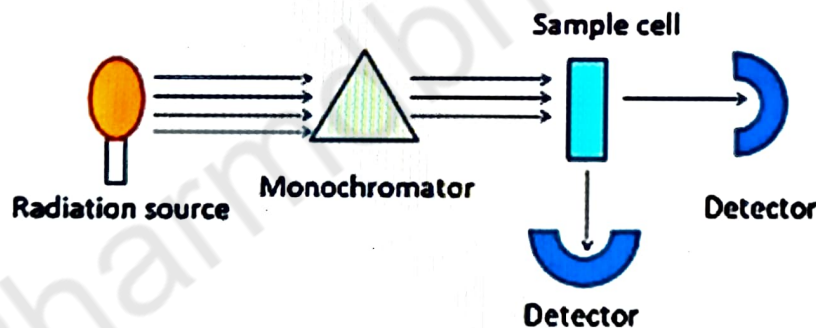
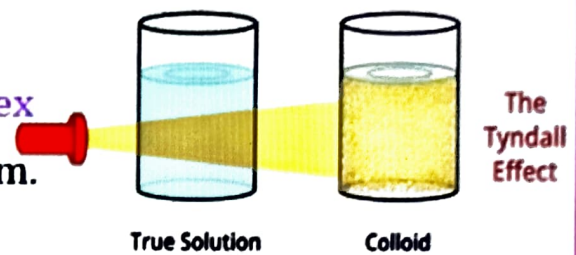
Points to be covered in this topic

- ❖ Introduction
- ❖ Principle
- ❖ Instrumentation
- ❖ Applications

NEPHELOTURBIDOMETRY

❖ INTRODUCTION

- Nephelometric and turbidometric methods depend on the **scattering of light by particle suspended in a liquid.**
- The suspended particles have **refractive index values** different from the suspending medium.
- The overall effect mimics **Tyndal effect.**
- Nephelometry is the measurement of **scattered light as a function of concentration** of suspended particles where the concentration is less than 100 mg/ litre.
- Turbidometry is the measurement of **transmitted light as a function of concentration of suspended particles** where the concentration is more than 100 mg/litre that is high concentration samples.

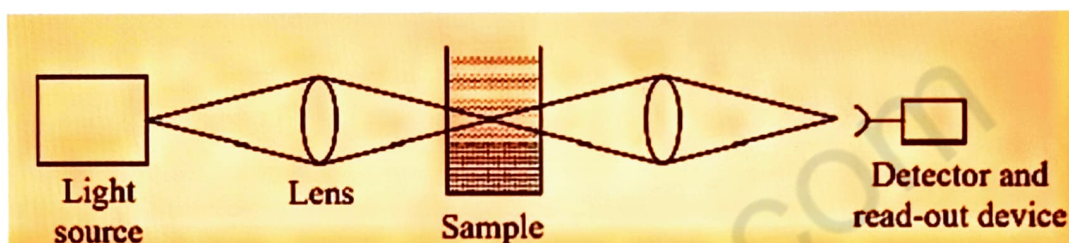


Nepheloturbidometry

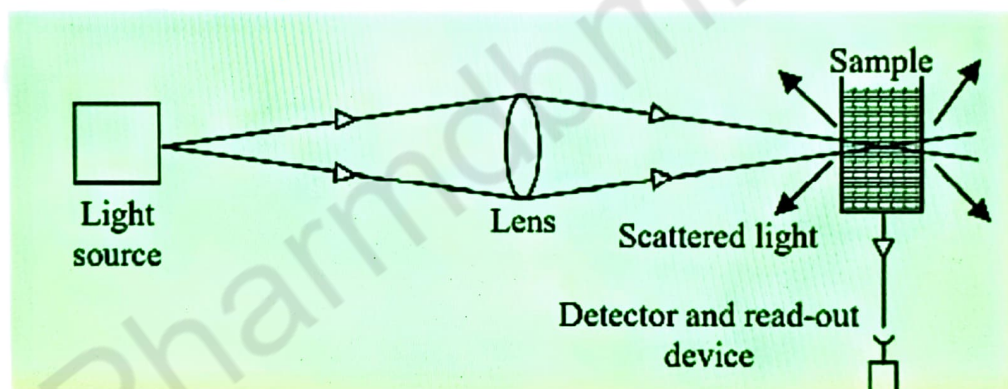
❖ PRINCIPLE

- At lower concentration of the suspension uniform scattering of particles is noticed. So the **intensity of scattered light is directly proportional to the concentration of solute.**
- The intensity of scattered light can be measured at **45°, 60°, 90° and 135° also.**
- For **higher concentration** suspensions scattering is **non uniform** and light becomes scattered in all possible directions. Hence, it is **difficult to measure the intensity of scatter radiation** at specific angles.

- So, the intensity of transmitted light (that is unscattered) direction is measured at 180° .
- The intensity of transmitted light (I_t) is a function of concentration i.e. when the concentration increases the intensity of transmitted light is less and when concentration is less the intensity is high.
- Depending on the sample concentration of the suspension either nephelometry or turbidometry is chosen.
- Suspensions with lower concentration nephelometry and for higher concentration turbidometry are utilised.



Concept of Turbidimetric Analysis



Principle of Nephelometry

❖ INSTRUMENTATION

- The components of a nephelometer and turbidimeter are:

- 1) Sources,
- 2) Detectors, and
- 3) Cells

❖ **Source of light:**

- ✓ **White light** could be used in nephelometers but preference is given to **monochromatic radiation** which is also used in turbidimeters to **minimise absorption**.

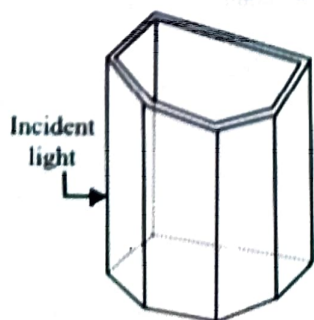
- Sources that give **high intensity monochromatic radiation** is a **better choice** and also employment of short wavelengths may increase the Rayleigh scattering efficiency.
- The most convenient source is a **mercury arc or a laser** along with suitable filter combinations that isolates one of its emission lines.
- For **determining the concentration** of a specific entity, a **polychromatic source** (e.g., a tungsten lamp) could be a better option.
- Employing the blue spectral region along with filters to block other wavelengths, provides better results.

☐ Detectors

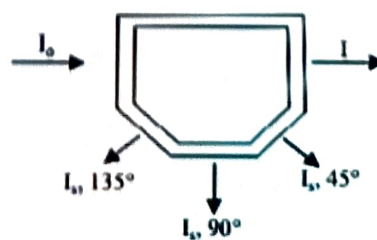
- ✓ Nephelometers use **photomultiplier tubes** since scattered radiation intensity is very small.
- ✓ The **detector is fixed at 90°** to the primary beam in nephelometers.
- ✓ In order to obtain **maximum versatility and sensitivity**, the detector angle is changed and positioned close to the primary beam.
- ✓ Also certain nephelometers contain detector mounted on a circular disc allowing measurement at different angles like at 0° and from 30-135°.
- ✓ In turbidimeters, ordinary detectors such as **phototubes** may be used.

☐ Cells

- ✓ **Cylindrical cells** with flat faces are used for facilitating the entry and exit of beams.
- ✓ This also **reduces the reflections and multiple scatterings** from the cell walls.
- ✓ Preference is given to a cell having **rectangular cross section**. Semi-octagonal cells are employed for measurements at angles other than 90°.



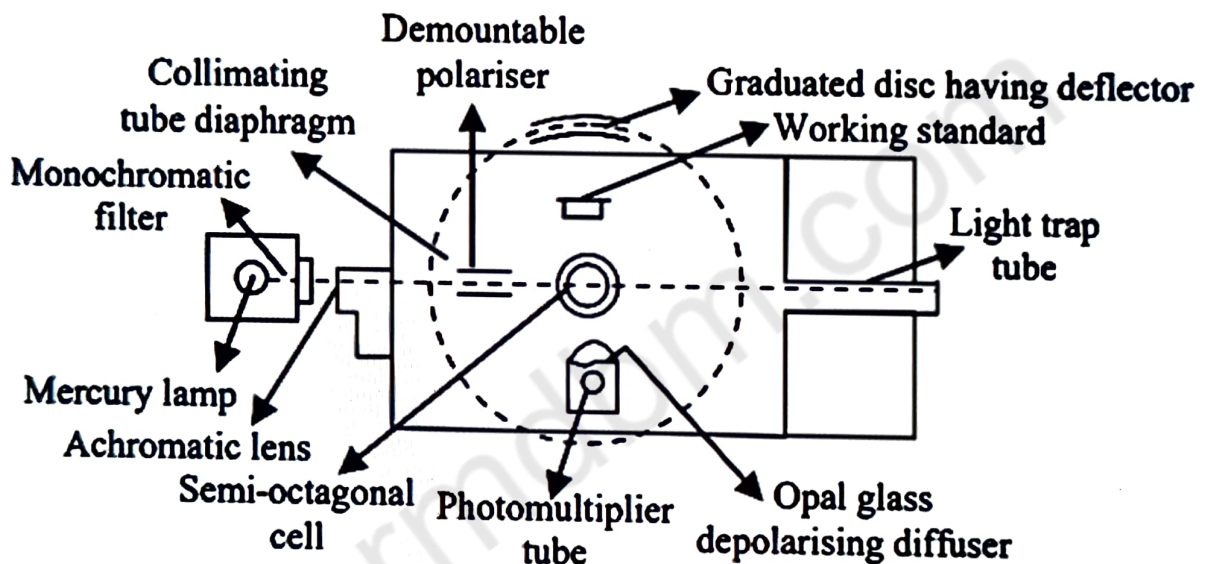
Semi-Octagonal Cells



The Octagonal Face

☐ Nephelometer

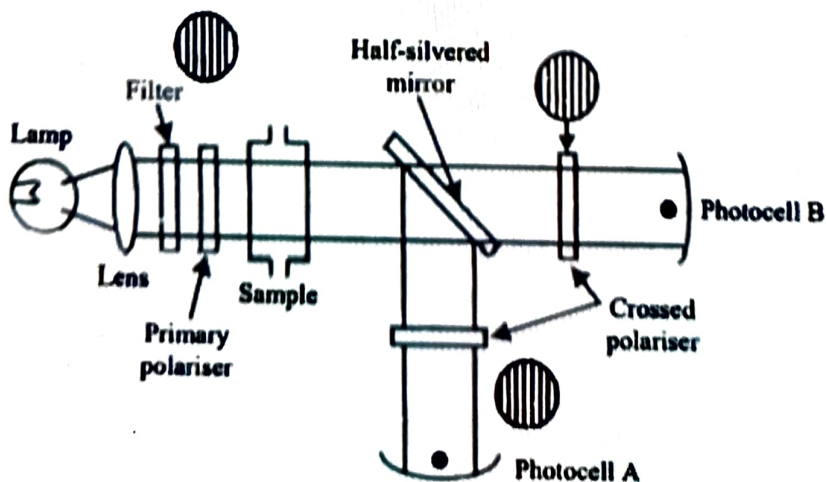
- ✓ It contains a **tungsten lamp** as the source of light and the **sample cell** is placed on the top of the source.
- ✓ Light passing through **filter** falls on the **suspended particles** and these particles **scattered the light**.
- ✓ These scattered lights are collected by **optical system** and reflected to a **photovoltaic cell** which is kept at the bottom of the instrument.
- ✓ It's a very **simple and inexpensive** and easy to handle method and has good precision and accuracy.



Nephelometer

☐ Turidimeter

- ✓ A **colorimeter** can be used as a **turidimeter** by selecting 530nm or by using a blue filter. Its construction can be seen as given below:



Turidimeter

❖ APPLICATIONS

❑ Inorganic Analysis:

- If precipitates cannot be filtered due to small sized particles or gelatinous nature, gravimetric operations cannot be performed. In such cases, nephelometry and turbidimetry are employed in which the precipitates are converted into ideal suspension under controlled conditions.
- In nephelometry or turbidimetry analysis for **quantitative determination**, calibration curves are prepared using **samples of known metal concentrations**. These calibration curves give results for **suspensions of unknown concentrations**.
- Nephelometry and turbidimetry **determine sulphate** (as BaSO_4), **carbonate** (as BaCO_3), **chloride** (as AgCl), **fluoride** (as CaF_2), **cyanide** (as AgCN), calcium (as oxalate or oleate), and zinc (as ferrocyanide).
- Nephelometry and turbidimetry are also used for **carbon dioxide determination** by bubbling the gas through the alkaline solution of barium salt, and analysing the barium carbonate suspension.

❑ Organic Analysis:

- Turbidimeter is used to determine the **turbidity in sugar products** (like food and beverages) and to determine the **clarity of citrus juices**.
- It is also used for **detection of benzene in alcohol** by dilution with water to produce an immiscible suspension.

❑ Biochemical Analysis:

- Turbidimetry measures the **growth of a test bacterium in a broth medium**.
- This method aids in estimation of amount of **amino acids, vitamins, and antibiotics**.
- Nephelometry detects **protein, yeast, glycogen, and β - and γ -globulin** in blood serum and plasma.

❑ Determination of Molecular Weights of High Polymers:

- The molecular weights of macromolecules can be determined by **asuring the intensity of light scattered by polymer solutions**.

☐ **Turbidimetric Titrations:**

- These titrations are performed in a manner similar to **photometric titrations**. Here **absorbance is plotted against the titrant volume**. With rise in titrant volume, the **concentration of precipitate rises** and thereby **absorbance also increases**.

☐ **Phase Titrations:**

- Turbidimetry is employed for titrating a **mixture of two liquids with a third liquid** that is miscible with one of the two liquids.
- Upon introducing **adequate quantity of the third liquid**, separation of phase occurs, **causing turbidity**.
- For result interpretation, either **one should have knowledge about the three** - component phase diagram or **should titrate the unknown** with known mixtures.