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 cm^{-1})** of the 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 the electromagnetic spectrum is divided into the following **three regions**, named for their relation with the visible spectrum:

1) The far-infrared, approximately 400 – 10 cm^{-1} (1000–30 μm)

Lies adjacent to the microwave region, has low energy and is used for **rotational spectroscopy**.

2) The mid-infrared, approximately 4000 – 400 cm^{-1} (30–2.5 μm)

Used to study the **fundamental vibrations** and associated rotational-vibrational structure.

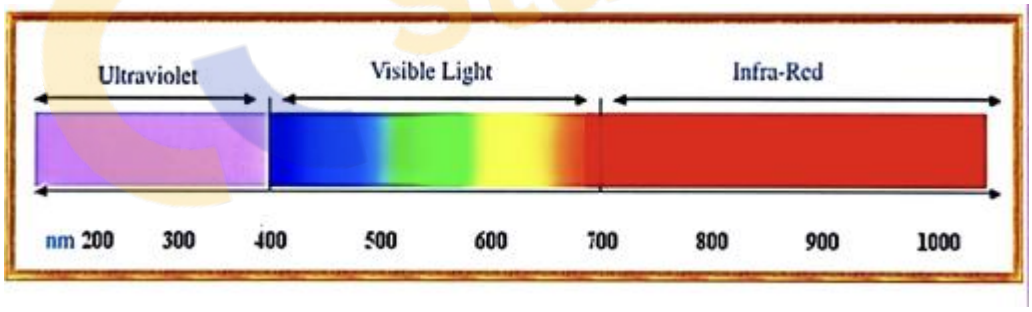
This region has wavelengths between **3×10^{-4} and 3×10^{-3} cm**.

3) The near-infrared, approximately 14000–4000 cm^{-1} (2.5–0.8 μm)

Has higher energy and can **excite overtone or harmonic vibrations**.

(image: electromagnetic spectrum UV–Visible–IR)

(Table: Near / Mid / Far IR ranges)



Region	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	10–37 Kcal/mole

Region	λ (cm)	λ (μm)	λ (cm^{-1}) Wavenumber	Energy (E)
Mid	3×10^{-4} to 3×10^{-3} (0.0003–0.003)	30 to 2.5	4,000 to 400	1–10 Kcal/mole
Far	3×10^{-3} to 3×10^{-2} (0.003–0.03)	1000 to 30	400 to 10	0.1–1 Kcal/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.**

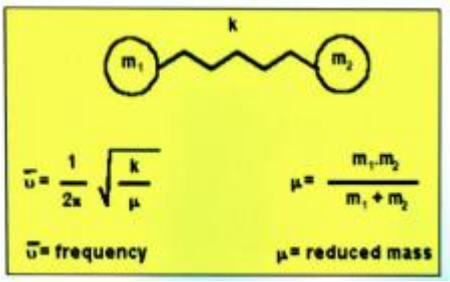
❖ Principle

● 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 two atoms increases or decreases**, keeping atoms in the same bond axis.

Stretching vibrations are of two types:

i) Symmetric Stretching Vibrations:

Movement of atoms with respect to a **particular atom in a molecule is in the same direction**.

ii) Asymmetric Stretching Vibrations:

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** (higher energy) than bending absorptions of the same bond.

Bending vibrations are of the following four types:

i) Scissoring:

Two atoms approach each other.

ii) Rocking:

Movement of atoms in the **same direction**.

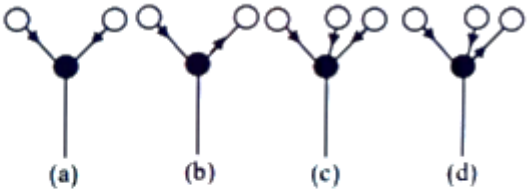
iii) Wagging:

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

(a) **Scissoring**

(b) **Rocking Vibrations of AB_2 Molecule; The out-of-plane deformation vibrations**

(c) **Twisting and**

(d) **Wagging Vibrations of AB_2 Molecule;**

(e) **Symmetric and**

(f) **Asymmetric Vibrations of AB_3 Molecule.**

Bending or Deformation Vibrations

(a) Scissoring
(b) Rocking Vibrations of AB_2 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.

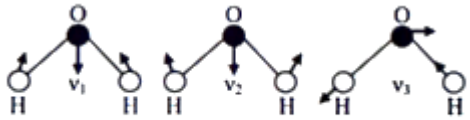
• **Water is a triatomic non-linear molecule** with $3\times3 - 6$ or $3(3n-6)$ normal modes of vibrations, which can be calculated by applying the following two primary forces:

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



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.**

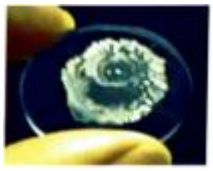
• As infrared spectroscopy has been used for the characterization of solid, liquid or gas samples, it is evident that samples of different phases have to be handled.

• 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:

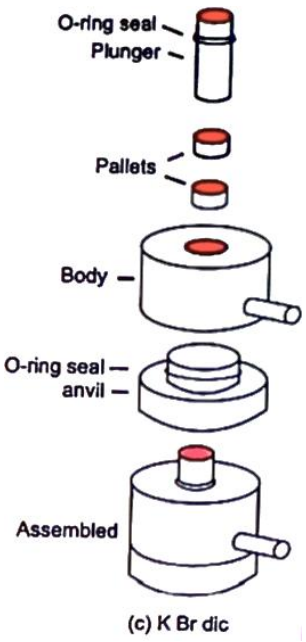
✓ In this technique, the finely ground **solid sample is mixed with Nujol** (mineral oil) to make a thick paste which is then made to **spread between IR-transmitting windows.**

✓ This is then **mounted in a path of infrared beam** and the spectrum is run. Although **Nujol is transparent** throughout the IR region.

✓ When IR spectrum of solid sample is taken in **Nujol mull**, absorption bands of the sample that happen to **coincide with 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 (at least 25,000 psi)** to form a **small pellet** (about 1–2 mm thick and 1 cm in diameter).

✓ The resulting pellet is **transparent to IR radiation** and is run as such 1–2 mm thick and 1 cm.

✓ Particle size must be fine to **avoid scattering** that is greater than wavelength of infrared radiation — less than 2 μm.

➤ Sampling of liquids

This is the **simplest infrared sampling technique**.
A liquid as a thin film squeezed between two infrared-transparent windows.

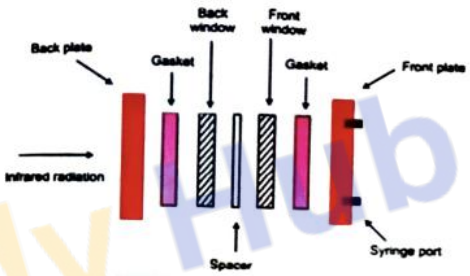
There are several different types of transmission solution cells available:

1. Fixed path length sealed cells

Liquid sample holder (demountable cell)

• Useful for volatile liquids but cannot be taken apart for cleaning.

2. Semi-permanent cells

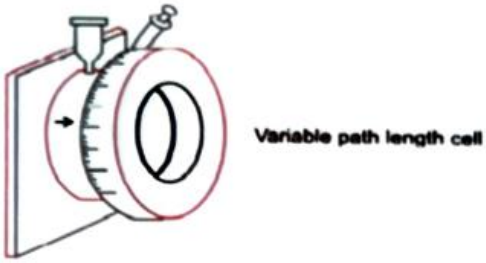


Demountable liquid cell internal structure

• Are demountable so that windows can be cleaned.
• Spacer is usually made of **PTFE (Teflon)** and is available in many thicknesses, allowing one cell to be used for various path lengths.

3. Variable path length cells

• Incorporate a mechanism for **continuously adjusting the path length**,
• Vernier scale allows accurate adjustment.



Variable pathlength cell

• All of these cell types are filled using a syringe and ports are sealed with PTFE plugs.
• Important consideration in IR cell choice is the **window material.**
• Must be transparent to IR; **alkali halides** normally used.
• Liquid cells made of **NaCl, KBr or ThBr flats.**

➤ Sampling of Gases

✓ The gas sample cell is **similar to the cell for liquid samples**.

✓ Gas sample cell surfaces in the light path are made of **KBr, NaCl.**

✓ To compensate for the **small number of molecules**, gas cells are **larger.**

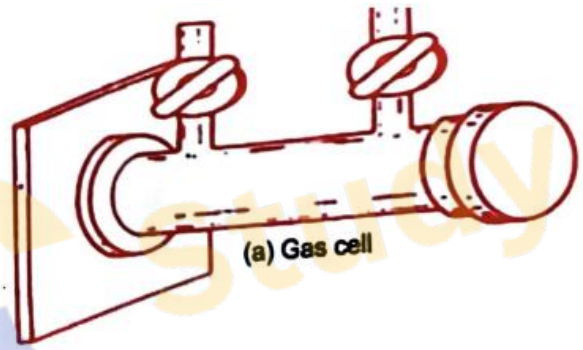
✓ They are **about 10 cm long**, but may be **up to 101 m long.**

✓ Multiple reflections can be used to make the **effective path length** **as long as 40 m**, so gas constituents can be determined.

✓ Gas must **not react** with cell windows or reflecting surfaces.

✓ Gas analyses are performed with IR but the method is **not much used because of lack of sensitivity.**

✓ **Moisture must be avoided**.



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 C=O bonds (O═C═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 **v_1, v_2, v_3**, in order of **decreasing frequency** within each symmetry group, starting from the symmetric mode of vibration.

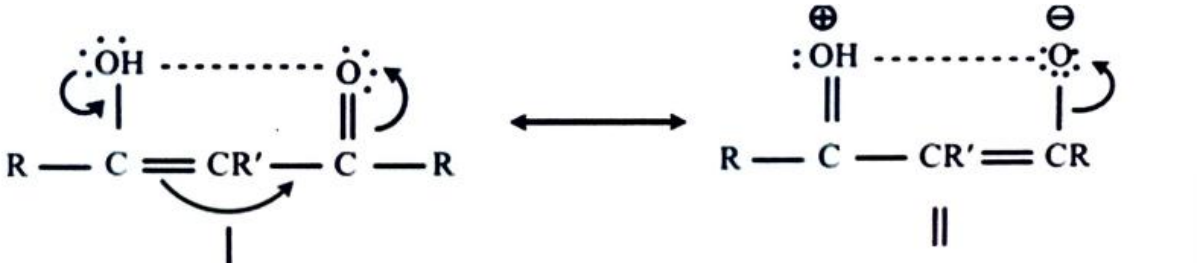
The important requirements for effective coupling interactions are:

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.
iii) Maximum interaction occurs when the coupled groups **individually absorb near the same frequency**.
iv) Coupling between **bending and stretching** vibrations occurs when a stretching bond forms one side of the changing angle.
v) A **common bond** is required for coupling of bending vibrations.

vi) **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, two types of hydrogen bonds can be distinguished.
- **Inter-molecular hydrogen bonds give rise to broad bands**, while **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 intermolecular hydrogen bonding.
- 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 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 CH_3 **groups combine together** to exhibit two coupled vibrations (asymmetric and symmetric) of different frequencies.
- Vibrational frequencies of **C–H coupled vibrations in** CH_3 **groups** differ from CH_2 groups; hence, detection of all four C–H stretching vibrations in high-resolution IR spectra becomes easy.
- Fermi resonance most commonly occurs in the **IR and Raman spectra**.

For Fermi resonance to occur:

i) The vibrational levels should be of the **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 an **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 decreases** (as force constant decreases because of lengthening or weakening of bond).
- For example: The **C═O stretching absorption** of HCHO and CH_3CHO occurs at **1735** cm^{-1} **and 1730** cm^{-1}, respectively.

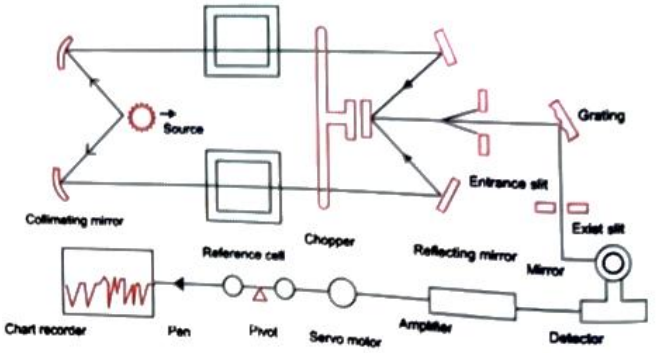
❖ INSTRUMENTATION

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**
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:**
   - Consists of a rod or hollow tube (2 cm long, 1 mm diameter)
   - Made by **sintering a mixture of cerium, zirconium, thorium and yttrium oxides**
   - Heated between **1000–1800°C**
   - Provides maximum radiation at **7100 cm^{-1}** region
2. **Globar:**
   - A **silicon carbide rod**, electrically heated between **1300–1700°C**
3. **Nichrome Wire:**
   - Heated by passing current
   - Used when required wavelength range & intensity are insufficient
4. **Rhodium Wire:**
   - Sealed in a **cylinder**
5. **Tungsten Filament Lamp:**

- Used for **near infrared region**

❑ Monochromators (Wavelength Selectors)

- Since the sample absorbs at **certain frequencies**, the desired frequencies must be **selected** and radiations of other frequencies **rejected**.

This selection is achieved using:

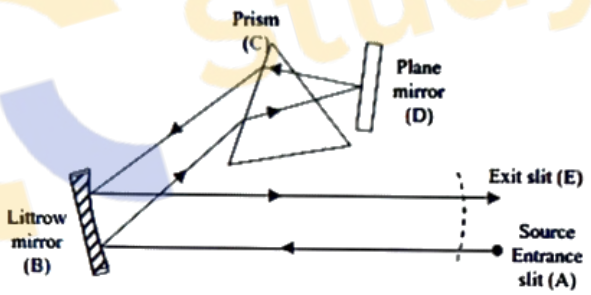
1. **Prism monochromator**
2. **Grating monochromator**

➤ 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

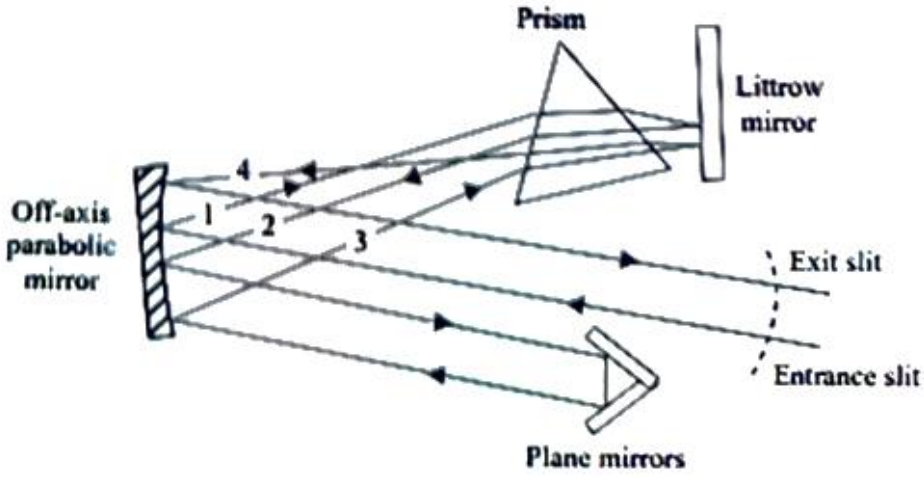
Single pass monochromator

• 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 single pass monochromator in the radiation before reaching the detector.

• In both mono- and double-pass monochromators, **sodium chloride (rock-salt) prism** is used for **4000-650 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 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,

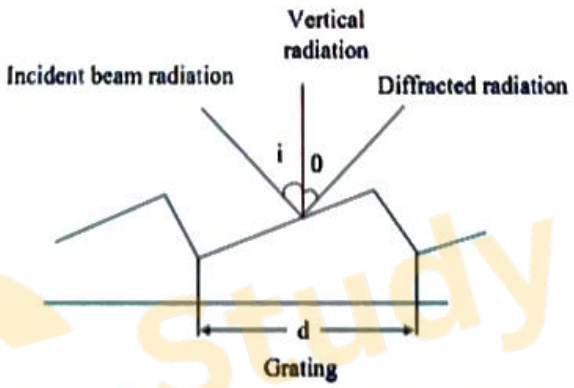
n = The order (a whole number)

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

5. Pyroelectric detector

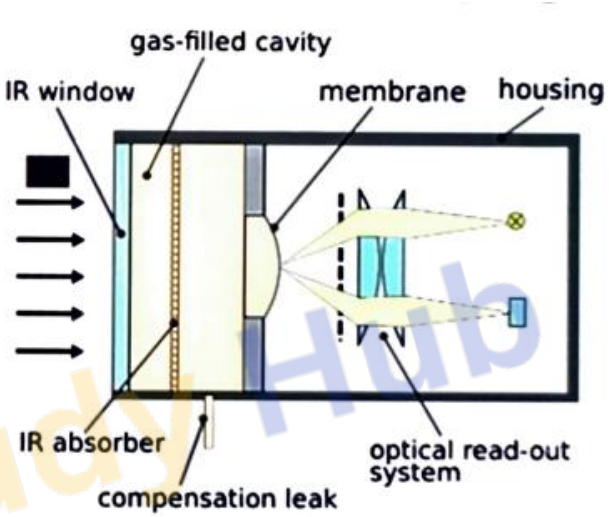
➤ Golay Cell

✓ 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.

✓ IR radiation falls on the blackened metal plate, heating the gas which expands.

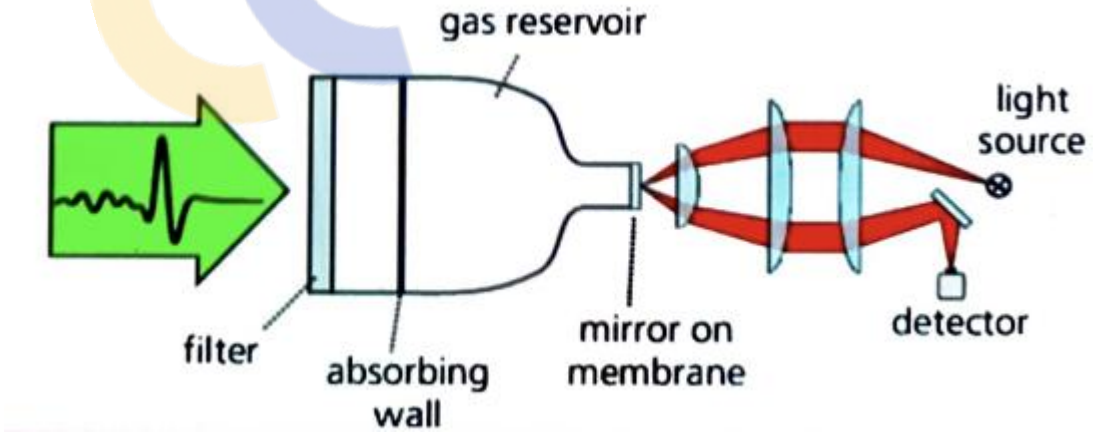
✓ Pressure increases and **deforms the metalised diaphragm** dividing the cell into two chambers.



✓ A light beam falls on the diaphragm and is **reflected onto a photocell**.

✓ The diaphragm motion changes the output of the cell.

✓ The signal seen by the phototube is modulated with respect to radiant power of the incident IR beam.

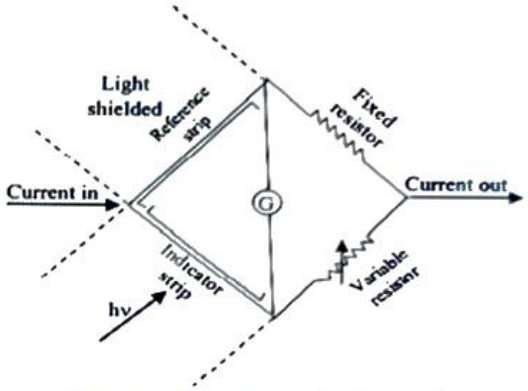


➤ Bolometer

✓ Works on the **principle** that the electrical resistance of a metal **increases by 0.4% for every °C rise in temperature**.

✓ Contains a **thin metal conductor** whose resistance changes when IR radiation falls on it.

✓ The amount of radiation falling on the bolometer is measured by **change in resistance**.



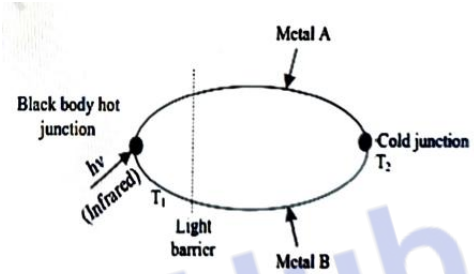
Schematic presentation of a bolometer

➤ Thermocouple

✓ Works on the principle that when **two dissimilar metal wires are joined**, a **temperature difference** develops and current flows.

✓ The end exposed to IR radiation is a **black body** to increase energy absorption.

✓ The other end is **thermally insulated** and screened from stray light (cold junction).



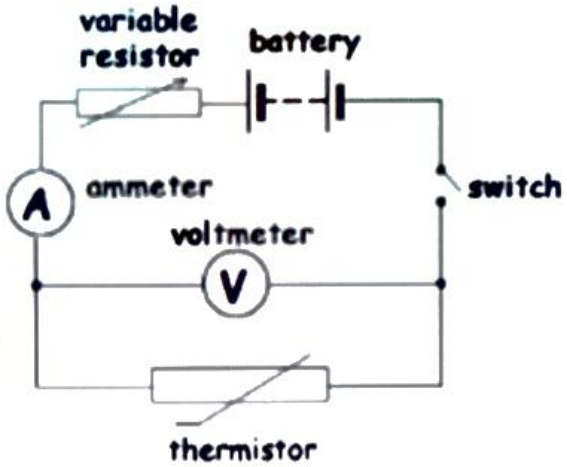
Schematic presentation of a Thermocouple

➤ Thermistor

✓ A thermistor is made up of a **fused mixture of metal oxides**.

✓ The electrical resistance **decreases with increase in temperature**.

✓ This relation allows thermistors to be used as IR detectors like bolometers.



Schematic presentation of a Thermistor

Pyroelectric Detector

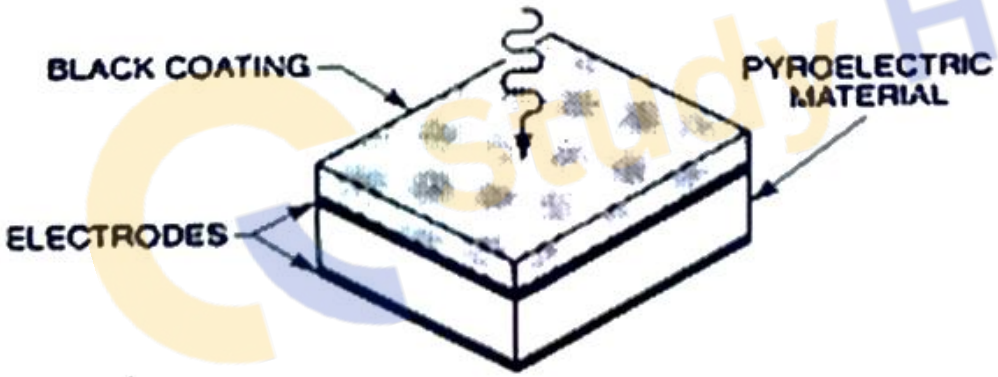
✓ Pyroelectric detector is made up of a **non-centrosymmetrical crystal**, which has an **internal electrical field** along its **polar axis**.

✓ On applying IR radiation, a **change in polarisation** is observed due to an **alteration of the crystal lattice**.

✓ The pyroelectric detector acts as a **capacitator** 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.

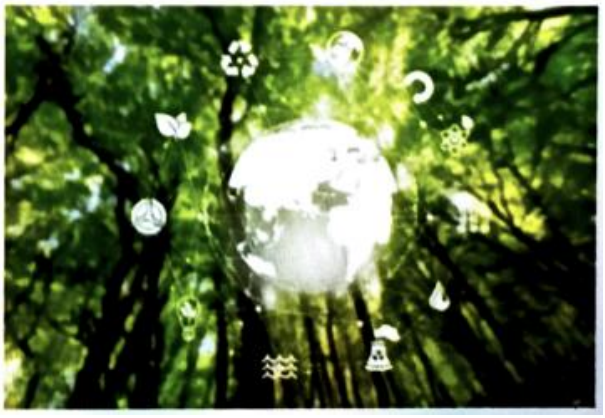
➤ May also be employed to **identify pigments in paints**, which is of particular importance in the fields of **art conservation** and **forensic analysis**.

➤ 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 (PART - 2)

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

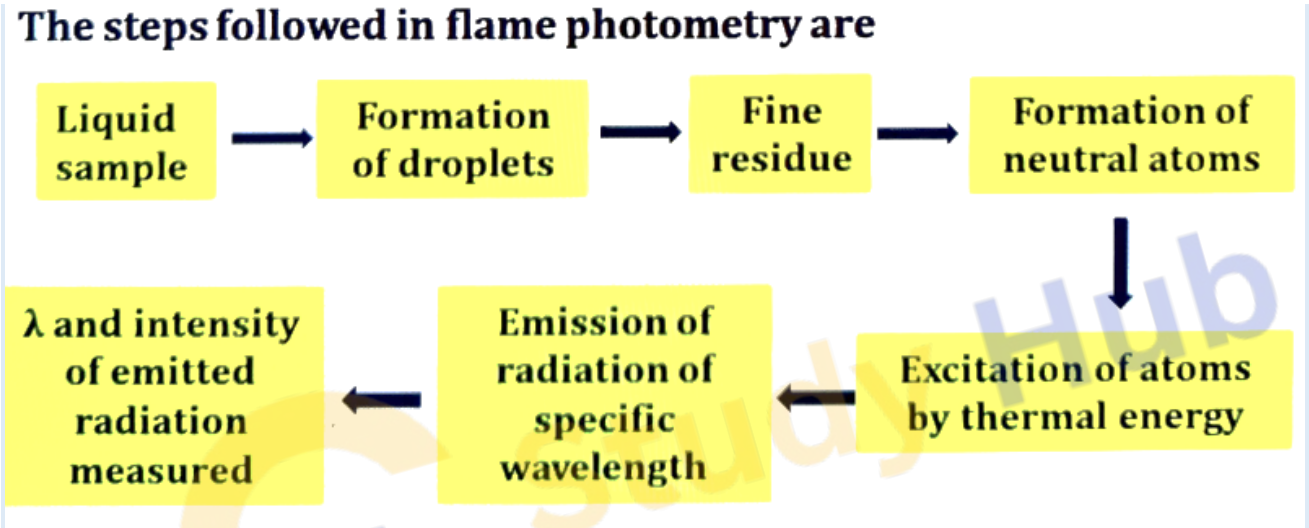
excited state atoms.

• The 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.



❖ 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.

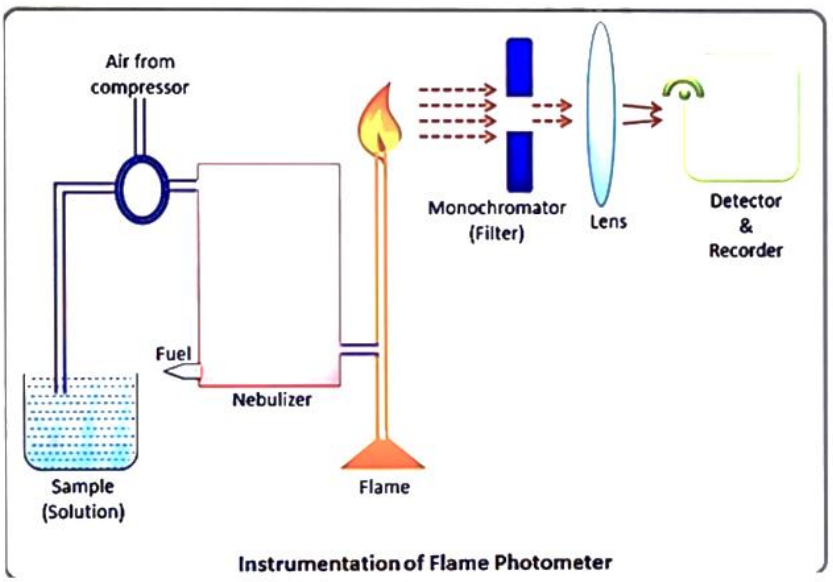
• The basis of flame photometric working is that **the types of metals are dissociated due to the thermal energy** provided by the flame source.

• 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 wavelengths.

• The emitted wavelengths are **specific for specific elements**.

elements.



Instrumentation of Flame Photometer

Whole process can be categorize as below

Desolvation:

✓ The **metal particles** in the flame are **dehydrated by the flame** and the process of desolvation takes place.

✓ Water or other solvent is vaporised 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 or 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.

✓ 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 shift 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 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

✓ 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 occurs 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:**

$$Na \rightleftharpoons Na^{+} + e^{-}$$

- 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 anions** 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.

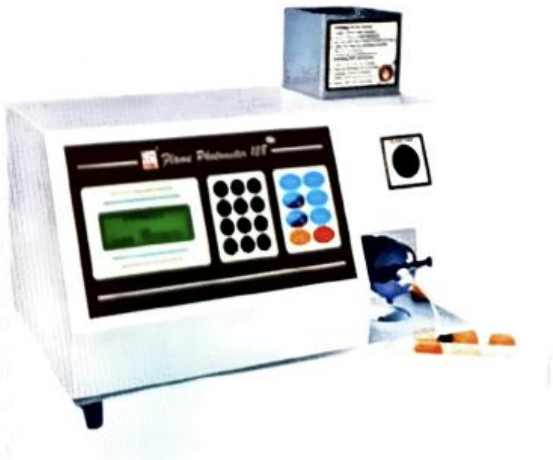
Oxide Formation Interferences

- 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

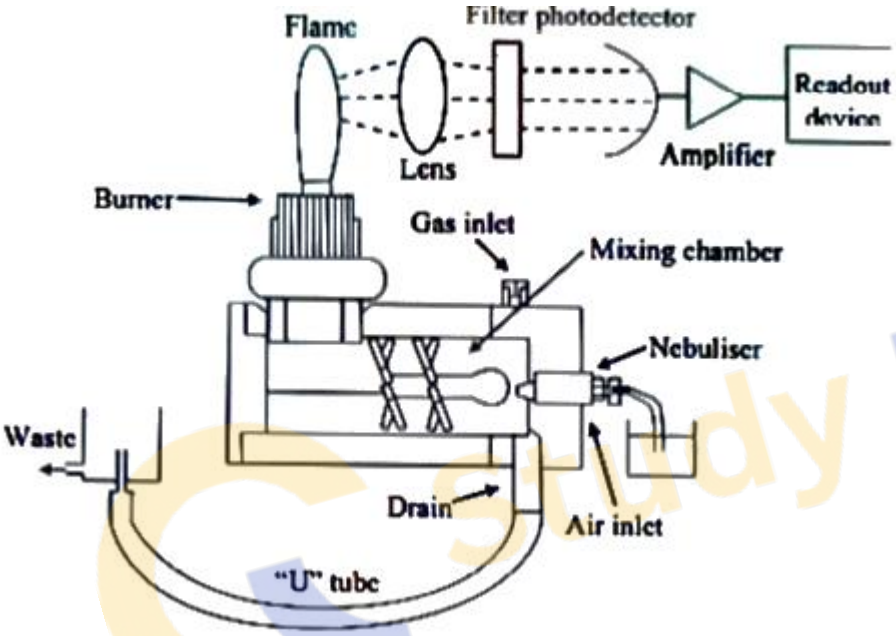
✓ **applying very high temperature flames**, which break the oxide-producing free atoms for their excitation

✓ 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.**

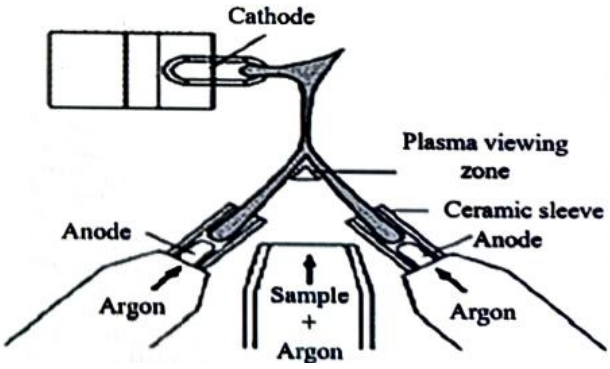


Atomisers

- 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 is 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:



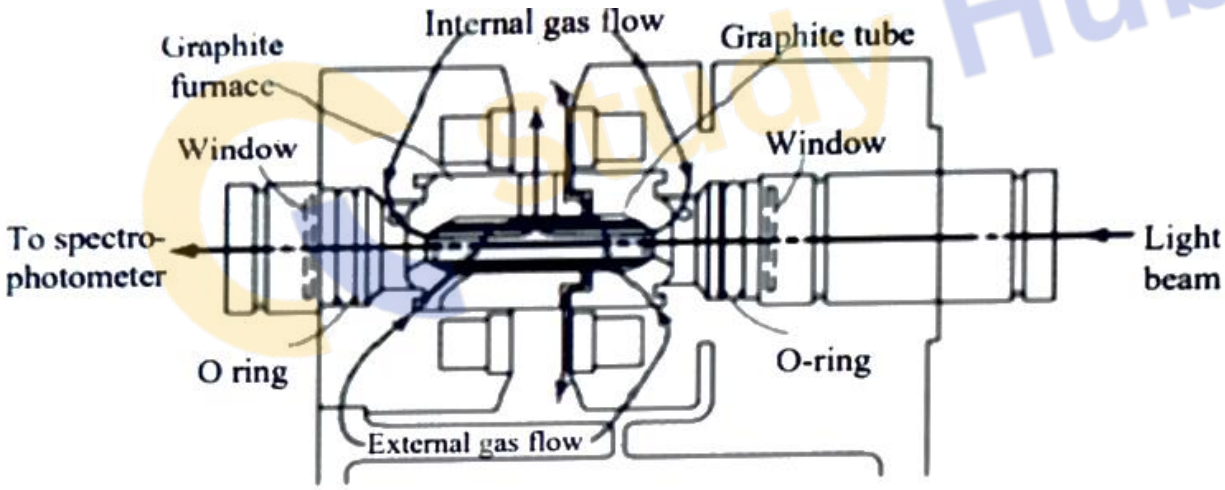
These atomisers utilise a **pneumatic nebuliser** for converting the sample solution into mist or aerosol.

✓ 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.



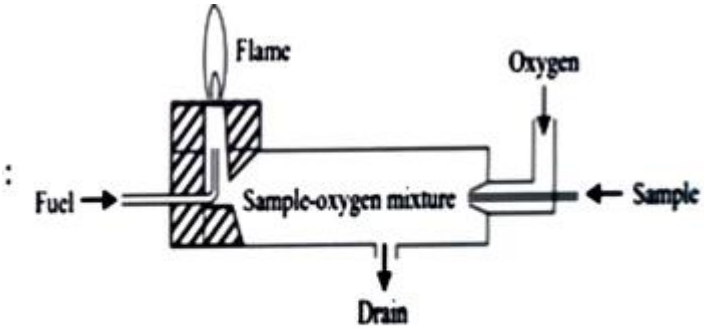
Nebulisers

- 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**
- **Lundergardh Burner**



Lundergarph Burner

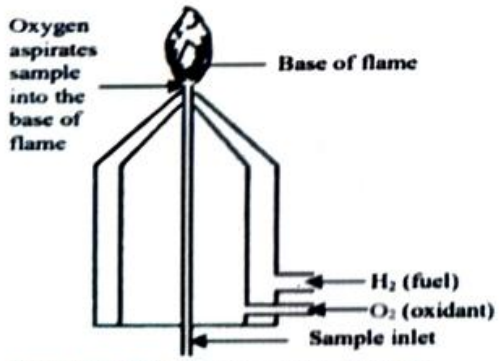


Figure 4.5: Total Consumption Burner

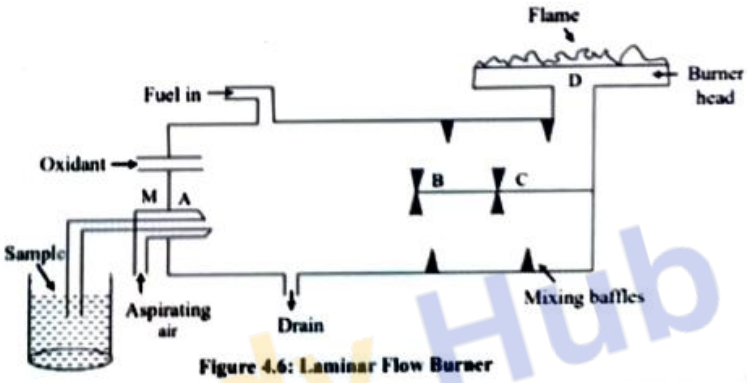


Figure 4.6: Laminar Flow Burner

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.**

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.

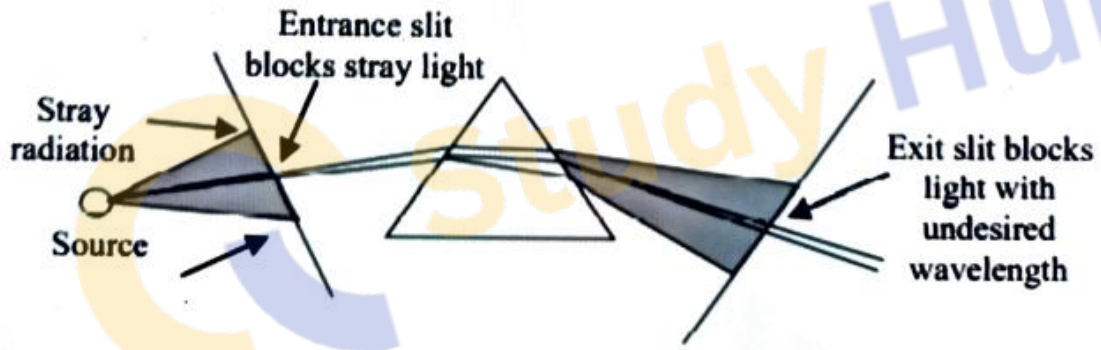


Figure 4.9: Monochromator System without Collimator Lenses for Simplification

❖ 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.

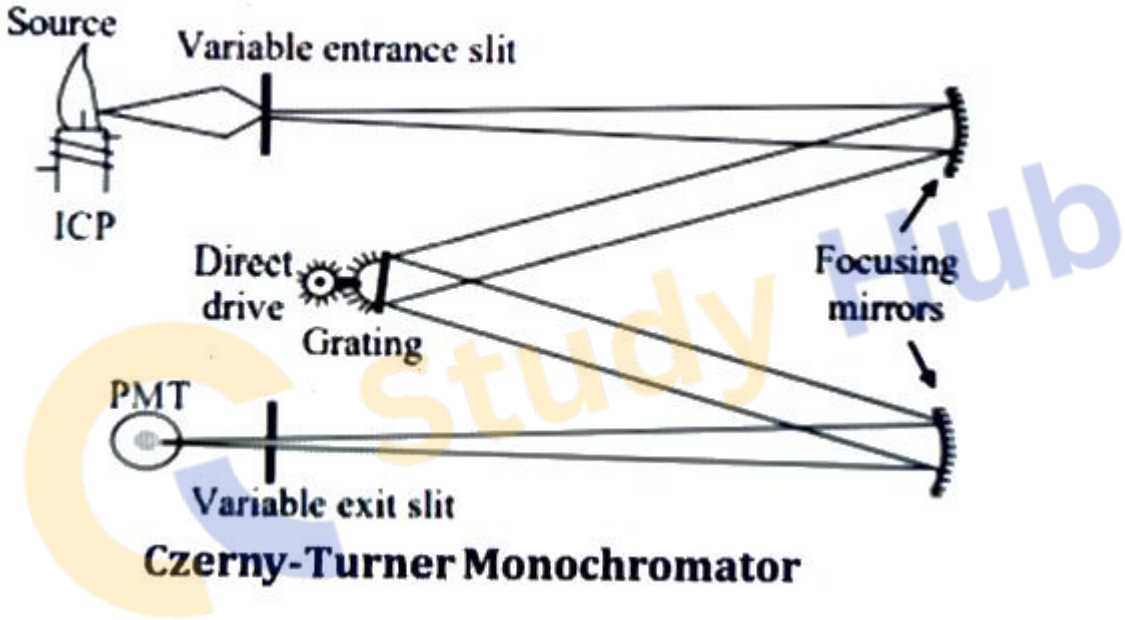
It mostly operates on a **computer-driven rotation** of gratings in diverse ways to **select a required wavelength.**

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 **5 ppm** in comparison to **10–20 ppm** 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.

UNIT–II ATOMIC ABSORPTION SPECTROSCOPY (PART – 2)

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:

= (πe / mc) Nf

Where,

e = charge on electrons

m = mass of light

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

f = oscillator strength

c = speed of light.

❖ INTERFERENCES

There are the following types of interferences in AAS:

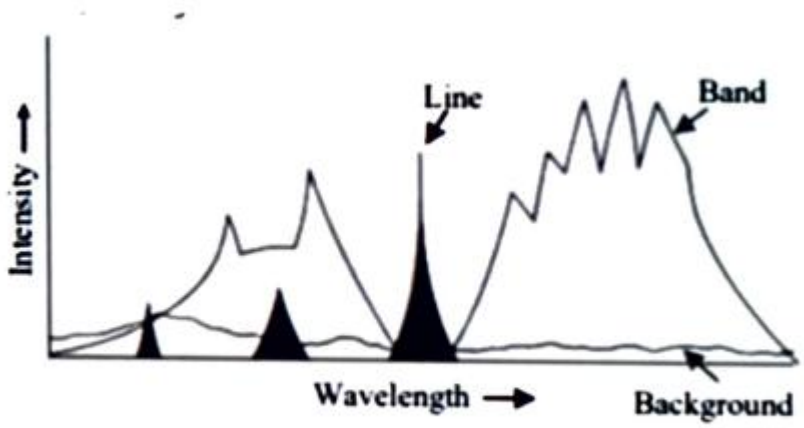
1. Spectral interferences,
2. Chemical interferences,
3. Ionisation interferences,
4. Matrix or bulk interferences,
5. Solvent interferences, and
6. Dissociation of metal compounds.

❖ 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

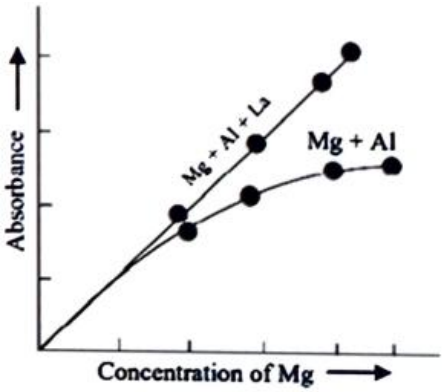
✓ These interferences must be considered in **atomic absorption procedures**.

✓ 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**



Chemical Interferences

the presence of aluminium.

The interference may be removed by the **addition of lanthanum (La)** to the system.

❖ 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.

INSTRUMENTATION

A typical AAS has the following instrumental components in it.

1. Radiation Source
2. Flame Nebulization 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:

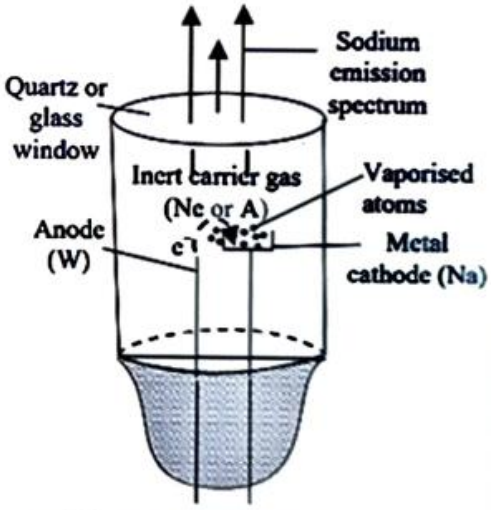
✓ This lamp consists of a hollow cup containing the element to be determined.

✓ 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.

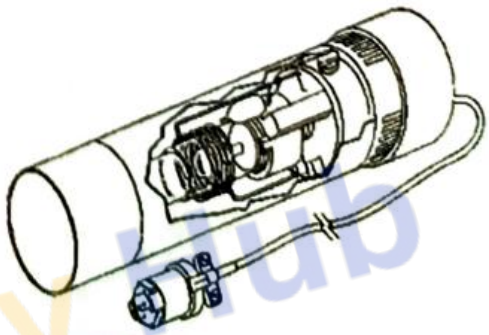


Hollow Cathode Lamp

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 the flame.

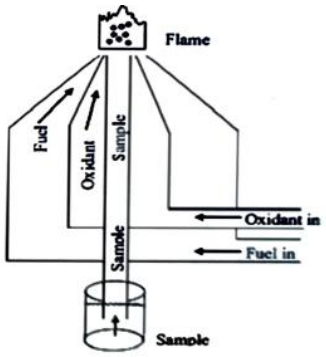
✓ But only the pulsating (or alternating) current is amplified and recorded and thus, the absorption of light will be measured without interference from the light emitted by the flame itself.

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:

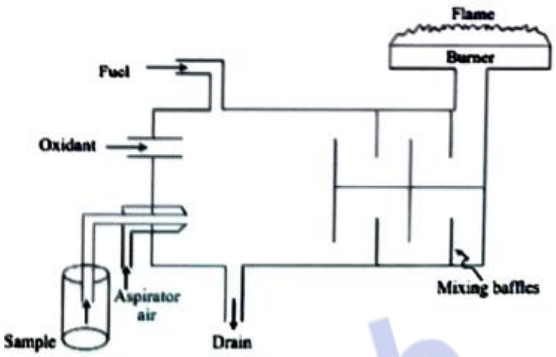
In this burner, the sample solution, fuel, and oxidising gases are **passed through separate passages** to meet at the opening of the flame base.
This burner is however noisy, hard to use, and its efficiency is not very good.



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 becomes complicated and **high dispersion is essential**.

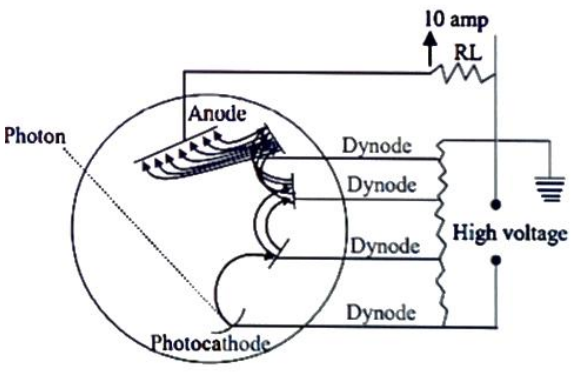
✓ For such cases, **large dispersion and high resolving** monochromators are advantageous for resolving spectra.

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



Photomultiplier tube and power supply

envelope which contains a **photocathode**, a series of **electrodes called dynodes**, and an **anode**.

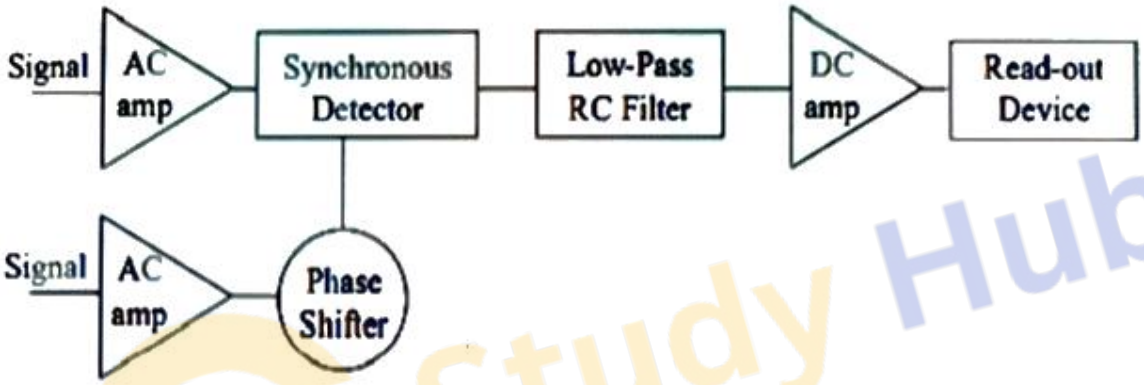
The photocathode is fixed to the power supply terminal.

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.

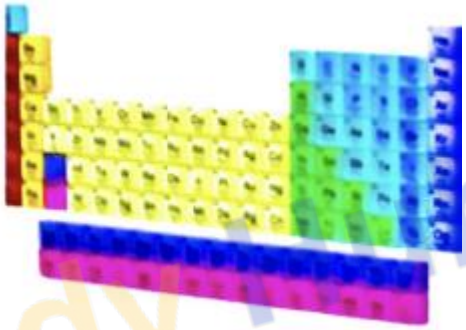
• **Quantitative Analysis:** The AAS is very **sensitive** and is **accurate** than any other technique.

• **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 ultrA 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 (PART - 3)

Points to be covered in this topic

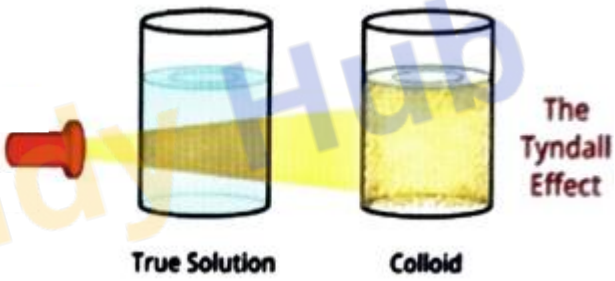
- ❖ **Introduction**
- ❖ **Principle**
- ❖ **Instrumentation**
- ❖ **Applications**

NEPHELOTURBIDOMETRY

❖ INTRODUCTION

• Nephelometric and turbidometric methods depend on the **scattering of light by particle suspended in a liquid**.

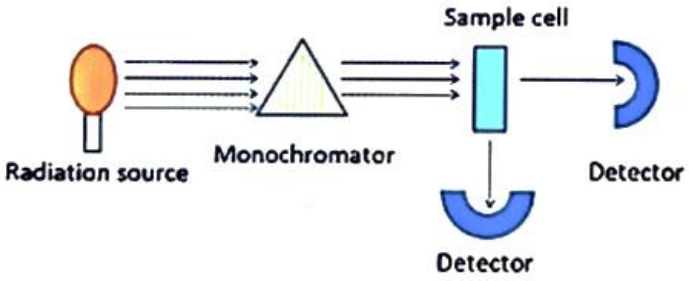
• The suspended particles have **refractive index values** different from the suspending medium.



• 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**.

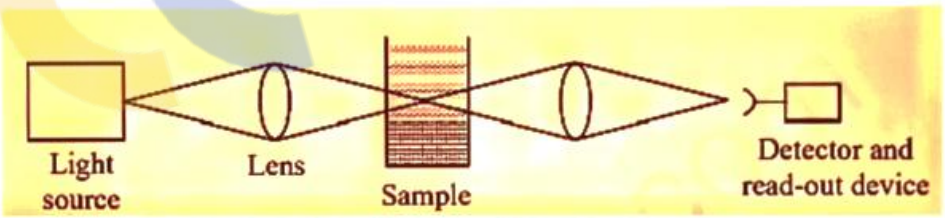
• For **higher concentration** suspensions scattering is **non uniform** and light becomes scattered in all possible directions. Hence, it is **difficult to measure the intensity of scatter radiation at specific angles.**

● So, the intensity of transmitted light (that is unscattered) direction is **measured at 180°**.

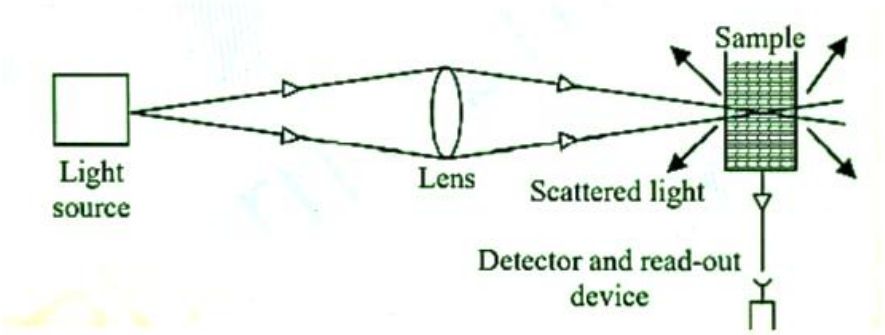
● The intensity of transmitted light (It) is a function of concentration i.e. when the **concentration increases the intensity of transmitted light is less** and when concentration is less the intensity is high.

● 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.

✓ To obtain **maximum versatility and sensitivity**, the detector angle is changed and positioned close to the primary beam.

✓ Certain nephelometers contain detector mounted on a circular disc allowing

measurement at **0° and from 30–135°**.

✓ In turbidimeters, ordinary detectors such as **phototubes** may be used.

Cells

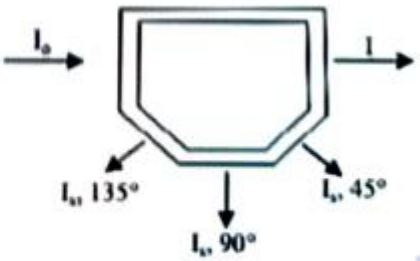
✓ **Cylindrical cells** with flat faces are used for facilitating the entry and exit of beams.

✓ This also **reduces 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

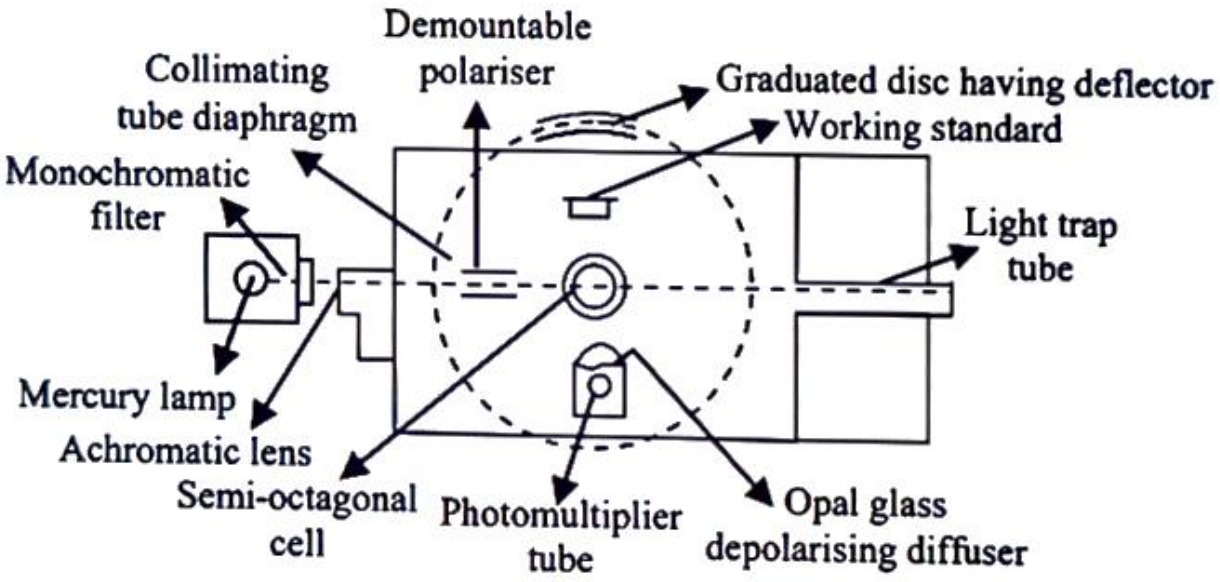
Nephelometer

✓ 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 **scatter the light**.

✓ These scattered lights are collected by **optical system** and reflected to a **photovoltaic cell** at the bottom of the instrument.

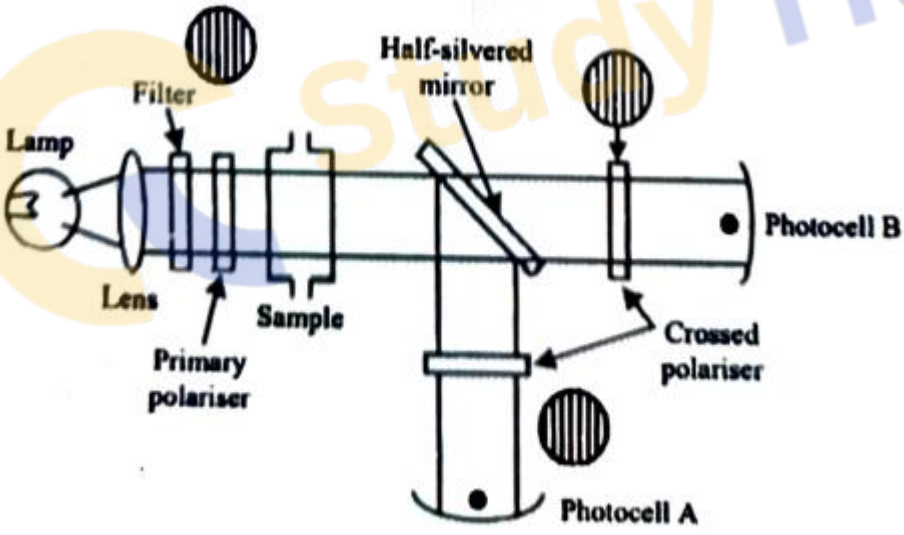
✓ It's a very **simple and inexpensive** and easy to handle method and has good precision and accuracy.



Nephelometer

Turidimeter

✓ A **colorimeter can be used as a turidimeter** by selecting 530 nm or 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 amounts 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 **assuring 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**.