IFAS

SPECTROSCOPY!

Separation → filtration, distillation, solvent extraction, chromatography

'Spectroscopy → Quantitative aspects'

Chemical analysis includes two parts- Separation And Quantitative estimation.

Quantitative determination is carried out by either spectral method or instrumental method.

❖SPECTROSCOPY?

Widely used technique for quantitative determination is spectroscopy.

components of EM Rad^n = Electrical, Magnetic

→ interaction with radiation → Electromagnetic radiation

move with speed of light

Q. What is spectroscopy?

Spectroscopy is interaction of matter with electromagnetic radiation.

Q. Electromagnetic radiation?

Form of radiation (radiant energy) released by certain electromagnetic processes.

Electromagnetic radiations consists of electromagnetic waves which are synchronized oscillations of electric and magnetic field that propagate at the speed of light.

→ wave nature + particle nature.

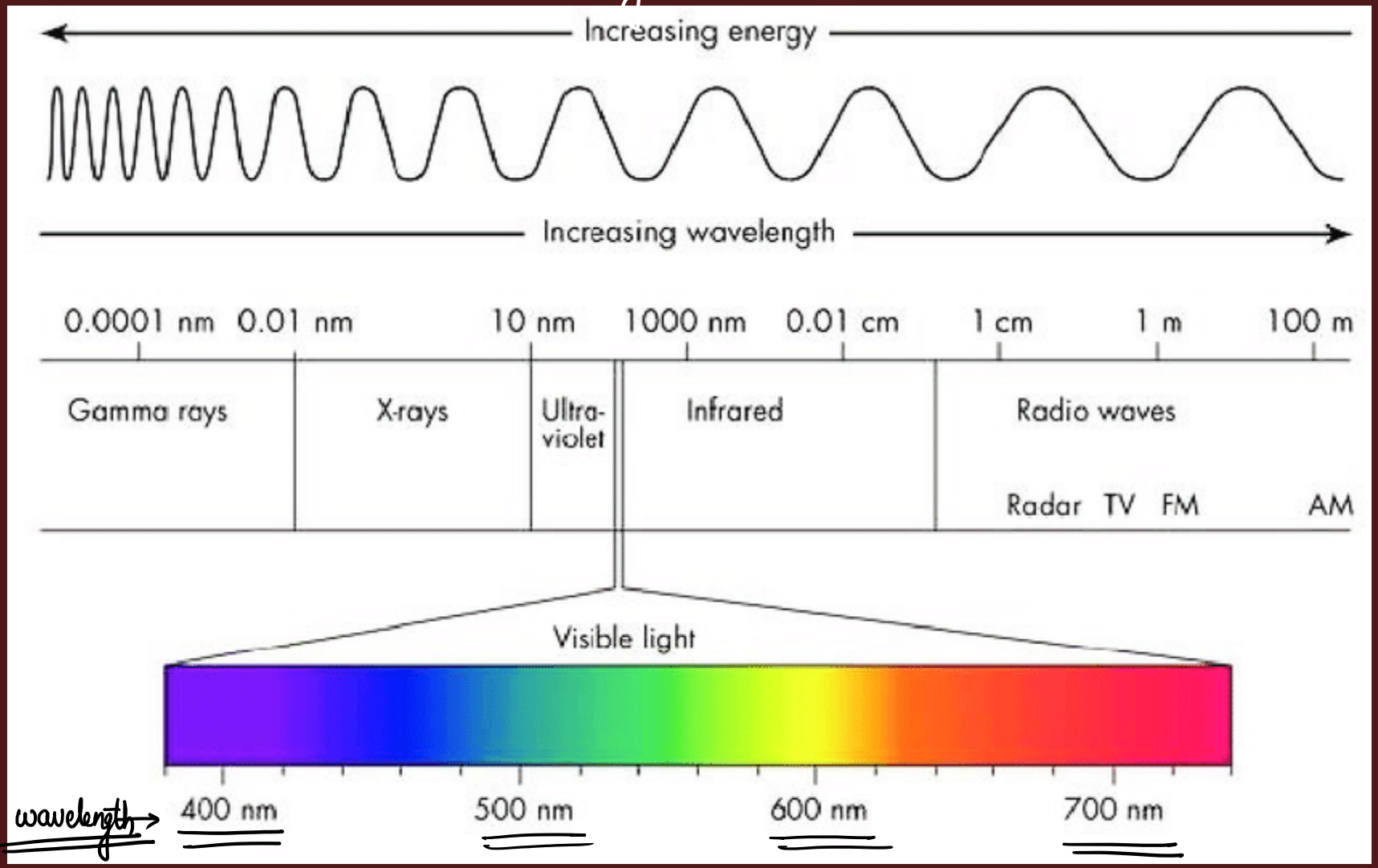
Electromagnetic waves behave as wave as well as particles in nature.

They can be characterised by their frequency or wavelength of oscillations to form the electromagnetic spectrum.

frequency ⟷ wavelength

$$\text{frequency } (\nu) = \frac{\text{speed of light } (c)}{\text{wavelength } (\lambda)}$$

Electromagnetic Radiation



❖ ADVANTAGES OF SPECTROSCOPIC TECHNIIQUES:

- ✓ Process is specific for a particular element however sometimes line of elements can overlap with one another.
- ✓ The method is time saving
- ✓ Quantitative determination of element in trace quantity can also be determined
- ✓ A permanent record can be obtained on a photographic plate
- ✓ It can be applied to any quantity of sample or for sample with trace quantities of impurities.

- General:

atoms of element in flame → absorb thermal energy from flame
→ remain in ground state.

When an element is introduced in the flame, a few of its atom absorb thermal energy from the flame and get excited. This excitation is due to transition of an electron from lower energy state to higher energy state. The energy required for transition is provided by a high temperature aflame or an electric arc or spark.

The lifetime of the excited electron is small. Hence excitation is quickly followed by emission of radiation due to return of electron to lower energy state.

The emitted radiation can have more than one way if de-excitation. The emitted radiation can have more than frequency. These emitted radiation produce distinct line on the spectrometer.

1. Atomic Absorption Spectroscopy: Sir Allan Walsh in 1955 (AAS)

When beam of radiation is passed through a flame containing atoms in ground state, certain atoms absorb the thermal energy and move to excited state.

* Majority of atoms are present in the ground state. These atoms absorb radiation which is of a characteristic wavelength. If the beam emerging form the flame is analyzed in a spectrometer, an absorption spectrum is obtained.

It contains dark lines on bright background.

AAS is study of absorption of radiation by the ground state atom when a sample is introduced into the flame.

Thus AAS helps in identification of the absorbing element.
The intensity of absorption depends upon the amount of sample introduced in the flame.

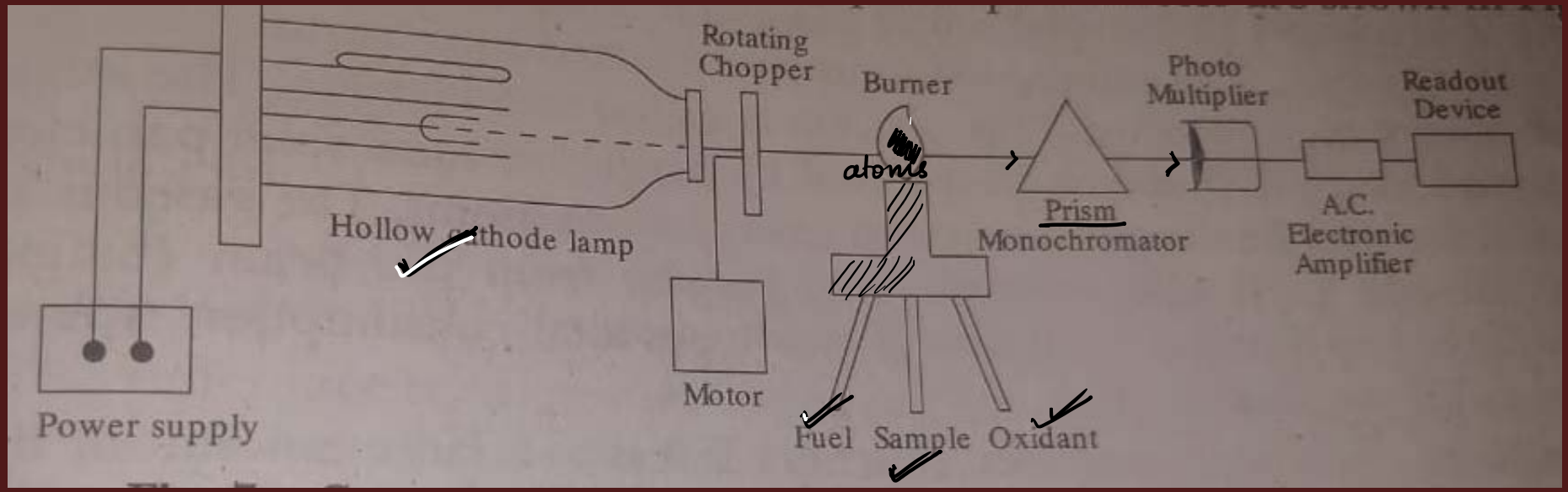
atoms → flame → majority of them are in ground state → beam of light → absorb light of characteristic wavelength

metal salt + solvent ⟶ metal salt (solid)

When Metal salt solvent is introduced in the flame, solvent evaporated giving back the metal salt. The solid metal salt is vaporized to gas phase and then converted into gaseous atoms.

MX (solid) $\xrightarrow{\text{flame}}$ MX (gas) $\xrightarrow{\text{flame}}$ M (gas) + X (gas)

The absorption depends upon the number of unexcited atoms in the flame and is thus independent of the flame temperature.



Atomic Absorption spectroscopy.

1. Source of radiation:
   Source should emit radiation which can excite atoms of the element from ground state t excited state.

   Copper cup → Cu^{2+} → energetic gas particle
   (excited state) → ground

   A hollow cathode lamps is used.

   A hollow cathode lamp consists of hollow cathode cup made of element under study.
   The cathode is protected with a glass shield. Tungsten acts as anode.
   The two electrodes are enclosed in the glass envelope containing inert gas like neon or argon at low pressure.

   Pressure is applied between the two plates and atoms of inert gas ionise. The positively charged ions are attracted towards cathode and hit the cathode surface as they are fast moving. They remove metal atoms form the cathode surface by process called sputtering.
   These metal atoms now collide with highly energetic gas ions and get excited.
   The excited metal atoms emit characteristic radiation which is usually small number of individual wavelength. This emitted radiation appears as bright glow in hollow cathode cup.
   Thus a characteristic wave length is emitted by the hollow cathode lamp.

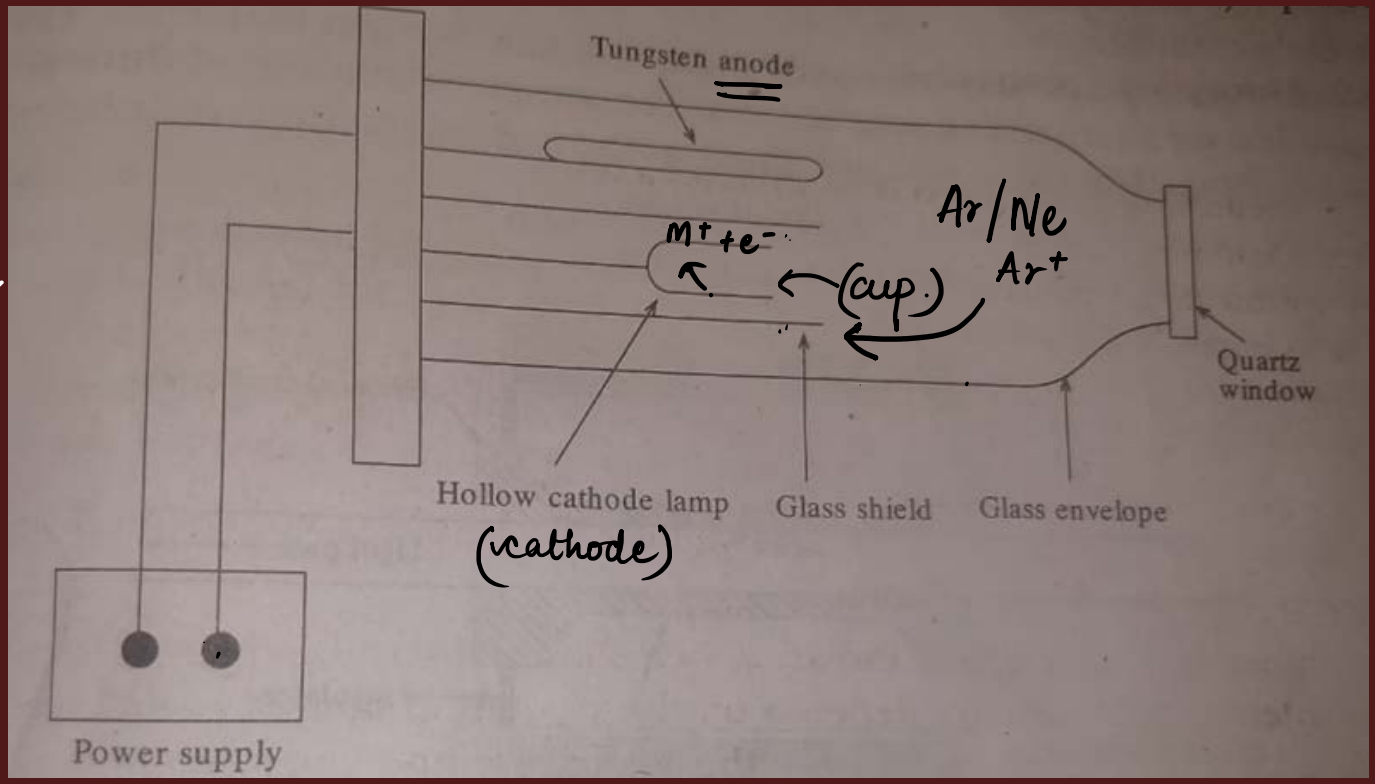
Ar/Ne gas atoms → ionized → fast moving ions (+vely charged)
e^-

① $Ar \rightarrow Ar^+$

② $Ar^+ + Cu \rightarrow Cu^+ + Ar$

③ $Cu^+ + Ar^+$ ↓ Cu^+ (excited) $+ Ar^+$

④ Cu^+ (ES) → Cu^+ (GS)



Hollow cathode lamp.

emission of radiation = characteristic property of that element.

2. Rotating Chopper: (produces Alternating Current)

Rotating wheel breaks the beam of light coming from hollow cathode cup and the resulting light produce s(alternating current) in PMT. The pulsating current is amplified in an AC electronic amplifier.

The beam of light from the flame is continuous and produces steady current in PMT. This current is not amplified. Thus the light by the metal atoms in the frame can be studied without interference form the light of the flame.

3. Flame Atomiser (Burner)

Also called as [burner. = Fuel gas + Oxidant
(H_2, propane) (air, oxygen)]

Flame is produced by burning fuel gas like hydrogen in presence of oxidant like oxygen.

Sample is converted into tiny droplets by gas ions moving with high velocity. This is called as nebulization.

Sample droplets are then sprayed into the flame and aspirate by oxygen to form solid particles. The solid particles vaporize and then get converted into gaseous atoms. The gaseous atoms in ground state absorb characteristic wavelength coming from the hollow cathode tube.

(solid) $MX \longrightarrow MX(gas) \longrightarrow M(gas) + X(gas)$.

Burner are of two types:

a. Total consumption type/ turbulent flow
   - Droplets are sometimes too large to undergo atomisation.

b. Pre mix type/ laminar flow

Sensitivity is less as a large amount of sample is drained off

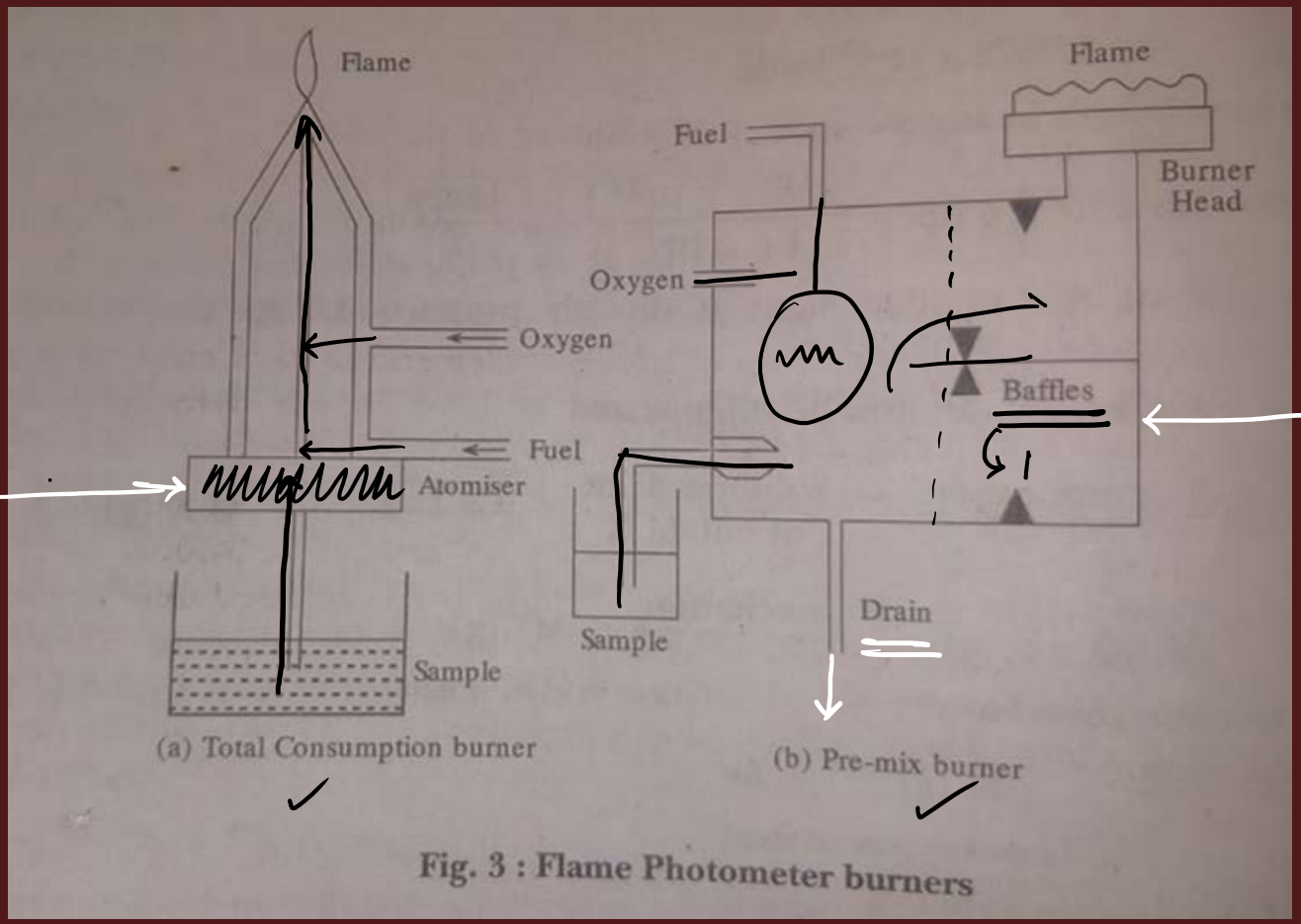


Fig. 3 : Flame Photometer burners

Nebulizn takes place

restricts larger sample droplets from going to flame

(more efficient)

Electro thermal atomisers are more sensitive as entire sample is atomised and the stay of atoms in the optical beam is 1 second.

1. Heated at low temperature- to remove solvent
2. Ashed at higher temperature on electrically heated carbon surface (shape= hollow tube, cup, boat or trough)
3. Heated to 2000-3000°C – atomise the sample.

→ Graphite furnace.

Electro thermal atomiser (also called graphite furnace) consists of graphite tube open at both ends. It is 5 cm long and 1 cm in inner diameter. Sample is introduced though central window. Two electrodes are present at the two ends of the tube. A stream of inert gas like neon/argon is passed to avoid oxidation of sample. The entire assembly is kept in water cooled metal jacket.

avoid any possible oxd^n rxn.

cooling of the burner.

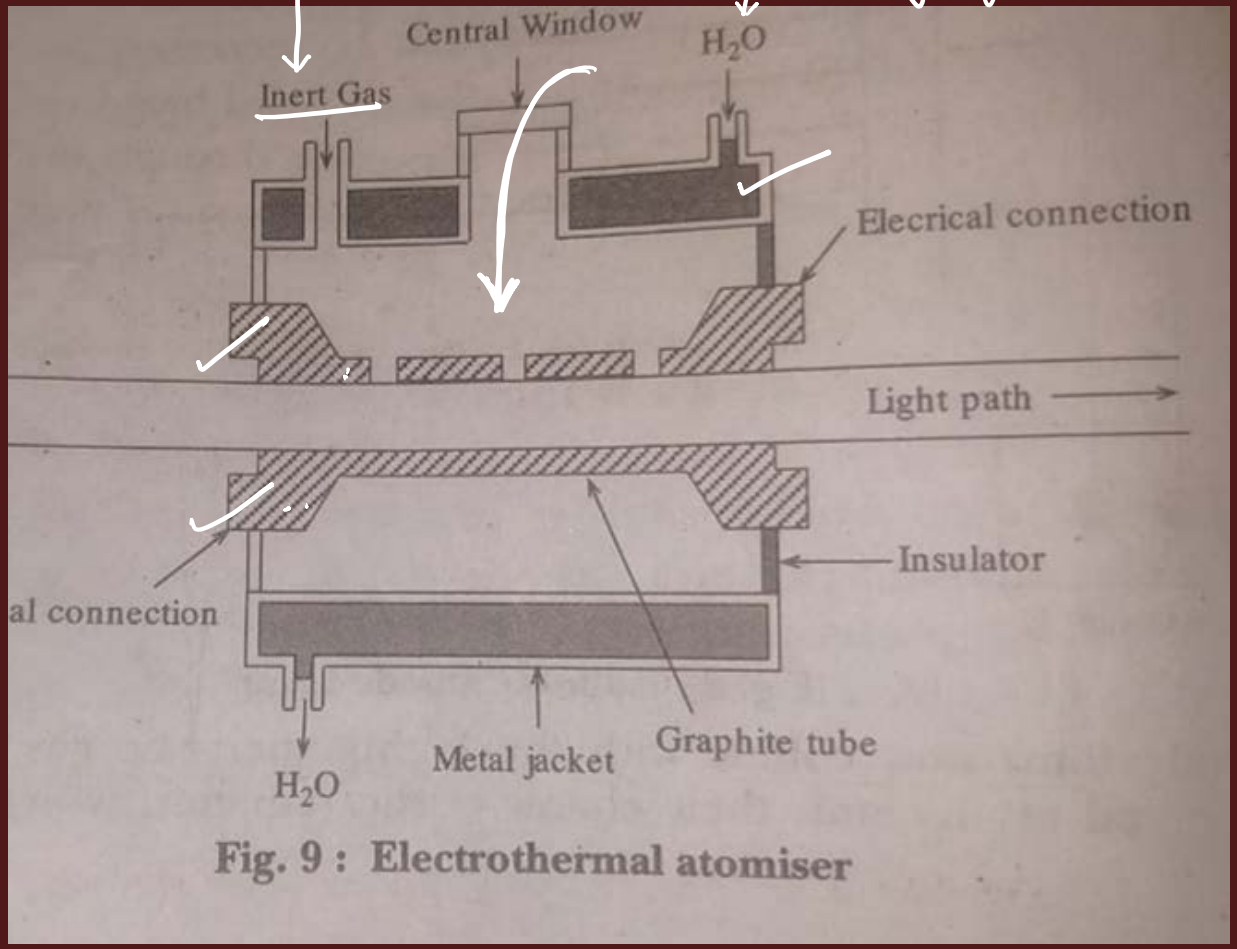


Fig. 9 : Electrothermal atomiser

4. Monochromator: ✓ → Prism or diffraction grating
Disperse the light into individual wavelength. When monochromator is rotated, these wavelengths are focussed one by one on photocathode of PMT.
These are of two types: Prisms or diffraction gratings.

5. Photomultiplier tube: (PMT) → produce electric current.
Each wavelength on the photocathode of the PMT produces electric current which is proportional to intensity of the incident radiation. The electric current is amplifies.

The intensity of the radiation corresponding to he most intense line is measured.

Amount of light absorbed by the sample is given by the difference in the intensities of the transmitted radiation in absence of sample and in presence of metal atoms.
This difference in the intensities of radiation is measured as the difference in electric current produced at the photocathode of the PMT before and after introduction of the metal sample into the flame.

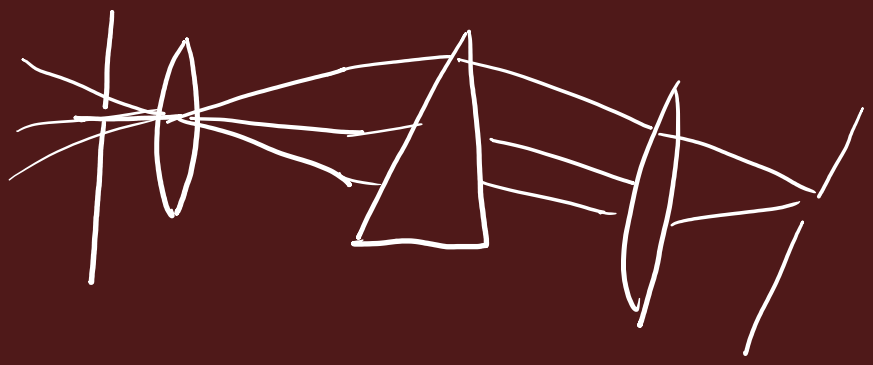
$$\begin{pmatrix}\text{Amt of light}\\ \text{absorbed}\end{pmatrix} = \begin{pmatrix}\text{Amt of light}\\ \text{without}\\ \text{Sample}\end{pmatrix} - \begin{pmatrix}\text{Amt of light}\\ \text{with sample}\end{pmatrix}$$

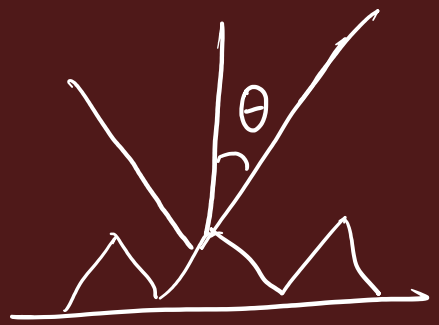
The given atomic spectrum is recorded on the chart paper or read on a digital readout device.

sample
blank / solvent → 2 beams = using mirrors

A single beam spectrophotometer is relatively less stable than double beam spectrophotometer.

Prism





$n\lambda = 2d\sin\theta$

Diffraction grating

AAS is used for identification of elements. It can estimate low and trace metals in biological system, detect toxic metals, etc.

LIMITATIONS:

1. Separate lamp is required for analysis of each element. Multi-element hollow cathode cup can be used but it is very costly.
2. Metals like La, Al, Ti, W, Mo, V and Si cannot be analyzed as they form stable refractory oxides in flame. They can be analyzed using nitrous oxide- acetylene flame.
3. Anions like phosphate forms stable phosphates with metals like calcium and magnesium. This interference is avoided by adding La or Th. Sometimes cations interfere in analysis though less. Al interferences in alkaline earth metal analysis, B with Ca, Mg with Ca.
4. Two elements absorbing at the same wavelength cannot be analyzed.
5. Elements in aqueous medium are more difficult to ionize than elements in non-aqueous medium.
6. Elements like Na, K with low ionization potential will ionize easily at high temperature.

Element → flame → atoms are excited = short lived = come back to GS by emission of rad?

→ majority of them are in ground state

2. Flame emission spectroscopy:

When an element is introduced in the flame, a few atoms absorb thermal energy from the flame and get excited. The majority of atoms remain in the unexcited state (ground state)

The excited atoms then emit the characteristic radiation and return to ground state. The intensity of the emitted radiation is directly proportional to the number of excited atoms and hence the concentration of the element.

The elements are identified from the color they impart.

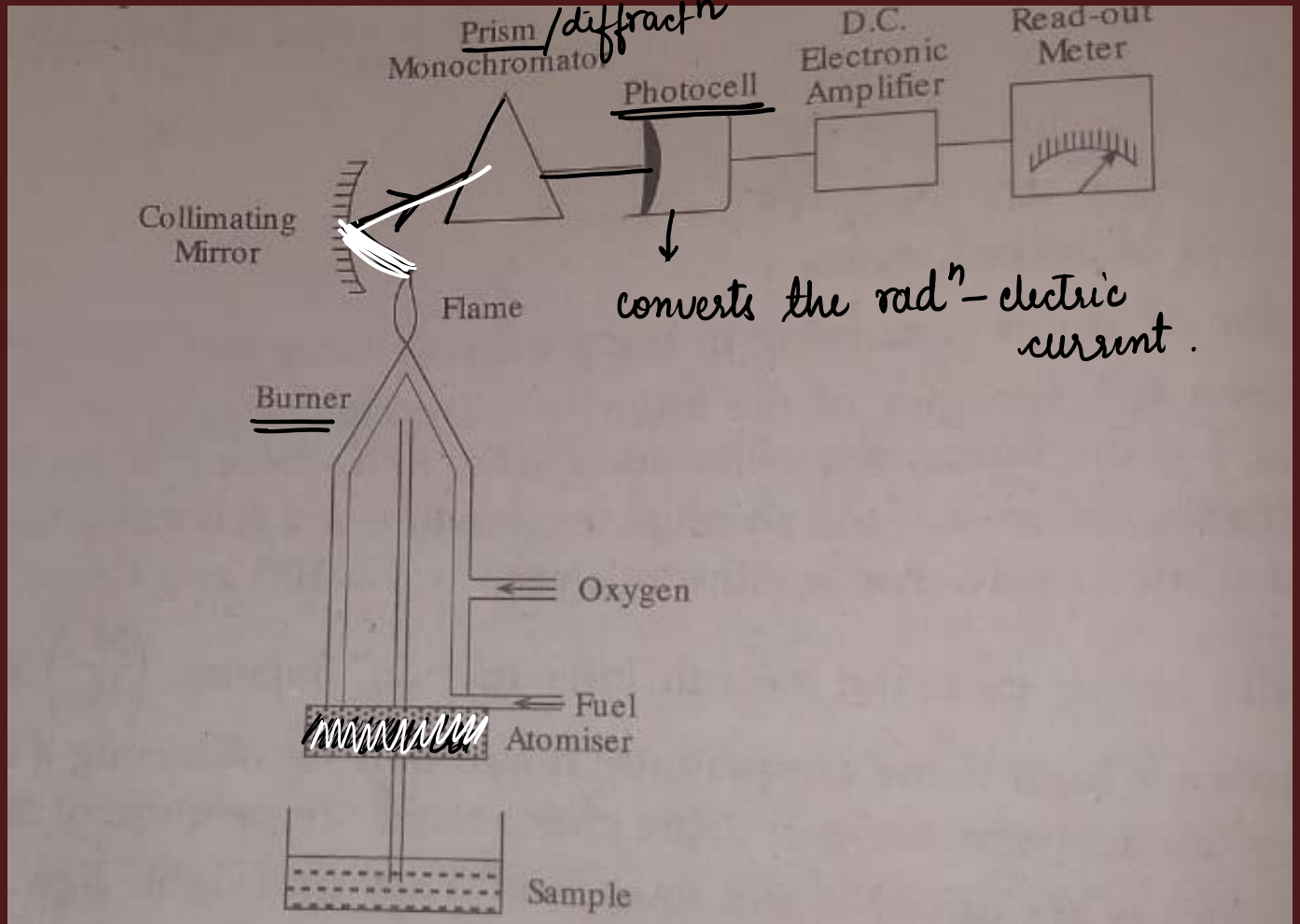


Fig. 2 : Components of a Flame Photometer

When Metal salt solvent is introduced in the flame, solvent evaporated giving back the metal salt. The solid metal salt is vaporized to gas phase and then converted into gaseous atoms. These gaseous atoms are then excited.

MX (solid) --------- MX (gas) ----------> M (gas) + X (gas)

M (gas) -----(thermal)----> M* (gas) ----(emits)----> M (gas)

The fraction of metal atoms in the excited state is given from Boltazman distribution equation.

The excited atoms are unstable and short lived. They emit radiation in the visible region and return to ground state.

Samples which are not soluble in normal solvents like hair, blood, etc. are decomposed using nitric acid, sulphuric acid, perchloric acid, or ashed at high temperature etc. and then dissolved to form solution.

The sample is nebulized i.e. converted into small droplets by the process of nebulization using nebulizer.

1. Flame atomizer:/Burner

Burner are of two types:

a. Total consumption type/ turbulent flow
   Droplets are sometimes too large to undergo atomisation.
b. Pre mix type/ laminar flow

Sensitivity is less as a large amount of sample is drained off

2. Mirror:

Light coming from flame is reflected by concave mirror placed behind the burner

3. Monochromator: ✓ Prism/ Diffraction
Disperse the light into individual wavelength. When monochromator is rotated, these wavelengths are focussed one by one on photocathode of PMT.
These are of two types: Prisms or diffraction gratings.

4. Photomultiplier tube: (PMT) → converts the (signal wavelength) into electric current.
Each wavelength on the photocathode of the PMT produces electric current which is proportional to intensity of the incident radiation. The electric current is amplifies.

Flame photometry is used for identification of elements.

LIMITATIONS:

1. Cannot be used to detect non-radiating metals like C, H, halogens.
2. Two elements with same emission wavelength cannot be detected.
3. Certain easily ionizing elements like Li, K, Na ionize at higher temperature. Thus high temperature cannot be used.

(low ionization potential) = easily ionizable elements.

3. Spectrophotometer: (UV-Visible Spectroscopy).

a. Source of radiation: Tungsten lamp

b. Monochromator: Prism or diffraction gratings

c. Sample holder: Glass or Quartz

d. Photocell or PMT

e. Read out device

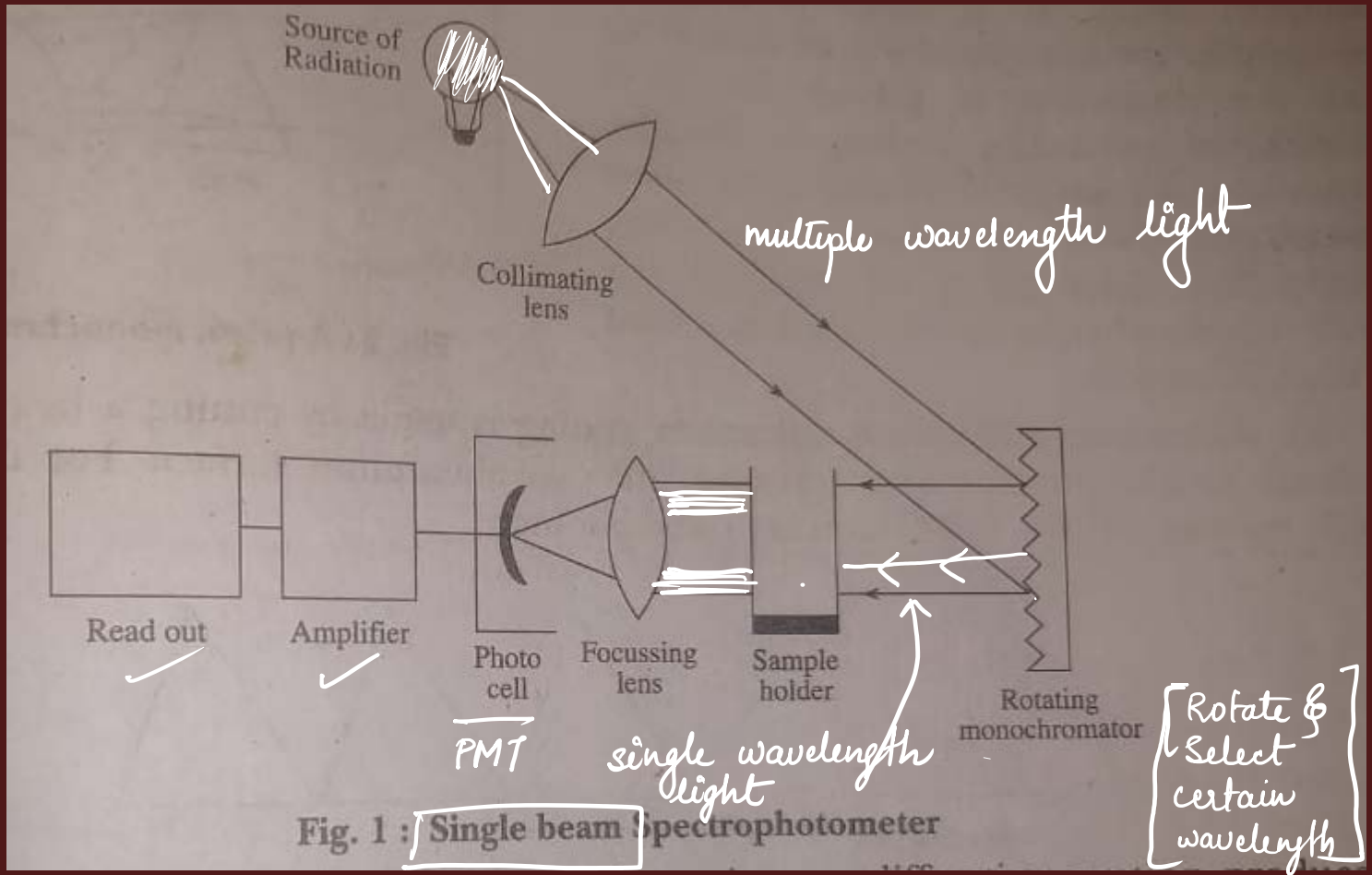


Fig. 1 : Single beam Spectrophotometer

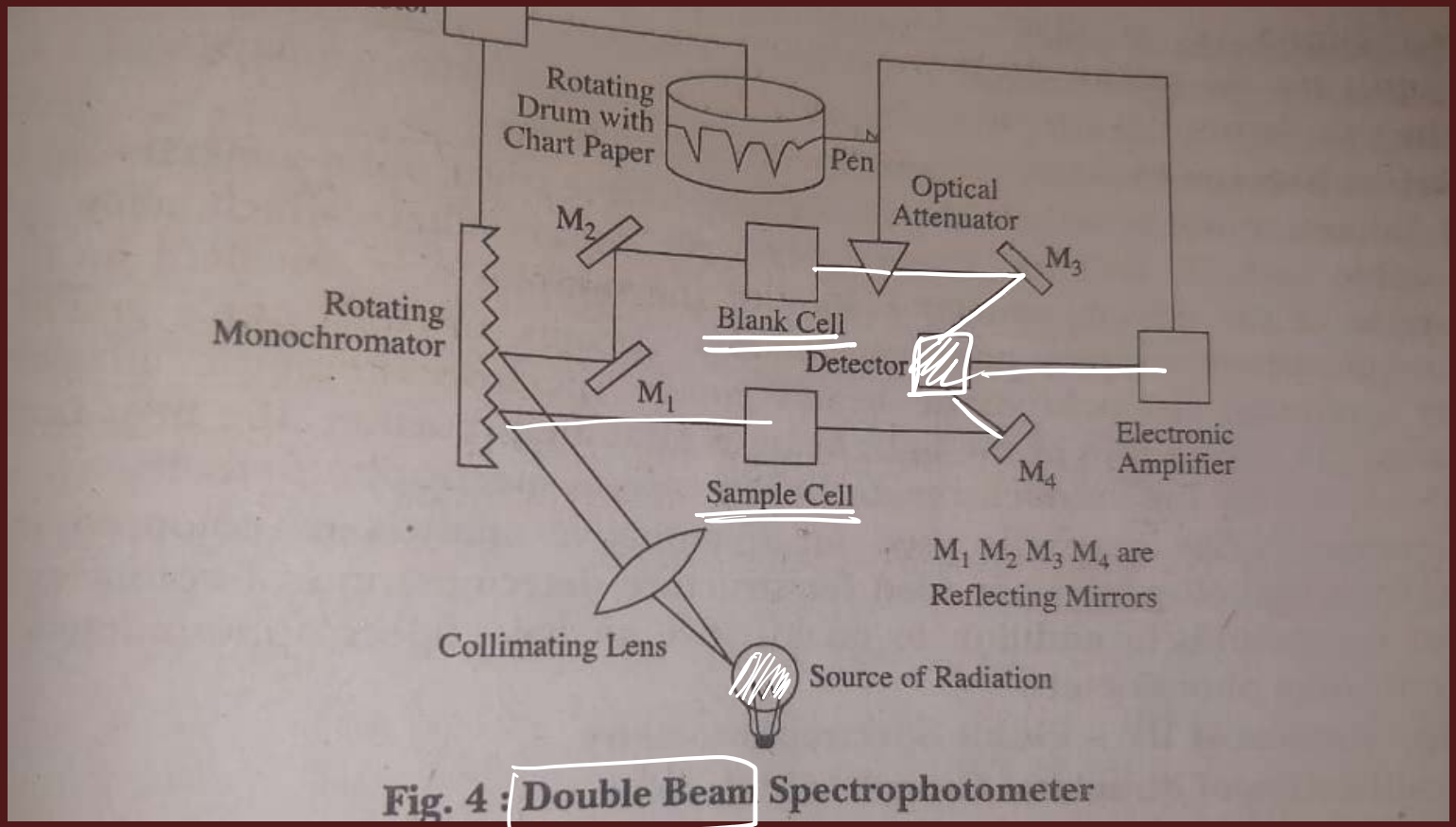


Fig. 4 : Double Beam Spectrophotometer

ε_{max} → molar absorpti

λ_{max} → max. wavelength

1. Identification of structural groups of molecules. ✓ COOH, CHO, .
2. Chromophore and auxochrome identification
3. Cis and trans isomer detection = [trans isomer has longer λ_{max} value than the cis isomer.]

→ chromophore → conjugated unsaturated groups that lead to absorption of light.
- → hence we have colour.
- → chromogens.

→ as conjugation energy ⟹ λ_{max} increases.

* Fluorescence :- Fluorimetry = emission of light.

↓

Mercury Vapour Lamp.

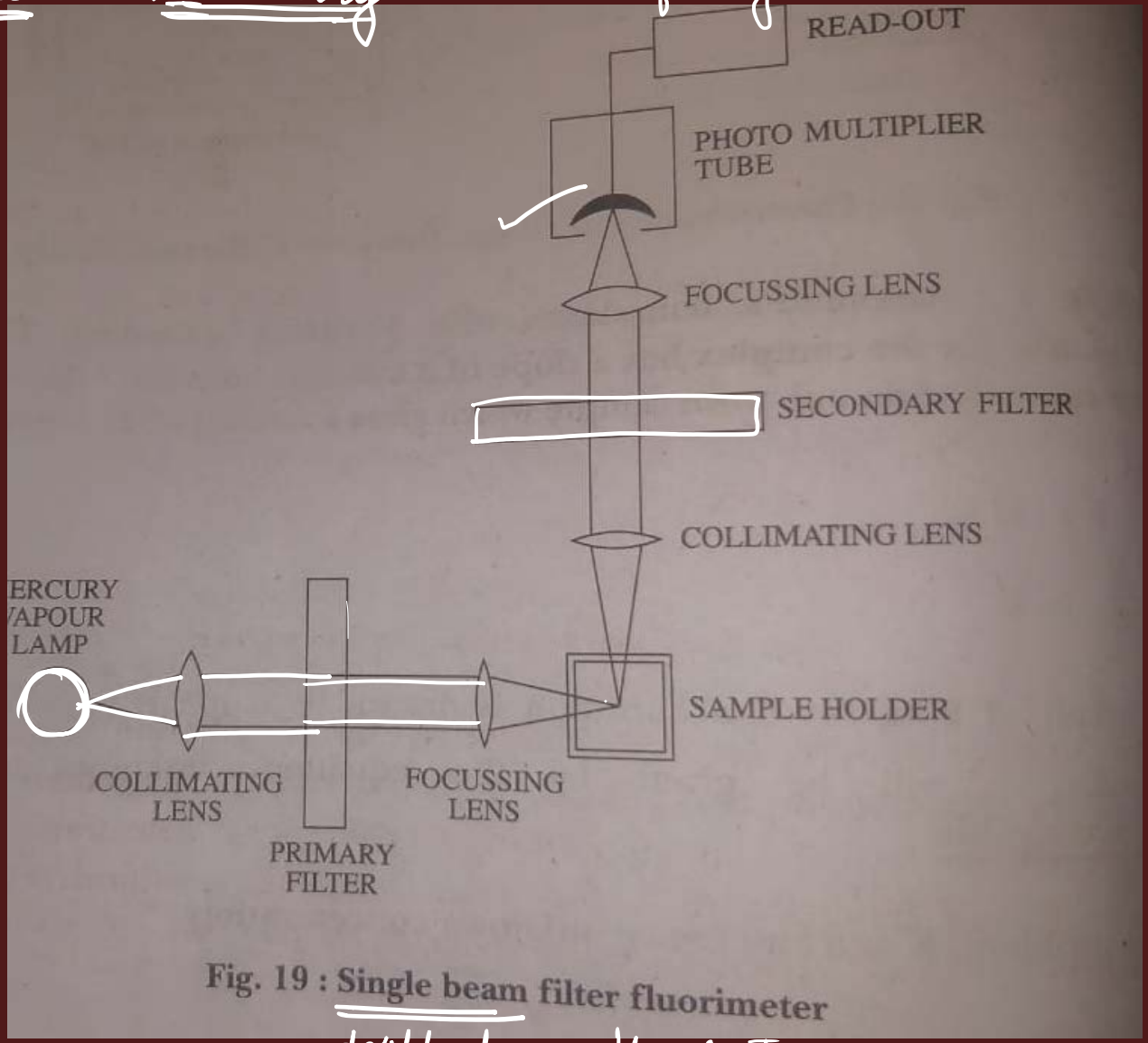


Fig. 19 : Single beam filter fluorimeter

double beam fluorimeter

(Phosphorescence :- delayed emission of light)

Xenon lamp

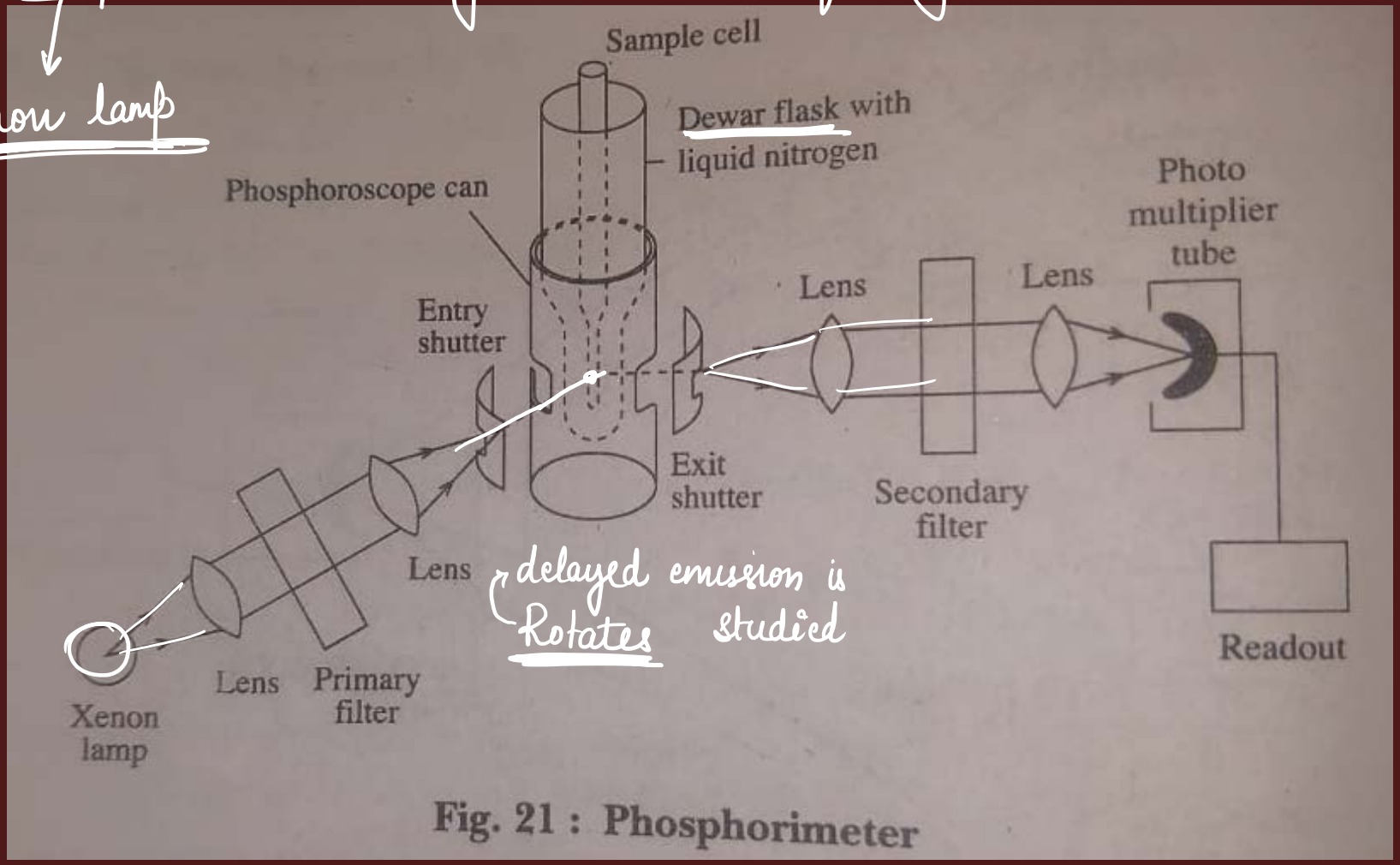


Fig. 21 : Phosphorimeter

* Turbidimeter :- turbidity of sol^n = measuring the transmitted (scattering of rad^n) radiation

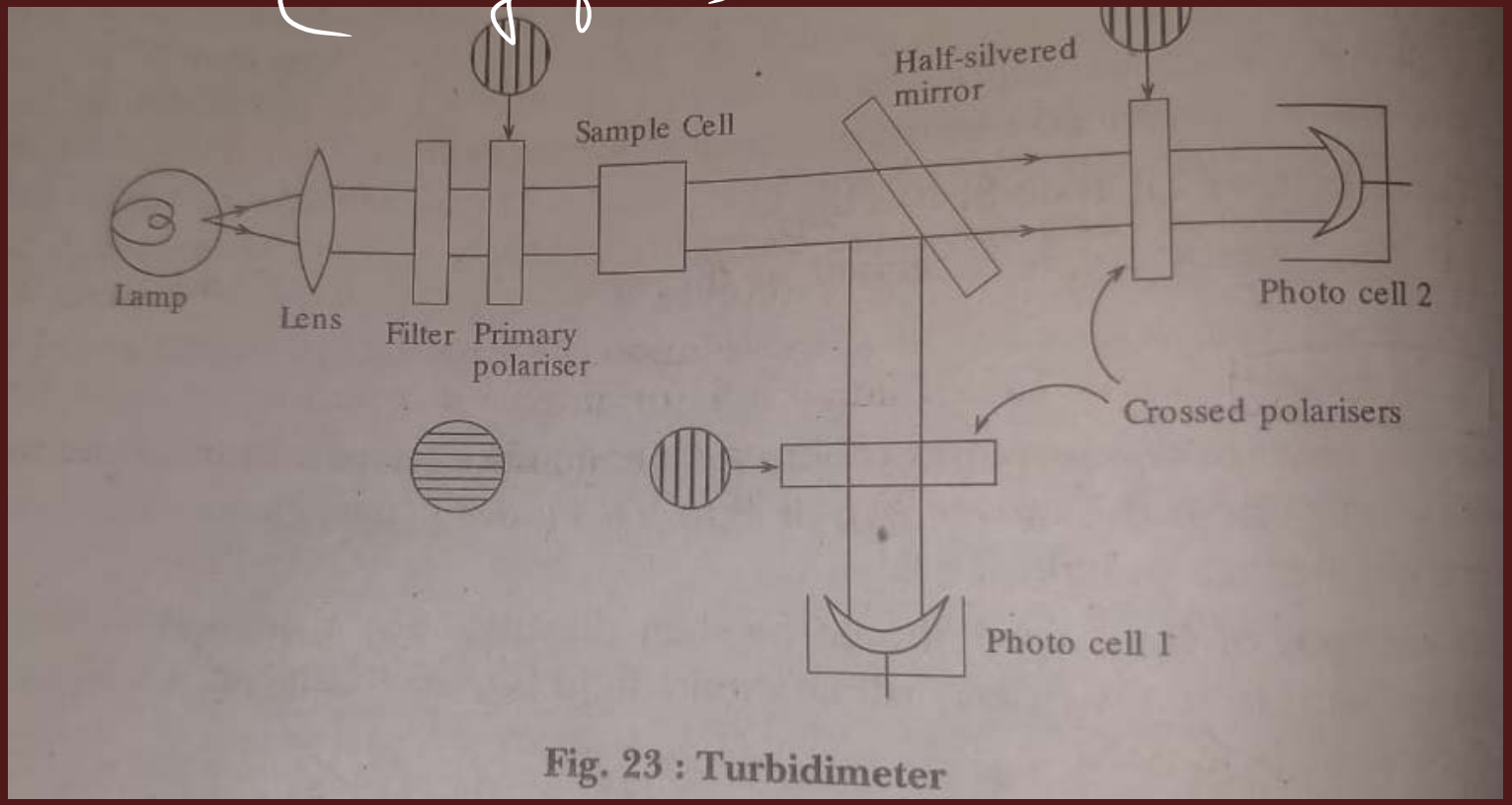


Fig. 23 : Turbidimeter

* Nephlometry = scattering of light = using scattered radiation
(turbid sol^n)

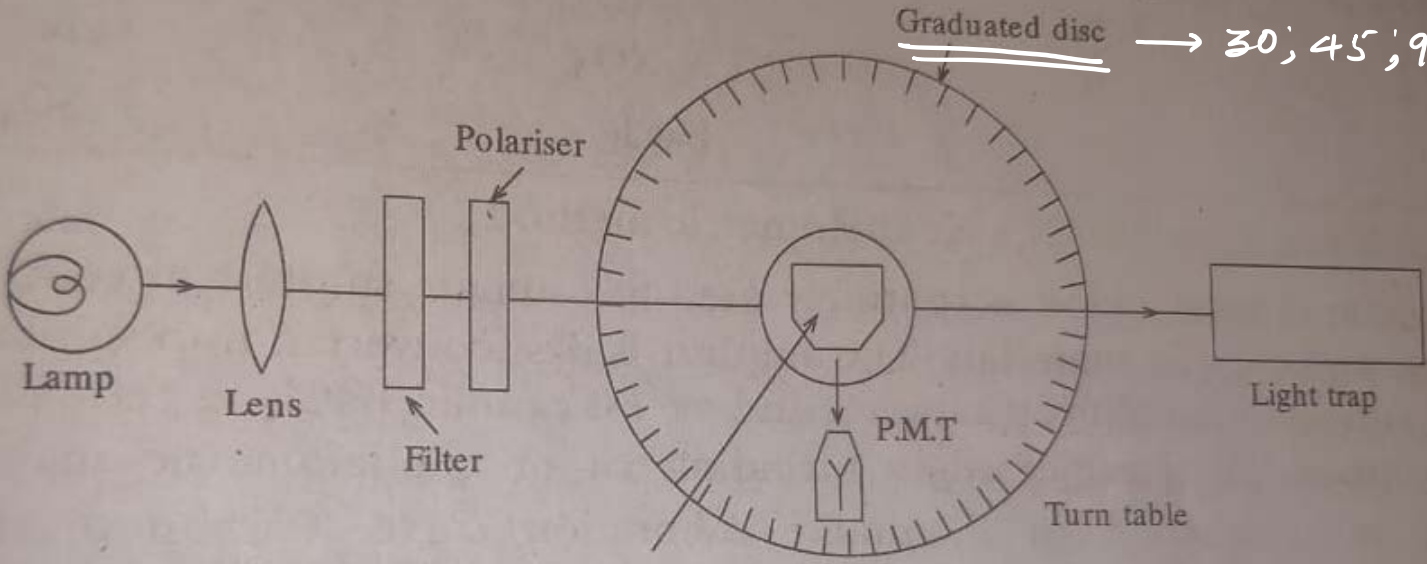


Fig. 24 : Nephelometer

*) Beer - Lambert's law :-

$$A = \varepsilon b c$$

A = absorbance

ε = molar absorptivity constant / Optical density

b = path length

c = concentration.

→ sample doesnot undergo change in molecular cond^{n}.

* Boltzman distribution law :-

$$\text{fraction of molecule in excited state} = \frac{M^*}{M} = A e^{-\Delta E/RT}$$

k = Boltzman constant

T = temperature (k)

ΔE = energy diff = $E_{\text{excited state}} - E_{\text{ground state}}$

1) AAS
2) AES
3) Spectrometry
4) Other mis. techniques
   - Fluorimetry.
   - Phosphorimetry.
   - Turbidimetry.
   - Nephelometry.

Thank - You!