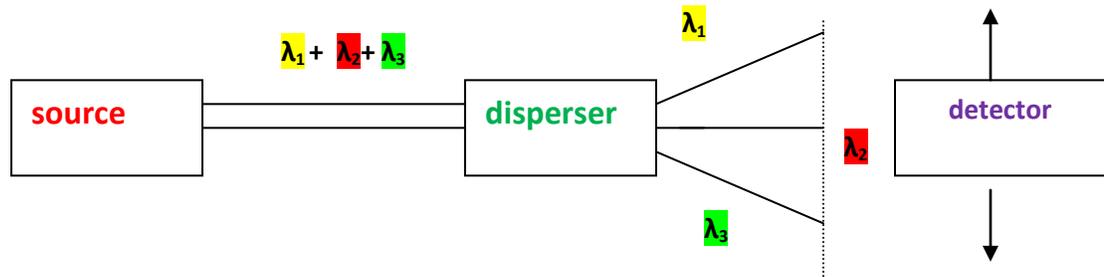


## Basics of spectroscopy

Any spectroscopic system consists essentially of 3 basic elements:



**Continuous radiation** : radiation consisting of a wide range of frequencies or wavelengths

**Monochromatic radiation** : (one colour)- radiation consisting of a narrow range of frequencies or wavelengths .

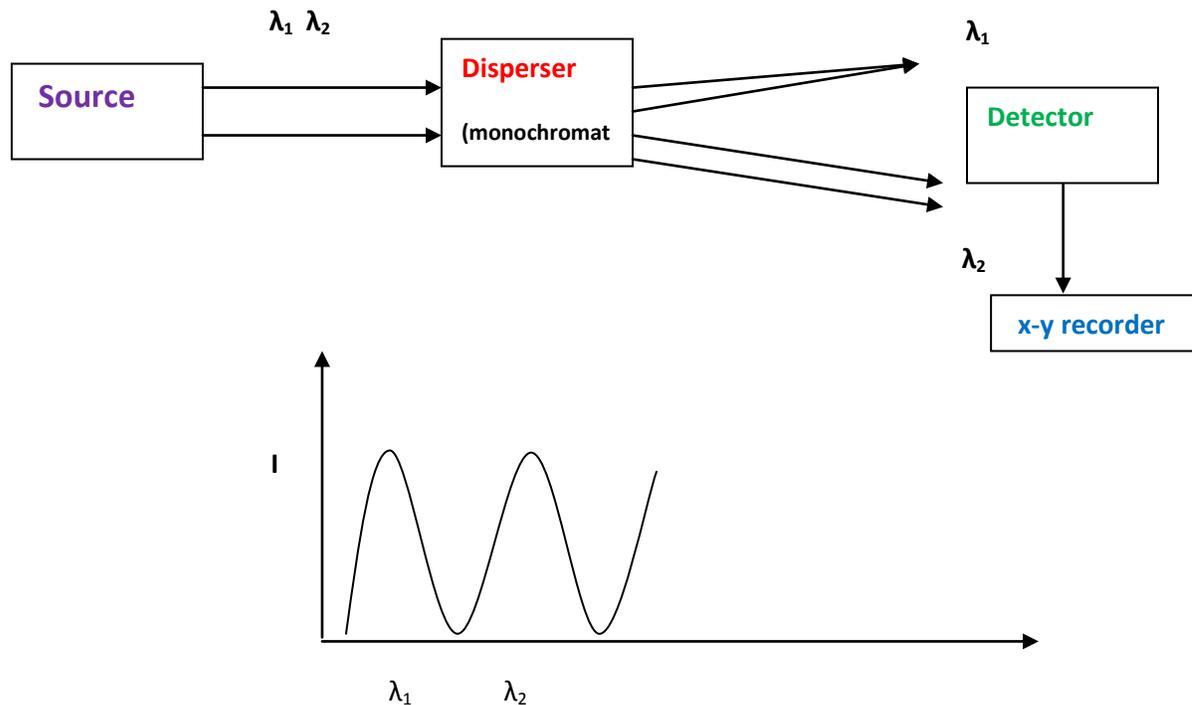
**Source** : Source of radiation under investigation .

**Disperser** : spreads or separates the light out spatially into its constituent wavelengths  
(or spectrum)

**Detector** : records the incident intensity of the separated monochromatic radiation as a function of position (ie wavelengths).

In practice , the disperser is scanned , and the o/p signal from the detector is fed directly to the y – axis of a chart recorder (or pc) , and the wavelength signal is derived from the scanning disperser & fed to the x-axis of a chart recorder (or pc).

Such system gives a direct plot of radiation intensity versus wavelength.



## The Nature & Propagation of Light

Light was thought to consist of a stream of some sort of **particles or corpuscles** emitting from a light source (the middle of the seventeenth century), (**Newton** and others).

**Huygens** proposed that light is **wave phenomena**, (1678).

In the 19<sup>th</sup> century evidence of the wave theory of light grew up.

**Fresnel** and **young** experiments on **interference** and **diffraction** supported the wave theory.

Existence of electromagnetic waves  $\Rightarrow$  Hertz

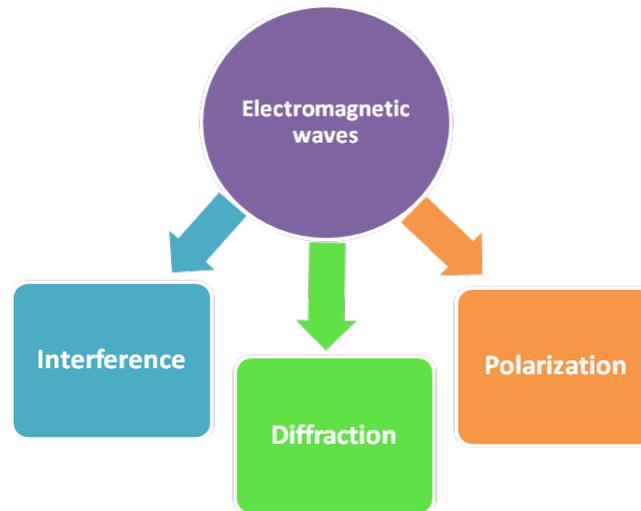


Figure (2): Electromagnetic waves.

Light is an electromagnetic wave  $\Rightarrow$  **Maxwell** (speed of propagation in 1873).

**Classical electromagnetic theory failed to explain several phenomena associated with absorption and emission of light.**

### Example

Photoelectric emission (ejection of electrons when a light incidented on a conductor).  
**photoelectric effect:** by Hertz 1887

Which is a Liberation of electrons from the surface of a conductor when light strikes the surface.

Also **x-ray production** greater frequency than visible light &  $\lambda \sim 1-20 \text{ \AA}$  Scattered x-ray of larger  $\lambda$ .

All these led to  $\Rightarrow$  **quantum theory of radiation** called **photons** or **quanta**.

In 1905 **Einstein** extended **Planck's** idea that the energy in a light beam was concentrated in packets or **photons**.

The wave nature was retained that **this photon is still has frequency**, and its energy is proportional to the frequency  $E = hv$

So, Propagation of light  $\Rightarrow$  waves.

Interaction of light with water  $\Rightarrow$  corpuscles (particles).

i.e, Dual nature of E.M. radiation.

## Sources of light

All bodies emit electromagnetic radiation due to their molecules thermal motion (thermal radiation)

This radiation is a mixture of different wavelengths.

At 300°C the most intense of these waves is 5000 nm or 50000 Å (infrared region).

At 800°C the body emits visible (red hot).

At 3000°C the body appears white (emits 4000-7000 Å).

## Examples:

- 1- (the tungsten lamp filament) Argon gas introduced to reduce evaporation of filament.
- 2- Carbon arc (very intense).  
Two Carbon rods 10-20 cm long, 1 cm dia connected to 110-220 V dc, touched together momentarily and pulled apart few millimeters causes intense light due to electron bombardment of the positive rod (temperature 4000°C).

- 3- Arc discharge in a metal vapor (Na, Hg).
- 4- Fluorescent light (a glass tube with argon and droplet of mercury (Hg)).

**The amount of U.V. is absorbed** by thin layer of **phosphor** (while coating on the glass wall).

- 5- **LASER** (narrow beam, monochromatic, very intense, many applications).

## Absorption & Emission of light

### Absorption

No material is perfectly transparent. When light passing a medium, it partially absorbed increasing the internal energy in the material. The intensity (power per unit area) is correspondingly attended. When a beam of light of intensity ( $I$ ) passes through a sheet of thickness ( $dx$ ), the decrease  $dI$  in intensity is proportional to the initial intensity and thickness.

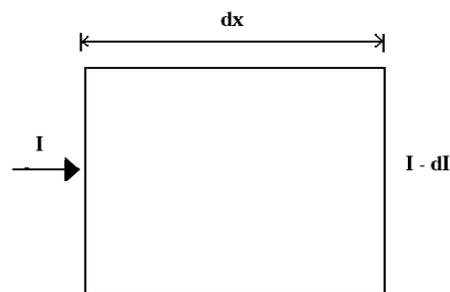


Figure 1): Transparent medium.

$$i.e. \quad dI \propto I dx \Rightarrow dI = \alpha I dx$$

$\alpha \equiv$  absorption coefficient.

$$dI = -I \alpha dx$$

$$\int_{I_0}^I \frac{dI}{I} = \int_0^x \alpha dx \quad \text{for finite thickness } x \text{ of the slab}$$

$$\ln \frac{I}{I_0} = -\alpha x$$

$$I = I_0 e^{-\alpha x} \quad \text{Lambert's law}$$

where  $I_0$  is the intensity at  $x = 0$ .

$\alpha$  is dependent on  $\lambda$  and polarization.

### Example

$\alpha = 10 \text{ m}^{-1}$  light passing a glass slab decrease by 5%, what is the value of  $x$  ?

### Solution:

$$\ln \frac{I}{I_0} = -\alpha x \Rightarrow$$

$$x = -\frac{1}{\alpha} \ln \frac{I}{I_0} = -\frac{1}{10} \ln 0.95 = 0.5 \text{ cm.}$$

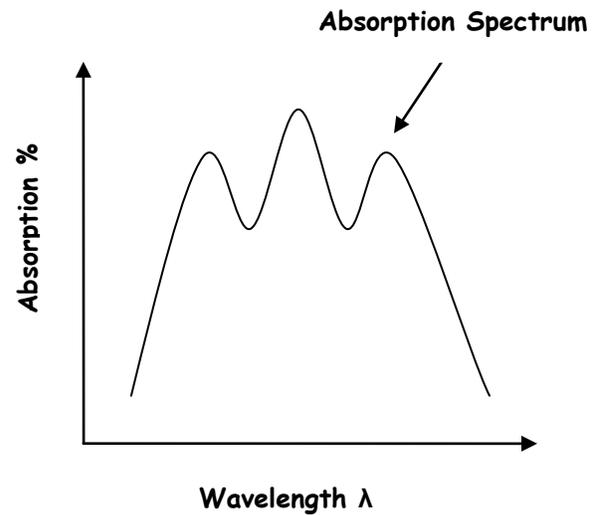
### **Absorption spectroscopy:**

Absorption spectrum of a sample is the amount of radiation absorbed at each wavelength as a function of wavelength.

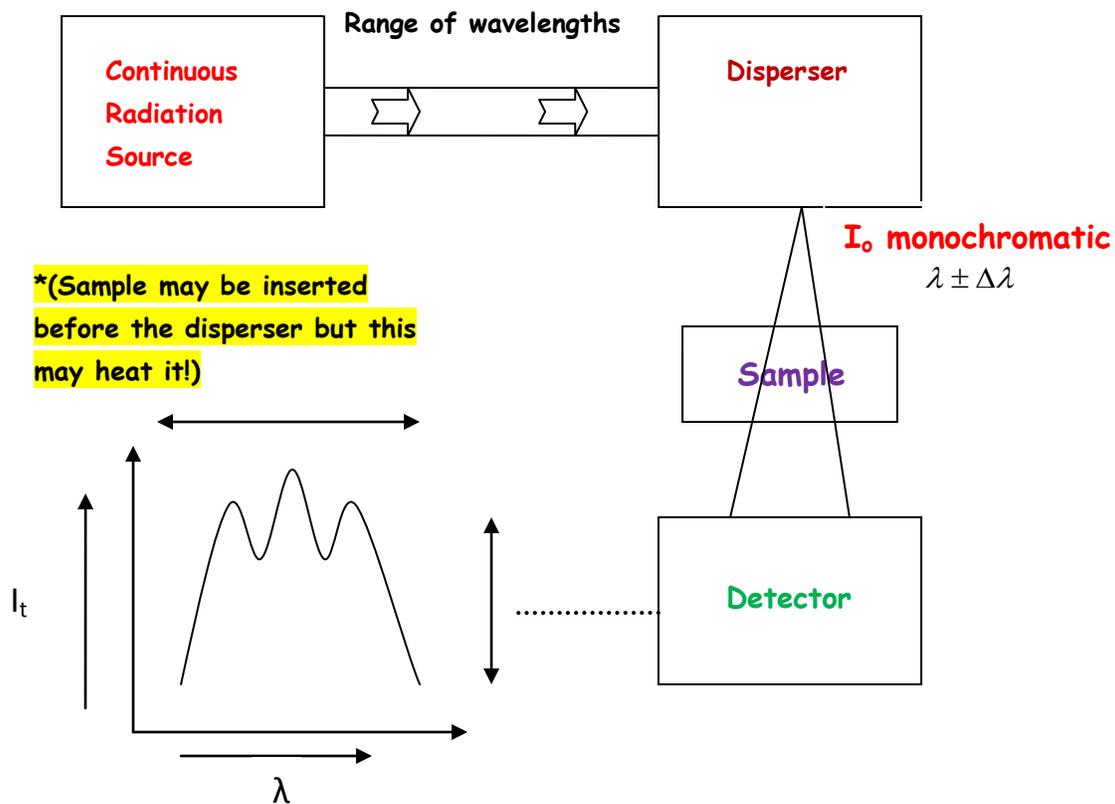


$$\text{Percentage Transmission} = \frac{I_t}{I_o} * 100$$

$$\text{Percentage Absorption} = \frac{(I_o - I_t)}{I_o} * 100$$



The apparatus required to produce such a spectrum is common to all regions of the spectrum, although the nature of components will vary for the different regions of the spectrum.

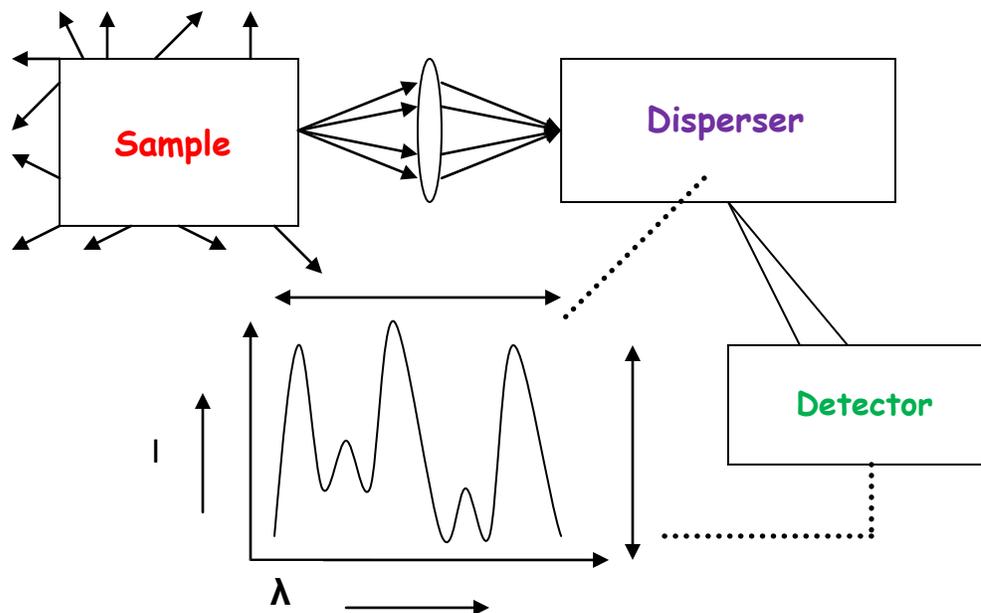


## Emission spectroscopy:-

The emission spectrum of a sample is a display of the intensity of radiation at each wavelength.

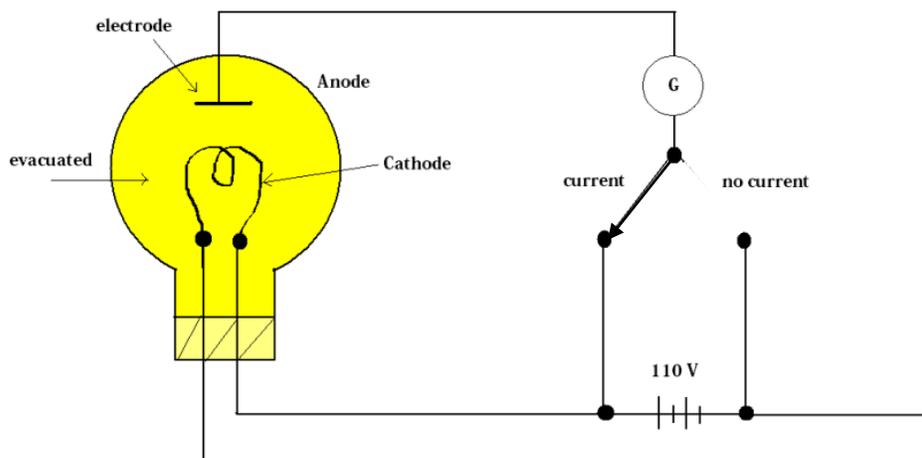
\*In emission spectroscopy the sample acts as the radiation source.

\*The sample must be excited to emit radiation; e.g. gaseous samples may be excited by an electrical discharge.



**Emission of line spectra**  $\Rightarrow$  light emitted from atoms heated in flame or excited electrically such as neon tubes  $\Rightarrow$  Contains lines **not** continuous wavelength  $\Rightarrow$  can be resolved by spectrometer (prism, diffraction grating, ...).

**Thermionic emission** discovered by Edison (1883)



\*Minimum energy required to escape from the surface is the **work function**, which varies for different materials.

Work function  $\sim$  few e.v.

$$1 \text{ e.v.} = 1.6 \times 10^{-19} \text{ J}$$

$$\begin{aligned} \text{Energy} \equiv U &= qv \\ &= 1.6 \times 10^{-19} \text{ coulomb} \times 1v \end{aligned}$$

$$1 \text{ Ke.v.} = 10^3 \text{ e.v.}$$

$$1 \text{ Me.v.} = 10^6 \text{ e.v.}$$

$$1 \text{ Ge.v.} = 10^9 \text{ e.v.}$$

### Example

A particle having charge of  $2e$  moves between 2 points of potential difference  $1000 \text{ v}$ , find P.E. in J and e.v.?

Solution:

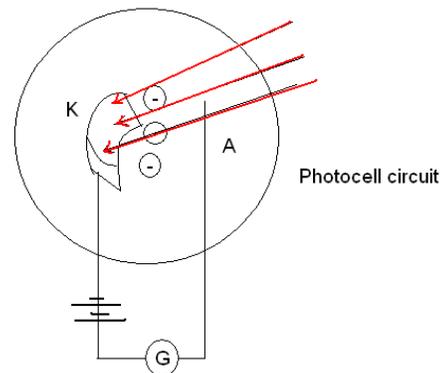
$$U = qv = 2 \times 1.6 \times 10^{-19} \times 10^3 = 3.2 \times 10^{-16} \text{ J}$$

$$\text{Then } \frac{3.2 \times 10^{-16}}{1.6 \times 10^{-19}} = 2000 \text{ e.v.}$$

At room temperature, no electrons escape.

## The Photoelectric Effect

If a metal is illuminated by light of short  $\lambda$ , electrons can have enough energy to escape from a metal surface even at low temperature (this is P.E. effect).



**Figure (3): Photocell circuit.**

The battery causes the electric field in the direction from (A) (Anode or collector) to (K) (cathode), and (e) (electron) emitted from (K) and went to (A).

(A) and (K) are enclosed in an evacuated container, photoelectric current is measured by the Galvanometer (G).

For a given cathode material (called emitter) there is minimum frequency of light incidented on it to emit electrons called **Threshold frequency** which is for metals mostly in U.V., ( $\lambda_{emit}$  200-300 nm) but for Potassium and Cesium oxide it is (400-700 nm).

To stop electrons, polarity reversed and potential energy  $e.v. < k.E.$  of electrons ( $\frac{1}{2}mv_{max}^2$ ).

To make direct measurement of k.E. of electron:

$$\frac{1}{2}mv_{max}^2 = eV_0 \quad \dots \dots \dots (1)$$

This electrical reversed potential is called **stopping potential** ( $V_0$ ).

To make direct measurement of k.E. of electrons:

## Explanation

By Einstein light quanta (photons) has energy

$$E = hf$$

Where  $h \equiv \text{Planck's constant} = 6.63 \times 10^{-34} \text{ J.s}$

So the photon when hits a metal surface will give energy to the electron, so it will escape from the surface.

In leaving the surface, the e loses energy ( $\phi$ ) (the work function of the surface).

$$\therefore \frac{1}{2}mv_{max}^2 = hf - \phi \quad \dots\dots\dots (2)$$

Combining with equation (1), get:

$$eV_0 = hf - \phi \quad \dots\dots\dots (3)$$

## Example

If stopping potential is 3V for light wavelength 300nm, 2V for 400 nm and 1V for 600 nm determine the work function for this material and find the value of Planck's constant?

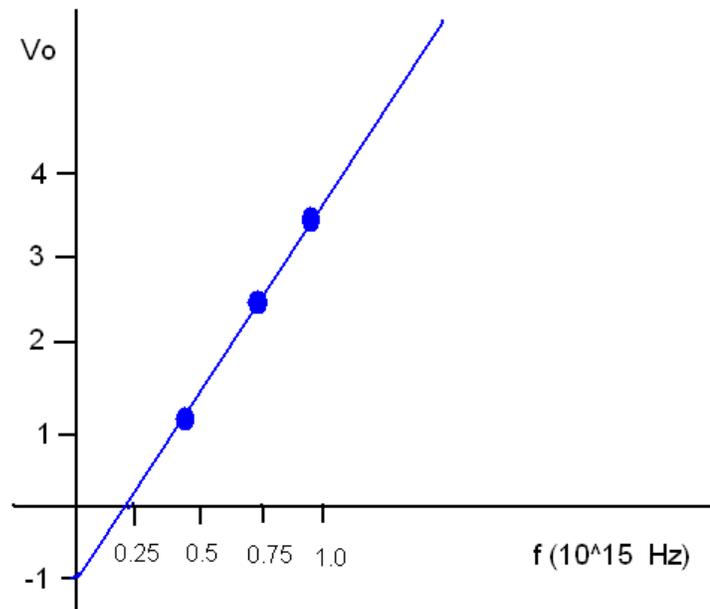


Figure (4): Stopping potential curve.

### Solution:

According to equation (3):

$$eV_0 = hf - \phi$$

$$\therefore V_0 = \frac{h}{e}f - \phi$$

$$\frac{h}{e} = \text{slope} = \frac{\Delta y}{\Delta x} = \frac{1}{0.25 \times 10^{15}}$$

$$\text{Using } f = \frac{c}{\lambda}$$

$$\therefore f = (0.5, 0.75, 1) \times 10^{15} \text{ s}^{-1}$$

$$-\frac{\phi}{e} \equiv \text{intercept of graph} = -1 \text{ v}$$

$$\therefore \phi = 1 \text{ e.v.}$$

$$\text{and } \frac{h}{e} = \text{slope} = \frac{\Delta y}{\Delta x} = \frac{1}{0.25 \times 10^{15}}$$

$$= 4 \times 10^{-15} \text{ J.C}^{-1}.\text{s}$$

$$\begin{aligned} \therefore h &= (4 \times 10^{-15}) \times 1.6 \times 10^{-19} \\ &= 6.4 \times 10^{-34} \text{ J.s} \end{aligned}$$

\*The energy of photon  $E = hf$

$$E = \frac{hc}{\lambda} \quad \text{since } f = \frac{c}{\lambda}$$