UNIT – I

OPTICAL ROTATORY DISPERSION

POLARIZED LIGHT AND OPTICAL ROTATION

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OPTICAL ROTATORY DISPERSION

- Optical rotatory dispersion (ORD) is the **variation in the optical rotation of a substance with a change in the wavelength of light**

- ORD can be used to find the absolute configuration of metal complexes.

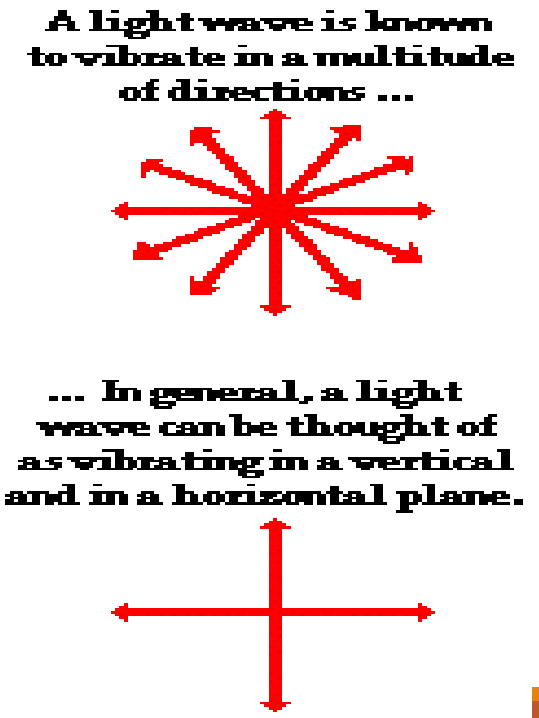
- Example, when plane-polarized white light from an overhead projector is passed through a cylinder of sucrose solution, a spiral rainbow is observed perpendicular to the cylinder.

- This leads to optical rotation which is measured by using a '**polarimeter**'.

- Measuring optical rotation as a function of wavelength is termed '**Optical rotatory dispersion (ORD) spectroscopy**'.

POLARIZATION – 'LIGHT'

- A light wave is an **electromagnetic wave** that travels through the vacuum of outer space.
- A light wave that is vibrating in more than one plane is referred to as **unpolarized light**.
- **Polarized light** waves are light waves in which the vibrations occur in a single plane. Thus, the process of transforming unpolarized light into polarized light is known as '**polarization**'.



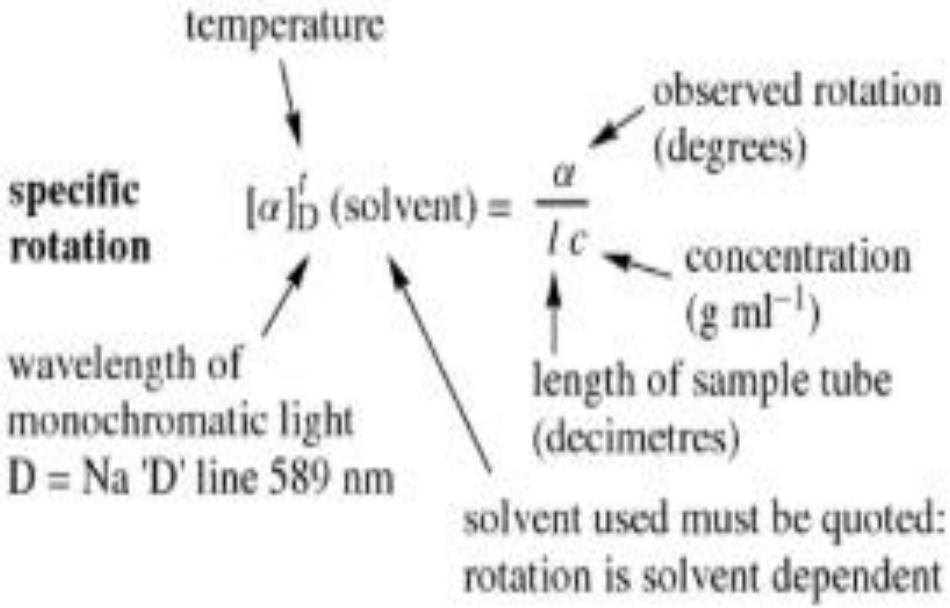
TYPES OF POLARIZED LIGHT

a) **Liner or plane polarized light -** Vibrating in a **single plane** perpendicular to the direction of propagation is called ‘plane polarised light’.

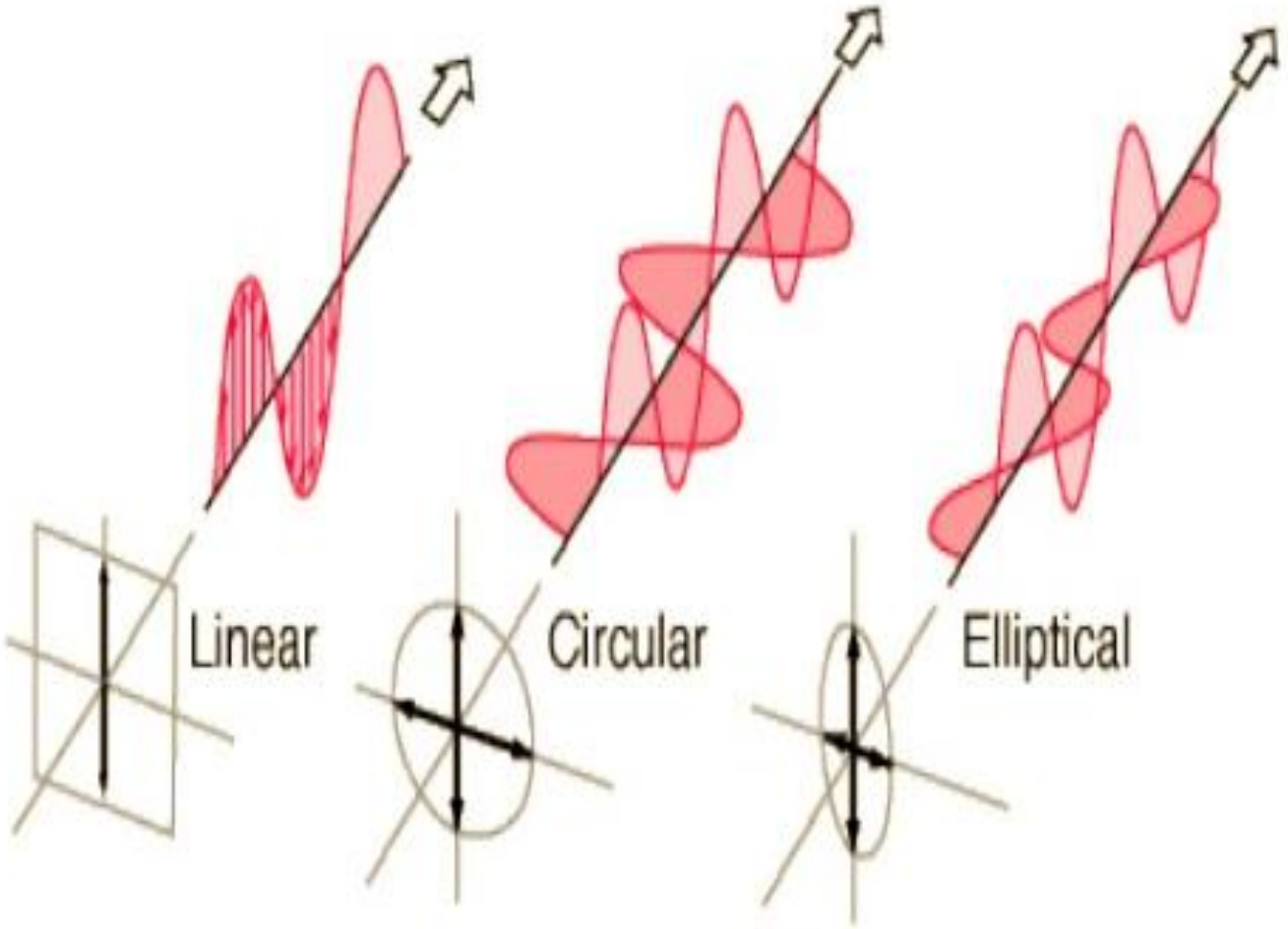
b) **Circular polarized light -** When vibration of light are along a **circle lying in a plane** perpendicular to the direction of propagation the light is called ‘circular polarized light’.

c) **Elliptical polarized light -** When vibration are along a **ellipse lying in a plane** perpendicular to the direction of propagation the light is called ‘elliptically polarized light’.

The Formula of Optical Rotation

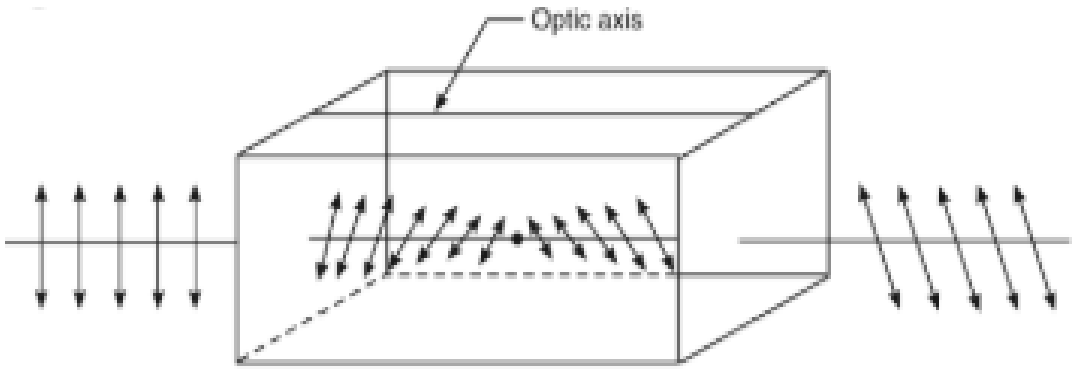


TYPES



OPTICAL ROTATION

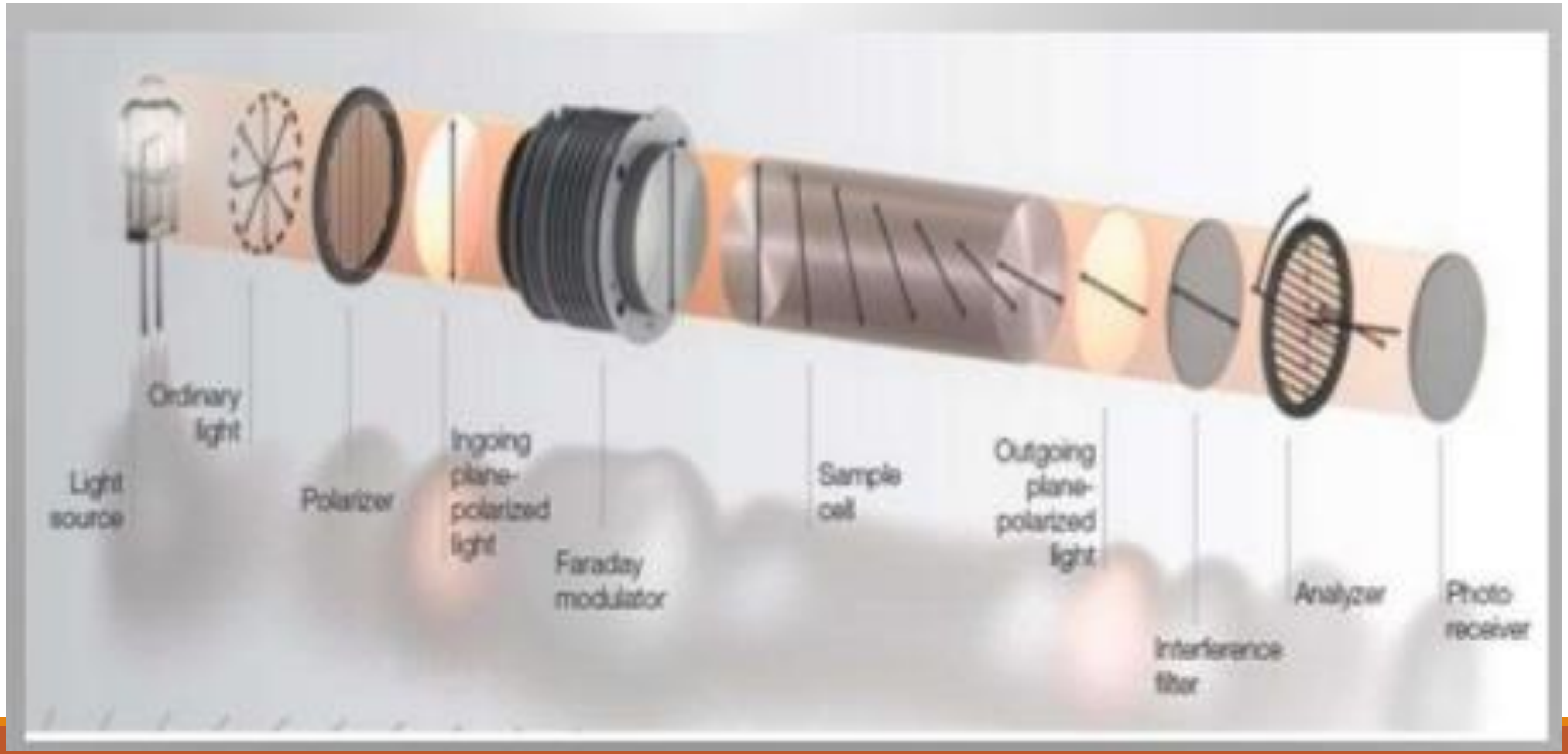
- ✓ The angle through which the plane of polarization is rotated when **polarized light passes** through a layer of liquid.
- ✓ The ability to rotate the plane of polarization of plane-polarized light by a certain substance is called **optical activity.**
- ✓ Quartz and cinnabar are examples of optically active crystals while aqueous solutions of sugar, tartaric acid are optically active solutions.



Optically active substances are classified into two types.

a. **Dextrorotatory substances –** Substances that rotate the plane of polarization of the light towards the right are known as right-handed.
b. **Laevorotatory substances –** Substances which rotate the plane of polarization of the light toward the left are known as left-handed.

INSTRUMENTATION - POLARIMETER



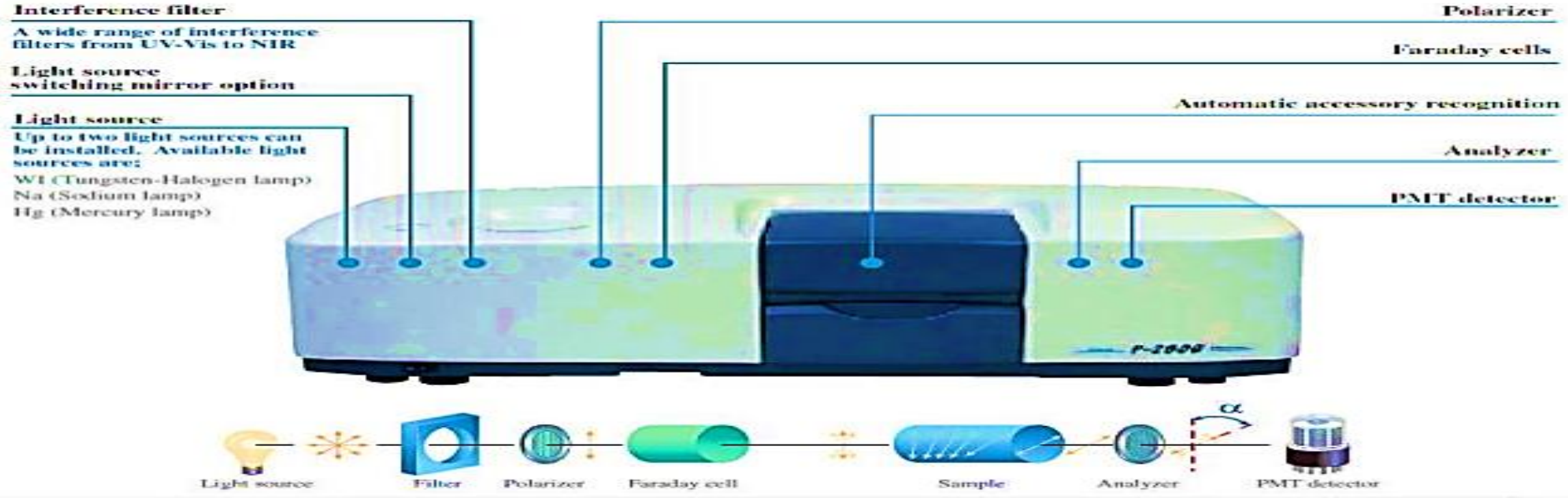
- A polarimeter consists of a polarized Light source
  - ✓ Sodium vapor lamp
  - ✓ Polarizer
  - ✓ Quartz prism
  - ✓ Material
  - ✓ Analyzer

Light source – Sodium vapor lamp

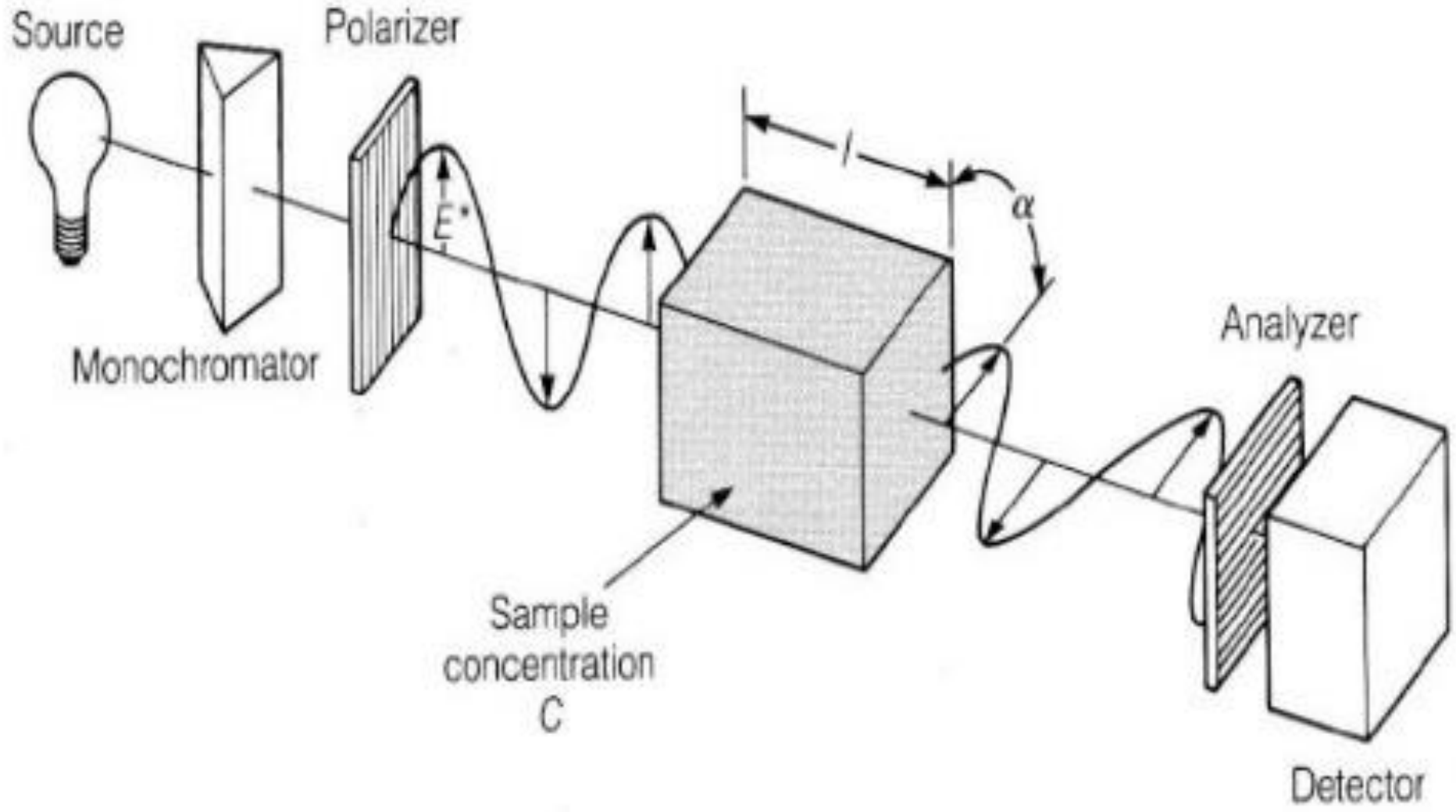
Analyzer– another Nicol prism aligned to intercept the linearly polarized ray as it emerges from the sample solution

Nicol prism aligned to intercept the linearly polarized ray as it emerges from the sample solution.

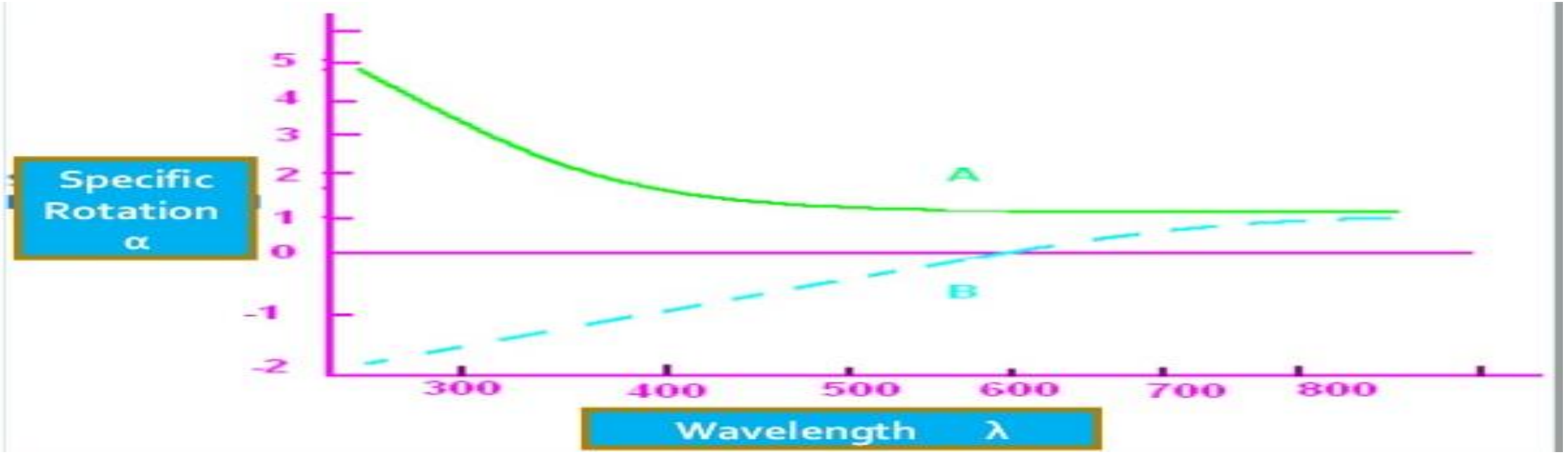
a graduated circle- to measure the rotation angle and sample tubes



INSTRUMENTATION – ORD Spectroscopy



ORD Curve



- From graph,
- A-Represents the plain *positive* ORD curve : The specific Rotation increases with decreasing wavelength.
- B – Represents the plain *negative* ORD curve :
- *Plain* – implies that there exist no maximum or minima in the curve.

APPLICATIONS OF OPTICAL ROTATION

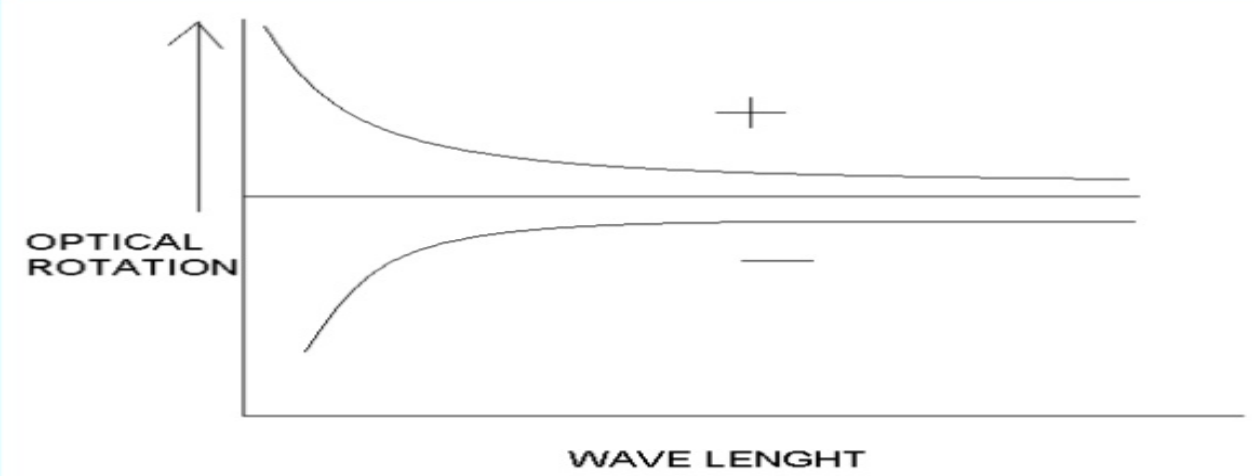
- Optical rotation is a function of time and it is used to determine kinetic reactions
- This is also used to plot optical rotatory dispersion curves for a various range of wavelengths this helps in analysing molecular structure
- The optical rotation is measured on a layer of suitable thickness at the wavelength specified in the monograph.
- If the specific rotation of a sample is known its concentration in the solution can be estimated.
- If the concentration of the material in the sample is known then its specific rotation can be determined.
- The technique may be extended to the determination of optical substances in the presence of optically inactive species.

Types Of ORD Curves:-

- They are of two types
  - 1) Plain curves
  - 2) Anamolous curves
    - a) Single cotton effect curves
    - b) Multiple cotton effect curves

Plain curves (Normal smooth curves or single curves)

- The curves obtained do not contain any peak and that curve do not cross the zero rotation line
- Such waves are obtained for compounds which do not have absorption in the wavelength region where optical activity is being examined
- E.g. .compounds exhibiting such plane curves are alcohols and hydrocarbons

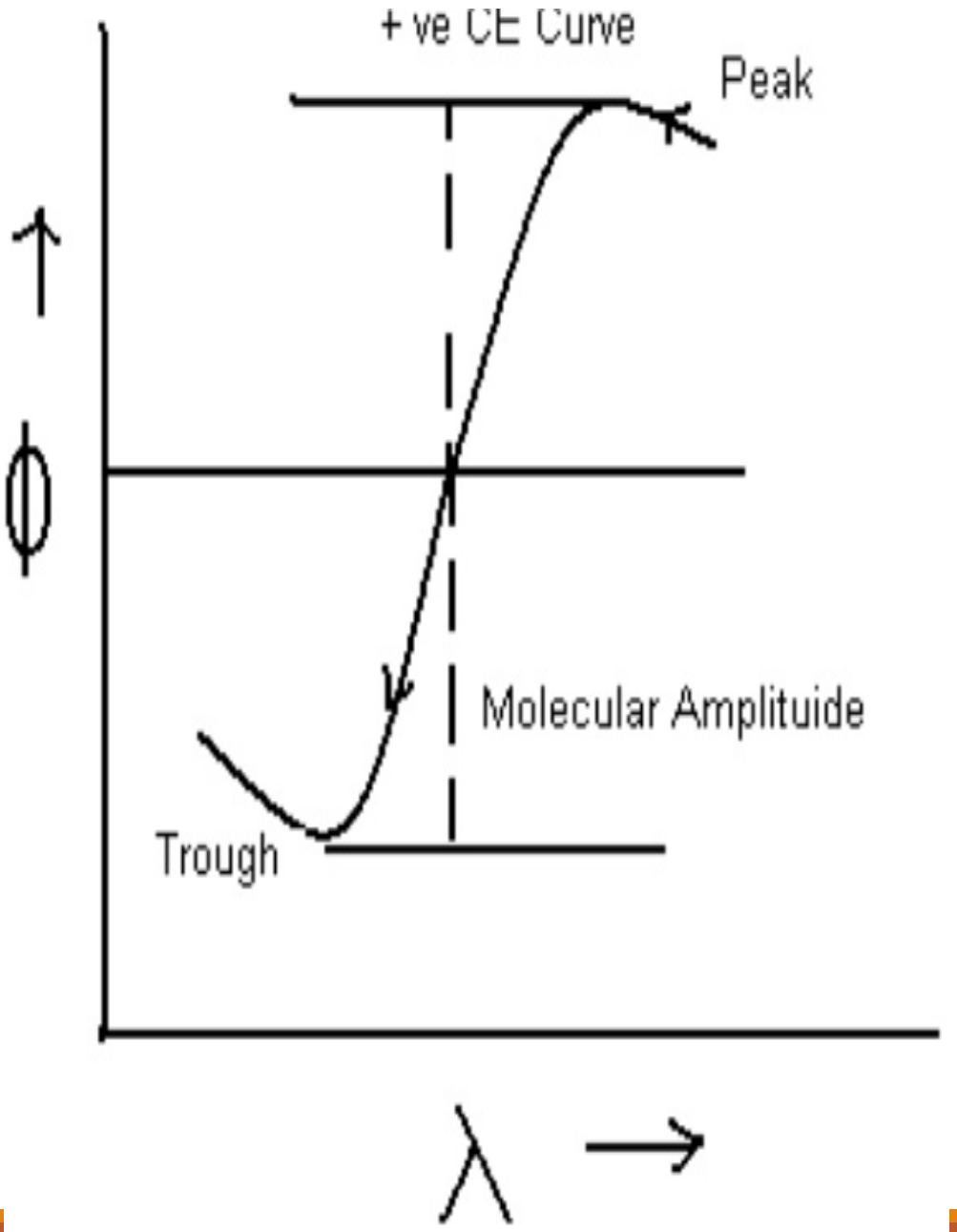


Anamolous curves:–

- These curve on the other hand shows a number of extreme ***peaks and troughs*** depending on the number of absorbing groups and therefore known as anomolous dispersion of optical rotation.
- This type of curve is obtained for compounds ,which contain an asymmetric carbon atom and also contains chromophore.

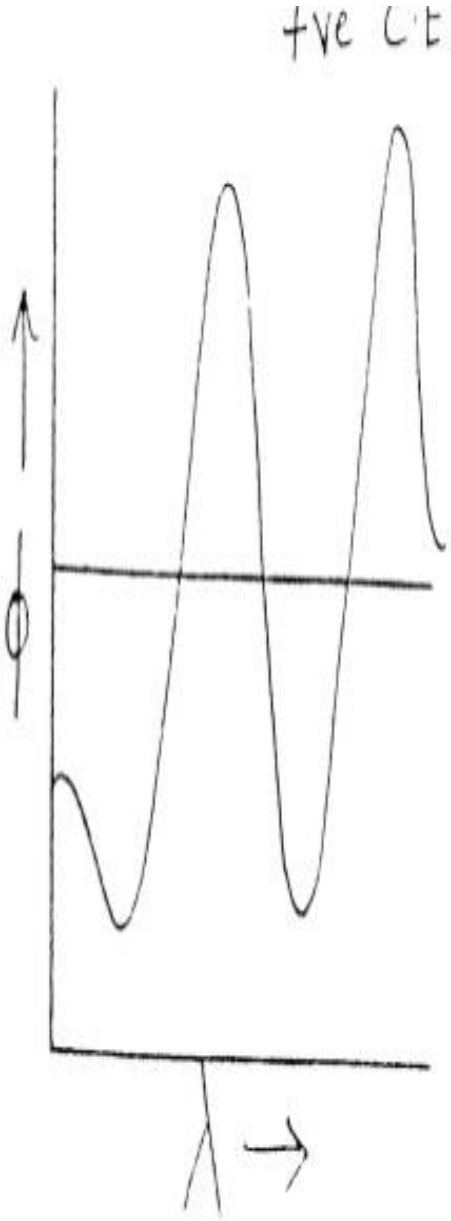
Single cotton effect curves:–

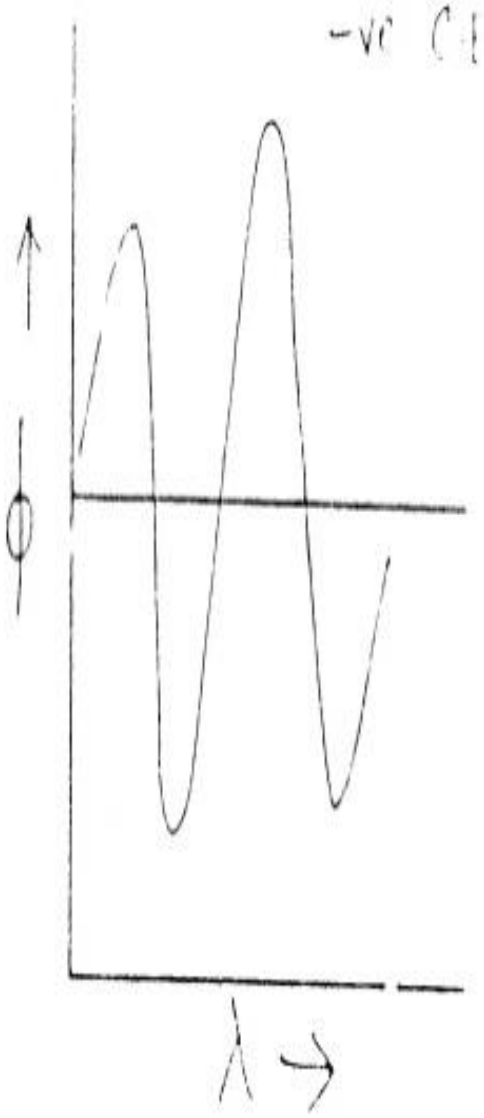
- These are anomolous dispersion curves which shows maximum and minimum both of them occurring in the region of maximum absorption.
- If an approaching the region of cotton effect from the long wavelength ,one passes first through maximum (peak) and then a minimum (trough) ,the cotton effect said to be positive . (Positive Cotton effect is where the peak is at a higher wavelength than the trough).



Multiple cotton effect curves:-

- In this type of curves two or more peaks and trough are obtained .
- E.g. functional group i.e. Ketosteriods , Camphor etc exhibits such curves .





CIRCULAR DICHROISM (CD)

- Measurement of how an optically active compound absorbs circular polarized light both left and right handed.
- Plotted as $\varepsilon_l - \varepsilon_r$ vs λ
- Instrument used is CD spectroscopy  It is used for study of biomolecules, their structure and interaction with metals and other molecules.