19CH103– ENGINEERING CHEMISTRY

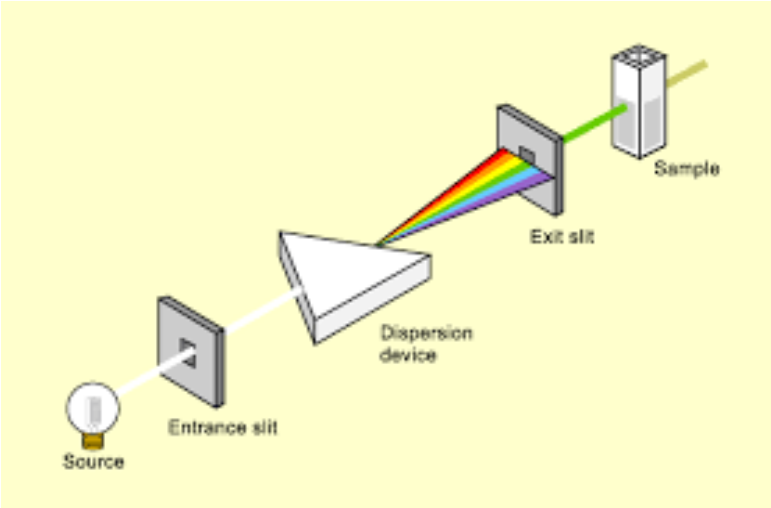
Unit-5 INSTRUMENTAL METHODS OF ANALYSIS

SPECTROSCOPIC TECHNIQUE

- Spectroscopy is the branch of science that deals with the study of interaction of electromagnetic radiation with matter.
- It is the most powerful tool available for the study of atomic & molecular structure and is used in the analysis of a wide range of samples .

TWO MAIN TYPE

- Atomic Spectroscopy -This Spectroscopy is concerned with the interaction of electromagnetic radiation with atoms are commonly in the lowest energy statecalled as grown state .
- Molecular Spectroscopy - This Spectroscopy deals with the interaction of electromagnetic radiation with molecule



- Electromagnetic radiation consist of discrete packets of energy which are called as photons.
- A photon consists of an oscillating electric field (E) & an oscillating magnetic field (M) which are perpendicular to each other.
- The principle is based on the measurement of spectrum of a sample containing atoms / molecules.
- Spectrum is a graph of intensity of absorbed or emitted radiation by sample verses frequency (ν) or wavelength (λ).
- Spectrometer is an instrument design to measure the spectrum of a compound.

Absorption Spectroscopy:

- An analytical technique which concerns with the measurement of absorption of electromagnetic radiation.
- The UV radiation region extends from 10 nm to 400 nm and the visible radiation region extends from 400 nm to 800 nm.
- Near UV Region: 200 nm to 400 nm, Far UV Region: below 200 nm
- Far UV spectroscopy is studied under vacuum condition.
- The common solvent used for preparing sample to be analyzed is either ethyl alcohol or hexane

LAWS OF ABSORPTION

The absorption of light by any absorbing material is governed by two laws .

- Bouger-Lambert law
- Beer's law

Bouger-Lambert law:

This law is suggested by Picre Bouguer in 1729, its often attributed to Johann Heinrich Lambert . This law is states that " The amount of the light absorbed is proportional to the thickness of the absorbing material & is independent of the intensity of the incident light "
It states that, the amount of light absorbed by a material is proportional to the number of Absorbing molecules(concentration)

Beer Lamberts Law:

This combined law states that the amount of light absorbed is proportional to the Concentration of the absorbing substance & to the thickness of the
absorbing material.

$$A = \varepsilon b c$$

A=absorbance
ε =molar absorbtivity with units of L /mol.cm b=path length of the sample (cuvette)
c =Concentration of the compound in solution, expressed in mol /L

- At room temperature molecules are in the lowest energy levels E_0.
- When molecules absorb UV-visible light from EMR, one of the outermost bond / lone pair electron is promoted to higher energy state such as E_1, E_2, …E_n, etc is called as electronic transition and the difference is as:

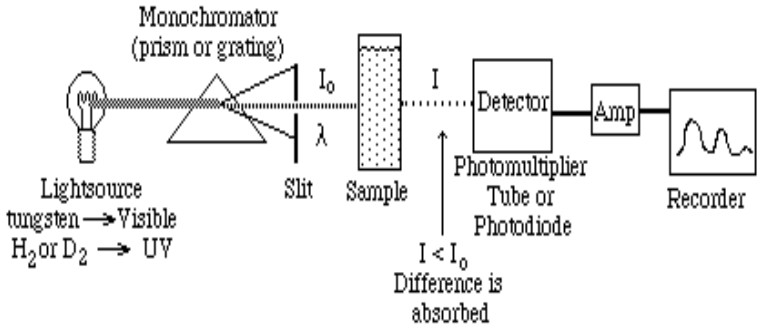
$\Delta E = h\nu = E_n - E_0$ where (n = 1, 2, 3, … etc)

ΔE = 35 to 71 kcal/mole

- $\sigma \rightarrow \sigma^*$ transition and shows absorbance maxima at 125 nm
- $\pi \rightarrow \pi^*$ transition absorb in the region 170 to 205 nm.
- $n \rightarrow \pi^*$ & $\pi \rightarrow \pi^*$ electronic transitions show absorption in region above 200 nm

Components of UV-Visible spectrophotometer

- Source
- Filters & Monochromator
- Sample compartment
- Detector
- Recorder



1) Source – A stable source of radiant energy at the desired wavelength (range).

2) Wavelength Selector – A device that isolates a restricted region of the EM spectrum used for measurement (monochromators, prisms & filters).

3) Sample Container – A transparent container used to hold the sample (cells, cuvettes, etc).

4) Detector/Photoelectric Transducer – Converts the radiant energy into a useable signal (usually electrical).

5) Signal Processor & Readout – Amplifies or attenuates the transduced signal and sends it to a readout device as a meter, digital readout, chart recorder, computer, etc.

Various UV radiation sources are as follows

a. Deuterium lamp
b. Hydrogen lamp
c. Tungsten lamp
d. Xenon discharge lamp
e. Mercury arc lamp

Various Visible radiation sources are as follow

a. Tungsten lamp
b. Mercury vapour lamp
c. Carbonone lamp

- Wavelength selectors output a limited, narrow, continuous group of wavelengths called a *band.*

Two types of wavelength selectors:

A) **Filters**
B) **Monochromators**

Filters

Two types of filters:

a) Interference Filters
b) Absorption Filters

Monochromators

- Wavelength selector that can continuously scan a broad range of wavelengths.
- Used in most scanning spectrometers including UV, visible, and IR instruments.

- PRISM TYPE
  - Refractive type
  - Reflective type
- GRATING TYPE
  - Diffraction type
  - Transmission Type

- **SAMPLE COMPARTMENT -** Spectroscopy requires all materials in the beam path other than the analyte should be as transparent to the radiation as possible.
- The geometries of all components in the system should be such as to maximize the signal and minimize the scattered light.
- The material from which a sample cuvette is fabricated controls the optical window that can be used. Some typical materials are:
  - Optical Glass - 335 - 2500 nm
  - Special Optical Glass – 320 - 2500 nm
  - Quartz (Infrared) – 220 - 3800 nm
  - Quartz (Far-UV) – 170 - 2700 nm

- **DETECTORS -** After the light has passed through the sample, we want to be able to detect and measure the resulting light.
- These types of detectors come in the form of transducers that are able to take energy from light and convert it into an electrical signal that can be recorded, and if necessary, amplified.
- **Three common types of detectors are used**
  - ✓ Barrier layer cells
- ✓ Photo emissive cell detector
  - ✓ Photomultiplier

Detection of Impurities

- It is one of the best methods for determination of impurities in organic molecules.
- Additional peaks can be observed due to impurities in the sample and it can be compared with that of standard raw material.
- By also measuring the absorbance at specific wavelength, the impurities can be detected.

Quantitative analysis

- UV absorption spectroscopy can be used for the quantitative determination of compounds that absorb UV radiation. This determination is based on Beer's law which is as follows.

$$A = \log I_0 / I_t = \log 1/ T = - \log T = abc = \varepsilon bc$$

Where :
ε -is extinction co-efficient,
c- is concentration, and
b- is the length of the cell that
is used in UV spectrophotometer.

Chemical Kinetics

- Kinetics of reaction can also be studied using UV spectroscopy.
- The UV radiation is passed through the reaction cell and the absorbance changes can be observed.

Detection of Functional Group

- This technique is used to detect the presence or absence of functional group in the compound
- Absence of a band at particular wavelength regarded as an evidence for absence of particular group