UV-VISIBLE SPECTROSCOPY

Principle

Ultraviolet and Visible spectra arise from the transition of valance electrons within a molecule or ion from a lower electronic energy level to higher electronic energy level. This transition occurs due to the absorption of UV or Visible light by a molecule or ion. The wave length region of ultraviolet (UV) and visible radiations are 200 – 400 and 400 – 750 nm respectively.

Origin of UV-Visible absorption spectra

When a monochromatic light is passed through a solution, the electrons present in the outermost shell of atoms or molecules orions (valence electrons) absorb radiant energy and undergo transitions from lower energy level (G.S.) to higher energy state (E.S.). The actual amount of energy required for transition depends on the energy difference between the ground state energy level (E_1) and the excited state energy level (E_2).

$$\Delta E = E_2 - E_1 = h\nu$$

The two groups, chromophore and auxochrome are responsible for absorption and position of absorption in UV -Vis. spectra respective

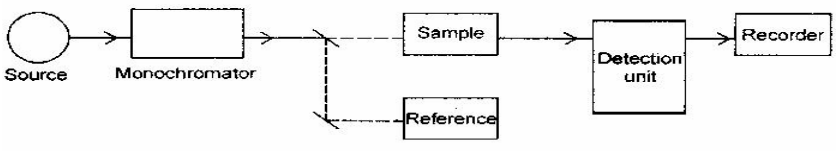
Chromophore

The presence of one or more unsaturated linkages (π -electrons) in a compound are responsible for the absorption of UV-Visible radiation. These linkages are referred as chromophores. Chromophores undergo $\pi \rightarrow \pi^*$ transitions in the short wavelength regions of UV-radiations.

Examples: C=C,– C ≡C– , C≡ N, –N =N ,–C =O–

Auxochrome

A saturated atom/group of atoms having unpaired electrons which does not give any absorption band with its own. But, when they are attached to chromophoric group, it alters the position of the peak. Examples: –OH, $–NH_2$, –Cl, Br, –I, –SH, etc.



Block diagram of UV-Visible spectrophotometer

The various components of a UV-Visible spectrophotometer are as follows:

1. Radiation source

In UV-Visible spectrometers, the most commonly used radiation sources are hydrogen (or) deuterium lamps for UV region and tungsten-filament lamp for visible region.

Requirements of a radiation source

- It must be stable and supply continuous radiation.
- It must be sufficient intensity.

2. Monochromators (or) filters

The monochromator is used to separate the radiation according to the wavelength. The essential elements of a monochromator are an entrance slit, a dispersing element and an exit slit. The dispersing element may be a prism or grating.

3. Cells (Sample cell and Reference cell)

The cells containing sample or reference for analysis should fulfil the following conditions

- They must be uniform in construction.
- The material used for construction should be inert to solvents.
- It must transparent to UV-Vis., light. For UV-Visible region, the cell is made of colour-corrected fused glass or quartz glass

4. Detectors

There are three common types of detectors used in UV-Visible spectrophotometers. They are Barrier layer cell, Photomultiplier tube or Photocell. The detector converts the radiation falling on it into electric current. The current is directly proportional to the concentration of the solution.

5. Recording system

The signal from the detector is finally received by the recording system. The recording is done by recorder pen.

Working of UV-visible spectrophotometer

The radiation from the source is allowed to pass through the filter. It allows a narrow range of wavelength to pass through an exit slit. The beam of radiation coming out from the filter is split into two equal beams. One-half of the beam (the sample beam) is directed to pass through a transparent cell containing a solution of the compound to be analysed. The another half (the reference beam) is directed to pass through an identical cell that contains only the solvent. The instrument is designed in such a way that it can compare the intensities

of the two beams. If the compound absorbs light at a particular wavelength, then intensity of the sample beam (I) will be less than that of the reference beam (Io). The instrument gives output graph, which is a plot of wavelength Vs absorbance of the light. This graph is known as absorption spectrum.