UV-VISIBLESPECTROSCOPY

Principle

- Ultraviolet (UV) visible – spectra arises fromthe transition of valency electrons within a molecule or ion from a lower electronic energy level (ground state E_o)to higher electronic energy level (excited state E_1).
- This transition occurs due to the absorption of UV (wavelength 100- 400 nm) or visible (wavelength 400-750 nm) region of the electronic spectrum by a molecule (or) ion.

OriginofUV– visiblespectroscopy

- The actual amount of energy required depends on the difference in energy between the ground state and the excited state of the electrons.

$$\Delta E=E_1-E_0=hv$$

1. Chromophores

- The presence of one or more unsaturated linkages (π-electrons) in a compound is responsible for the colour of the compound, these linkages are referred to as chromophores .
- Examples: C=C;-CC-;-C-N;-N-N;C-O; etc.,

3. Auxochromes

- Itreferstoanatomoragroupofatomswhichdoesnotrisetoabsorptionbandonits own, but when conjugate to chromophore will cause a red shift.
  - Examples:-OH,-NH_2,-Cl, -Br, -I,etc.,

Someimportantdefinitionsrelatedtochangeinwavelengthandintensity

1.	Bathochromicshift.(redshift)	Shift tohigherwave length(lower frequencies).
2.	Hypsochromicshift.(blueshift)	Shifttolowerwave length(higher frequencies).
3.	Hyperchromiceffect.	Anincrease in intensity.
4.	Hypochromiceffect.	Andecreasein intensity.

Illustration

Inchloroethylene,CH_2–CHCl,

C=CisachromophoreandClisanauxochrome.

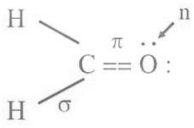
Typesofelectronsinvolvedinorganicmolecule

- The energyabsorbed bya organic molecule involvestransitionofvalence electrons. The following three types of electrons are involved in the transition.

S. No	Electrons	Examples	Energyrequiredto excite electrons	Presentin
1.	σ-electrons	Saturated long chain hydrocarbons. (paraffins) (CH_3-CH_2-CH_2-CH_3)	HigherthanUVlight	Singlebond
2.	π-electrons	Unsaturatedhydrocarbons like trienes and aromatic compounds.	UV(or)visiblelight	Doublebond and triple bonds. (unsaturated bond)
3.	n-electrons	Organiccompounds containingN, O(or) halogens.	UVradiation	Unshared(or) non bonded electrons.

- Thus,theunsaturatedhydrocarbonsandcompoundscontainingN,O,Smayabsorb visible (or) UV radiations.

Examples:The threetypesofelectronsareshowninthemolecule(HCHO).



Instrumentation

Components

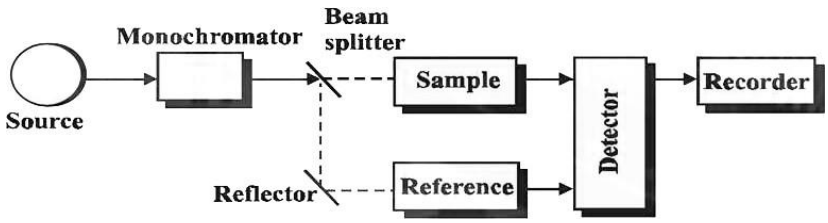
1. Radiationsource
   - Invisible – UV spectrometer, the most commonlyused radiationsources are hydrogenor deuterium lamps.
   - Requirementsofaradiationsource
     (a) Itmustbestableandsupplycontinuous radiation.
     (b) It mustbeofsufficientintensity.
2. Monochromators
   - The monochromatorisusedtodispersetheradiationaccordingtothe wavelength.
   - The essentialelements ofa monochromator are anentrance slit, a dispersing element and an exit slit.
   - Thedispersingelementmaybeaprismorgrating(or)afilter.
3. Cells(samplecellandreferencecell)
4. Detectors

- barrier layercell,photomultipliertubeandphotocell.
- The detector converts the radiation, falling on which, into current. The current is directly proportional to the concentration of the solution.

5. Recordingsystem
   - The signal from the detectors is finally received by the recording system. The recordingis done by the recording pen.

IIWorking ofUVand visiblespectrophotometer

- Theradiation fromthesourceisallowed topassthroughthemonochromatorunit.
- Themonochromatorallowsanarrowrangeofwavelengthto passthroughanexitslit.
- Thebeamofradiationcomingoutofthemonochromatorissplitintotwo equalbeams.
- One-half of thebeams(thesamplebeam)isdirectedtopassthrougha transparentcell containing a solution of the compound to be analyzed.
- Anotherhalf(thereferencebeam)isdirectedtopassthroughanidenticalcellthatcontains only the solvent.
- Theinstrumentisdesignedin such away thatitcan comparetheintensitiesof the two beams.
- Ifthecompoundabsorbslightataparticularwavelength,thenintensityofthesample beam (I) will be less than that of the reference beam (I_O).
- The instrument gives output graph, which is a plot of wavelength Vs absorbance of thelight. This graph is known as an absorption spectrum.



Applications

1. Predictingrelationshipbetweendifferent groups
2. Qualitativeanalysis
3. Detectionofimpurities
4. Quantitativeanalysis
5. Determinationofmolecular weight
6. Dissociationconstantsofacidsandbases

7. Studyoftautomericequilibrium
8. Studyingkineticsofchemicalreactions
9. Determinationofcalciuminblood serum