आईएफटीएम विश्वविद्यालय, मुरादाबाद, उत्तर प्रदेश

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VISIBLE SPECTROSCOPY

- Introduction
- The wavelength range of visible radiations is 4000 to 8000 Å or (400 to 800 nm).
- Spectrophotometry is mainly concerned with the following regions of the spectrum; near ultraviolet (2000 to 4000 Å), visible (4000 to 8000 Å).
- Colorimetry is concerned with the visible region of spectrum.

LAWS GOVERNING ABSORPTION OF RADIATIONS

- When light is incident upon a homogeneous medium a part of the incident light is reflected, a part is absorbed by the medium and the remainder is allowed to transmit as such.
- If I denotes the incident light, I_r denotes the reflected light, I_a denotes the absorbed light, I_t denotes the transmitted light.
- The we can write-:

$I = I_a + I_t + I_r$ .....eq 1

Assuming I_r to be very small for dilute transparent solutions, the relationship becomes-:

$I = I_a + I_t$ .....eq 2

- The two separate laws governing absorption are generally known as **Lambert's law** and **Beer's law.**
- Lambert's Law
  - This law states that "When a beam of **monochromatic radiation** passes through a homogeneous absorbing medium, the **rate of decrease in intensity of radiation** with the thickness of absorbing medium is **directly proportional** to the **intensity of the incident radiations".**
  - Mathematically the Lambert's law may be stated as follows-:

$$-\frac{dI}{dt} \propto I$$

$$-\frac{dI}{dt} = kI$$

$$-\frac{dI}{I} = kdt$$

Where

I = Intensity of Incident light or radiations

dI = Exceedingly small decrease in the intensity of radiation on passing through exceedingly small thickness, dt of the medium

$-\frac{dI}{dt}$ = Rate of decrease of intensity of radiation with thickness of the absorbing medium

k = Proportionality constant

- Let I_0 be the intensity of radiation before entering the absorbing medium (t=0).
- Then I_t will be the intensity of radiation after passing through any thickness, say (t) of the medium -:

$$-\int_{I_0}^{I_t} \frac{dI}{I} = \int_0^t k\,dt$$

$$-\ln \frac{I_t}{I_0} = kt$$

Substracting Both the Sides

$$\ln \frac{I_t}{I_0} = -kt$$

$$\frac{I_t}{I_0} = e^{-kt}$$

So,

$$I_t = I_0 e^{-kt} \quad \text{——} (1)$$

We have

$$\ln \frac{I_t}{I_0} = -kt$$

$$2.3026 \log \frac{I_t}{I_0} = -kt$$

We know

$$\ln = 2.3026 \log$$

$$\log \frac{I_t}{I_0} = -\frac{1 \times k \times t}{2.3026}$$

$$\log \frac{I_t}{I_0} = -0.4343\,kt$$

$$\frac{I_t}{I_0} = 10^{-0.4343kt}$$

$$I_t = I_0 \times 10^{-0.4343kt} \quad \text{——} (2)$$

We know

$$K = 0.4343k$$

So,

$$I_t = I_0 \, 10^{-kt} \quad \text{---} \quad (3)$$

- In eq 3, K is the **absorption coefficient** which is defined as-
- "It is the reciprocal of the thickness which is required to reduce the light to **1/10th of its intensity".**
- So, $K \propto 1/t$
- The ratio I_t / I_o is called **transmittance (T).**

  and the ratio **log** I_o / I_t is termed as **absorbance.**

Formally, Absorbance was termed as **Optical Density (D) or extinction coefficient (E).**

$A = \log I_o / I_t = \log 1/T = -\log T$

- Beer's law - "Intensity of incident light shows an exponential decrease with increase in the concentration of the absorbing medium."

$I_t = I_o\ e^{-k'c}$ .....eq 4

- On changing the natural logarithm to the base 10

$I_t = I_o\ 10^{-0.4343\ k'c}$ .....eq 5

$I_t = I_o\ 10^{-K'c}$ .....eq 6

Where k' and K' are constants and c is the concentration of absorbing substance

- On combining eq 3 and eq 6; we get

$$I_t = I_0 \, 10^{-KK'ct}$$

$$I_t = I_0 \, 10^{-act}$$

$$\frac{I_t}{I_0} = 10^{-act} \quad \text{---} \quad (7)$$

Taking logarithm

$$\log \frac{I_t}{I_0} = -act$$

$$\log \frac{I_0}{I_t} = act \quad \text{---} \quad (8)$$

- Eq 8 is termed as **Mathematical statement of Beer's -Lambert Law**
- Here **a is the absorptivity**, a constant depends upon the **wavelength (λ)** of the incident light and the absorbing material

- If **c** is expressed in mole dm^{-3} and t is expressed in centimeters, then **a is replaced by ε** and is termed as **Molar absorptivity or Molar extinction coefficient or Molar absorption coefficient.**
- It is important to remark here that there exists a relationship between the absorbance (A), the transmittance (T) and the molar extinction coefficient **ε; i.e.-:**
- **A = εct.....eq 9**
- eq 9 may be put as follows-:
- **ε=A/ct.....eq 10**
- **If c=1** mole dm^{-3} and t = 1 cm; eq 10 becomes as -:
- **ε=A.....eq 11**
- **From eq 11; it follows that the molar absorption coefficient is specific absorption coefficient for a concentration of 1** mole dm^{-3} and a path length of 1 cm.

DEVIATION FROM BEER'S LAW

- From Beer's law it follows that if we plot absorbance (A) against concentration (C), a straight line passing through the origin should be obtained.

- But there is usually a deviation from a linear relationship between concentration and absorbance and an apparent failure of Beer's law may ensure.

- Deviation from the law are reported as positive or negative according to whether the resultant curve is **concave upwards or concave downwards.**


Positive
Deviation
Negative
Deviation
Absorbance
Concentration

- Deviation From Beer's Law may arise due to following factors-:
  - Beer's law will hold over a wide range of concentration provided the structure of the colored ion or of the colored non-electrolyte in the dissolved state does not change with the concentration. If a colored solution is having a foreign substance whose ions react chemically with the colored components, its small concentration (foreign substance) may effect light absorption and may also alter the value of extinction coefficient.
  - Deviation may occur due to presence of impurities.
  - Deviation may occur if monochromatic light is not used.

- Deviation may occur if the width of the slit is not proper and therefore it allows undesirable radiations to fall on the detector.

- These undesirable radiations might be absorbed by the impurities present in the sample which would cause an apparent change in the absorbance of the sample.

- Chemical deviation results from chemical changes in the absorbing species For example, Acid-Base dye (Phenol red) undergoes a pH based transformation from yellow form (acidic) to red (basic) form showing that its absorption characteristics are dependent on pH which alters its chemical form.

- **Radiation Source**
  - The following are the requirements of a radiation source:
  - It must be stable.
  - It must be of sufficient intensity for the transmitted energy to be detected at the end of the optical path.
  - It must supply continuous radiation over the entire wavelength region in which it is used.
- The tungsten filament lamp is the most common source of visible radiations. The wavelength range of visible light lies between 4000 to 8000 Å.
- In this region tungsten-filament lamp is most widely used. Its construction is similar to the house hold lamp. However, it contains a piece of tungsten wire which is heated in a controlled atmosphere.

- In order to get best results, it is important that the tungsten lamp should emit radiant energy which should be constant over long period of time.
- This can only be achieved by employing a constant power supply.
- Tungsten is the most satisfactory material for lamp filaments but the carbon arc is used when a more intense source of visible light is required.

- Filters
  - A light filter is a device that allows light of the required wavelength to pass but absorbs or reflect light of other wavelengths wholly or partially.

- Thus a suitable filter can select a desired wavelength band. It means that a particular filter may be used for specific analysis.
- Filters are of two types-:
  - Absorption Filters- Absorption filters work by selective absorption of unwanted wavelengths.

    Dyed gelatin can be used as absorption filter.

  - Interference Filters- Narrower band widths are obtained with interference filters. These filters function on interference phenomenon at desired wavelengths, thus permitting rejection of unwanted radiations by selective reflection.

- In order to prepare interference filter, a semitransparent metal film is deposited on a plate of glass. Then it is coated with a thin layer of magnesium fluoride (MgF_2), followed by another coating of a thin film of metal. Finally another plate of glass is kept over the film.

- Interference filters provide narrower band-pass compared to absorption filters.

- They are inexpensive.

Note:
*An **interference filter** or dichroic **filter** is an optical **filter** that reflects one or more spectral bands or lines and transmits others.
Metal - tungsten

Monochromators

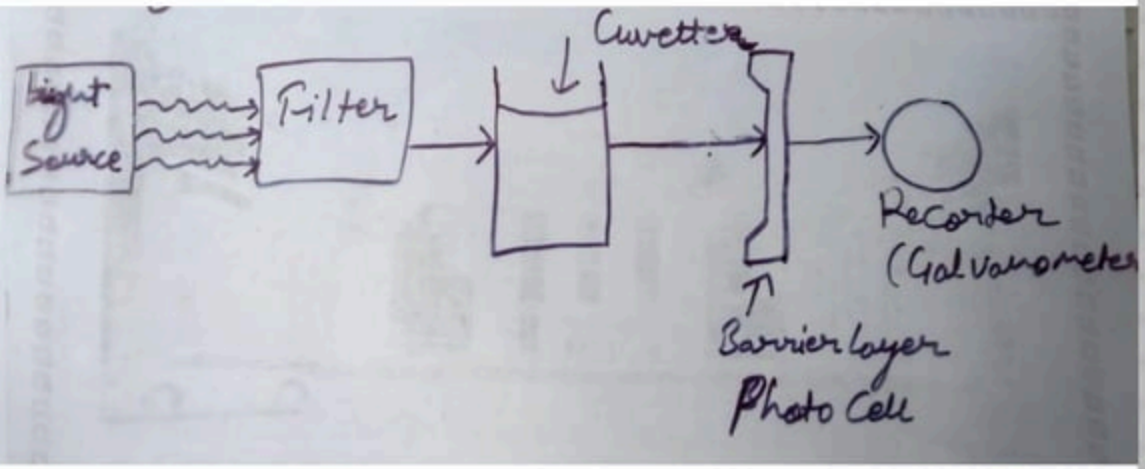
- The essential elements of a monochromator are an entrance slit, dispersing element (a prism or grating) and an exit slit.
- The function of a prism or grating is to disperse the heterochromatic radiation into its component wavelength.
- Material of construction of a prism should be selected with care to suit the range in which it has to work. For example, normal glass for the visual range, quartz for ultraviolet.

- There are two slits: Entrance slit and Exit slit
- The entrance slit sharply defines the incoming beam of heterochromatic radiations.
- Exit slit selects a narrow band of desired wavelength for observation by the detector.

- **Cells or Cuvettes**
  - The cell holding the sample (usually a solution) should be transparent to the wavelength region being recorded.
  - For visible region, the cell is generally made of fused glass.
  - The thickness of the cell is generally 1 cm.
  - Cells may be rectangular or cylindrical in shape or cylindrical with flat ends.

Detector – Same as discussed in UV spectroscopy.

Power Supply - Same as discussed in UV spectroscopy.



- Essential parts are as follows-:
  - Source of light
  - Colored glass filters for monochromatising light.
  - Cuvette for keeping the sample and blank solvent.
  - Photocell (Detector) to receive the radiation.
  - A recorder (galvanometer)

- The cuvette is filled up with blank solvent (reference).
- It is positioned into the optical path and light shutter is open so that the meter reads full scale (100 % transmittance).
- Subsequently blank solvent is replaced by sample and is placed in light path in a cuvette. Then the meter will read the transmittance from which the absorbance of solution can be evaluated.

APPLICATIONS

- For Quality Control of Samples
  - In Industry many products are manufactured and there are chances of contamination. Colorimetry can be used to assess the quality and purity of finished products.

- Qualitative Analysis
  - The percentage concentration of a substance in the given sample can be determined by absorption characteristics.

- **Structural Elucidation**
  - The structure of organic compounds can be elucidated using spectrophotometry. The absorbance spectrum of the test substance can be compared with the known ones.
  - This helps to define the most probable structure of the given test sample.
  - Other spectroscopic methods like IR Spectroscopy, NMR Spectroscopy, Mass Spectroscopy are also used for structure elucidation.

- **Determination of Geometrical Isomerism**
  - Spectrophotometry is used to distinguish between cis and trans isomer of a compound.

THANK YOU