OPTICAL ANALYTICAL INSTRUMENTATION

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Interaction of EM Radiation with Media

- Different Forms of Spectra:
  - Absorption – Emission - Fluorescence
- Polarization
- Scattering
  - Rayleigh Type
  - Tyndal Type

A major class of analytical instruments is based on the interaction of radiation with matter.
Examples:
- Spectrophotometers
  - UV and Vis.
  - IR
  - Raman
- Spectrofluorometers
- Polarimeter
- Turbidimeter – Nephelometer
- LASER
CHAPTER ONE

PROPERTIES OF ELECTROMAGNETIC RADIATION AND MATTER
1.1 Nature of EM Radiation

EM RADIATION has double nature

1- Wave Nature

2- Quantum (Particle) Nature
1.1.1 Wave Nature of EM radiation

the equation:

\[ Y = f(x - Ct) \]

Represents a disturbance with contour \( y=f(x) \) at \( t=0 \), and is traveling in a medium or in the space with constant velocity \( C \) in +ive \( x \)-direction.
Partial differential equation for waves traveling with velocity $C$ in the x axis may be written as:

$$\frac{\partial^2 f}{\partial t^2} = C^2 \frac{\partial^2 f}{\partial x^2}$$

General Wave Equation:

$$\frac{\partial^2 f}{\partial t^2} = C^2 \nabla^2 f$$
Harmonic (sinusoidal) waves

The general form of sinusoidal wave traveling in the positive x-axis is,

\[ Y = Y_o \sin (Kx - wt + \phi) \]

- \( Y_o \): The Amplitude
- \( \lambda \): The Wavelength
- \( K \): The wavenumber = \( \frac{2\pi}{\lambda} \)
- \( w \): The angular velocity = \( 2\pi\nu \)
- \( \nu \): The frequency
- \( T \): Periodic time = \( \frac{1}{\nu} \)
- \( \phi \): The phase angle = \( (wt-Kx+\phi) \)
- \( C \): Velocity of propagation = \( \nu\lambda = \frac{w}{k} \)
EM Waves

- It consists of an electric field \( E \) and magnetic field \( B \) oscillating perpendicular to each other and to the direction of propagation.

Equation of EM wave shown in the figure may be written in terms of its electric field component, i.e., for EM wave propagated in z-direction:

\[
E = E_o \sin (wt - Kz + \phi)
\]
Properties of EM Waves

- A transverse wave which needs no medium to propagate and has its maximum speed $C_o$ in vacuum, $C_o = 3 \times 10^8 \text{ m/s}$.

- In any other medium, the speed $C$ is less than $C_o$, where,

\[
\frac{C_o}{C} = n
\]

($n$) is the refractive index of the medium. It is characteristic of the medium and varies with the wavelength of the wave.

- For dielectric media

\[
n = \sqrt{\varepsilon_r}
\]
• The frequency ($\nu$) of a certain EM wave remains the same when traveling in different media while its wavelength ($\lambda$) varies for different media, due to variation of speed of propagation in these media according to the following relation:

$$\frac{\lambda_o}{\lambda_m} = \frac{(C_o/\nu)}{(C/v)} = \frac{C_o}{C} = n$$

where ($\lambda_o$) and ($\lambda_m$) are the values of the wavelengths of the same EM wave in vacuum and any other medium of refractive index ($n$).
<table>
<thead>
<tr>
<th>RADIATION</th>
<th>TYPE</th>
<th>Wavelength ((\lambda)) (\text{nm})</th>
<th>Frequency ((v) \text{Hz})</th>
</tr>
</thead>
<tbody>
<tr>
<td>COSMIC RAYS</td>
<td></td>
<td>(3 \times 10^{-7} - 10^{-5})</td>
<td>(3 \times 10^{22} - 10^{24})</td>
</tr>
<tr>
<td>GAMMA RAYS</td>
<td></td>
<td>(10^{-5} - 0.3)</td>
<td>(10^{18} - 3 \times 10^{22})</td>
</tr>
<tr>
<td>X-RAYS</td>
<td></td>
<td>(3 \times 10^{-4} - 30)</td>
<td>(10^{16} - 10^{21})</td>
</tr>
<tr>
<td>ULTRA-VIOLET</td>
<td></td>
<td>(3 - 400)</td>
<td>(7.5 \times 10^{14} - 10^{17})</td>
</tr>
<tr>
<td>VISIBLE (Vis.)</td>
<td>Violet-Red</td>
<td>(400 - 700)</td>
<td>(4.28 \times 10^{14} - 7.5 \times 10^{14})</td>
</tr>
<tr>
<td>INFRA RED (I.R.)</td>
<td>NEAR</td>
<td>(700 - 2500)</td>
<td>(1.2 \times 10^{14} - 4.28 \times 10^{14})</td>
</tr>
<tr>
<td></td>
<td>MEDIUM</td>
<td>(2500 - 50000)</td>
<td>(6 \times 10^{12} - 1.2 \times 10^{14})</td>
</tr>
<tr>
<td></td>
<td>FAR</td>
<td>(50000 - 10^{6})</td>
<td>(3 \times 10^{11} - 6 \times 10^{12})</td>
</tr>
<tr>
<td>MICRO-WAVES</td>
<td></td>
<td>(10^{5} = 1.0 \text{ m})</td>
<td>(3 \times 10^{8} - 3 \times 10^{12})</td>
</tr>
<tr>
<td>RADIO WAVES</td>
<td></td>
<td>(1.0 \text{ m} - 10^{3} \text{ m})</td>
<td>(3 \times 10^{5} - 3 \times 10^{8})</td>
</tr>
</tbody>
</table>
In Practical spectrophotometry, we always use the range:

Infra red (IR) - Visible (Vis) - Ultraviolet (UV)

- **IR:** Near 700 – 2500 nm  
  Med 2500 – 50000 nm  
  Far 50000 – $10^6$ nm

- **Vis:** 400 - 700 nm

- **UV:** 3 - 400 nm
1.1.2 Quantum Nature of EM radiation

- By Plank's Quantum Theory:

"The EM radiation is not a continuous flow of energy, but consists of discrete packets of Energy", called "Photons".

The Energy (\(\xi\)) of each Photon, is proportional to its frequency (\(\nu\)), and is given by the following formula:

\[
\xi = h \ \nu
\]

where \((h) = 6.625 \times 10^{-34} \ \text{joule.sec} = \text{Planck's constant.}\)
By *Einstein's special theory of relativity*:

Energy ($\xi$) and matter (of mass $m$), are equivalent and are related by the following formula:

$$\xi = m C_o^2$$

accordingly the photon has the following properties:

* It has **zero rest mass**
* Its **mass at $C_o$** is given by:

$$m = \frac{\xi}{C_o^2} = \frac{h \nu}{C_o^2} = \frac{h}{C_o \lambda}$$

*Its **momentum** is given by:

$$p = m C_o = \frac{\xi}{C_o} = \frac{h}{\lambda}$$
1.2 Radiant Power (P):
It is the radiant energy per unit time, i.e,
\[ P = \frac{dW}{dt} = d(N\xi)/dt \]
\[ = \xi (dN/dt) = (h\nu) (dN/dt) \]

1.3 The Intensity of Radiation (I):
The Intensity of Radiation (I) in any direction, is defined as the radiant power per unit normal area in that direction, i.e,
\[ I = \frac{P}{A} \text{ Watt/m} \]
1.4 SOURCES OF RADIATION:

1.4.1 Sources of Continuous Spectrum:

1- Black Body (B.B.)
2- Tungsten Lamp
3- Gas Filled Electric Discharge Lamp
   * High Pressure Xenon lamp
   * High pressure Mercury vapor Lamp
   * High pressure Sodium vapor Lamp
   * Fluorescent Lamp

1.4.2 Sources of Discontinuous Spectrum:

1- Gas Filled Electric Discharge Lamp
   * Low pressure Mercury vapor Lamp
   * Low pressure Sodium vapor Lamp
   * Neon lamp
2- Hydrogen or Deuterium lamp
3- LED
4- LASER sources
1.4.1 Sources of continuous spectra

1.4.1.1 Black Body

The figure shows the spectral energy distribution \( (E_\lambda - \lambda) \) for a black body at different temperatures.

\( (E_\lambda) \) is called monochromatic Emissivity.

\( (E_\lambda) \) is defined as the "The emitted power radiated per unit surface area of Black Body per unit wavelength band width in the range \((\lambda)\) to \((\lambda + d\lambda)\) ".

![Diagram showing spectral energy distribution for different temperatures]
From this definition, one can calculate the radiated power per unit surface area in the band from $\lambda_1$ to $\lambda_2$ as follows:

$$P = \int_{\lambda_1}^{\lambda_2} E_\lambda \, d\lambda \text{ watt/m}^2$$

**LAWS OF BLACK BODY RADIATION:**

(1) *Stefan's law* of total radiation:

$$P_T = \int_{0}^{\infty} E_\lambda \, d\lambda = \sigma T^4$$
(2) Wien’s Displacement Law:

\[ \lambda_{\text{max}} \ T = \text{Constant} = 2.93 \times 10^{-3} \ m.^\circ K \]

(3) Planck’s spectral energy distribution formula:

It is deduced Theoretically by Planck, using his quantum hypothesis as follows,

\[
E_{\lambda} = \frac{c_1 \lambda^{-5}}{e^{c_2/\lambda} - 1}
\]

where:

(C1) and (C2) are the first and second radiation constants.
1.4.1.2 **Tungsten Lamp:**

It is an *incandescent lamp type* giving, when heated, radiation of continuous spectrum ranging between 320 to 3500 nm i.e. consisting mainly of VIS and NEAR IR spectral regions.

It can be considered as a *Gray body*.

I.e. may be approximated by black body radiation.

1.4.1.3 **High pressure gas discharge Lamp:**

- **Xenon lamp**
  It gives, when excited by suitable potential difference between its electrodes, radiation of continuous spectrum ranging between 250 to 1000 nm i.e. consisting of UV, VIS and NEAR IR spectral regions.
High pressure Mercury vapor Lamp

It gives continuous spectrum with spikes showing the characteristic lines of Mercury at 404.6, 407.7, 435.8, 491.6, 546, 577 and 579 nm. This gives the output spectrum its bluish color.
High pressure sodium vapor Lamp

It gives continuous spectrum spreads mostly in VIS. and very near I.R. around the characteristic lines of Sodium at 588.9 and 589.5 nm give the output spectrum its yellowish color.
1.4.1.4 Fluorescent lamp

It consists of a glass tube filled with Argon gas mixed with evaporated Mercury atoms at low pressure. The tube supplied in each terminal with a pole from tungsten wire. The inner surface of the tube is coated with fluorescent material giving white spectrum mostly in the range from 300 nm to 700 nm.

The figure shows the spectral energy distribution for the Daylight lamp type.
1.4.2 Sources of *Discontinuous Spectrum*:

1.4.2.1 Low Pressure Gas Filled Electric Discharge Lamp:

*Low pressure Mercury vapor Lamp*:

which gives the spectrum shown in figure (bluish – green colors)
at characteristic lines of mercury.
*Low pressure sodium vapor Lamp*

which gives the spectrum shown in figure (yellow color) at characteristic lines of Sodium (588.9 and 589.5 nm).
*Neon lamp:* gives characteristic line at 633 nm.

*Hydrogen or Deuterium lamp:* It is used as a source of U.V. radiation (160 to 365 nm) in the instruments of the spectral analysis due to its high intensity and its long live.

1.4.2.2 LED which is a *P-N junction*

- Silicon LED (1100 nm at near IR)
- Gallium-Arsenide LED (Ga As) (900 nm at near I.R.)
- Gallium-Phosphorus LED (700 nm)
- Gallium—Arsenide with phosphor coating (green 540 nm)
1.4.2.3 LASER sources

which are highly monochromatic, collimated and coherent sources.

Examples of LASER sources are:

- Ruby LASER (693 nm).
- Argon LASER (515 nm).
- Helium-Neon LASER (633 nm).
- CO$_2$ LASER (Gaseous LASER) (10600 nm).
1.7 METHODS OF EXCITATION OF MATIER:

- (1) **Thermal excitation**: by absorbing heat energy.

- (2) **Electrical excitation**: by applying potential difference or a strong electric field.

- (3) Excitation by **Electron Bombardment**: a beam of accelerated electrons is applied to atoms of matter to gain kinetic energy.

- (4) Excitation by **Irradiation**: with a beam of radiation of continuous spectrum from an external Source.