**Chapter 6 – Introduction to Spectrometric Methods**

Read pp. 132-159   Problems: 1,2,3,4,7,8,9,14,15

**Spectrometric methods** = general term for the science that deals with the interactions of various types of electromagnetic radiation (e.g., visible light) with matter.

What can happen to the light intensity as it passes through the sample?

For many measurements, the amount of light absorbed (only) is related to the analyte concentration!

\[ I_{\text{abs}} \sim [\text{analyte}] \]

Ultraviolet = \(<\ 180\ \text{nm}\)
Ultraviolet/visible = \(180 – 780\ \text{nm}\)
Infrared = \(0.78 – 300\ \mu\text{m}\)

\[ E = h \nu = hc/\lambda \]

photon
Electromagnetic radiation (EMR) has properties of a wave.

Energy → $E = h\nu = hc/\lambda$

Velocity → $v_i = \nu i$

Oscillating electric field

$h = 6.62 \times 10^{-34}$ Js
$c = 3.00 \times 10^8$ m/s

Amplitude, frequency ($s^{-1},$ Hz), period (time in s for passage of successive maxima or minima), wave length (linear distance between two equiv. Pts., nm), velocity of propagation (m/s).

Monochromatic means **one** wavelength of light (EMR).
\[ y = A \sin (\omega t + \Phi) \]

- \( y \) = magnitude of the electric field
- \( A \) = amplitude or max value of \( y \)
- \( \omega = 2\pi v \)

**TABLE 6-1** Common Spectroscopic Methods Based on Electromagnetic Radiation

<table>
<thead>
<tr>
<th>Type of Spectroscopy</th>
<th>Usual Wavelength Range*</th>
<th>Usual Wavenumber Range, cm(^{-1})</th>
<th>Type of Quantum Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gamma-ray emission</td>
<td>0.005–1.4 Å</td>
<td>–</td>
<td>Nuclear</td>
</tr>
<tr>
<td>X-ray absorption, emission,</td>
<td>0.1–100 Å</td>
<td>–</td>
<td>Inner electron</td>
</tr>
<tr>
<td>fluorescence, and diffraction</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vacuum ultraviolet absorption</td>
<td>10–180 nm</td>
<td>(1 \times 10^6) to (5 \times 10^4)</td>
<td>Bonding electrons</td>
</tr>
<tr>
<td>Ultraviolet-visible absorption,</td>
<td>180–780 nm</td>
<td>(5 \times 10^4) to (1.3 \times 10^6)</td>
<td>Bonding electrons</td>
</tr>
<tr>
<td>emission, and fluorescence</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Infrared absorption and Raman</td>
<td>0.78–300 μm</td>
<td>(1.3 \times 10^4) to (3.3 \times 10^1)</td>
<td>Rotation/vibration of molecules</td>
</tr>
<tr>
<td>scattering</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Microwave absorption</td>
<td>0.75–375 mm</td>
<td>13–0.03</td>
<td>Rotation of molecules</td>
</tr>
<tr>
<td>Electron spin resonance</td>
<td>3 cm</td>
<td>0.33</td>
<td>Spin of electrons in a magnetic field</td>
</tr>
<tr>
<td>Nuclear magnetic resonance</td>
<td>0.6–10 m</td>
<td>(1.7 \times 10^{-2}) to (1 \times 10^3)</td>
<td>Spin of nuclei in a magnetic field</td>
</tr>
</tbody>
</table>

*1 Å = 10\(^{-10}\) m = 10\(^{-8}\) cm

1 nm = 10\(^{-9}\) m = 10\(^{-7}\) cm

1 μm = 10\(^{-6}\) m = 10\(^{-4}\) cm

**FIGURE 6-3** Regions of the electromagnetic spectrum.
What can happen to EMR when interacting with matter (e.g., an analyte sample)?

- Diffraction
- Transmission
- Refraction
- Reflection
- Scattering
- Absorption (quantized event!)

\[
T = \frac{P}{P_0}
\]

\[
A = \log \frac{P_0}{P} = -\log T
\]

Power = Energy/cm²-s

Intensity = Power/angle
**Diffraction** = process whereby a parallel beam of radiation is bent as it passes a sharp barrier or through a narrow opening.

Transmission = rate at which radiation propagates through a transparent medium is less than in vacuum and depends on kinds and concentrations of atoms, ions and molecules making up the medium.

Refractive index = $\eta_i = \frac{c}{\nu_i}$

Stepwise process that involves polarized atoms, ions or molecules.
**Refraction** = when radiation passes at an angle through the interface between two transparent media that have different optical densities, an abrupt change in the direction of propagation occurs.

\[
\sin \theta_1 = \eta_2 = v_2 \\
\sin \theta_2 = \eta_1 = v_1
\]

**Reflection** = when radiation crosses an interface between media that differ in refractive index, reflection occurs.

\[
I_r = \frac{(\eta_2 - \eta_1)^2}{I_o = (\eta_2 + \eta_1)^2}
\]

> 60% ~ 100% \(I_r\)
Scattering  = small fraction of radiation is transmitted in all angles from the original path.

Transmission of radiation in matter can be pictured as a momentary retention of the radiant energy. When atomic or molecular particles are large with respect to the wavelength of light, radiation can be transmitted in all directions. Scattered radiation increases with particle size.

\[ I_s \alpha \frac{1}{\lambda^4} \]
Converting Light (Energy) Into Electricity

\[ \text{Ru(II)} + h\nu \rightarrow \text{Ru(II)*} \]
\[ \text{Ru(II)*} \rightarrow \text{Ru(III)} + e^- \quad \text{(injected into the TiO}_2\text{)} \]
\[ \text{I}_3^- + 2e^- \rightarrow 3\text{I}^- \]
\[ 3\text{I}^- + 2\text{Ru(III)} \rightarrow \text{I}_3^- + 2\text{Ru(II)} \]

(*denotes an excited species)

At Pt electrode
High surface area (~100-300 m²/g) TiO₂ “support”

## Major Classes of Spectrometric Methods

<table>
<thead>
<tr>
<th>Class</th>
<th>Radiant Power Measured</th>
<th>Conc. Relationship</th>
<th>Method Types</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emission</td>
<td>Emitted, $P_e$</td>
<td>$P_e = kC$</td>
<td>Atomic emission</td>
</tr>
<tr>
<td>Luminescence</td>
<td>Luminescent, $P_l$</td>
<td>$P_l = kC$</td>
<td>Atomic and molecular fluorescence and chemiluminescence</td>
</tr>
<tr>
<td>Scattering</td>
<td>Scattered, $P_{sc}$</td>
<td>$P_{sc} = kC$</td>
<td>Raman spectroscopy and turbidimetry</td>
</tr>
<tr>
<td>Absorption</td>
<td>Incident, $P_o$ &amp; transmitted, $P$</td>
<td>$A = -\log \frac{P}{P_o} = \varepsilon b C$</td>
<td>Atomic and molecular absorption</td>
</tr>
</tbody>
</table>
Quantized Nature of EMR and its Interaction with Matter

\[ h\nu = eV_o + \omega \]

(KE) (WF)

When EMR is emitted or absorbed, a permanent transfer of energy from the emitting object or to the absorbing medium occurs.

1. Photocurrent proportional to intensity of incident radiation.
2. Magnitude of stopping voltage depends on frequency (energy) of incident radiation.
3. Stopping voltage depends on photocathode material.
4. Stopping voltage is independent of intensity of incident radiation.

EMR is form of energy that releases electrons from metallic surfaces and imparts to these electrons some kinetic energy.

Figure 6-13 Apparatus for studying the photoelectric effect.

\[ h\nu \]
Quantized Nature of EMR and its Interaction with Matter

- \( E_{\text{total}} = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}} + E_{\text{translational}} \)

- Excitation photon, \( h\nu \), must equal the energy difference between the ground energy state (lower) and the excited energy state (higher).

- Energy differences are unique for each chemical species (atom or molecule).

- Relaxation from the excited state – (i) radiative and (ii) nonradiative.
Quantitative Aspects of Spectrochemical Measurements

\[ A = \varepsilon b C = -\log T = \log \frac{P_0}{P} \]

**Figure 6-20** Partial energy-level diagrams for a fluorescent organic molecule.