24 Introduction to Spectrochemical Methods

Spectroscopic method: based on measurement of the electromagnetic radiation produced or absorbed by analytes.

emagnetic radiation: include γ-ray, X-ray, ultraviolet(UV), visible, infrared(IR), microwave and radio-frequency(RF).

24A Properties of Electromagnetic Radiation

photons or quanta

24A-1 Wave properties

Fig. 24-1 wave nature of a beam of single-frequency electromagnetic radiation. In (a) a plane-polarized wave is shown propagating along the x-axis. In (b), only the electric field oscillations are shown.

Wave Characteristics

\[ V_i = \nu \lambda_i \]

\( V_i \): velocity;
\( \nu \): frequency(1/period p), Hz(= S\(^{-1}\));
\( \lambda_i \): wavelength;

Wavelength units for various spectral regions (Table 24-1)

<table>
<thead>
<tr>
<th>Region</th>
<th>Unit</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray</td>
<td>Angstrom unit, Å</td>
<td>10(^{-10}) m</td>
</tr>
<tr>
<td>Ultraviolet/visible</td>
<td>Nanometer, nm</td>
<td>10(^{-9}) m</td>
</tr>
<tr>
<td>Infrared</td>
<td>Micrometer, μm</td>
<td>10(^{-6}) m</td>
</tr>
</tbody>
</table>

The speed of light

\[ c = \nu \lambda = 3.00 \times 10^{10} \text{ cm/s} = 3.00 \times 10^{8} \text{ m/s} \]

\( \nu \): frequency, wavenumber, \( \bar{\nu} \), (cm\(^{-1}\)) no. of wave/cm = 1/\( \lambda \)

Fig. 24-2 Change in wavelength as radiation passes from air into a dense glass and back to air.
Ex. 24-1 Calculate the wavenumber of a beam of infrared radiation with a 
  wavelength of 5.00 μm.
  \[
  \bar{\nu} = \frac{1}{5.00 \mu m \times 10^{-4} \text{ cm/μm}} = 2000 \text{ cm}^{-1}
  \]

Radiant Power and Intensity
  
  *power*, P: the energy of a beam that reaches a given area per second
  *intensity*: power-per-unit solid angle

24A-2 The Particle Nature of Light Photons
  
  \[E = h \nu = \frac{hc}{\lambda} = hcv\]
  
  \[\hbar: \text{Planck’s constant (6.63} \times 10^{-34} \text{ J s)}\]
  
  Joules (J): the work done by a force of one newton (N) acting over a distance of one meter.

Ex 24-2 Calculate the energy in joules of one photon of the radiation described in 
  ex. 24-1
  
  \[E = h \bar{\nu} = 6.63 \times 10^{-34} \text{ J s} \times 3.00 \times 10^{10} \text{ cm/s} \times 2000 \text{ cm}^{-1} = 3.98 \times 10^{-20} \text{ J}\]

24B Interaction of Radiation and Matter

24B-1 The Electromagnetic Spectrum

Regions of the UV/Visible and IR Spectrum (Table 24-2)

<table>
<thead>
<tr>
<th>Region</th>
<th>Wavelength Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV</td>
<td>180 - 380 nm</td>
</tr>
<tr>
<td>Visible</td>
<td>380 - 780 nm</td>
</tr>
<tr>
<td>Near-IR</td>
<td>0.78 - 2.5 μm</td>
</tr>
<tr>
<td>Mid-IR</td>
<td>2.5 - 50 μm</td>
</tr>
</tbody>
</table>

Fig 24-3 the regions of the electromagnetic spectrum.
24B-2 Spectroscopic Measurements

Emission or chemiluminescence spectroscopy
Absorption spectroscopy
Photoluminescence spectroscopy (fluorescence and phosphorescence spectroscopy)

Fig. 24-4
Emission or chemiluminescence processes. In (a), the sample is excited by the application of thermal, electrical, or chemical energy. These processes do not involve radiant energy and are therefore called nonradiative processes. In the energy-level diagram (b), the dashed lines with upward-pointing arrows symbolize these nonradiative excitation processes, whereas the solid lines with downward-pointing arrows indicate that the analyte loses its energy by emission of a photon. In (c), the resulting spectrum is shown as a measurement of the radiant power emitted $P_E$ as a function of wavelength, $\lambda$.

Fig. 24-5 Absorption methods. Radiation of incident radiant power $P_0$, can be absorbed by the analyte, resulting in a transmitted beam of lower radiant power $P$. For absorption to occur, the energy of the incident beam must correspond to one of the energy differences shown in (b). The resulting absorption spectrum is shown in (c).

Fig. 24-6 Photoluminescence methods (fluorescence and phosphorescence). Fluorescence and phosphorescence result from absorption of electromagnetic radiation and then dissipation of the energy by emission of radiation (a). In (b), the absorption can cause excitation of the analyte to state 1 or state 2. Once excited, the excess energy can be lost by emission of a photon (luminescence shown as solid line) or by nonradiative processes (dashed lines). The emission occurs over all angles, and the wavelengths emitted (c) correspond to energy differences between levels. The major distinction between fluorescence and phosphorescence is the time scale of emission, with fluorescence being prompt emission and phosphorescence being delayed emission.
24C Radiation Absorption

24C-1 The Absorption Process

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

Absorbing solution of Concentration c

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

Measuring Transmittance and Absorbances

\[ A = \log \frac{P_0}{P} \approx \log \frac{\text{solvent}}{\text{solution}} \]

Beer'S Law

\[ A = \log \frac{P_0}{P} = abc \]

Using Beer's Law

Ex. 24-3 A 7.25 \times 10^{-5} \text{ M solution of KMnO}_4 \text{ has a transmittance of 44.1\% when measured in a 2.10-cm cell at a wavelength of 525 nm. Calculate (a) the absorbance of this solution; (b) the molar absorptivity of KMnO}_4.}

(a) \[ A = -\log T = -\log 0.441 = -(0.3554) = 0.355 \]

(b) \[ \varepsilon = \frac{A}{bc} = \frac{0.3554}{2.10 \text{ cm} \times 7.25 \times 10^{-5} \text{ mol L}^{-1}} = 2.33 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1} \]

Table 24-3 Important Terms and Symbols used in Absorption Measurements

<table>
<thead>
<tr>
<th>Term and Symbol</th>
<th>Definition</th>
<th>Alternative Name and Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Incident radiant power, ( P_0 )</td>
<td>Radiant power in watts incident on sample</td>
<td>Incident intensity, ( I_0 )</td>
</tr>
<tr>
<td>Transmitted radiant power, ( P )</td>
<td>Radiant power transmitted by sample</td>
<td>Transmitted intensity, ( I )</td>
</tr>
<tr>
<td>Absorbance, ( A )</td>
<td>( \log \left( \frac{P_0}{P} \right) )</td>
<td>Optical density, ( D ); extinction, ( E )</td>
</tr>
<tr>
<td>Transmittance, ( T )</td>
<td>( \frac{P}{P_0} )</td>
<td>Transmission ( T )</td>
</tr>
<tr>
<td>Pathlength of sample, ( b )</td>
<td>Length over which attenuation occurs</td>
<td>( l, d )</td>
</tr>
<tr>
<td>Absorptivity, ( a )</td>
<td>( \frac{A}{bc} ), ( c(\text{g/L}) )</td>
<td>Extinction coefficient, ( k )</td>
</tr>
<tr>
<td>Molar absorptivity, ( \varepsilon )</td>
<td>( \frac{A}{bc} ), ( b(\text{cm}), c(\text{mol/L}) )</td>
<td>Molar extinction coefficient</td>
</tr>
</tbody>
</table>
Applying Beer's Law to Mixtures

\[ A_{\text{total}} = A_1 + A_2 + \cdots + A_n = \varepsilon_1 b c_1 + \varepsilon_2 b c_2 + \cdots + \varepsilon_n b c_n \]

24C-2 Absorption Spectra

Atomic Absorption

Fig. 24-10 Methods for plotting absorption spectra. The numbers for the curves indicate ppm of KMnO$_4$; \( b = 2.00 \text{ cm} \).

Fig. 24-11 Partial energy-level diagram for sodium, showing the transition resulting from absorption at 590, 330 and 285 nm.

Ex. 24-4 The energy difference between the 3p and the 3s orbitals in Figure 24-11b is 2.107 eV. Calculate the wavelength of radiation that would be absorbed in exciting the 3s electron to the 3p state (1 eV = 1.60 \( \times \) \( 10^{-19} \) J).

\[
\lambda = \frac{hc}{E} = \frac{6.63 \times 10^{-34} \text{ J s} \times 3.00 \times 10^{-10} \text{ cm/s} \times 10^7 \text{ nm/cm}}{2.107 \text{ eV} \times 1.60 \times 10^{-19} \text{ J/eV}} = 590 \text{ nm}
\]

Molecular Absorption

*ground state*: the lowest energy state of an atom or molecule

*excited state*: excitation \( M + h\nu \rightarrow M^* \)

- a chemical species absorbs thermal, electrical, or radiant energy and is promoted to a higher energy state called an *excited state*.

*Relaxation*: an excited species gives up its excess energy and returns to a lower energy state.

\( M^* \rightarrow M + \text{heat} \)

photochemical decomposition: by *fluorescent* or *phosphorescent* reemission of radiation.
**electronic transition**: transition of an electron between two orbitals

**vibrational transitions**

**rotational transitions**

Fig. 24-12 Energy-level diagram showing some of the energy changes that occur during absorption of infrared (IR) radiation, visible (VIS), and ultraviolet (UV) radiation.

\[
E = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}}
\]

\[
\Delta E_{\text{electronic}} \approx 10 E_{\text{vibrational}} \approx 100 E_{\text{rotational}}
\]

Fig. 24-13 Types of molecular vibrations. The plus sign indicates motion from the page toward the reader, the minus sign indicates motion in the opposite direction.

**Absorption of Ultraviolet and Visible Radiation**

Fig. 24-14 Typical ultraviolet absorption spectra. The compound is 1,2,4,5-tetrazine. In (a), the spectrum is shown in the gas phase where many lines due to electronic, vibrational, and rotational transitions are seen. In a nonpolar solvent (b), the electronic transitions can be observed, but the vibrational and rotational structure have been lost. In a polar solvent (c), the strong intermolecular forces have caused the electronic peaks to blend together to give only a single, smooth absorption peak.
24C-3 Limits to Beer's Law

1. Real Limitations to Beer's Law

   in relatively concentrated solution of the analyte or in concentrated electrolyte solutions

2. Chemical Deviations

   The absorbing species participates in a concentration-dependent equilibrium such as a dissociation or association reaction.

**Ex. 24-5** Solutions containing various concentrations of the acidic indicator HIn (Ka = 1.42 × 10^{-5}) were prepared in 0.1 M HCl and 0.1 M NaOH. In both media, a linear relationship between absorbance and concentration was observed at 430 and 570 nm. From the magnitude of the acid dissociation constant, it is apparent that, for all practical purposes, the indicator is entirely in the undissociated form (HIn) in the HCl solution and completely dissociated as In⁻ in NaOH. The molar absorptivities at the two wavelengths were found to be

<table>
<thead>
<tr>
<th></th>
<th>ε_{430}</th>
<th>ε_{570}</th>
</tr>
</thead>
<tbody>
<tr>
<td>HIn (HCl solution)</td>
<td>6.30 × 10^2</td>
<td>7.12 × 10^3</td>
</tr>
<tr>
<td>In⁻ (NaOH solution)</td>
<td>2.06 × 10^4</td>
<td>9.60 × 10^2</td>
</tr>
</tbody>
</table>

Derive absorbance data (1.00-cm cell) at the two wavelengths for unbuffered solutions with indicator conc. ranging from 2 × 10^{-5} to 16 × 10^{-5} M. Plot the data.

in a unbuffered 2.00 × 10^{-5} M solution of indicator

\[ [H^+] = [In^-], \quad [HIn] = 2.00 \times 10^{-5} \text{ M} - [In^-] \]

\[ K_{HIn} = \frac{[H_3O^+][In^-]}{[HIn]} = \frac{[In^-]^2}{2.00 \times 10^{-5} - [In^-]} = 1.42 \times 10^{-5} \]

\[ [In^-] = 1.12 \times 10^{-5} \]

\[ [HIn] = 2.00 \times 10^{-5} - 1.12 \times 10^{-5} = 0.88 \times 10^{-5} \]

\[ A_{430} = (6.30 \times 10^2 \times 1.00 \times 0.88 \times 10^{-5}) + (2.06 \times 10^4 \times 1.00 \times 1.12 \times 10^{-5}) = 0.236 \]

\[ A_{570} = (7.12 \times 10^3 \times 1.00 \times 0.88 \times 10^{-5}) + (9.60 \times 10^2 \times 1.00 \times 1.12 \times 10^{-5}) = 0.073 \]

<table>
<thead>
<tr>
<th>C_{HIn}, M</th>
<th>[HIn]</th>
<th>[In⁻]</th>
<th>A_{430}</th>
<th>A_{570}</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.00 × 10^{-5}</td>
<td>0.88 × 10^{-5}</td>
<td>1.12 × 10^{-5}</td>
<td>0.236</td>
<td>0.074</td>
</tr>
<tr>
<td>4.00 × 10^{-5}</td>
<td>2.22 × 10^{-5}</td>
<td>1.78 × 10^{-5}</td>
<td>0.381</td>
<td>0.175</td>
</tr>
<tr>
<td>8.00 × 10^{-5}</td>
<td>5.27 × 10^{-5}</td>
<td>2.73 × 10^{-5}</td>
<td>0.596</td>
<td>0.401</td>
</tr>
<tr>
<td>12.00 × 10^{-5}</td>
<td>8.52 × 10^{-5}</td>
<td>3.48 × 10^{-5}</td>
<td>0.771</td>
<td>0.640</td>
</tr>
<tr>
<td>16.00 × 10^{-5}</td>
<td>11.9 × 10^{-5}</td>
<td>4.11 × 10^{-5}</td>
<td>0.922</td>
<td>0.887</td>
</tr>
</tbody>
</table>

(Fig. 24-15)
Fig. 24-15 Chemical deviations from Beer’s law for unbuffered solutions of the indicator HIn.

Fig. 24-16 Deviations from Beer’s law with polychromatic radiation. The absorber has the indicated molar absorptivities at the two wavelengths $\lambda'$ and $\lambda''$.

3. Instrumental Deviations: Polychromatic Radiation

$$A' = \log \frac{P'_0}{P'} = \varepsilon' \varepsilon_{bc} \text{ or } \frac{P'_0}{P'} = 10^{-\varepsilon' \varepsilon_{bc}}$$

For $\lambda'$, $P' = P'_0 10^{-\varepsilon' \varepsilon_{bc}}$,

For $\lambda''$, $P'' = P''_0 10^{-\varepsilon'' \varepsilon_{bc}}$

$$A_m = \log \frac{P'_0 + P''_0}{P' + P''} = \log \frac{P'_0 + P''_0}{P'_0 10^{-\varepsilon' \varepsilon_{bc}} + P''_0 10^{-\varepsilon'' \varepsilon_{bc}}}$$

$$= \log(P'_0 + P''_0) - \log(P'_0 10^{-\varepsilon' \varepsilon_{bc}} + P''_0 10^{-\varepsilon'' \varepsilon_{bc}})$$

when $\lambda' = \lambda''$

$$A_m = \log(P'_0 + P''_0) - \log[(P'_0 + P''_0)(10^{-\varepsilon' \varepsilon_{bc}})]$$

$$= \log(P'_0 + P''_0) - \log(P'_0 + P''_0) - \log(10^{-\varepsilon' \varepsilon_{bc}})$$

$$= \varepsilon' \varepsilon_{bc} = \varepsilon'' \varepsilon_{bc}$$

Fig. 24-17 The effect of polychromatic radiation on Beer’s low.

4. Instrumental Deviations: Stray Light

$$A' = \log \frac{P_0 + P_s}{P + P_s} \quad \text{P: power of the stray radiation}$$

Fig. 24-18 Deviation from Beer’s law caused by various levels of stray light.

5. Mismatched Cells

$$A = \varepsilon bc + k$$
24D Emission of Electromagnetic Radiation

24D-1 Emission Spectra

**Line spectra:** $10^{-2} \sim 10^{-3}$ nm, Bands for Na, K, Sr, Ca and Mg in Fig. 24-19

Fig. 24-19 Emission spectrum of a brine sample obtained with an oxyhydrogen flame.

**Band spectra:** made up of many closely spaced lines that are difficult to resolve
Bands for OH, MgOH and MgO in Fig. 24-19.

**Continuum spectra:** no line character and generally produced by heating solids to a high temperature.

**Blackbody radiation**
The energy peak shift to shorter wavelength with increasing temperature.

Fig. 24-20 Energy-level diagram for Na.

24D-2 Emission by Fluorescence and Phosphorescence

**Atomic Fluorescence:**

**Molecular Fluorescence:**

**Fluorescence:** an analytically important emission process in which atoms or molecules are excited by the absorption of electromagnetic radiation.

The excited species then relax to the ground state, giving up their excess energy as photons.
**Relaxation Processes** (Fig. 24-22)

a. Nonradiative relaxation

1. **Vibrational deactivation, or relaxation:**
   - collisions between excited molecules and molecules of the solvent → temp. of the medium ↑
   - average lifetime: $10^{-10} \sim 10^{-11}$ s

2. **Internal conversion:**
   - between the lowest vibrational level of an excited electronic state and the upper vibrational level of another electronic state
   - average lifetime: $10^{-12}$ s

b. **Fluorescence emission**

   electronically excited molecules relax to any of the several vibrational states of the ground electronic state.

   average lifetime: $10^{-5} \sim 10^{-10}$ s

---

Fig. 24-22 Energy-level diagram shows some of the processes that occur during absorption, nonradiative relaxation and fluorescence by a molecular species.

Resonance Lines and the Stokes Shift

Resonance fluorescence has an identical wavelength to the radiation that caused the fluorescence.

Stokes-shifted fluorescence is **longer** in wavelength than the radiation that caused the fluorescence.