Chapter 21
Lecture # 18 – Atomic Spectroscopy

Weekly Outline

Week 13 Apr. 21 Atomic Spectroscopy (Almirall)
Apr. 22 Mass Spectrometry (Almirall)

Week 14 Apr. 26 Introduction to Analytical Separation and Chromatography/ Electrophoresis
Apr. 28 Extraction; Sample Preparation

Week 15 Apr. 24 Gas Chromatography (Almirall)
Apr. 25 Liquid Chromatography and Fines Review (Almirall)

Week 16 Apr. 24 FINAL EXAM – 12:45-3:30 pm (Almirall and L. de la Vega)

Energy and Electromagnetic Radiation

Light is a particle = Photon

\[ E (\text{energy of photon}) = h \nu \]

\( h \) (Planck’s constant) = \( 6.626 \times 10^{-34} \) J \( \cdot \) s

\[ c = \nu \lambda \Rightarrow \frac{\nu}{\lambda} = \frac{c}{\lambda} \]

\[ E = \frac{hc}{\lambda} = h\nu \]

\( \nu \equiv \text{wavenumber} \)

Blackbody Radiation

\[ M_{\lambda} = \frac{2\pihc^2}{\lambda^5} \left( e^{\frac{hc}{\lambda kT}} - 1 \right) \]

Energy States and UV-Vis/Fluorescence Spectroscopy

Jablonski Energy Diagram

- \( S_0 \): electronic ground state
- \( S_n \): excited states
- \( P \): photon absorption
- \( T_2 \): triplet state
- IC: internal conversion
- ISC: intersystem crossing

\( A \equiv \text{absorption} \)

\( P \equiv \text{phosphorescence} \)

Transition Process Timescale (Seconds)

- \( S(0) \Rightarrow S(1) \text{ or } S(n) \): Absorption (Excitation)
  \( \text{Instantaneous} \)
  \( 10^{-15} \text{ to } 10^{-14} \)

- \( S(n) \Rightarrow S(1) \): Internal Conversion
  \( k(ic) \)
  \( 10^{-14} \text{ to } 10^{-10} \)

- \( S(1) \Rightarrow S(1) \): Vibrational Relaxation
  \( k(vr) \)
  \( 10^{-12} \text{ to } 10^{-10} \)

- \( S(1) \Rightarrow S(0) \): Fluorescence
  \( k(f) \text{ or } G \)
  \( 10^{-9} \text{ to } 10^{-7} \)

- \( S(1) \Rightarrow T(1) \): Intersystem Crossing
  \( k(pT) \)
  \( 10^{-8} \text{ to } 10^{-7} \)

- \( S(1) \Rightarrow S(0) \): Non-Radiative Relaxation Quenching
  \( k(nr), k(q) \)
  \( 10^{-7} \text{ to } 10^{-5} \)

- \( T(1) \Rightarrow S(0) \): Phosphorescence
  \( k(p) \)
  \( 10^{-3} \text{ to } 100 \)

- \( T(1) \Rightarrow S(0) \): Non-Radiative Relaxation Quenching
  \( k(nr), k(qT) \)
  \( 10^{-3} \text{ to } 100 \)
**Spectroscopy vs. Spectrometry**

Spectroscopy is “the study of the interaction between electromagnetic radiation and matter.”

Spectrometry is “the measure of these interactions.”

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**Atomic Spectroscopy**

“determination of elemental composition”

*Sample → Atomization → Excited States → Ground State*

**Atomic Absorption**

- Hollow Cathode (made of element being analyzed)
- Insulating Disk
- Ne/Ar + Wavelength
- Intensity
- Bandwidth

**Atomization**

1. Flame
2. Furnace (e.g. graphite furnace)
3. Plasma (e.g. Inductively Coupled Plasma)
**Flame Atomization**

- Oxidant (e.g., air)
- Fuel (e.g., acetylene)
- Premix Burner

**Graphite Furnace**

- Pre-Concentration
- Sample Volume: 1-100 µL
- Detection Limit: 0.02-0.06 ng/mL

1. **Pre-Concentration**
2. **Automated Injection**
3. **Transverse Heating**
4. **Matrix Modifiers**
   - Matrix More Volatile
   - Analyte Less Volatile

**Graphite Furnace**

- Dry
- "Char" (pyrolysis)

**Graphite furnace**

- Front View
- Sample (~1 µL)
- Pre-Concentration (= multiple sample applications)

**Graphite furnace**

- Top View
- Time-Integrated Absorbance

**Graphite Furnace**

- Time (s)
- Temperature (°C)
Analysis of Mercury by Cold Vapor Atomic Fluorescence

Inductively Coupled Plasma (ICP)

Plasma Tube (ionized Ar collide with atoms; transfer energy)

Quartz

Inductively Coupled Plasma (ICP)

*can measure as many as ~70 elements simultaneously*

Comparison of Detection Limits for Ni\textsuperscript{+} Ion (at 231 nm)*

<table>
<thead>
<tr>
<th>Detection Technique</th>
<th>Limits (ng/mL = ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ICP/atomic emission</td>
<td>3-50</td>
</tr>
<tr>
<td>ICP/atomic emission (pneumatic nebulizer)</td>
<td>0.3-4</td>
</tr>
<tr>
<td>Graphite Furnace/atomic absorption</td>
<td>0.02-0.06</td>
</tr>
<tr>
<td>ICP/mass spectrometry</td>
<td>0.001-0.2</td>
</tr>
</tbody>
</table>

*Sensitivity of Atomic Spectroscopy*

*Note: Atomic Fluorescence (of Hg) < 0.1 ppt*
**Boltzmann Distribution**

\[
\frac{N_e}{N_o} = \frac{g_e e^{-\Delta E/kT}}{g_o}
\]

*\(N_e/N_o = \text{Relative Population of Excited/Ground States}\)*

*\(g_e, g_o = \text{“degeneracy” (number of states)}\)*

*\(T = \text{Temperature (K)}\)*

*\(k = \text{Boltzmann Constant (1.381 x 10^{-23} J/K)}\)*

*\(\Delta E = \text{Excited State (Ex: } g = 3 \text{ states)}\)*

*\(E_o = \text{Ground State (Ex: } g_o = 2 \text{ states)}\)*

**Effect of Energy Difference and Temperature on population of excited states**

<table>
<thead>
<tr>
<th>Wavelength difference of states (nm)</th>
<th>Energy difference of states (J/atom)</th>
<th>Excited-state fraction ((N_e/N_o))*</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>(7.95 \times 10^{-19})</td>
<td>0.80 x 10^{-3}</td>
</tr>
<tr>
<td>500</td>
<td>(3.97 \times 10^{-19})</td>
<td>0.85 x 10^{-3}</td>
</tr>
<tr>
<td>750</td>
<td>(2.65 \times 10^{-19})</td>
<td>0.88 x 10^{-3}</td>
</tr>
</tbody>
</table>

*Based on the equation* \(N_e/N_o = (g_e/g_o) e^{-\Delta E/kT}\) *in which* \(g^* = g_o = 1\).*

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**“Bandwidth” in Spectroscopy**

- Bandwidth \(\approx 10^{-2}\) nm

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**Linewidth in Atomic Spectroscopy**

**Heisenberg Uncertainty Principle:** “the shorter the lifetime of the excited state, the more uncertain is its energy”

\[
\delta E \delta t \geq \frac{\hbar}{4\pi}
\]

- \(\delta E = \text{Uncertainty in Energy}\)
- \(\delta t = \text{Lifetime of the Excited State}\)
- \(\hbar = \text{Planck’s Constant (6.6 x 10^{-34} J \cdot s)}\)

**Example: Atomic Absorption Intrinsic Linewidth @ 10^{-4} nm**

\[
\begin{align*}
\delta t &\approx 10^{-9} \text{ s} \Rightarrow \frac{\delta E}{\delta t} \geq \frac{\hbar}{4\pi} \\
&= \frac{(6.6 \times 10^{-34} \text{ J} \cdot \text{s})}{(4\pi)} \approx 10^{-25} \text{ J} \cdot \text{s} \\
\Delta E &= \hbar \lambda = 4.0 \times 10^{-19} \text{ J} \cdot \text{s} \\
(\text{e.g. 500 nm})
\end{align*}
\]

\[
\begin{align*}
\frac{\delta E}{\Delta E} &= \frac{(10^{-25})}{(4.0 \times 10^{-19})} \\
&= 2 \times 10^{-7}
\end{align*}
\]

\[
\begin{align*}
\frac{\delta \lambda}{\lambda} &= (2.5 \times 10^{-7})/(500) \approx 10^{-4}
\end{align*}
\]
“Linewidth” in Atomic Spectroscopy

Linewidth Broadening

1. Doppler Effect
   \[ \delta \lambda = \frac{\lambda}{c} \left( \frac{v}{c} \right)^2 \ \text{eV} \]
   where \( \lambda \) is the wavelength, \( c \) is the speed of light, \( v \) is the velocity of the atom, and the factor \( \left( \frac{v}{c} \right)^2 \) is the Doppler factor.

   Example: \( \delta \lambda = 300 \text{ nm} \) for Fe (M = 56 amu) at 2500 K.

2. Pressure Broadening
   \[ \delta \lambda \approx \frac{2}{3} \lambda \left( \frac{T}{M} \right)^{1/2} \]
   where \( T \) is the temperature in Kelvin and \( M \) is the molecular mass in amu.

Example:

\[ \delta \lambda = 300 \text{ nm} \left( \frac{2}{3} \right) \left( \frac{7 \times 10^{-7}}{56} \right)^{1/2} = 0.0014 \text{ nm} \]

LIBS Setup

Nd:YAG ns lasers
- Big Sky Laser 1064nm
- 220 mJ max energy

New Wave Research 3rd Harmonic 266nm
- 27 mJ max energy

Collection optics
- perpendicular to sample surface

Andor Mechelle iCCD Camera
- (200-900nm)
- Computer controlled xyz sample stage

Plasma Evolution

Early stages dominated by broadband continuum 0-1.0 \( \mu \)s
Rapid expansion and cooling
Neutral and ionic dominated emission

LIBS for Forensics

Advantages
- Large amount of information obtained
- Qualitative and quantitative
- Almost non-destructive direct solid sampling
- Speed, versatility, ease of operation, affordability and portability
- Good detection limits (~ 10 ppm - 50 ppm)

Challenges
- Calibration
- Matrix effects

NIST Standard Reference Materials
- 610 = 515 ppm Sr
- 1831 = 112 ppm Sr

Interference

1. Spectral Interference
   - Background (e.g. optical scattering, residual smoke, other elements)
   - Zeeman or D2 Background Correction

2. Chemical Interference
   - “any component of the sample that decreases the extent of atomization of analyte”

3. Ionization Interference
   - \( M(g) \leftrightarrow M^+(g) + e^- \)
   \[ K = \frac{[M^+][e^-]}{[M]} \]
   - Ionization Supressors (more easily ionized)
ICP-Mass Spectrometry

<table>
<thead>
<tr>
<th>Method</th>
<th>Detection Limit (ppt)</th>
<th>Linear Range</th>
<th>Sample Volume</th>
<th>Sample Throughput</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flame Absorption</td>
<td>10-1000</td>
<td>10^3</td>
<td>Large</td>
<td>10-15 s/element</td>
</tr>
<tr>
<td>Furnace Absorption</td>
<td>0.01-1</td>
<td>10^3</td>
<td>Very Small</td>
<td>3-4 min/element</td>
</tr>
<tr>
<td>Plasma Emission</td>
<td>0.1-10</td>
<td>10^3</td>
<td>Medium</td>
<td>3-4 min/element</td>
</tr>
<tr>
<td>Plasma-Mass Spec</td>
<td>0.00001-0.0001</td>
<td>10^3</td>
<td>All elements</td>
<td>2-5 min/element</td>
</tr>
</tbody>
</table>

Atomic Fluorescence

ICP-MS

ICP-Mass Spectrometry

Atomic Fluorescence

ICP-MS

ICP-Mass Spectrometry
HR-ICP-MS (ELEMENT 2)

Chapter 21

Assigned Problems: 21-4, 21-7, 21-9, 21-11, 21-18