Ch. 8  Introduction to Optical Atomic Spectroscopy

3 major types of Spectrometry – elemental
- Optical Spectrometry    Ch 9, 10
- Mass Spectrometry      Ch 11
- X-ray Spectrometry     Ch 12

In this chapter
- theories on sources
- properties of optical atomic spectra
- atomizing techniques
- sample introducing methods

8.2

8A. Optical Atomic Spectra
8A-1. Energy Level Diagram

Splitting of p, d, f orbitals

Spin & orbital motion create magnetic field due to rot of charge carried by electrons
- Same direction – rep.
- Opposite - attractive

Figure 8.1  Energy level diagrams for (a) atomic sodium and (b) magnesium(I) ion. Note the similarity in pattern of lines but not in actual wavelengths.

by Prof. Myeong Hee Moon
8A-1. Energy Level Diagram

- **Atomic Emission**
  - 3S → 3P
  - Excited state
  - Energy: 5890, 5896 Å
  - Na

- **Atomic Absorption**
  - 3P → 3S
  - Energy absorbing
  - Na

**Heat source:**
- Flame
- Plasma
- Arc
- Spark

**Atomization needed**

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8A-4. Energy Level Diagram

- **Atomic Fluorescence**
  - Atoms or Ions
  - Transition: 6s^2 7s^2 2S_1/2 → 6s^2 6p^2 2P_1/2
    - λ = 3776 Å
  - Transition: 6s^2 6p^2 2P_3/2 → 6s^2 7s^2 2S_1/2
    - λ = 5350 Å
  - Rapid transition
  - Heat loss

**Figure 8-5** Energy level diagram for thallium showing the source of two fluorescence lines.
8A-2. Atomic Line Widths

Line Widths: Narrower, Better for absorption spectroscopy emission

Definition: $\Delta \lambda_{1/2}$ line widths at half the max. signal

Sources of broadening

1. Uncertainty effect in transition time
2. Doppler effect
3. Pressure effects due to collisions
4. Electric & magnetic field effect

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8A-2. Atomic Line Widths

• Broadening from Uncertainty effect

From Heisenberg’s Uncertainty Principle

$$\Delta t \cdot \Delta \nu \geq 1$$

Minimum time for a measurement

Life time of transition state - finite

$\Delta t \geq \frac{1}{\Delta \nu}$

Spectral lines have finite widths

• Pressure Broadening

Caused from collisions among atoms or ions.

Collision alters ground state E. level

changes range of abs or emission $\lambda$

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8A-2. Atomic Line Widths

• Broadening from Doppler effect

Figure 8.7 Cause of Doppler broadening. (a) Atom moving toward incoming radiation sees wave crests more frequently and thus absorbs radiation that is actually higher in frequency. (b) Atom moving with the direction of radiation encounters wave crests less often and thus absorbs radiation that is actually of lower frequency.

Doppler shift

8A-3. Effect of Temp. on Atomic Spectra

Temperature affects number of excited ($N_j$) & unexpected atomic particles

$$\frac{N_j}{N_0} = \frac{P_j}{P_0} \exp\left(-\frac{E_j}{kT}\right)$$

$k$: Boltzman cons.  $1.38 \times 10^{-23}$ J/K
$E_j$: E difference bet. Ex.-gr.state
$P_j$, $P_0$: statistical factor
$3S - 2$: quantum number
$3P - 6$

$\Delta T$: 10K  ----- 4% increase in # of ex. Na atoms excited at 2500K --- 0.017% Na excited

Emission Spec.: based on this limited number
Absorption Spec.: based on 99.98% unexcited
8B. Atomization Methods

For spectroscopy, sample should be converted in gaseous atom or ionized atom then determined by:

- emission
- absorption
- fluorescence
- mass spectrometry

Atomization:
sample conversion to atomic vapor

<table>
<thead>
<tr>
<th>Type of Atomizer</th>
<th>Typical Atomization Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flame</td>
<td>1700–3150</td>
</tr>
<tr>
<td>Electrothermal vaporization (ETV)</td>
<td>1200–3000</td>
</tr>
<tr>
<td>Inductively coupled argon plasma (ICP)</td>
<td>4000–6000</td>
</tr>
<tr>
<td>Direct current argon plasma (DCP)</td>
<td>4000–6000</td>
</tr>
<tr>
<td>Microwave-induced argon plasma (MIP)</td>
<td>2000–3000</td>
</tr>
<tr>
<td>Glow-discharge plasma (GD)</td>
<td>Nonthermal</td>
</tr>
<tr>
<td>Electric arc</td>
<td>4000–5000</td>
</tr>
<tr>
<td>Electric spark</td>
<td>40,000 (?)</td>
</tr>
</tbody>
</table>

8C. Sample Introduction Methods (Achilles Heal)

Critical for Accuracy, Precision, Detection limit

With high Efficiency
With no interference
mostly from solution status
low reproducibility for solids

<table>
<thead>
<tr>
<th>Method</th>
<th>Type of Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pneumatic nebulization</td>
<td>Solution or slurry</td>
</tr>
<tr>
<td>Ultrasonic nebulization</td>
<td>Solution</td>
</tr>
<tr>
<td>Electrothermal vaporization</td>
<td>Solid, liquid, or solution</td>
</tr>
<tr>
<td>Hydride generation</td>
<td>Solution of certain elements</td>
</tr>
<tr>
<td>Direct insertion</td>
<td>Solid, powder</td>
</tr>
<tr>
<td>Laser ablation</td>
<td>Solid, metal</td>
</tr>
<tr>
<td>Spark or arc ablation</td>
<td>Conducting solid</td>
</tr>
<tr>
<td>Glow-discharge sputtering</td>
<td>Conducting solid</td>
</tr>
</tbody>
</table>
Continuous sample introduction into a plasma or flame.

8C-1. Solution samples

Nebulization methods: finely divided droplets (aerosols) by jet or compressed gas

- Pneumatic Nebulizer
  a) Concentric tube: Bernoulli effect
  b) Cross-flow
     a) Fritted disk: finer than a, b
     b) Babington type
        less clogging of high salt samples
8C-1. Solution samples

- Ultrasonic Nebulizers
  piezoelectric crystal, vibrating at 20kHz ~ Mhz
- Electrothermal vaporizers (ETV)

\[
\text{Ar} 
\rightarrow 
\text{Conductor (carbon rod)} 
\text{Good for small vol. liquid or solid sample} 
\]

Apply currents to evaporate samples

- Hydride Generation

For volatile metals to enhance D.L. (10~100)
As, Sb, Sn, Se, Bi, Pb

\[
3\text{BH}_4^- + 3\text{H}^+ + 4\text{H}_3\text{AsO}_3 \rightarrow 3\text{H}_3\text{BO}_3 + 4\text{AsH}_3 + 3\text{H}_2\text{O} 
\]

8C-2. Solid samples

: directly to flame or plasma as a form of powder, metals, particulates

- adv: reduce sample dissolution process
- dis-adv: calibration
  sample conditioning
  precision
  accuracy
- main difference from solution introduction
discrete signal vs. continuous
8C-2. Solid samples

• Types

A. Direct insertion: powder on atomizing probe
   use electric arc or spark

B. Electrothermal vaporization

C. Arc & Spark ablation
   Ablation: plume (particulate & vaporized sample)
   at surface, transferred to atomizer by inert gas flow

D. Laser ablation
   work for both conducting and non-cond. Solid
   inorganic & organic
   powder & metallic

E. Glow Discharge Technique

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**Figure 8.10** A glow discharge atomizer. (From D. S. Gough,
permission.)

DC 250~1000V causes Ar into Ar⁺ + e-
By electric field, Ar⁺ hits cathode (sample)  
   SPUTTERING
 : Eject neutral sample atoms  100µg/min

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