Optical Atomic Spectroscopy

- Atomic spectra: one electron

**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.
Atomic spectrum Mg

Figure 8-2  Energy level diagram for atomic magnesium. The relative line intensities are indicated very approximately by the width of the lines between states. Note that a singlet/triplet transition is considerably less probable than a singlet to singlet transition.
Atomic spectroscopy

- Emission
- Absorption
- Fluorescence
Atomic spectroscopy

- Interaction of an atom in the gas phase with EMR

- Samples are solids, liquids and gases but usually not ATOMS!
Atomic Spectroscopy

- Sample Introduction
  - Flame
  - Furnace
  - ICP

- Sources for Atomic Absorption/Fluorescence
  - Hollow Cathode Lamps

- Sources for Atomic Emission
  - Flames
  - Plasmas

- Wavelength Separators + Slits + Detectors
How to get things to atomize?

**TABLE 8-1 Types of Atomizers Used for Atomic Spectroscopy**

<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>
How to get samples into the instruments?

<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, 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>
A diagram illustrating the process of flame atomic absorption spectroscopy. An atom in a flame emits a signal that is detected by a detector. The signal is passed through a monochromator. A laser and a hollow-cathode lamp are also depicted, with transitions between ground and excited states shown.
What is atomization?

Figure 9-1  Processes occurring during atomization.
FLAMES

Figure 9-2  Regions in a flame.

Figure 9-3  Temperature profiles in °C for a natural gas/air flame. (From B. Lewis and G. van Elstic, J. Chem. Phys., 1943, 11, 94. With permission.)
## TABLE 9.1  Properties of Flames

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Oxidant</th>
<th>Temperatures, °C</th>
<th>Maximum Burning Velocity (cm s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural gas</td>
<td>Air</td>
<td>1700–1900</td>
<td>39–43</td>
</tr>
<tr>
<td>Natural gas</td>
<td>Oxygen</td>
<td>2700–2800</td>
<td>370–390</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>Air</td>
<td>2000–2100</td>
<td>300–440</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>Oxygen</td>
<td>2550–2700</td>
<td>900–1400</td>
</tr>
<tr>
<td>Acetylene</td>
<td>Air</td>
<td>2100–2400</td>
<td>158–266</td>
</tr>
<tr>
<td>Acetylene</td>
<td>Oxygen</td>
<td>3050–3150</td>
<td>1100–2480</td>
</tr>
<tr>
<td>Acetylene</td>
<td>Nitrous oxide</td>
<td>2600–2800</td>
<td>285</td>
</tr>
</tbody>
</table>
Boltzmann Equation: Relates Excited State Population/Ground State Population Ratios to Energy, Temperature and Degeneracy

\[ \frac{N^*}{N_0} = \left( \frac{g^*}{g_o} \right) \times e^{-\frac{E}{RT}} \]

<table>
<thead>
<tr>
<th>Wavelength difference of states (nm)</th>
<th>Energy difference of states (J/atom)</th>
<th>Excited-state fraction ((N^*/N_0)^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>(7.95 \times 10^{-19})</td>
<td>(1.0 \times 10^{-10})</td>
</tr>
<tr>
<td>500</td>
<td>(3.97 \times 10^{-19})</td>
<td>(1.0 \times 10^{-5})</td>
</tr>
<tr>
<td>750</td>
<td>(2.65 \times 10^{-19})</td>
<td>(4.6 \times 10^{-4})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>(2\ 500\ \text{K})</th>
<th>(6\ 000\ \text{K})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1.0 \times 10^{-10})</td>
<td>(6.8 \times 10^{-5})</td>
<td></td>
</tr>
<tr>
<td>(1.0 \times 10^{-5})</td>
<td>(8.3 \times 10^{-3})</td>
<td></td>
</tr>
<tr>
<td>(4.6 \times 10^{-4})</td>
<td>(4.1 \times 10^{-2})</td>
<td></td>
</tr>
</tbody>
</table>

a. Based on the equation \(N^*/N_0 = (g^*/g_o)e^{-\Delta E/RT}\) in which \(g^* = g_o = 1\).

Table 21-3  Effect of energy difference and temperature on population of excited states
What happens inside the flame?
Sample Introduction

- **Venturi Effect and Atomization**

- **Pneumatic Nebulizers (for ICP techniques)**
  - Break the sample solution into small droplets.
  - Solvent evaporates from many of the droplets.
  - Most (>99%) are collected as waste
  - The small fraction that reach the plasma have been de-solvated to a great extent.
What is a nebulizer?

SAMPLE AEROSOL

Sample

Argon gas
Different configurations
Samples are nebulized (broken into small droplets) as they enter the spray chamber via a wire capillary. Only about 5% reach the flame. Larger droplets are collected. Some of the solvent evaporates.

- Flow spoilers
  » Cheaper, somewhat more rugged
- Impact beads
  » Generally greater sensitivity
ElectroThermal AAS (ETAAS or GFAAS)

- The sample is contained in a heated, graphite furnace.
- The furnace is heated by passing an electrical current through it (thus, it is electro thermal).
- To prevent oxidation of the furnace, it is sheathed in gas (Ar usually).
- There is no nebulization, etc. The sample is introduced as a drop (usually 5-20 uL), slurry or solid particle (rare).
ElectroThermal AAS (ETAAS or GFAAS)

- The furnace goes through several steps…
  - Drying (usually just above 110 °C)
  - Ashing (up to 1000 °C)
    - Sometimes there is also a “charring” step
  - Atomization (Up to 2000-3000 °C)
  - Cleanout (quick ramp up to 3500 °C or so). Waste is blown out with a blast of Ar.

- The light from the source (HCL) passes through the furnace and absorption during the atomization step is recorded over several seconds. This makes ETAAS more sensitive than FAAS for most elements.
Solid sample weighed onto graphite platform

Direct solid sampling — end view of furnace
Figure 9-7  Typical output from a spectrophotometer equipped with an electrothermal atomizer. The sample was 2 μL of canned orange juice. The times for drying and ashing are 20 and 60 s, respectively. (Courtesy of Varian Instrument Division, Palo Alto, CA.)
**Sources (for FAAS and ETAAS)**

- Hollow Cathode Lamps (HCL) are the main source.
- These are element specific, constructed of the same element you are analyzing.
- A current is passed through the lamp, exciting the element of interest. As it returns to the ground state, it emits light which is focused through the sample.
- Since emission/absorption is quantized, this is the same wavelength of light that the analytes will absorb!
- Multielement lamps are available.
- Limited lifespan, treat carefully, do not exceed specified maximum current!
FAAS and ETAAS Considerations...

- Temperature level and consistency are key.
- Alignment of the source light is important.
- Since temperatures are relatively low, refractory species and excessive amounts of complexes can form in the flame:
  - Hinder ATOMIC absorption
- Analytes may also be lost by volatilization prior to the absorption of light.
- Matrix modifiers may overcome these two barriers:
  - Reduce oxide and oxyhydroxide formation
  - Reduce sample loss from volatilization
  - Complex with interfering species (molecular)
  - Ammonium chloride, palladium nitrate, magnesium nitrate, for example
ICP-AES (ICP-OES)

- Inductively coupled plasmas are at least 2X as hot as flames or furnaces.
- The Ar plasma is the result of the flow of Ar ions in a very strong, localized radio field.
- 6000-10000 K are common.
- Hot enough to excite most elements so they emit light.
- Hot enough to prevent the formation of most interferences, break down oxides and eliminate most molecular spectral interferences.
- The way to do atomic emission spectroscopy today.
ELECTROTHERMAL VAPORIZATION FOR ICP

Diagram of the process:
- ICP
- Sample
- Graphite rod
- Heater power
- Water coolant
- Argon
Wavelength Separators for Atomic Spectroscopy

- Must be able to separate light that might be only a fraction of nm from the next nearest wavelength of light
  - Atomic spectra are complex!
  - High blaze (groove) density gratings!
- Usually Czerny-Turner configuration or a modification of it.
  - Polychromator for simultaneous instruments.
- Need to incorporate background correction if possible
  - Atomic spectra are complex with many possible spectral interferences
  - Lamp intensities may fluctuate
  - Flame composition may fluctuate
    - Over time on the same sample
    - From sample to sample
  - ICP uses background subtraction based on spectral and peak shape details
DOUBLE BEAM FAA SPECTROMETER
Background Correction

**Figure 9-14** Schematic of a continuum-source background correction system. Note that the chopper can be dispensed with by alternately pulsing each lamp.
Zeeman Effect Background Correction:

Analyte absorption is cancelled out in a strong magnetic field. When the field is on, the instrument measures background absorption. When the field is off, the instrument measures analyte absorption. The difference is the corrected absorption.
Wavelength Separators/Detectors for ICP-AES

- Must have greater resolving power than those for AAS methods.
  - Plasmas are hotter, therefore the spectra are more complex.
- ICP techniques usually cover a wider range of wavelengths
  - 190 – 900 nm
  - Different detectors for different wavelengths
  - PMTs still #1 choice, but CCD arrays also common.
    - Changing in the past few years CCD>>PMT
- The light emitted by an ICP is also more intense! Slits must have greater adjustability…..
- Sequential (scanning) ICP-AES instruments are much more common…
Echelle Spectrograph system

Diagram showing components of an Echelle Spectrograph system:
- Source
- Entrance slit
- Computer-adjusted source mirror
- Echelle grating
- Aperture plate
- Prism/lens
- Plane mirror
- Collimating mirror
Rowland circle polycromator

![Rowland circle diagram](image1)

![Polycromator image](image2)
<table>
<thead>
<tr>
<th>Method</th>
<th>&lt;1 ppb</th>
<th>1–10 ppb</th>
<th>11–100 ppb</th>
<th>101–500 ppb</th>
<th>&gt;500 ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inductively coupled plasma emission</td>
<td>9</td>
<td>32</td>
<td>14</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>Flame atomic emission</td>
<td>4</td>
<td>12</td>
<td>19</td>
<td>6</td>
<td>19</td>
</tr>
<tr>
<td>Flame atomic fluorescence</td>
<td>4</td>
<td>14</td>
<td>16</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>Flame atomic absorption</td>
<td>1</td>
<td>14</td>
<td>25</td>
<td>3</td>
<td>14</td>
</tr>
</tbody>
</table>

*Detection limits correspond to a signal that is twice as great as the standard deviation for the background noise. Data abstracted with permission from V. A. Fassel and R. N. Kniseley, *Anal. Chem.*, 1974, 46(13), 1111A. Copyright 1974 American Chemical Society.
<table>
<thead>
<tr>
<th>Element</th>
<th>AAS‡ Flame</th>
<th>AAS‡ Electrothermal</th>
<th>AES‡ Flame</th>
<th>AES‡ ICP</th>
<th>AES‡ Flame</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>30</td>
<td>0.005</td>
<td>5</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>As</td>
<td>100</td>
<td>0.02</td>
<td>0.0005</td>
<td>40</td>
<td>100</td>
</tr>
<tr>
<td>Ca</td>
<td>1</td>
<td>0.02</td>
<td>0.1</td>
<td>0.02</td>
<td>0.001</td>
</tr>
<tr>
<td>Cd</td>
<td>1</td>
<td>0.00001</td>
<td>800</td>
<td>2</td>
<td>0.01</td>
</tr>
<tr>
<td>Cr</td>
<td>3</td>
<td>0.01</td>
<td>4</td>
<td>0.3</td>
<td>4</td>
</tr>
<tr>
<td>Cu</td>
<td>2</td>
<td>0.002</td>
<td>10</td>
<td>0.1</td>
<td>1</td>
</tr>
<tr>
<td>Fe</td>
<td>5</td>
<td>0.005</td>
<td>30</td>
<td>0.3</td>
<td>8</td>
</tr>
<tr>
<td>Hg</td>
<td>500</td>
<td>0.1</td>
<td>0.0004</td>
<td>1</td>
<td>20</td>
</tr>
<tr>
<td>Mg</td>
<td>0.1</td>
<td>0.00002</td>
<td>5</td>
<td>0.05</td>
<td>1</td>
</tr>
<tr>
<td>Mn</td>
<td>2</td>
<td>0.0002</td>
<td>5</td>
<td>0.06</td>
<td>2</td>
</tr>
<tr>
<td>Mo</td>
<td>30</td>
<td>0.005</td>
<td>100</td>
<td>0.2</td>
<td>60</td>
</tr>
<tr>
<td>Na</td>
<td>2</td>
<td>0.0002</td>
<td>0.1</td>
<td>0.2</td>
<td>—</td>
</tr>
<tr>
<td>Ni</td>
<td>5</td>
<td>0.02</td>
<td>20</td>
<td>0.4</td>
<td>3</td>
</tr>
<tr>
<td>Pb</td>
<td>10</td>
<td>0.002</td>
<td>100</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>Sn</td>
<td>20</td>
<td>0.1</td>
<td>300</td>
<td>30</td>
<td>50</td>
</tr>
<tr>
<td>V</td>
<td>20</td>
<td>0.1</td>
<td>10</td>
<td>0.2</td>
<td>70</td>
</tr>
<tr>
<td>Zn</td>
<td>2</td>
<td>0.00005</td>
<td>0.0005</td>
<td>2</td>
<td>0.02</td>
</tr>
</tbody>
</table>

* Nanogram/milliliter = $10^{-3}$ μg/mL = $10^{-3}$ ppm.
‡ AAS = atomic absorption spectroscopy; AES = atomic emission spectroscopy; AFS = atomic fluorescence spectroscopy; ICP = inductively coupled plasma.
Hydride generation

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

**Figure 9.9** A hydride generation and atomization system for atomic absorption spectrometry.
Glow discharge atomization

Figure 9-8  (a) Cross section of a cell for glow-discharge atomization of solid samples. (b) Craters formed on sample surface by six jets of ionized argon.  (Courtesy of Leeman Labs, Inc., Bedford, MA.)