Excellent series of methods for determining the elemental composition in environmental samples, foods and drinks, potable water, biological fluids, and materials.
**Atomic Absorption Spectrophotometer**

Sample – aerosol mist, desolvation, atomization – atoms in gas phase!

Flame – sample holder – creates atoms to absorb wavelengths from lamp.

Radiation source – hollow cathode lamp, emission lines for the element being analyzed
An absorption measurement was used to determine the levels of different metals in bronze. Measurement made by oxidizing the metal sample (dissolving) and then measuring the solution concentrations of the different metal ions.
Origins of Atomic Spectra

Spectroscopy of atoms or ions do not involve vibrational or rotational transitions. Transition involves promoting an electron from a ground state to a higher empty atomic state orbital, this state is referred to as the excited state.

Shown to the right is the three absorption and emission lines for Na. Atomic p-orbitals are in fact split into two energy levels for the multiple spins of the electron. The energy level is so small however that a single line observed. A high resolution would show the line as a doublet.
The first excited state of Ca is reached by absorption of 422.7 nm light. Calculate the energy difference (kJ/mole) between the ground and excited states.

$$E = h\nu = \frac{hc}{\lambda}$$

$$E = \frac{(6.62 \times 10^{-34} \text{ J-s})(3.00 \times 10^8 \text{ m/s})}{(422.7 \text{ nm})(1.00 \times 10^{-9} \text{ m/nm})} = 4.69 \times 10^{-19} \text{ J/photon}$$

$$(4.69 \times 10^{-19} \text{ J/photon})(6.02 \times 10^{23} \text{ photons/mol}) = 2.83 \times 10^5 \text{ J/photon}$$

$$(2.83 \times 10^5 \text{ J/photon}) \left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right) = 283 \text{ kJ/mol}$$
Optical Atomic Spectra

- Outer shell or valence electrons are promoted to unoccupied atomic orbitals by incident radiation.

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

- Small energy differences between the different transitions – excited states, therefore, high resolution instruments are needed.

- Transitions are observed only between certain energy states.
Excitation Wavelengths and Detection Limits

Table 17.3
Representative Detection Limits by Atomic Absorption (AAS) and Flame Emission (FES) Spectrometry

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelength (nm)</th>
<th>Detection Limit (ppm)</th>
<th>AAS&lt;sup&gt;a&lt;/sup&gt;</th>
<th>FES&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>328.1</td>
<td>0.004 (A)</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>309.3</td>
<td>0.1 (N)</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td></td>
<td>396.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Au</td>
<td>242.8</td>
<td>0.03 (N)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>267.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>422.7</td>
<td>0.003 (A)</td>
<td>0.0003</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>324.8</td>
<td>0.006 (A)</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>Eu</td>
<td>459.4</td>
<td>0.06 (N)</td>
<td>0.0008</td>
<td></td>
</tr>
<tr>
<td>Hg</td>
<td>253.6</td>
<td>0.8 (A)</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>766.5</td>
<td>0.004 (A)</td>
<td>0.00008</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>285.2</td>
<td>0.004 (A)</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>589.0</td>
<td>0.001 (A)</td>
<td>0.0008</td>
<td></td>
</tr>
<tr>
<td>Tl</td>
<td>276.8</td>
<td>0.03 (A)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>213.9</td>
<td>0.001 (A)</td>
<td>15</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>Fuel is acetylene. Letter in parentheses indicates oxidant: A = air; N = nitrous oxide.

<sup>b</sup>Nitrous oxide–acetylene flame.

These are wavelengths with relatively large ε(λ) values so signals are good to use for quantitation.
Chemical Problem

Calculate the emission wavelength (nm) of excited atoms that lie $3.371 \times 10^{-19}$ J per molecule above the ground state.

$$E = \frac{hc}{\lambda} \quad \text{or} \quad \lambda = \frac{hc}{E}$$

\[
\lambda = \frac{(6.62 \times 10^{-34} \text{ J-s})(3.00 \times 10^8 \text{ m/s})}{3.371 \times 10^{-19} \text{ J}} = 5.89 \times 10^{-7} \text{ m}
\]

$$\frac{(5.89 \times 10^{-7} \text{ m}) (1)}{1.00 \times 10^{-9} \text{ m/nm}} = 589 \text{ nm}$$

Visible light!!
Atomic Line Widths

Sources of Line Broadening

1. Uncertainty effect

2. Pressure effects due to collisions

3. Doppler effect

4. Electric and magnetic field effects

Spectral line widths are typically 0.01 nm or so.

Figure 8-6 Profile of an atomic line showing definition of the effective line width $\Delta \lambda_{1/2}$. 
The Uncertainty Effect

- Spectral lines always have finite widths because the lifetimes of one or both of the transitions states are finite, which leads to uncertainties in the transition times.

\[ \Delta \nu \cdot \Delta t > 1 \]

- Lifetime of the ground state is long but the lifetime of the excited state is brief, 10^{-8} s.
- If one wants to know \( \Delta \nu \) with high accuracy, then the time of the measurement, \( \Delta t \), must be very long!
- Line widths due to uncertainty broadening are sometimes called natural line widths, and are about 10^{-4} Å.
Doppler Broadening - When molecules are moving towards a detector or away from a detector the frequency will be offset by the net speed the radiation hits the detector. This is also known as the Doppler effect and the true frequency will either be red shifted (if the chemical is moving away from the detector) or blue shifted (if the chemical is moving towards the detector).

- Wavelength of radiation emitted or absorbed by rapidly moving atom decreases if motion is toward the detector and increases if motion is away from the detector.
- $10^{-2}$ to $10^{-1} \text{ Å}$ Situation is the same for an absorbing atom moving toward or away from the source.
Pressure Broadening

• Broadening that arises from collisions of the emitting or absorbing species with other atoms or ions in the heated medium.

• Collisions cause small changes in the ground state energy levels and hence a range of absorbed or emitted wavelengths.

• ~ $10^{-1}$ Å or so
Atomization Process

- Temperature effects are significant
  \[ \frac{N_j}{N_o} = \frac{P_j}{P_o} \exp\left(-\frac{E_j}{kT}\right) \]

- The process by which a sample is converted into atomic vapor is called *atomization*. 
Neutral atoms in the gas phase are desired!!

Process of sample introduction into the flame where absorption occurs. It is the “sample”holder”.
Atomic Spectroscopy

Atomic spectroscopy is a principal tool for measuring metallic elements at trace levels in industrial and environmental laboratories.

Atomic absorption = requires a lamp with light absorbed by atoms

Atomic emission = luminescence from excited atoms – no lamp required.
Atoms have no vibrations and rotations (energy levels associated with molecules), therefore, spectral bands are more narrow so high resolution instrument
Hollow Cathode Lamp (Line Source)

A lamp with a matching cathode material is required for each element.

Gaseous metal atoms sputtered from cathode by impacting Ar+ in an excited state. They release this “extra energy” by emitting photons and return to ground state.

Atomic radiation emitted by the lamp has the same frequencies at that absorbed by atoms in the flame or furnace.
Narrow Absorption Lines from Source

High resolution instruments needed. Monochromator with a longer focal length, more narrow slit widths and a higher resolution grating are needed.
1. Nebulization

2. Desolvation

3. Atomization

Atomization is the process of breaking analyte into gaseous atoms, which are then measured by their absorption or emission of radiation.

Acetylene – air

(2400 -2700 K)
Graphite Tube Furnace

Furnaces offer increased sensitivity (significantly lower detection limits) and require less sample than a flame.

1 – 100 μL sample volume

All sample is atomized and all atoms remain in optical path for several seconds.
Multiple narrow bands are typical for atomic absorption or emission spectra. Gaseous atoms absorbing or emitting light.
Monochromator or Wavelength Selector

Key component properties: (i) good stray light rejection, (ii) high resolution ($\Delta \lambda/\lambda = nN$), (iii) good light gathering power ($F = f (\text{focal length})/d$ (diameter of mirror))
Photomultiplier Tube (Single Channel)

A photomultiplier tube, useful for light detection of very weak signals, is a photoemissive device in which the absorption of a photon results in the emission of an electron. These detectors work by **amplifying** the electrons generated by a photocathode exposed to a photon flux.

\[ I_{ph} = kP \]

Each dynode is +90 V more positive than the previous one.

\[ I_{ph} = \text{photocurrent} \]

\[ P = \text{incident power of light} \]

Florida State University
All wavelengths detected simultaneously, fast scanning instruments, signal averaging possible to improve S/N
Types of Interferences

- **Spectral** – signals from other elements overlap signals for analyte of interest.

- **Chemical** – chemical reactions decrease the concentration of analyte atoms.

- **Ionization** – ionization of analyte atoms decreases the concentration of neutral atoms.

Analyte signal overlaps signals from other species or from flame.

\[ \text{Ca}^{2+} + \text{SO}_4^{2-} \rightarrow \text{CaSO}_4 \]  
(nonvolatile)  
*(Releasing and protecting agents)*

\[ M(g) \rightarrow M^+(g) + e^- \]  
*(Ionization suppressor)*