Atomic spectroscopy – need to convert the analyte to free, unbound atoms or ions (atomization).

Atomization

a. Flame – premix burner (fuel, oxidant and sample mixed before flame introduction)
- Drawn into pneumatic nebulizer by air (oxidant) and creates small droplets (aerosol).
b. Electrothermal – the graphite furnace
- greater sensitivity and less sample
- maintains constant temperature, reducing memory effects
c. Inductively coupled plasma (ICP), 0.001-50 ng L⁻¹
- high temperature, stability and chemically inert Ar environment

<table>
<thead>
<tr>
<th>Atomization method</th>
<th>Temperature (K)</th>
<th>Measurement Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flame</td>
<td>2300-3400</td>
<td>Abs, emission</td>
</tr>
<tr>
<td>Electrothermal</td>
<td>2000-3300</td>
<td>Abs, emission</td>
</tr>
<tr>
<td>ICP</td>
<td>6000-8500</td>
<td>emission</td>
</tr>
</tbody>
</table>

**Atomic Spectroscopy**

- Unbound atoms, rather than molecules, are the absorbing species.
- Monochromator in atomic absorption or emission is place after the sample (remove unwanted radiation during atomization process).
- Bandwidths are very narrow (0.002-0.005 nm), often referred to as lines.

**Temperature Effects**

Boltzmann Distribution – degeneration of energy states (describes the relative populations of diff. states at thermal equilibrium).
- Ground state atoms can absorb light to be promoted to the excited state.
- Excited state atoms can emit light to return to the ground state.
**Boltzmann distribution:**

\[ \frac{N^*}{N^0} = \frac{g^*}{g^0} e^{-\frac{\Delta E}{kT}} \]

Where \( T \) is temperature (K), \( k \) is Boltzmann’s constant (1.381 x 10^{-23} J/K).

**Example**

Calculate the fraction of sodium atoms in the excited state in an acetylene-air flame at 2600 K.

- lowest excited state = 3.371 x 10^{-19} J/atom above ground state
- Degeneracy of excited state = 2, ground state = 1

\[ \frac{N^*}{N^0} = \frac{g^*}{g^0} e^{-\frac{\Delta E}{kT}} = \frac{2}{1} e^{-\frac{(3.371 \times 10^{-19} \text{ J/atom})}{(1.381 \times 10^{-23} \text{ J/K}) \times 2600 \text{ K}}} = 1.67 \times 10^{-4} \]

- fewer than 0.02% of atoms are in the excited state

**The Effect of Temperature on Absorption and Emission**

- Excited state population changes by 4% when the temperature rises 10 K….therefore the emission intensity rises by 4%.

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**Table 21-3** 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^*/N^0)^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>7.95 x 10^{-19}</td>
<td>1.0 x 10^{-4} 6.8 x 10^{-5}</td>
</tr>
<tr>
<td>500</td>
<td>3.97 x 10^{-19}</td>
<td>1.0 x 10^{-5} 8.3 x 10^{-3}</td>
</tr>
<tr>
<td>750</td>
<td>2.65 x 10^{-19}</td>
<td>4.6 x 10^{-4} 4.1 x 10^{-2}</td>
</tr>
</tbody>
</table>

a. Based on the equation \( N^*/N^0 = (g^*/g^0)e^{-\Delta E/kT} \) in which \( g^* = g^0 = 1 \).