3 - Atomic Absorption Spectroscopy

Introduction
Atomic-absorption (AA) spectroscopy uses the absorption of light to measure the concentration of gas-phase atoms. Since samples are usually liquids or solids, the analyte atoms or ions must be vaporized in a flame or graphite furnace. The atoms absorb ultraviolet or visible light and make transitions to higher electronic energy levels. The analyte concentration is determined from the amount of absorption. Applying the Beer-Lambert law directly in AA spectroscopy is difficult due to variations in the atomization efficiency from the sample matrix, and nonuniformity of concentration and path length of analyte atoms (in graphite furnace AA). Concentration measurements are usually determined from a working curve after calibrating the instrument with standards of known concentration.

Schematic of an atomic-absorption experiment

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Relationship between Atomic Absorption and Flame Emission:
- **Flame Emission**: it measures the radiation emitted by the excited atoms that is related to concentration.
Atomic Absorption Spectroscopy

- **Atomic Absorption**: it measures the radiation absorbed by the unexcited atoms that are determined.
- **Atomic absorption depends** only upon the number of unexcited atoms; the absorption intensity is not directly affected by the temperature of the flame.
- **The flame emission intensity** in contrast, being dependent upon the number of excited atoms, is greatly influenced by temperature variations.

**Flame Atomic Absorption Spectrometer**

**Emission Flame Photometer**
Atomic Absorption Spectroscopy

Advantages of AAS:
1. Widespread application to metals more than X-ray, Fluo, FP
2. High sensitivity
3. No interference

Disadvantage of AAS:
1. Metal only (not for non–metals)
2. Cant be used for gas or solid (must dissolved first)
3. Only one element
4. Anionic interference (calibration curve with interfering sub.)

Instrumentation

Light source: The light source is usually a hollow-cathode lamp of the element that is being measured. The disadvantage of these narrow-band light sources is that only one element is measurable at a time.

1. Hollow-cathode Lamps
   - Hollow-cathode lamps (HCL) are a type of discharge lamp that produce narrow emission from atomic species. The hollow cathode lamp uses a cathode made of the element of interest with a low internal pressure of an inert gas.
   - A low electrical current (~10 mA) is imposed in such a way that the metal is excited and emits a few spectral lines characteristic of that element (for instance, Cu 324.7 nm and a couple of other lines; Se 196 nm and other lines, etc.).
Atomic Absorption Spectroscopy

- The light is emitted directionally through the lamp's window, a window made of a glass transparent in the UV and visible wavelengths.

*Schematic of a hollow-cathode lamp.*

How cathode lamps work

The lamp is filled with an inert gas like argon or neon. When a potential is applied, it causes gas to become excited and it is driven towards the cathode.

Metal atoms are then sputtered off the surface of the cathode:

\[ M^* \rightarrow M^0 + hv \]

Repeated bombardment of the metal atom by the gas causes it to be excited. It ultimately relaxes, producing specific atomic emission lines.
Electrodeless discharge lamps *EDL*

- These provide radiant intensities that are usually one to two orders of magnitude greater than hollow cathode lamps. A typical lamp is constructed from a sealed quartz tube containing a few torr of an inert gas such as argon and a small quantity of the metal (or its salt) whose spectrum is of interest.

- The lamp is energized by an intense field of radio-frequency or microwave radiation. Ionization of the argon occurs to give ions that are accelerated by the high-frequency component of the field until they gain sufficient energy to excite the atoms of the metal whose spectrum is sought. Electrodeless discharge lamps are available commercially for 15 or more elements.

- Common discharge lamps and their wavelength ranges are:
  - hydrogen or deuterium : 160 - 360 nm.
  - mercury : 253.7 nm, and weaker lines in the near-uv and visible.
  - Ne, Ar, Kr, Xe discharge lamps : many sharp lines throughout the near-uv to near-IR.
  - xenon arc : 300 - 1300 nm
Atomic Absorption Spectroscopy

- Deuterium lamps are the Uv source in Uv-Vis absorption spectrophotometers.

How an EDL Works

- An intense RF (or microwave) field is applied to the sealed quartz tube within the lamp
- Ar gas within the tube ionizes and gains kinetic energy from the RF field
- Energy is transferred to the metal upon collision
- Excited metal returns to ground state, emitting light (hn)

\[
\text{Ar}_{(g)} \rightarrow \text{Ar}^*_{(g)} + \text{M}_{(s)} \rightarrow \text{M}^*_{(g)} + \text{Ar}_{(g)}
\]

Atomizer

Flame Atomization: In a flame atomizer, a solution of the sample is nebulized by a flow of gaseous oxidant, mixed with a gaseous fuel, and carried into a flame where atomization occurs. The following processes then occur in the flame.

- Desolvation (produce a solid molecular aerosol)
- Dissociation (leads to an atomic gas)
- Ionization (to give cations and electrons)
- Excitation (giving atomic, ionic, and molecular emission)
The Atomization Process

Types of Flames:

Several common fuels and oxidants can be employed in flame spectroscopy depending on temperature needed. Temperatures of 1700°C to 2400°C are obtained with the various fuels when air serves as the oxidant. At these temperatures, only easily decomposed samples are atomized. For more refractory samples, oxygen or nitrous oxide must be employed as the oxidant. With the common fuels these oxidants produce temperatures of 2500°C to 3100°C.

Properties of Flames

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Oxidant</th>
<th>Temperature, °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>
Types of fuel/oxidant

1) air/acetylene    2300°C most widely used.

\[ C_2H + 2.5 O_2 + 10 N_2 \rightarrow 2CO_2 + H_2O + 10N_2 \]

2) nitrous oxide/acetylene   2750°C hot and reducing red feather zone

\[ C_2H + 5N_2O \rightarrow 2 CO_2 + H_2O + 5N_2 \]

Burning Velocity:

The burning velocities are of considerable importance because flames are stable in certain ranges of gas flow rates only. If the gas flow rate does not exceed the burning velocity, the flame propagates itself back into the burner, giving flashback. As the flow rate increases, the flame rises until it reaches a point above the burner where the flow velocity and the burning velocity are equal. This region is where the flame is stable. At higher flow rates, the flame rises and eventually reaches a point where it blows off of the burner.

Flame Structure:

Important regions of a flame include:

1. **Primary combustion zone**: Thermal equilibrium is ordinarily not reached in this region, and it is, therefore, seldom used for flame spectroscopy.

2. **Interzonal region**: This area is relatively narrow in stoichiometric hydrocarbon flames, is often rich in
free atoms and is the most widely used part of the flame for spectroscopy.

3. **Secondary combustion zone:** In the secondary reaction zone, the products of the inner core are converted to stable molecular oxides that are then dispersed into the surroundings.

**Temperature Profiles:**

A temperature profile of a typical flame for atomic spectroscopy is shown in Fig. 9-3. The maximum temperature is located in the flame about 1 cm above the primary combustion zone. It is important—particularly for emission methods—to focus the same part of the flame on the entrance slit for all calibrations and analytical measurements.

**Flame Atomizers:**

Figure below is a diagram of a typical commercial laminar flow burner that employs a concentric tube nebulizer. The aerosol is mixed with
fuel. The aerosol, oxidant, and fuel are then burned in a slotted burner that provides a flame that is usually 5 or 10 cm in length.

Advantages:
1. Uniform dropsize
2. Homogeneous flame
3. Quiet flame and a long path length

Disadvantages:
1. Flash back if $V_{\text{burning}} > V_{\text{flow}}$
2. $\sim 90\%$ of sample is lost
3. Large mixing volume

Electrothermal or Graphite Furnace Atomizer
- Atomization occurs in an electrically heated graphite tube
- The graphite tube is flushed with an inert gas (Ar) to prevent the formation of (non-absorbing) metal oxides
Performance Characteristics:

Electrothermal atomizers offer the advantage of unusually high sensitivity for small volumes of sample. Typically, sample volumes between 0.5 and 10 μL are used; absolute detection limits lie in the range of $10^{-10}$ to $10^{-13}$ g of analyte. Furnace methods are slow—typically requiring several minutes per element. A final disadvantage is that the analytical range is low, being usually less than two orders of magnitude.

Light separation and detection

AA spectrometers use monochromators and detectors for uv and visible light. The main purpose of the monochromator is to isolate the absorption line from background light due to interferences. Simple dedicated AA instruments often replace the monochromator with a band pass interference filter. Photomultiplier tubes are the most common detectors for AA spectroscopy.
Ionic spectra versus atomic spectra:

- Spectra of excited atoms differ from those of excited ions of the same atoms
- Spectrum of singly ionized atom is similar to the atomic spectrum of the element having an atomic number of one less e.g.:
  - spectrum of Mg + is similar to that of Na atom
  - spectrum of Al+ is similar to that of Mg atom
- Ionic spectra contain more lines than atomic spectra; however the intensity of ionic spectra is much less than that of atomic spectra.

Spectral Line width

- Narrow line desirable for absorption and emission work to reduce possibility of interference due to overlapping spectra.
- Theoretically atomic lines should have a zero line width but this does not exist
- The natural line should have a width of $10^{-5}$ nm