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Atomic Absorption Spectroscopy
Atomic Spectroscopy

Is the study of the **electromagnetic radiation** absorbed and emitted by atoms.

Since unique elements have characteristic (signature) spectra, atomic spectroscopy, specifically the electromagnetic spectrum or mass spectrum, is applied for determination of **elemental compositions**.

The science of atomic spectroscopy has yielded three techniques for analytical use:

- Atomic Absorption.
- Atomic Emission.
- Atomic Fluorescence.
Atomic absorption spectroscopy (AAS) is a spectroanalytical procedure for the qualitative and quantitative determination of chemical elements using the absorption of optical radiation (light) by free atoms in the gaseous state.

Typically, these methods can detect parts-per-million to parts-per-billion amounts, and in some cases, even smaller concentrations. Atomic spectroscopic methods are also rapid, convenient, and usually of high selectivity.

Flame atomic absorption spectroscopy is currently the most widely used of all the atomic methods because of its simplicity, effectiveness, and relatively low cost.
The most important problem in atomic absorption methods was directly related to problems created by the very narrow widths of atomic absorption lines. The widths of atomic absorption lines are much less than the effective bandwidths of most monochromators.

No ordinary monochromator is capable of yielding a band of radiation as narrow as the width of an atomic absorption line (0.002 to 0.005 nm). As a result, the use of radiation that has been isolated from a continuum source by a monochromator inevitably causes instrumental departures from Beer’s law.

The problem created by narrow absorption lines was surmounted by using radiation from a source that emits not only a line of the same wavelength as the one selected for absorption measurements but also one that is narrower. For example, **Hollow-cathode lamps**.
AAS Block diagram
Spectroscopic determination of atomic species can only be performed on a gaseous medium in which the individual atoms or elementary ions, such as Fe\(^+\), Mg\(^+\), or Al\(^+\), are well separated from one another.

Consequently, the first step in all atomic spectroscopic procedures is \textit{atomization}, a process in which a sample is volatilized and decomposed in such a way as to produce gas-phase atoms and ions.

The efficiency and reproducibility of the atomization step can have a large influence on the sensitivity, precision, and accuracy of the method. In short, atomization is a critical step in atomic spectroscopy.
Processes leading to atoms, molecules, and ions with continuous sample introduction into a **plasma** or **flame**. The solution sample is converted into a spray by the nebulizer. The high temperature of the flame or plasma causes the solvent to evaporate leaving dry aerosol particles. Further heating volatilizes the particles producing atomic, molecular, and ionic species. These species are often in equilibrium at least in localized regions.
Several methods that are used to atomize samples for atomic spectroscopy. Inductively coupled plasmas, flames and electrothermal atomizers are the most widely used atomization methods. Flames and electrothermal atomizers are found in atomic absorption spectrometry, while the inductively coupled plasma is used in optical emission and in atomic mass spectrometry.

Classification of Atomic Spectroscopic Methods

<table>
<thead>
<tr>
<th>Atomization Method</th>
<th>Typical Atomization Temperature, °C</th>
<th>Types of Spectroscopy</th>
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</thead>
</table>
| Flame                         | 1700–3150                           | -Absorption
                                      |                                    | -Emission
                                      |                                    | -Fluorescence                     |
| Electrothermal                | 1200–3000                           | -Absorption
                                      |                                    | -Fluorescence                     |
| Inductively coupled plasma    | 6000–8000                           | -Emission
                                      |                                    | -Mass                            |
| Direct-current plasma         | 5000–10,000                         | -Emission                       |
| Electric arc                  | 3000–8000                           | -Emission                       |
| Electric spark                | Varies with time and position       | -Emission                       |
Flame Atomizers

A laminar flow burner used in flame atomic absorption spectroscopy
Properties of Flames

When a nebulized sample is carried into a flame, the droplets are desolvated in the primary combustion zone.

The resulting finely divided solid particles are carried to a region in the center of the flame called the inner cone. Here, in this hottest part of the flame, the particles are vaporized and converted to gaseous atoms, elementary ions, and molecular species.

Finally, the atoms, molecules, and ions are carried to the outer cone, before the atomization products disperse into the atmosphere.
Types of Flames Used in Atomic Spectroscopy

When the oxidant is air, temperatures are in the range of 1700 to 2400°C. At these temperatures, only easily excitable species, such as the alkali and alkaline earth metals, produce usable emission spectra. For heavy-metal species, which are not so easily excited, oxygen or nitrous oxide must be used as the oxidant. These oxidants produce temperatures of 2500 to 3100°C with common fuels.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Oxidant</th>
<th>Temperature, °C</th>
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</thead>
<tbody>
<tr>
<td>Natural gas</td>
<td>Air</td>
<td>1700–1900</td>
</tr>
<tr>
<td>Natural gas</td>
<td>O₂</td>
<td>2700–2800</td>
</tr>
<tr>
<td>H₂</td>
<td>Air</td>
<td>2000–2100</td>
</tr>
<tr>
<td>H₂</td>
<td>O₂</td>
<td>2500–2700</td>
</tr>
<tr>
<td>C₂H₂</td>
<td>Air</td>
<td>2100–2400</td>
</tr>
<tr>
<td>C₂H₂</td>
<td>O₂</td>
<td>3050–3150</td>
</tr>
<tr>
<td>C₂H₂</td>
<td>N₂O</td>
<td>2600–2800</td>
</tr>
</tbody>
</table>
Effects of Flame Temperature

Both emission and absorption spectra are affected by variations in flame temperature. Higher temperatures increase the total atom population of the flame and thus the sensitivity. With elements such as the alkali metals, however, this increase in atom population is more than offset by the loss of atoms by ionization.

Flame temperature determines to a large extent the efficiency of atomization, which is the fraction of the analyte that is desolvated, vaporized, and converted to free atoms and/or ions.

The flame temperature also determines the relative number of excited and unexcited atoms in a flame.

-For example, in an air/acetylene flame, the ratio of excited to unexcited magnesium atoms is about $10^{-8}$, whereas in an oxygen/acetylene flame, which is about 700°C hotter, this ratio is about $10^{-6}$ (100 times higher).

-For example, with a 2500°C flame, a temperature increase of 10°C causes the number of sodium atoms in the excited 3p state to increase by about 3%. 
The optimum region of a flame used in a determination must change from element to element and that the position of the flame with respect to the source must be reproduced closely during calibration and measurement.

Height profiles for three elements in AAS. The plot shows absorbance versus height above the burner for Mg, Ag, and Cr.
**Instrumentation**

The instrumentation for AA can be fairly simple.

![Block diagram of a single-beam atomic absorption spectrometer](image)

single-beam AA spectrometer

Block diagram of a single-beam atomic absorption spectrometer. Radiation from a line source is focused on the atomic vapor in a flame or electrothermal atomizer. The attenuated source radiation then enters a monochromator that isolates the line of interest. Next, the radiant power from the source, attenuated by absorption, is converted into an electrical signal by the photomultiplier tube (PMT). The signal is then processed and directed to a computer system for output.
Line Sources

The most useful radiation source for atomic absorption spectroscopy is the **hollow-cathode lamp** (HCL). It consists of a tungsten anode and a cylindrical cathode sealed in a glass tube containing an inert gas, such as argon, at a pressure of 1 to 5 torr.

The cathode either is fabricated from the analyte metal or else serves as a support for a coating of that metal. If a potential difference of about 300 V is applied across the electrodes, the argon ionizes, and as the argon cations and electrons migrate to the two electrodes, a current of 5 to 10 mA is generated.

The cations strike the cathode with sufficient energy to dislodge some of the metal atoms and to produce an atomic cloud. This process is called **sputtering**. Some of the sputtered metal atoms are in an excited state and emit their characteristic wavelengths as they return to the ground state.
Hollow-cathode lamps for about 70 elements are available from commercial sources. For some elements, high-intensity lamps are available that provide about an order of magnitude higher intensity than normal lamps.

Because a different hollow-cathode lamp is required for each element, only a single element can be determined at a time, and this is the major drawback of AA.

However, some hollow cathode lamps have a cathode containing more than one element and thus provide spectral lines for the determination of several species.
**Hollow Cathode Lamp**
- Emits light of specific wavelength to be absorbed by element

**Atomiser**
- Atomise sample to atomic state
- Atom vapour (gas phase) produced

**Fuel**
- Burning mixture of ethyne with $\text{O}_2$ (combustion mix)
- Sample dehydrated/solvent removed

**Monochromator**
- Select light with specific frequency/wavelength of interest
- Provide the specific light which will be absorb by metal

**Detector**
- Measure the decrease in intensity of light absorb by analyte
- Convert the decrease in light intensity into electrical signal using photomultiplier