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كلية العلـــوم
قــســـــــم الادلة الجنائية

المحاضرة السادسة

Atomic Absorption Spectrometer (AAS)

المادة : كيمياء تحليلية
المرحلة : الثانية
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Introduction:

- Absorption at the molecular level occurs in **UV (Ultraviolet) Spectroscopy** and **Visible Spectroscopy**. As a result of energy absorption, **electronic transitions** take place within atoms in molecules.
- Molecular absorption also occurs in **Infrared (IR) Spectroscopy**, where the absorbed energy causes **vibrational transitions** within molecules. The molecule is excited from the **ground vibrational level** to higher vibrational energy levels.
- These vibrational transitions lead to **bond stretching or bond compression**, or changes in the **bond angles** between atoms within the molecule.
- In contrast, in **Atomic Absorption Spectroscopy (AAS)**, absorption occurs at the **atomic level only**, not at the molecular level.
- Therefore, the element to be measured must first be converted from its molecular form into the **free atomic state** before analysis.
- There are several methods to **excite the atoms of elements** and promote them from the **ground state** to the **excited state**. The simplest method to excite a sample is to **heat it to a high temperature**, which causes excitation due to **collisions between the atoms of the sample**. This method is commonly used in **flame atomic absorption spectrometry**.
- The **Atomic Absorption Spectrometer (AAS)** works by measuring the **wavelengths of photons absorbed** during the excitation of element atoms. By analyzing these absorption wavelengths, the **elements present in the sample** can be identified.
- **Atomic absorption spectrometers** estimate the elements in their solutions as a spectroscopic measurement method. The estimation process involves **atomizing the sample solution** into a fine mist, which is then mixed with a gas mixture such as **acetylene and air** or **acetylene and nitrous oxide**.
- The element is **vaporized into its atomic form** by the flame produced from this gas mixture and is then exposed to a **Hollow Cathode Lamp (HCL)** specific to the element being measured.

Several stages occur in the sample during flame atomic absorption:

1. **Evaporation (Dehydration):** The sample is dried by the flame, and the solvent evaporates.
2. **Dissociation:** Molecules break down into individual atoms.
3. **Atomization:** Metal ions dissolved in the sample are reduced to free atoms. For example:

$$\mathrm{Mg}^{2+}(aq) + 2e^{-} \rightarrow \mathrm{Mg}(g)$$

4. **Excitation:** Electrons in the metal atoms absorb energy from the flame and move to higher energy levels. The amount of energy absorbed depends on **electrostatic forces** between the negatively charged electrons and the positively charged nucleus (related to the number of protons). After absorbing energy, electrons reach an **excited state**.

*At this stage, the **energy required for excitation**—that is, the **absorbed energy**—can be measured using a **Flame Atomic Absorption Spectrometer (FAAS)**.

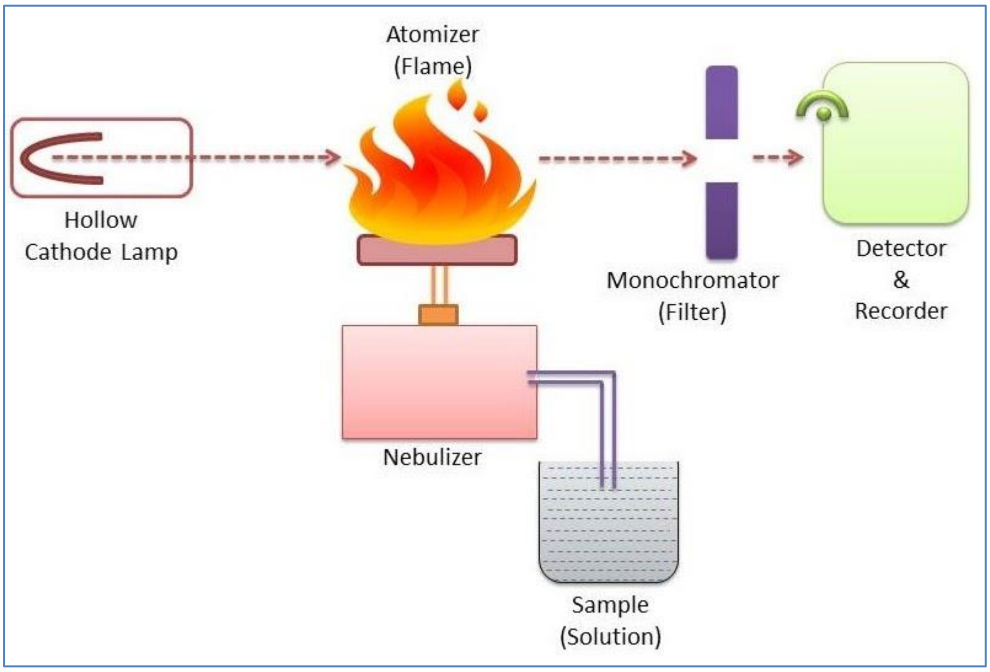

Figure 1:Flame atomic absorption spectrometer

Techniques for Atomic Absorption Determination:

There are several **techniques** to determine the atomic absorption of elements, which **vary depending on the type and concentration of the element** in the sample.

1. Flame Atomic Absorption (Direct Aspiration method)

- The element is **atomized in a flame**.
- A **Hollow Cathode Lamp (HCL)** of the same element passes light through the flame.
- The **absorbed light** is measured by a detector.
- Absorption depends on **ground-state free atoms**.
- Suitable for **element concentrations in the ppm range**.

2. Flameless Atomic Absorption

The element can be **converted to its atomic form by methods other than a flame**, such as:

- ✓ Using **electric furnaces**.
- ✓ Generating **volatile gaseous hydrides** for elements like **arsenic, selenium, antimony, and tin** by adding a reducing agent.
- ✓ Utilizing **chemical properties** like **sublimation** for elements such as **mercury**, where the element vaporizes **without flame or furnace heating**.

Here's a concise English summary in **bullet points** for the two methods of atomic absorption:

A. Graphite Furnace Method:

- ✓ More sensitive than flame methods, allowing **detection down to ppb (parts per billion) levels**.
- ✓ The sample is placed in a **graphite tube inside an electric furnace**, where it is **dried, ashed, and atomized**.
- ✓ The **fraction of atoms available for energy absorption** is higher than in direct flame, making it suitable for **trace element analysis**.

- The detection principle is similar to flame AAS, except the **furnace performs atomization** instead of the flame.

B. Hydride Generation Method:

- An older technique for atomic absorption used to **separate volatile gaseous hydrides** from elements like **arsenic, selenium, antimony, and tin**.
- A **reducing agent** (e.g., **borohydride** or **lithium aluminium hydride**) is added to a large sample volume.
- The **volatile hydride** is carried to the **burner head** of the atomic absorption system.
- The chemical reaction occurs in a **Hydride Generator**, which produces the hydrides for measurement.

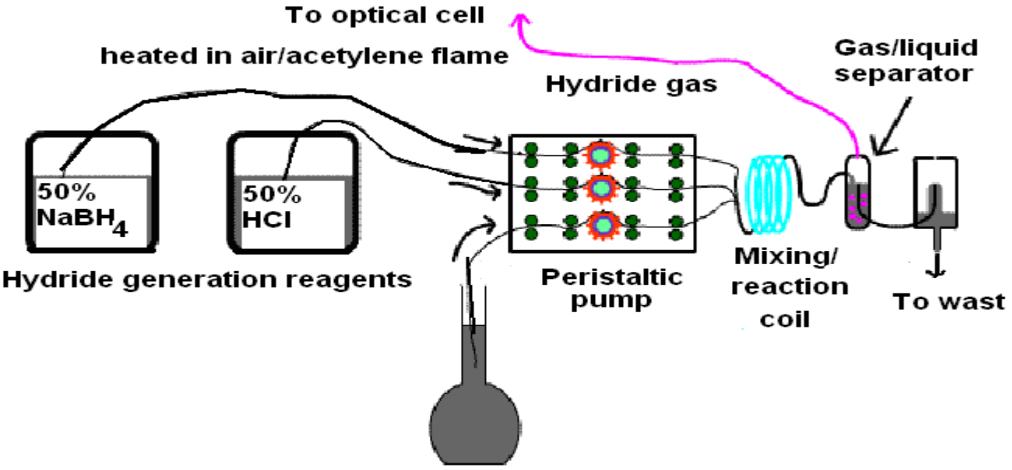

Figure 2: Hydride Generation Method

C. Cold Vapor Method:

- A chemical method used for **mercury (Hg) determination**.
- Based on **sublimation**, where mercury converts directly from solid or dissolved form to **atomic vapor**.
- Mercury vapor is **separated from the aqueous sample solution**.

- ☐ **Stannous chloride ($SnCl_2$)** is used as a **reducing agent** to release mercury from the solution.
- ☐ **Argon or air** is used to **flush the atomic vapor** through a **150 mm quartz flow-through absorption cell**.
- ☐ The absorption cell is **mounted on the burner head** of the atomic absorption spectrometer for measurement.

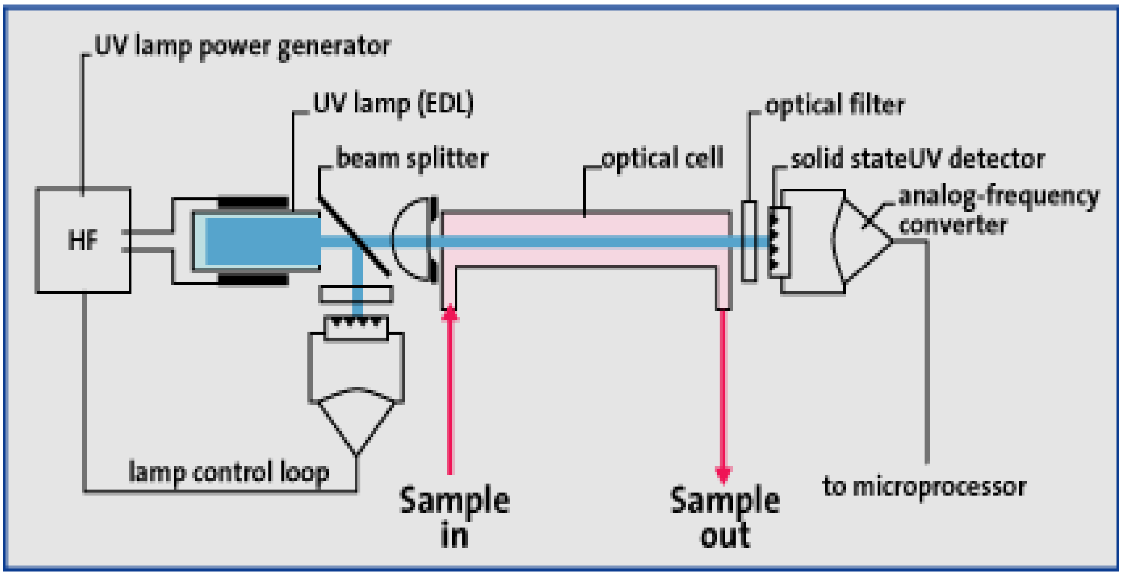

Figure3: Cold Vapor Method

Sample Preparation:

1) **Prepare an acidified standard solution** of the element.
2) **Prepare a series of concentrations** within a specific range:

- **ppm range** for direct flame AAS.
- **ppb range** for graphite furnace AAS.
- The sample should be in an **acidified aqueous solution** (e.g., 10% nitric acid in redistilled deionized water).

3) Introduce the blank for the standard solution, then the **element standard solution** into the instrument.

4) Introduce the blank for the samples, then the **sample solutions** containing the element to be measured:

- The sample is drawn into the instrument via a **sampling tube**.
- The solution is converted into a **fine mist**, which is then mixed with the gas for atomization and measurement.

Types of Atomic Absorption Spectroscopy (AAS) for elements:

1. **Single-Beam Atomic Absorption Spectrometer (Single Beam AAS)**
   Measurements in a single-beam atomic absorption spectrometer rely on passing a **single light beam** through the sample in the flame. One of the disadvantages of this spectrometer is that the readings are affected by any errors or fluctuations in the light source. To overcome these fluctuations in light intensity, the **hollow cathode lamp** is heated before starting the measurements, but this also affects the lamp's **lifetime**.

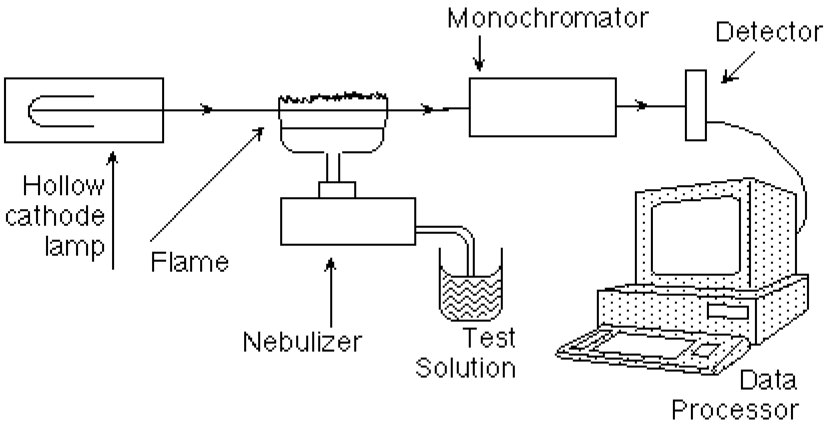

Figure4: Single-Beam Atomic Absorption Spectrometer

2. **Double-Beam Atomic Absorption Spectrometer (Double Beam AAS)**
   Measurements in a double-beam atomic absorption spectrometer are based on splitting the light from the source into **two parts**: one part passes through the sample in the flame (**sample beam**), and the other part bypasses the flame (**reference beam**).

This reference beam is used as a **monitor of the light source intensity**.

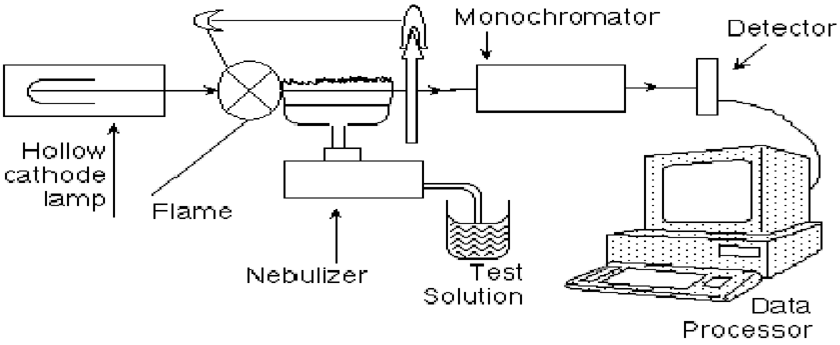

Figure 5: Double-Beam Atomic Absorption Spectrometer

Components of the Atomic Absorption Spectrophotometer (AAS)

1- Light Source

- The light source in Atomic Absorption Spectrophotometry (AAS) is the **Hollow Cathode Lamp (HCL)**. It emits radiation in the wavelength range of 190–800 nm.
- Each element has its own specific lamp that serves as its characteristic radiation source. The light source emits the atomic spectrum of the element to be determined, and the lamp is named after that element.
- For example, a lead lamp is used for the determination of lead, a copper lamp is used for the determination of copper, and so on.

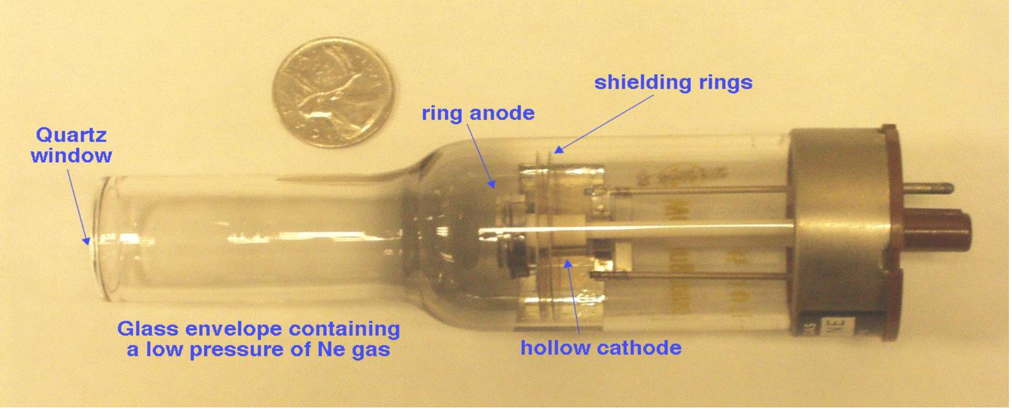

Figure 6:Hollow Cathode lamp

2- **Atomizer**

Converts the sample into free ground-state atoms. It can be:

- Flame atomizer (Flame AAS)
- Graphite furnace atomizer (Electrothermal AAS)

3- **Nebulizer and Spray Chamber**

The nebulizer converts the liquid sample into a fine aerosol, while the spray chamber removes larger droplets before the sample enters the flame or furnace.

4- **Monochromator**

Isolates the specific wavelength of interest from other emitted wavelengths and background radiation.

5- **Detector**

Usually a photomultiplier tube (PMT) that measures the intensity of transmitted light and converts it into an electrical signal.

6- **Signal Processor and Readout System**

Amplifies, processes, and displays the signal as absorbance or concentration.

Quantitative Analysis by Atomic Absorption Spectrophotometry (AAS)

When a light beam of intensity (I_0) passes through the flame containing the element to be determined, part of the radiation is **absorbed**, while the remaining part is **transmitted**.

The absorbed portion of the radiation is expressed as **percentage absorption (% Absorption)**. This relationship can be mathematically described using **Lambert–Beer's Law**.

Absorbancy (A) = Log ($I_\circ$ - I)

= Log 100 / %T

= Log 100 - Log % T

= 2 – Log % T

A = Absorbance

I_0 = Intensity of incident radiation

I = Intensity of transmitted radiation

ε = Molar absorptivity (extinction coefficient)

b = Path length (cm)

c = Concentration of the element

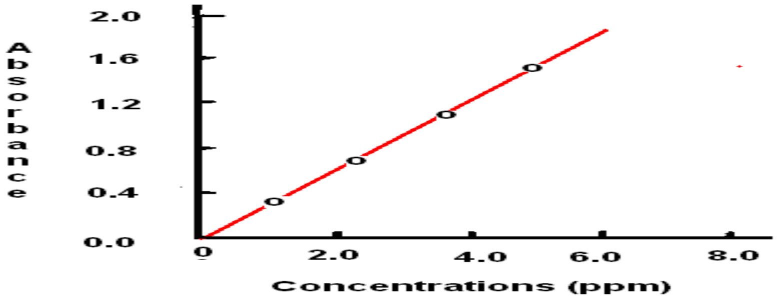

Figure 7: The Relationship Between Absorbance and the Concentration

Sensitivity

Sensitivity in Atomic Absorption Spectrophotometry (AAS) is defined as the concentration of the element to be determined in solution, expressed in **mg/L**, that absorbs **1% of the radiation** emitted from the element-specific light source.

Alternatively, sensitivity can be defined as the concentration of the element (mg/L) that produces an **absorbance of 0.0044**, according to **Lambert–Beer's Law**.

$A = \text{Log } 100 - \text{Log } \%T$

$\% A = 100 - \% T$ ……………………………(1)

$\% T = 100 - \% A$, $\% A = 1$

$\% T = 100 - 1 = 99$ …………………………..(2)

From (1) and (2)

$A = \text{Log } 100 - \text{Log } 99 = 2 - 1.9956 = 0.0044$

Sensitivity is the concentration that gives an absorbance of **0.0044** or **1% absorption** of the incident radiation.

Detection Limit (LOD) :is the lowest concentration that can be reliably detected (at 95% confidence), giving a signal distinguishable from background noise—typically equal to about **twice the standard deviation of the blank**.

Chemical Interference in Atomic Absorption Spectrophotometry (AAS)

Chemical interferences occur when other substances in the sample **affect the absorption of the analyte**, leading to inaccurate results. Common sources of chemical interference include:

1. **Formation of stable compounds**
    - The analyte may react with other components to form **non-volatile or stable compounds** that do not atomize properly in the flame or furnace.
2. **Precipitation**
    - The analyte may **precipitate** before atomization, reducing the free atom concentration.
3. **Oxidation or reduction reactions**
    - Other sample constituents may **oxidize or reduce the analyte**, altering its absorption characteristics.
4. **Matrix effects**
    - High concentrations of salts or other elements can change the **flame temperature** or **atomization efficiency**, affecting absorbance.
5. **Chemical modifiers**
    - Some additives may interact with the analyte or matrix, either **enhancing** or **suppressing** its signal.

Identifying and correcting for chemical interferences is essential for accurate quantitative analysis.

Methods to Overcome Chemical Interferences in AAS

To minimize or eliminate chemical interferences during Atomic Absorption Spectrophotometry, the following strategies are commonly used:

1. **Use of Chemical Modifiers**
    - Add reagents (e.g., **matrix modifiers** like ammonium phosphate, magnesium nitrate) that **stabilize the analyte** and prevent formation of non-volatile compounds.
2. **Dilution of Samples**
    - Diluting the sample can reduce the concentration of interfering species, **minimizing their effect** on atomization.
3. **Optimizing Flame or Furnace Conditions**
    - Adjust **flame composition** (fuel/oxidant ratio) or **graphite furnace program** to improve atomization of the analyte.
4. **Masking Agents**
    - Add chemicals that **bind interfering ions** without affecting the analyte.
5. **Matrix Matching / Standard Addition**
    - Prepare calibration standards with the **same matrix** as the sample, or use **standard addition** to compensate for matrix effects.
6. **Separation Techniques**
    - Remove interfering species before analysis using **precipitation, filtration, or extraction** methods.

By applying these methods, accurate and reliable determination of trace elements in complex samples can be achieved.