Chapter 3. Atomic Absorption Spectrophotometry :

1-Introduction

Atomic absorption spectroscopy (AAS) is a very powerful elemental analysis method, widely used in chemistry, biology, environment and in the pharmaceutical industry. It allows to **detect and quantify metallic elements** present in trace amounts in various samples. Based on the interactions between **light** and **atoms in the ground state** , this technique is based on a simple but rigorous principle: a **free atom selectively** absorbs a wavelength of light corresponding to the **electronic transition** of its electrons. Developed in the 1950s, AAS combines precision, sensitivity and selectivity, making it an essential tool in modern analytical laboratories.

2. Principle

The basic principle is based on **the absorption of light** by **free atoms** in a **gas** .

- A specific **light source** (often a hollow cathode lamp) emits a wavelength characteristic of an element.
- The sample is **atomized** (usually in a flame or graphite furnace), releasing the atoms in a gaseous state.
- These atoms **absorb** part of the incident light at a very specific wavelength.
- The **amount of light absorbed** is proportional to the **concentration of the element** in the sample, according to the **Beer -Lambert law** .

3. Applications

SAA is used in many areas:

- **Environmental analysis** : detection of heavy metals (lead, mercury, cadmium) in water, soil or air.
- **Pharmaceutical industry** : control of the purity of raw materials, dosage of trace elements.
- **Food industry** : metal detection in food and beverages.
- **Medical** : analysis of trace elements in blood, urine or tissues.
- **Metallurgy** : control of the composition of alloys.

Atomic absorption spectroscopy allows the detection and quantification of the majority of metallic elements in the periodic table, in particular transition metals, alkalis and alkaline earths, with high sensitivity even at trace levels.

4. Kirchhoff's experiments

Kirchhoff's three experiments demonstrate the principles of atomic absorption and emission.

- polychromatic light through a prism, a continuous spectrum is obtained.
- By replacing the polychromatic light with a Bunsen burner , in which a metallic salt burns, we see the bright lines that characterize the element appear. We therefore obtain the emission spectrum of this element.
- By combining the two experiments, we obtain the absorption spectrum of the metal salt. We therefore see the same thing appear as in the first experiment, except that in the places where the emission lines of the second experiment appeared, we notice dark lines. This is due to the presence in the flame of a large proportion of atoms remaining in the ground state which absorb the light radiation of polychromatic light at the characteristic wavelengths of the element, which is a manifestation of atomic absorption.

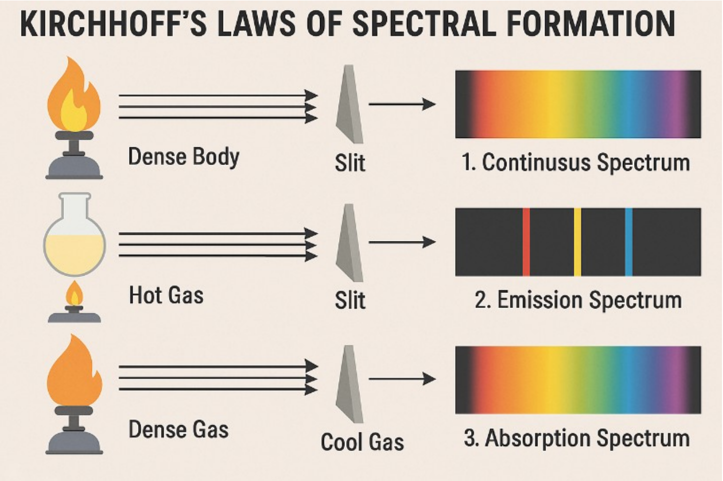


Fig.1: Kirchhoff's Laws of Spectral Formation

Understand how different materials emit or absorb light, and how chemical elements can be identified from their spectra.

Experimental device:

1. **Heat source** :A **Bunsen burner** heats a small amount of a chemical element (for example, sodium, lithium, or potassium).
2. **Gas or vapor** : Heat transforms the sample into **atomic gas or vapor** .
3. **Spectroscope or prism** : The light emitted by these hot vapors is directed towards a **prism** (or diffraction grating), which **separates the light into its different wavelengths** .
4. **Observation** : The decomposed light is observed through an **eyepiece** against a **black background** , revealing a **spectrum composed of colored lines** .

Result 1 – Emission spectrum

When the hot gas is observed **alone** , it produces an **emission spectrum with lines** :

- **bright lines** appear at specific positions, characteristic of the heated element. For example: **sodium** gives two very close yellow lines (sodium doublet around 589 nm).

Result 2 – Absorption spectrum

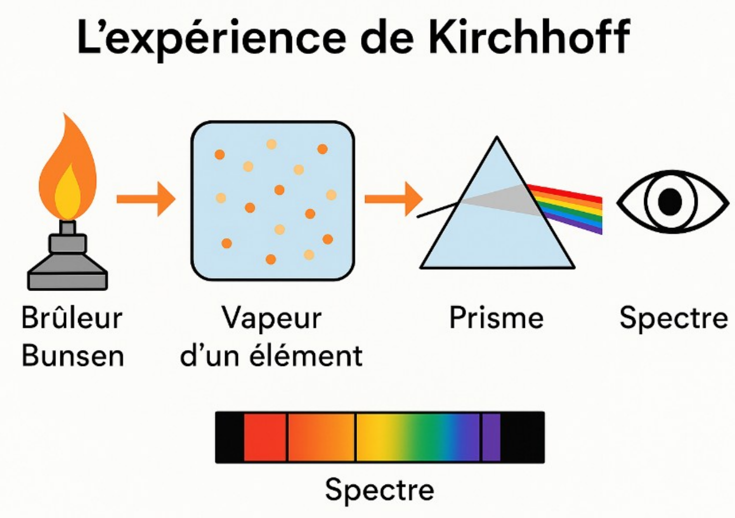
Next, Kirchhoff places a **white light source** (like a heated filament) behind a layer of **cold gas** (same gas as before).

- When white light passes through cold gas, certain **wavelengths are absorbed** by atoms in the gas.
- Looking at the spectrum, we see a **continuous spectrum** , but with **dark lines at the same positions** as the colored lines seen previously in the emission. This proves that **atoms absorb the same wavelengths that they emit** !

Scientific interpretation:

Kirchhoff understands that:

- Chemical elements **have a unique spectral signature** .
- **An element** can be identified from the **colored** (emission) or **dark** (absorption) lines in a spectrum.



Summary :

Case	Source	Result	Example
1. Continuous spectrum	Dense and warm body	Full rainbow	Sun, light bulb
2. Emission spectrum	Hot gas	Colored stripes on a black background	Neon tube
3. Absorption spectrum	White light + cold gas	Dark lines on continuous spectrum	Sunlight through atmosphere

5. Principle of Atomic Absorption Spectrometry (AAS)

Main steps:

a) **Radiation source:**

- A **hollow cathode lamp (HCL) emits** light characteristic of a specific chemical element.
- This light is **monochromatic** , that is to say it corresponds to precise wavelengths absorbed by the element to be analyzed.

b) **Modulation by the chopper (optical chopper):**
  - A **chopper (rotating disc)** periodically interrupts the light beam to **differentiate between the signal from the lamp and the stray or emission light from the flame/oven** .
  - This allows **the light to be modulated** for better sensitivity and to distinguish **absorbed radiation from emitted** radiation .

c) **Atomized sample (usually in gas form):**
  - The sample is **introduced in liquid or solid form** , then it is **nebulized and atomized** in:
    - A **flame** (flame SAA) or
    - A **graphite furnace** (electrothermal SAA).
  - At this stage, **free atoms in the gas phase** are present and can **absorb the light** emitted by the lamp.

d) **Light absorption:**
  - Light **passes through the cloud of gaseous atoms** in the sample.
  - The **atoms of the element under study absorb** part of this light at a specific wavelength.
  - The higher the concentration, **the greater the absorption (** Beer -Lambert law).

e) **Monochromator:**
  - It **selects the wavelength** of interest (the one absorbed by the element to be analyzed).
  - This **eliminates interference** from other wavelengths.

f) **Detector:**
  - It measures **the intensity of the beam after absorption** .
  - The difference between the initial intensity and the measured one allows **the concentration** of the element to be determined.

g) **Signal processing (amplification, display):**
  - The signal is amplified, processed by electronics, and then converted into a **concentration value** .

The term "chopper" can have several meanings depending on the context, but in the field of spectroscopy and atomic absorption, a **chopper** generally refers to a device that allows light or signal to be modulated.

5.1 Role of the Chopper in Spectroscopy

a) **Signal Modulation** : A chopper varies the intensity of the light emitted by the source. This creates alternating signals that can be more easily detected and analyzed.

b) **Noise Reduction** : By modulating the light signal, the chopper helps distinguish the signal of interest (coming from absorption) from background noise, which improves the sensitivity of the measurement.

c) **Synchronization** : The chopper can be synchronized with the detector to only pick up signals at specific times, improving measurement accuracy.

d) **Improved Selectivity** : By filtering wavelengths of light, the chopper allows you to focus on specific absorption lines for more precise analysis of elements.

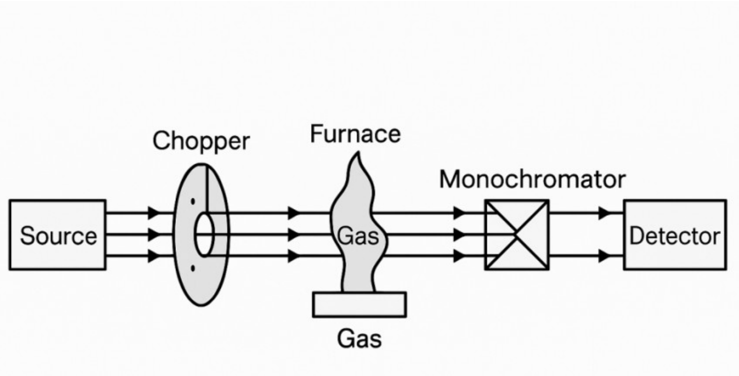


Fig 3. Diagram of the SAA principle

5.2 What is the role of the chopper?

The **chopper** is a **rotating disc** with openings (holes) that periodically interrupts the light beam coming from the **hollow cathode lamp** . It acts as an **optical switch** .

- **Why do we need it?**

When light passes through the **flame** or **graphite furnace** , there are two types of radiation that can reach the detector:

a) **Lamp light (HCL)** : this is the one we are interested in, because it is absorbed by the atoms in the sample.

b) **Light emitted by the flame or the oven** : this is **parasitic light** , which can distort the measurements.

How does the chopper solve this problem?

The chopper **quickly alternates** between two situations:

a) **When the light from the lamp passes through** (hole in the disc):

- The detector receives **the total intensity** : absorbed light + stray light.

b) **When light is blocked (opaque disc)** :

- The detector **only receives stray light** (because the lamp is switched off).

Then, the system **makes the difference** between the two measurements to **keep only the light absorbed by the sample** , that is to say that due to the lamp.

Conclusion: Chopper is a rotating device located between a hollow cathode lamp and a flame. This process eliminates macroscopic drops and facilitates the entry of drops of homogeneous dimensions into the combustion zone. The continuous light from the lamp is modulated in a pulsed form. The pulsed current in the solar cell is amplified and recorded without any known interference.

There are several other devices and techniques that can be used in atomic absorption spectroscopy to improve the quality of measurements, in addition to the chopper. Here are some examples:

a) **Frequency Modulators:** These devices modulate the frequency of the light emitted by the source to improve the detection of the signal by the detector.

b) **Optical Filters:** Filters can be used to select specific wavelengths, thereby minimizing background noise and improving measurement selectivity.

c) **Photomultiplier Detectors:** These detectors amplify the light signal and improve sensitivity, allowing the detection of very low concentration levels.

d) **Time-of-Flight Detection Systems:** Used to measure the time it takes for atoms to reach the detector, helping to distinguish signals from different elements.

e) **Pulsing Technologies:** Pulsing systems can be used to generate alternating light signals, similar to those produced by a chopper, but often with different methods.

f) **Spectrum Analyzer:** These instruments analyze the light spectrum in real time, allowing precise identification of the elements present in a sample.

5.3 Types of light sources:

In atomic absorption spectroscopy, several types of light sources are used to excite atoms and produce the absorption spectrum. Here are the main ones:

1. Hollow Cathode Lamp

- **Description** : This lamp contains an inert gas (such as argon) and a metal cathode of the element to be analyzed.
- **Use** : It emits a light characteristic of the element when a current passes through the gas, which excites the atoms of the cathode.

2. Discharge Lamp Lamp)

- **Description** : Similar to the hollow cathode lamp, but uses an electrical discharge to excite the gas.
- **Use** : Used for specific elements, it produces an emission spectrum that can be used for analysis.

3. Continuous Light Source

- **Description** : A source that emits continuous light over a broad spectrum, such as an incandescent lamp.
- **Use** : Less common in atomic absorption, it can be used for certain types of analyses where a continuous spectrum is required.

4. Laser Source

- **Description** : A laser emits a very precise and intense monochromatic light.
- **Use** : Used for specific applications requiring high wavelength accuracy.

5. Quartz Lamp

- **Description** : A lamp that uses a quartz tube to produce ultraviolet light.
- **Use** : Used in certain analytical methods, particularly for UV analyses.

5.4 Types of flame burners:

In atomic absorption spectroscopy, different types of flame burners are used to atomize samples. The main types of burners are:

1. Bunsen Flame Burner

- **Description** : Uses an open flame fueled by a mixture of gas (usually propane or acetylene) and air.
- **Use** : Commonly used for simple analyses; the flame is adjustable to reach different temperatures.

2. Nitrogen Flame Burner

- **Description** : Uses a mixture of fuel gas and nitrogen to create a cooler, more controlled flame.
- **Use** : Popular for the analysis of heat-sensitive elements.

3. Brass Flame Burner

- **Description** : Made of brass, this burner is designed for even heat distribution.
- **Use** : Used for applications requiring efficient atomization.

4. Quartz Flame Burner

- **Description** : Made of quartz, this burner withstands higher temperatures and allows better light transmission.
- **Use** : Used for analyses where signal clarity is essential.

5. Argon Flow Flame Burner

- **Description** : Uses an argon flow to stabilize the flame and improve atomization.
- **Use** : Used for trace or delicate element analyses.

Conclusion

The choice of flame burner depends on the element to be analyzed, the nature of the sample, and the requirements of the experiment. Each type of burner has its advantages in terms of temperature control, flame stability, and atomization efficiency. If you need more details on a specific type, please don't hesitate to ask!

5.6 Types of detectors

In atomic absorption spectroscopy, several types of detectors are used to measure the intensity of light absorbed by atoms in the flame. The main types of detectors are:

1. Photomultiplier (PMT)

- **Description** : A highly sensitive detector that amplifies the light signal using a secondary electron emission process.
- **Use** : Ideal for low-light measurements. Prized for its speed and sensitivity.

2. Diode Detector (Photodiode)

- **Description** : Uses a semiconductor to convert light into electric current.
- **Use** : Less sensitive than PMT but more compact and less expensive. Used for applications where extreme sensitivity is not required.

3. CCD (Charge- Coupled) Detector Device)

- **Description** : A type of image sensor that converts light into electrical signals, often used in modern spectrometers.

- **Use** : Allows multiple wavelengths to be captured simultaneously. Used for complex spectral analyses.

4. Thermopile Detector

- **Description** : Measures the heat generated by the absorption of light, transforming this heat into an electrical signal.
- **Use** : Used for measurements in wider wavelength ranges, including infrared.

5. Phototransistor Detector

- **Description** : A type of transistor that functions as a light detector.
- **Use** : Less sensitive than PMTs and photodiodes, but used in less demanding applications.

Conclusion

The choice of detector depends on various factors, including the required sensitivity, wavelength range, and sample type. Each type of detector has its advantages and disadvantages in terms of cost, sensitivity, and complexity. If you would like more information on a specific detector, please don't hesitate to ask!

6. Types of Atomic Absorption Spectrometers

1. Single Beam AAS

Principle:

- The **light** from the lamp passes **directly through the sample** , then goes to the **detector** .
- There is no direct real-time **reference .**
- To compare, the user **first measures a blank** (without the sample), then the sample.

Features :

Benefits	Disadvantages
- Less expensive	- Less stable in the long term
- Simpler design	- Sensitive to variations in lamp intensity, drifts, etc.

2. Double Beam AAS

Principle:

- The light beam of the lamp is **split into two** :
  - **A beam passes through the sample** .
  - **The other passes through a reference cell (white or air)** .
- The two signals are compared **in real time** by the system.

Features :

Benefits	Disadvantages
- Very good stability	- More **complex** and more expensive

- Automatically corrects lamp variations	- Requires good optical alignment

Atomic Absorption Spectroscopy (AAS) exists in several variants, depending on the **sample introduction method** , the **atomization source** , or the **detection technique** . Here are the **main types of AAS** :

- **a.** Flame AAS
- **b.** Electrothermal SAA (Graphite Furnace AAS or GFAAS)
- **c.** Cold Vapor AAS (CVAAS)
- **d.** Hydride Generation AAS (HGAAS)
- **e.** Flameless SAA (Flameless SAA)
- **f.** SAA coupled with modern techniques

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