ATOMIC ABSORPTION SPECTROSCOPY

SPECTROSCOPY

- Spectroscopy is **the study of the absorption and emission of light and other radiation by matter**.
- It involves the splitting of light (or more precisely electromagnetic radiation) into its constituent wavelengths (a spectrum), which is done in much the same way as a prism splits light into a rainbow of colours.

GENERAL PRINCIPLE

- The basic principle shared by all spectroscopic techniques is to shine a beam of **electromagnetic radiation** onto a sample, and observe how it responds to such a stimulus. The response is usually recorded as a function of radiation wavelength.

TYPE OF SPECTROSCOPY

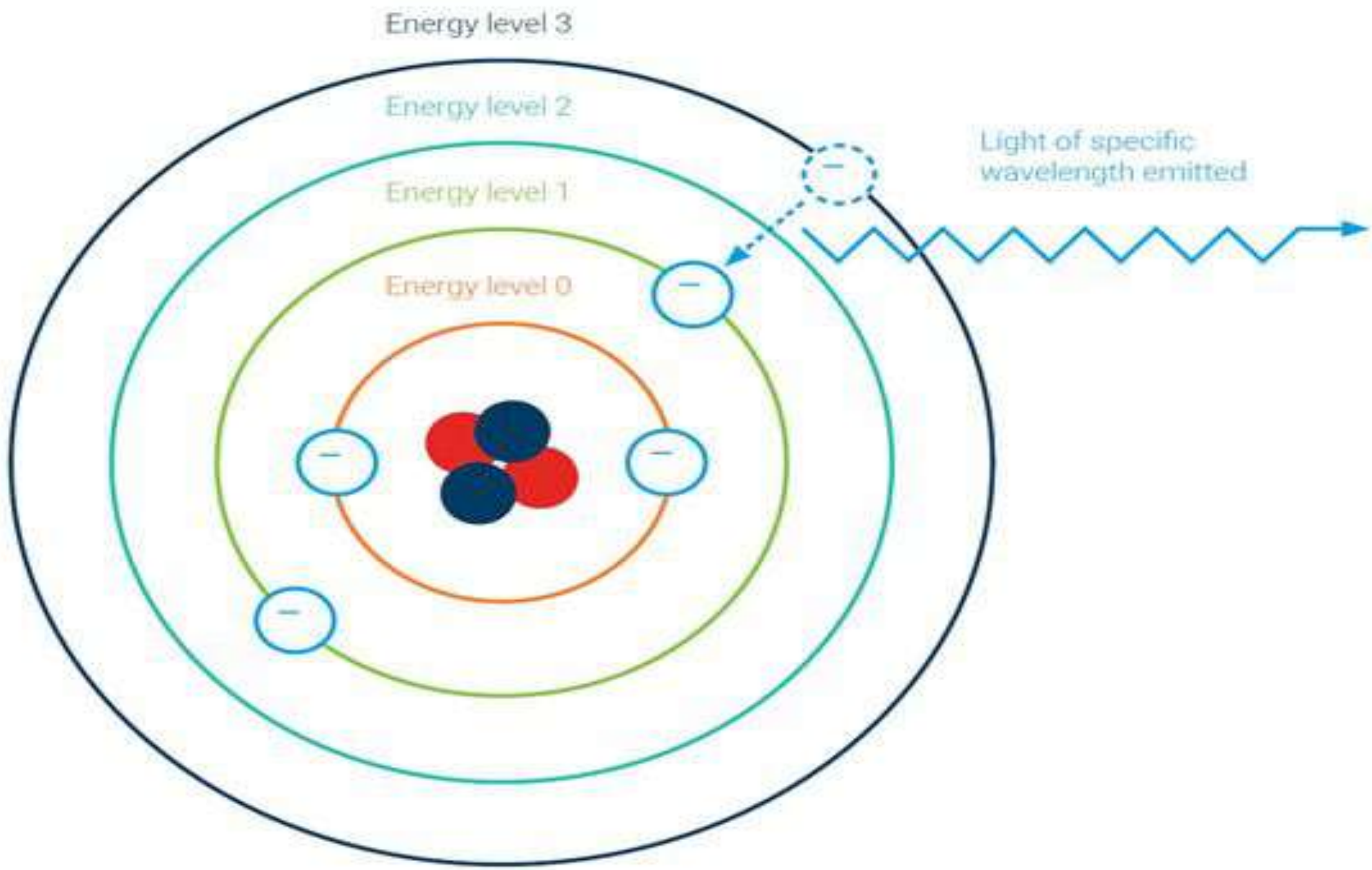
The main types of atomic spectroscopy include:

1. **Atomic absorption spectroscopy (AAS),**
2. **Atomic emission spectroscopy (AES)**
3. **Atomic fluorescence spectroscopy (AFS)**

Now, we will discuss Atomic Absorption spectroscopy in detail:

ATOMIC ABSORPTION SPECTROSCOPY

- AAS is an analytical technique used to determine how much of certain elements are in a sample. It uses the principle that atoms (and ions) can absorb light at a specific, unique wavelength.
- When this specific wavelength of light is provided, the energy (light) is absorbed by the atom. Electrons in the atom move from the ground state to an excited state. The amount of light absorbed is measured and the concentration of the element in the sample can be calculated.
- It can analyze over 62 elements.
- The first atomic absorption spectrometer was built by CSIRO scientist Alan Walsh in 1954.



An electron is excited from the ground state to higher energy level by absorbing energy (light) at a specific wavelength. In atomic absorption spectroscopy, the wavelength of absorbed light is determined by the type of atom (which element it is) and the energy levels the electrons are moving to. How much light is absorbed is determined by the concentration of the element in the sample.

Principle of AAS

- The technique uses basically the principle that free atoms (gas) generated in an atomizer can absorb radiation at specific frequency.
- Atomic-absorption spectroscopy quantifies the absorption of ground state atoms in the gaseous state.
- 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.
- Concentration measurements are usually determined from a working curve after calibrating the instrument with standards of known concentration.
- Atomic absorption is a very common technique for detecting metals and metalloids in environmental samples.

Theory behind AAS

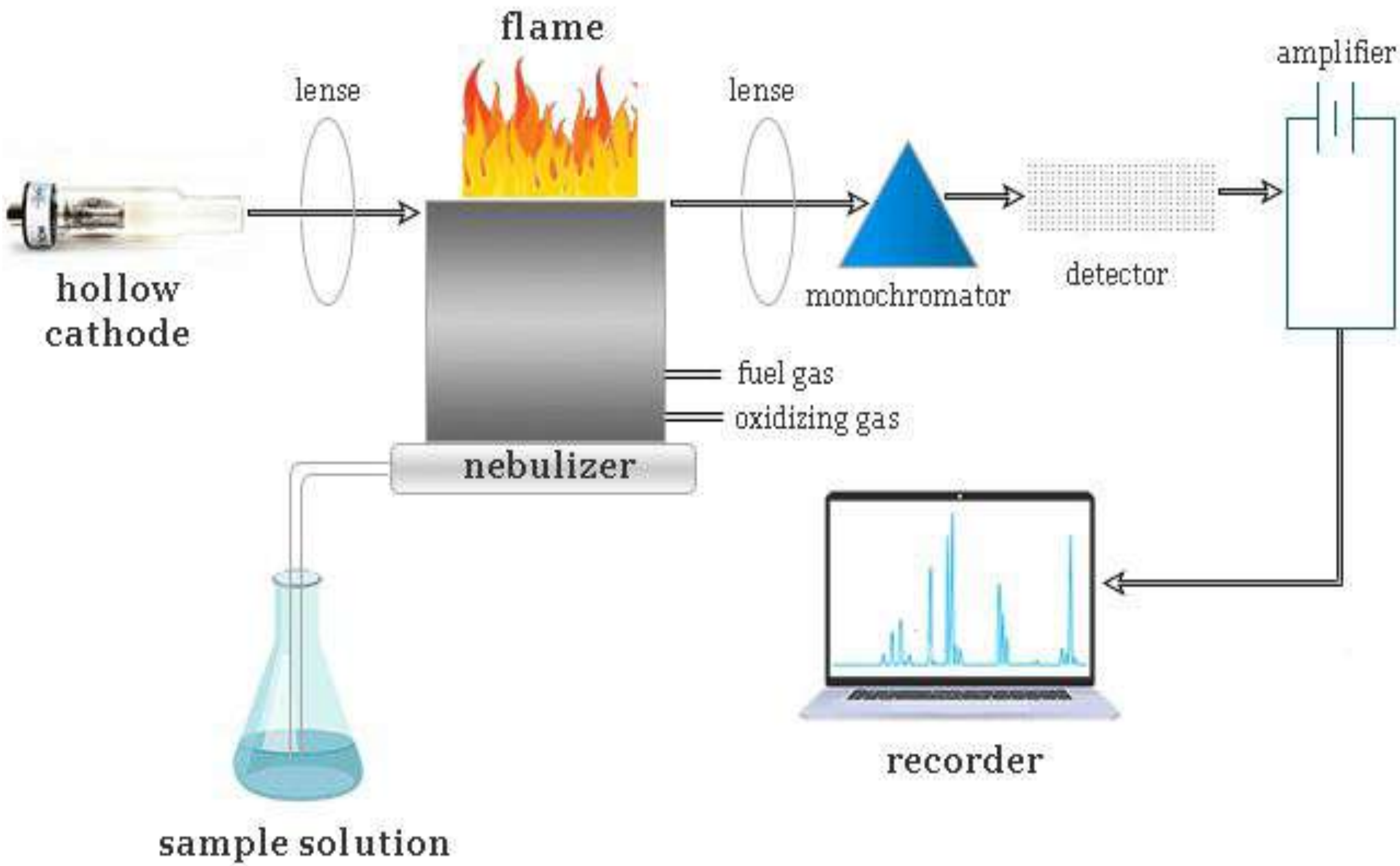
- When a solution containing the metallic species is introduced into a flame, the vapours of metallic species will be obtained. Some of the metal atoms may be raised to an energy level sufficiently high to emit the characteristic radiation of the metal during their return but a large percentage of metal will remain in the non-emitting ground state.
- Now, These ground state elements are receptive of light radiation of their own specific wavelength. Thus when a light of this wavelength is allowed to pass through a flame having atoms of metallic species, part of light is absorbed and the absorption is directly proportional to the density in the flame.

Atomic absorption spectrometer

The AA spectrometer works by:

- Creating a steady state of freely dissociated ground state atoms using a heat source (flame)
- Passing light of a specific wavelength through the flame. The wavelength corresponds to the amount of energy required to excite an electron from (typically) the ground to first excited state for a specific element.
- Measuring the amount of the light absorbed by the atoms as they move to the excited state (the atomic absorption).
- Using the measured absorbance to calculate the concentration of the element in a solution, based on a calibration graph.

Atomic absorption spectroscopy



1. BURNER

- The atomic absorption spectrometer (AAS) burner provides a steady state of ground state atoms. In flame AAS, the burner converts the aerosol/gas mixture created by the spray chamber and nebulizer, into free, ground state atoms.
- The burner is specially designed with a thin slit, that is 5–10 cm long, depending on the type of burner used. The slit defines the length of the flame in the spectrometer where the population of free ground state atoms exist. The length of the flame determines the light path passing through the atoms, which determines the sensitivity, according to the Beer-Lambert Law.
- The burner height is also able to be raised or lowered. This allows the light source to be passed through the area of the flame that provides the best sensitivity for the selected analyte.

1. BURNER

- The Flame burner is the most popular atomization source, there are other alternatives that provide specific advantages. The most common atomization sources are:
- **Graphite Furnace** : Using electrothermal heating, a graphite tube provides a small, contained area for atomization. The high temperature capabilities and containment of the sample allows for complete atomization. Graphite furnace AAS (GF-AAS) is able to detect some elements down to ppb levels.
- **Hydride Generator**: Hydride-forming elements; As, Se, Sb, Bi, and Pb, are reacted to form a gaseous hydride. An acidified sample solution is added to a solution of sodium borohydride in a specially designed reaction cell. The resultant volatile hydride gas is passed into an optical cell (fused silica glass tube), where it can be electrothermally or flame heated. At high temperature, volatile hydrides decompose into neutral metal atoms that can absorb light from a hollow cathode lamp.

2. HOLLOW CATHODE LAMP

- A HCL is the most common light source used with an AA spectrometer. The light source is a critical component. It is the absorbance of the light from the lamp as it passes through the atomized sample, that is measured.

Process:

- Hollow cathode lamps are filled with an inert ‘filler’ gas at low pressure, usually argon or neon. A metal cathode, coated in the element of interest, is positioned opposite an anode. A high voltage is applied, across the two electrodes, which ionizes the filler gas accelerating ions toward the cathode.
- The cathode is bombarded by these ions with enough energy that metal atoms from the cathode material are ejected or “sputtered” creating an atom plume. Inside the atom plume, further collisions between metal atoms occurs raising them to an excitation state.
- When the atoms return to their preferred ground state, radiation is emitted, as light, at the characteristic wavelengths of that specific element.

3. THE MONOCHROMATOR

- The hollow cathode lamp emits many narrow emission lines. A monochromator is used to isolate a single resonance emission line. This happens after the light passes through the sample within the atomization source, e.g. the flame.
- A Monochromator is an optical device with the sole purpose of collecting light containing many wavelengths and isolating (selecting) a narrow wavelength band.
- A simple monochromator consists of the:

1. Entrance slit: This is at the entry of the monochromator immediately after the light beam passes through the flame. The entrance slit effectively confines the source radiation to narrow beam.
2. Internal mirrors: These direct the light through monochromator.
3. Dispersing element: At the heart of the monochromator, the dispersing element takes the light and disperses the radiation into its component wavelengths (you may be familiar with a prism that separates white light into a rainbow).
4. Exit slit: This is the exit from the monochromator. The wavelength selected for analytical measurement is focused onto the exit slit where it will then pass to the optical detector for measurement. All other wavelengths will remain inside the monochromator.

4. THE DETECTOR

- The most used detector in atomic absorption spectrometer is the photomultiplier tube (PMT).
- The PMT converts incident light to an electrical signal allowing measurement of the light's intensity. The light from the exit slit of the monochromator enters the PMT and hits a photodiode, creating an electrical signal.
- A series of dynodes amplify the signal and then it is collected (measured) on an anode and used to provide a quantitative measurement of absorption.