Flame Atomic Absorption Spectrometry

F-AAS

Atomic Absorption Spectrometry

- It measures the radiation absorbed by the unexcited atoms that are determined.
- AAS is procedure applied by free atoms for the quantitative as well as qualitative determination of components that use a certain wavelength region in the gaseous state.
- The system is employed to determine metals in various specimens, including environment, foods, forensic, and industrial waste and drugs

Relationship Between Atomic Absorption and Flame Emission

- **Flame Emission measures** the radiation emitted by the excited atoms that is related to concentration, and the flame serves *a dual purpose*: it converts the sample **aerosol** into an vapor and then thermally elevates the **atoms to an excited state**. When these atoms return to the ground state, they **emit light** which is detected by the instrument.
- The intensity of light emitted is related to the concentration of the element of interest in solution.

- **Atomic Absorption** measures the radiation absorbed **by the unexcited atoms** that are determined and the *only function* of the flame is to convert the sample aerosol **into atomic vapor** which can then absorb light from the primary light source.
- **Atomic absorption depends only upon the number of unexcited atoms**, the absorption intensity is not directly affected by the temperature of the flame.

$$N^*/N = A\, e^{-(\Delta E/kT)}$$

Measured signal and analytical concentration in Atomic Absorption

- Signal = $\mathbf{I}_{\mathbf{absorbed}}$ = Absorbance = **k l C**

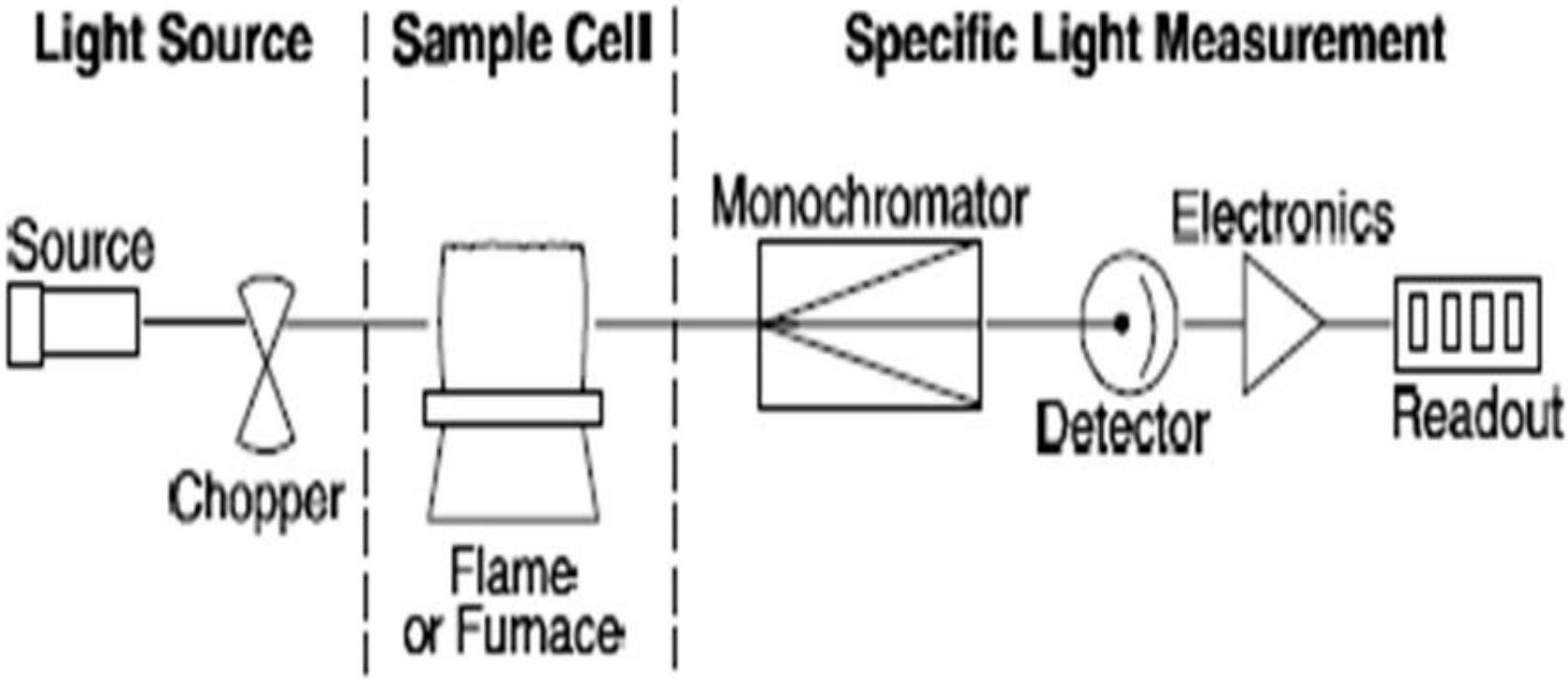
For the measurement to be reliable **k** must be constant;

- it should not change when a change in matrix or flame type takes place.
- it depends upon same factors as those for the atomic emission spectroscopy

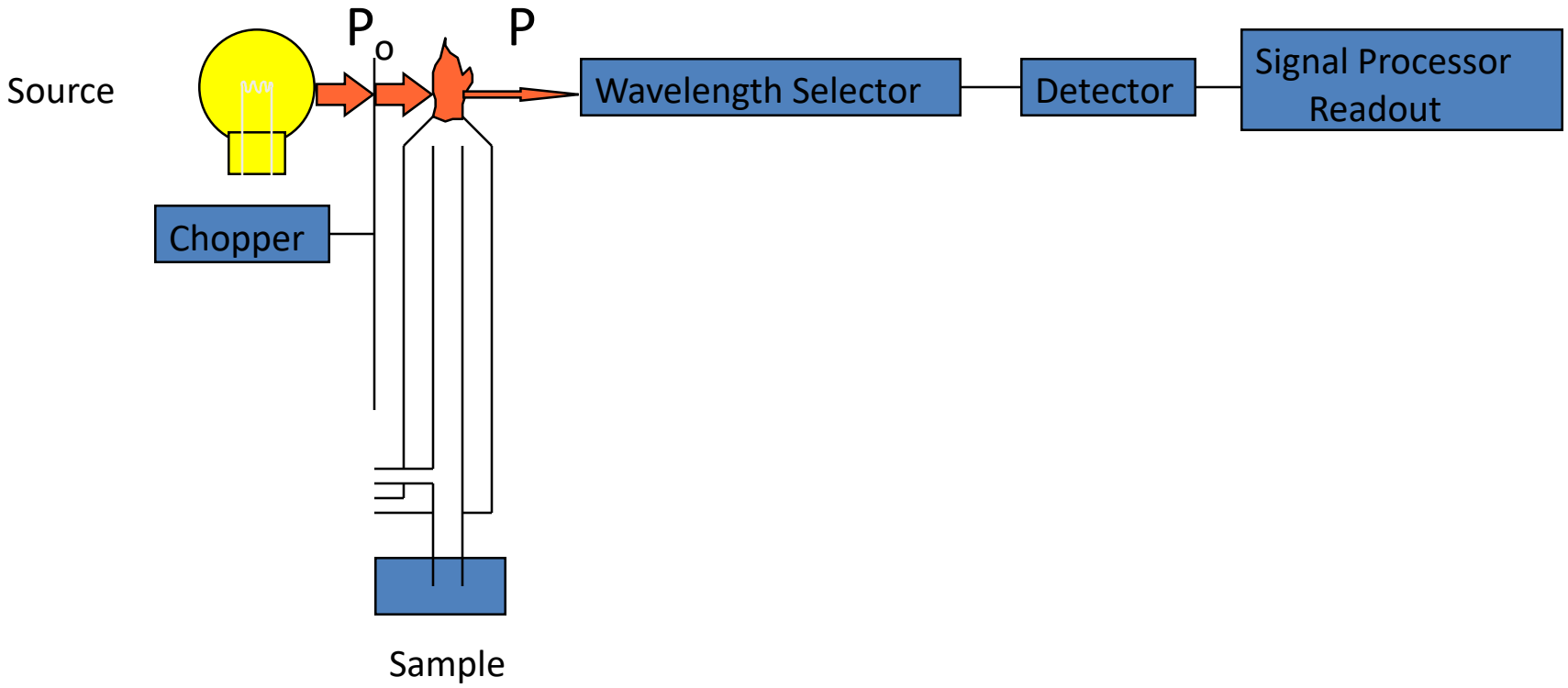
Atomic Absorption Instrumentation

There are five basic components

1. The light source that emits the spectrum of the element of interest(**H.C.L**)
2. An "absorption cell" in which atoms of the sample are produced (**flame, graphite furnace, ext…**)
3. A **monochromator** for light dispersion
4. A **detector**, which measures the light intensity and amplifies the signal
5. A **display that shows the reading** after it has been processed by the instrument electronics


Light Source
Sample Cell
Specific Light Measurement
Source
Chopper
Flame
or Furnace
Monochromator
Detector
Electronics
Readout

Atomic absorption techniques measure the **quantity of radiation passed through atoms**. A detector receives light photons wavelengths and correlates those with the wavelengths originally received by the sample.

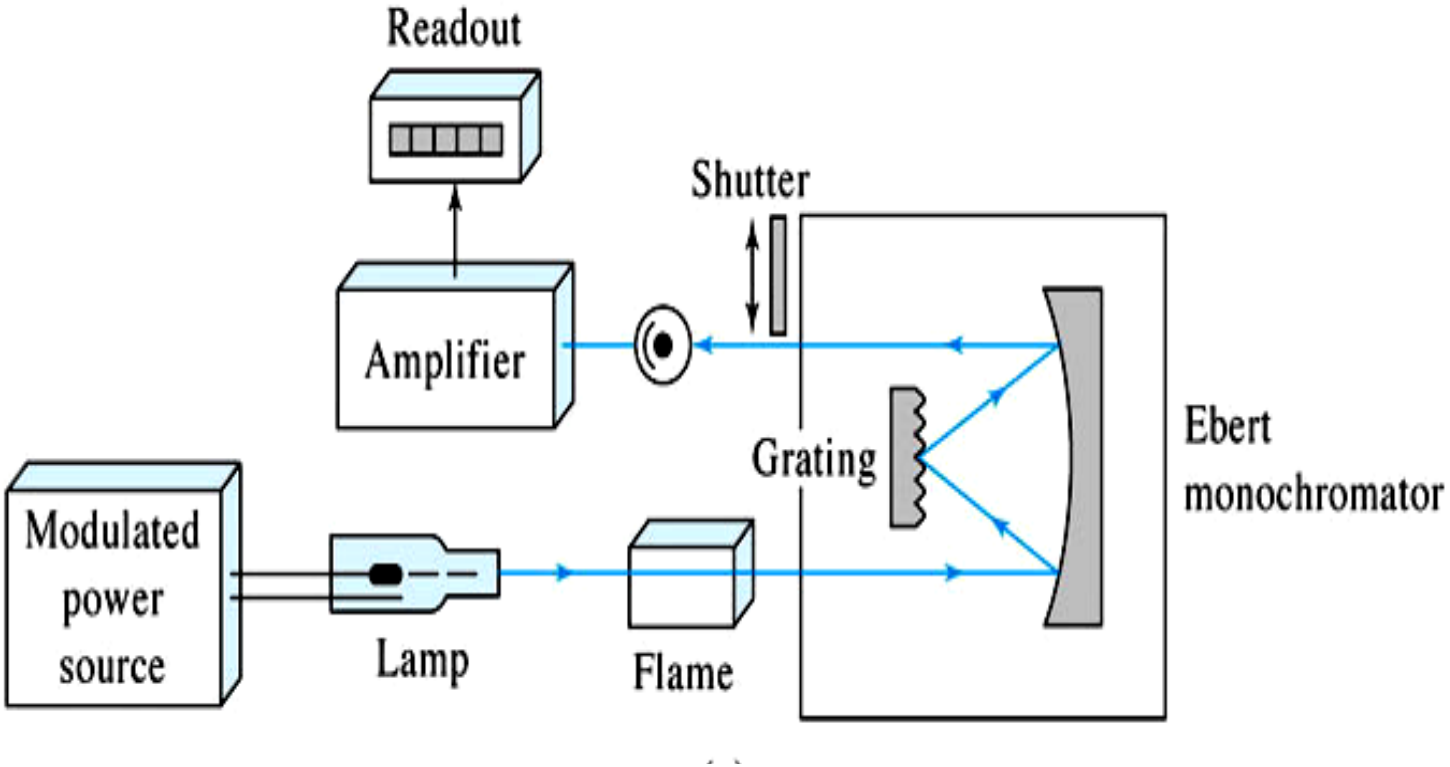


Flame Atomic Absorption Spectrometer

There are two basic types of atomic absorption instruments:

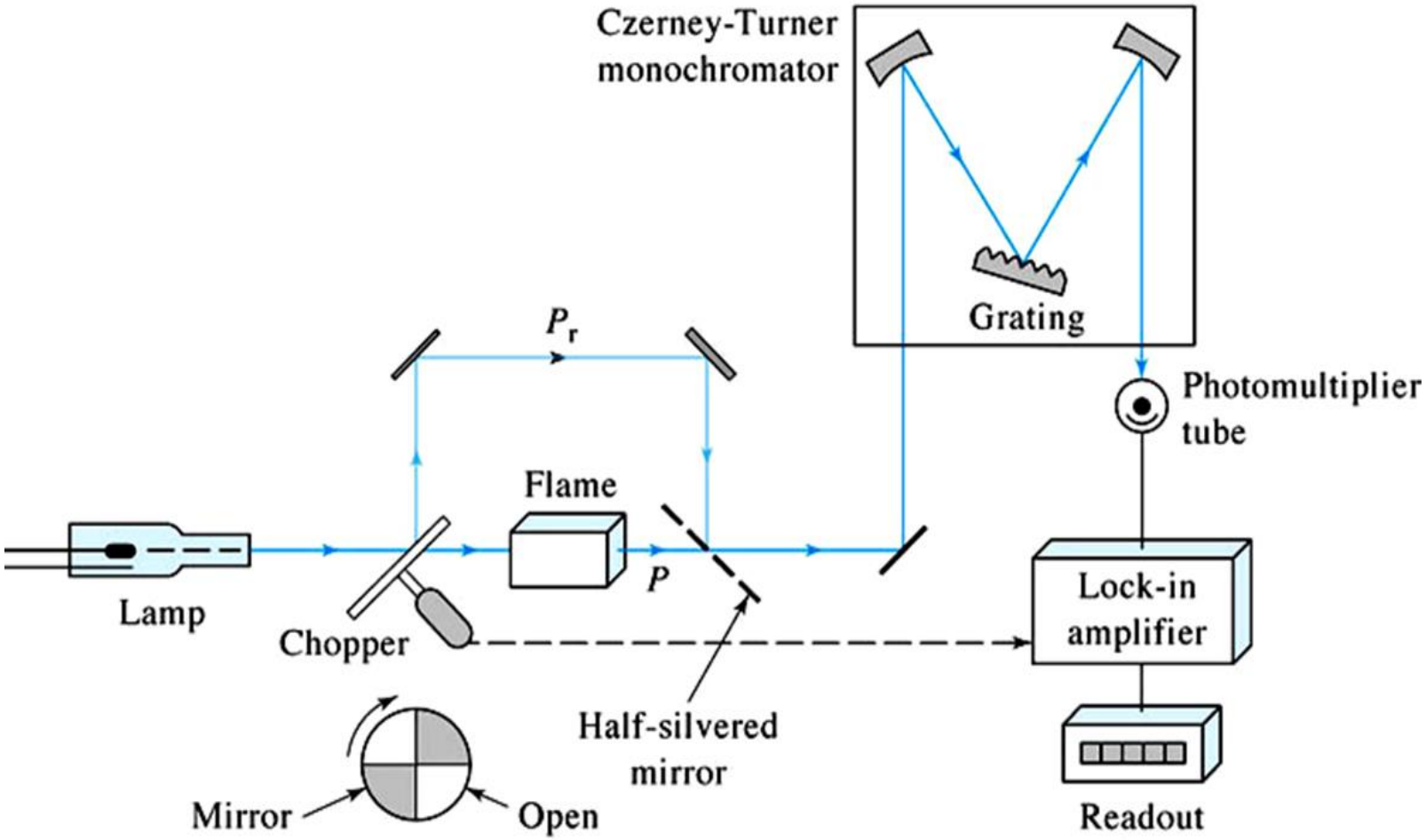
single beam and **double-beam**.

Single-Beam Instruments



- The **light source** emits a spectrum **specific to the element of which it is made**, which is focused through the **sample cell (flame)** into the monochromator. It must be mechanically **chopped** to differentiate between the **light from the source** and **the emission from the flame.**
- The **monochromator** disperses the light and the specific wavelength of light isolated passes to the **detector**, which is usually a photomultiplier tube.
- An electrical current is produced depending on the light intensity and processed by the instrument electronics. The electronics will **measure the amount of light attenuation in the sample cell and convert those readings** to the actual sample concentration.
- With single-beam systems, a short warm up period is required to allow the source lamp to stabilize

Double-Beam Instruments

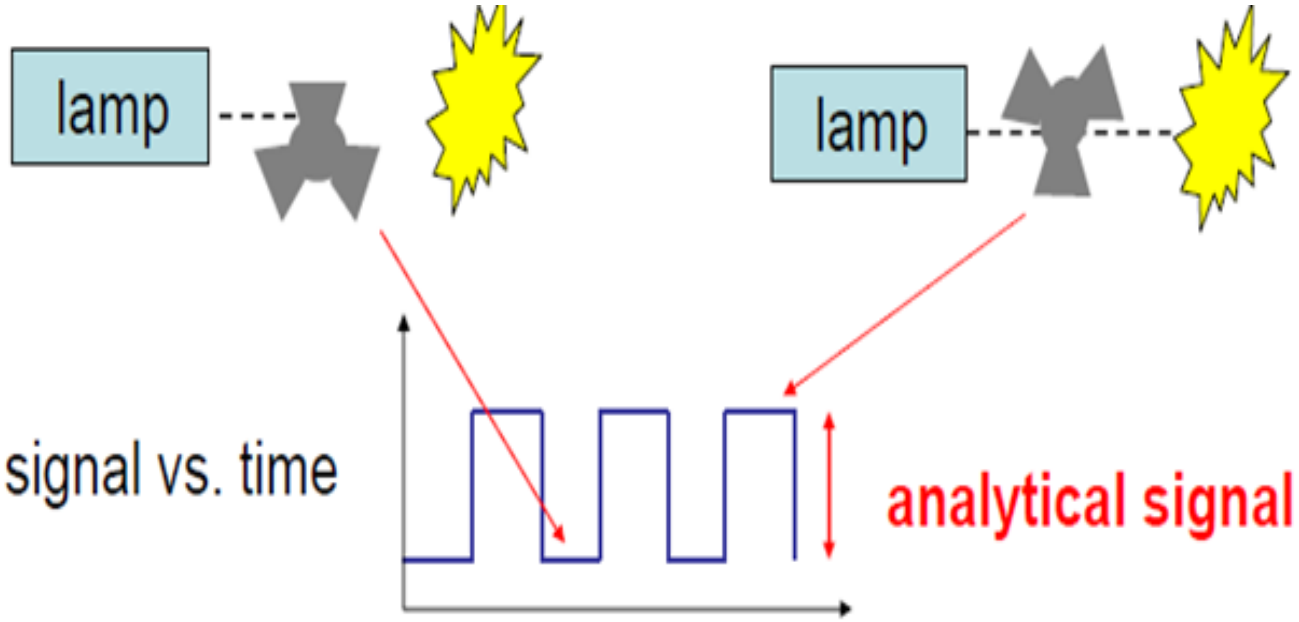


The light from the source lamp **is *divided into*** a **sample beam**, which is focused through the sample cell, and a **reference beam**, which is directed around the sample cell.

In a double-beam system, the readout represents the ratio of the sample and reference beams. **Therefore**:

- fluctuations in source intensity do not become fluctuations in instrument readout, and
- stability is enhanced.
- Generally, analyses can be performed immediately with no lamp warm-up required

The **rotating chopper** eliminates unwanted emissions from the flame.



Chopper

A chopper is used to provide signal modulation - in conjunction with a lock-in amplifier.

Its not practical to have two separate cells, so the light is simply split, with half being sent around the atomization source.

This reduces some noise from the atomization source and accounts for instrumental variations.

Light Sources for Atomic Absorption --Hollow Cathode Lamp (H.C.L.)

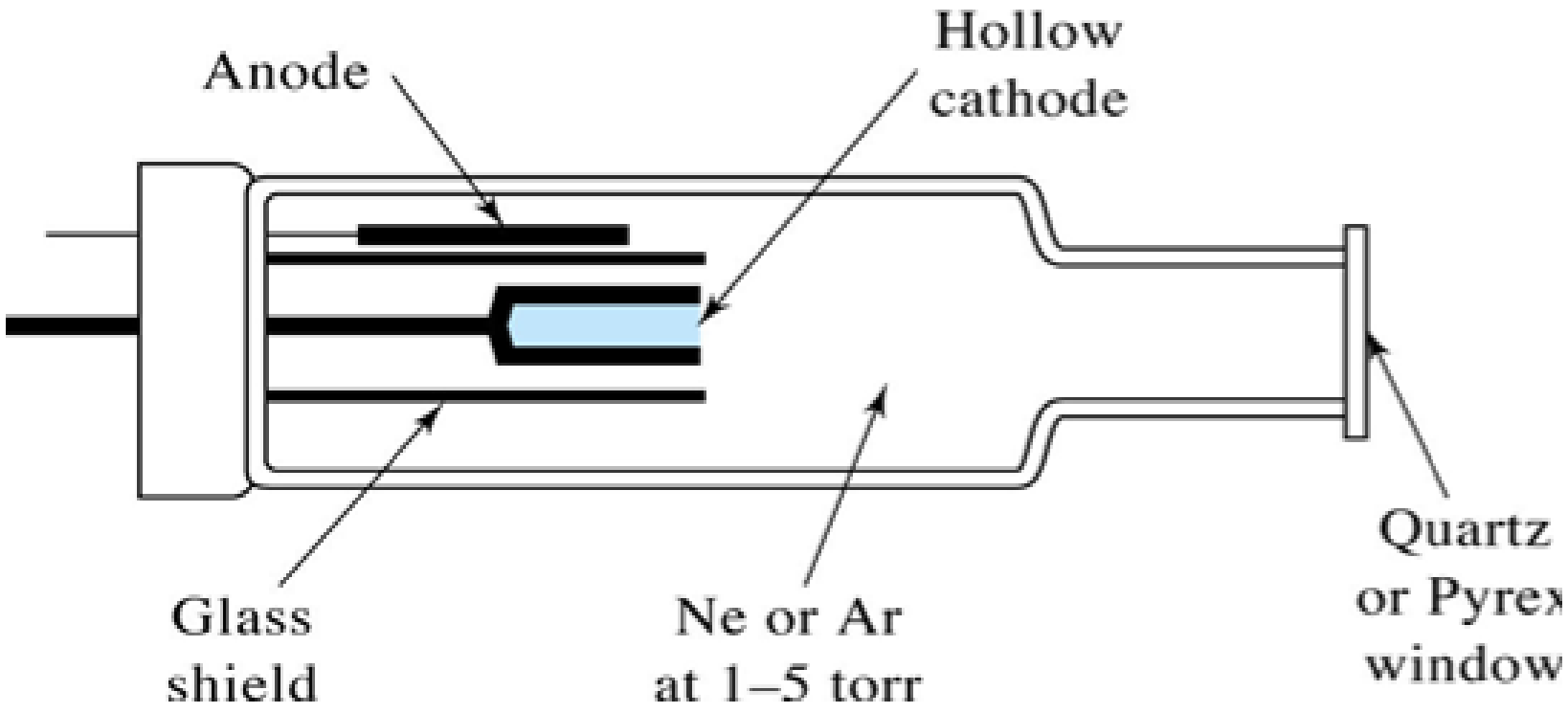
atoms absorb light at very specific wavelengths,

it is necessary to use a **narrow-line source** spectra of the element of interest and make atomic absorption **a specific analytical technique**.

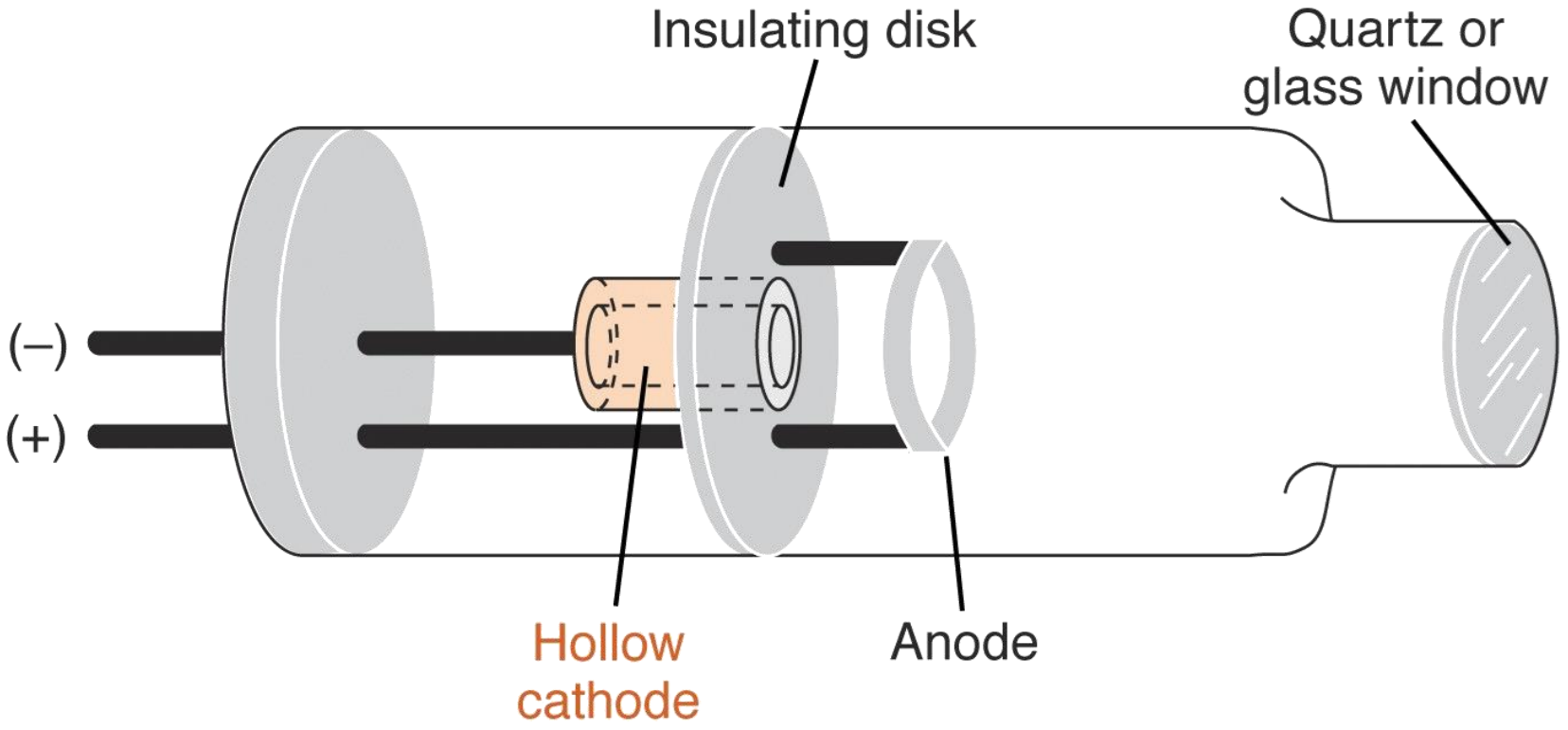
The main sources used for atomic absorption are the **hollow cathode lamp (H.C.L).**

The hollow cathode lamp is an excellent, bright, stable line source for most elements.

- The anode and cathode are sealed in a **glass cylinder filled with neon or argon** at a pressure of 1 to 5 torr**.**
- The glass cylinder has a quartz or UV glass window for optimum transmittance of the emitted radiation
- The **cathode** is cylinder constructed entirely of the metal whose spectrum is to be produced. generally constructed from **a very pure metal** resulting in a very pure emission spectrum
- A red glow is observed in lamps filled with neon, while argon filled lamps have a blue glow.
- Hollow cathode lamps are available for more than **60 elements.**


Anode
Hollow
cathode
Glass
shield
Ne or Ar
at 1–5 torr
Quartz
or Pyrex
window

Hollow-Cathode Lamps



Hollow Cathode Lamp

emission process

1- An electrical potential is applied between the anode and cathode

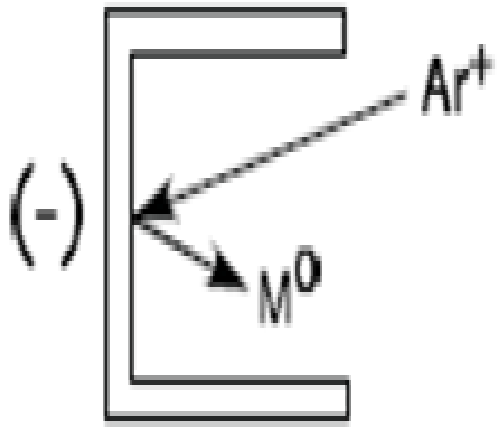
2-some of the fill gas atoms are ionized.

$$Ar \rightarrow Ar^{+} + e$$

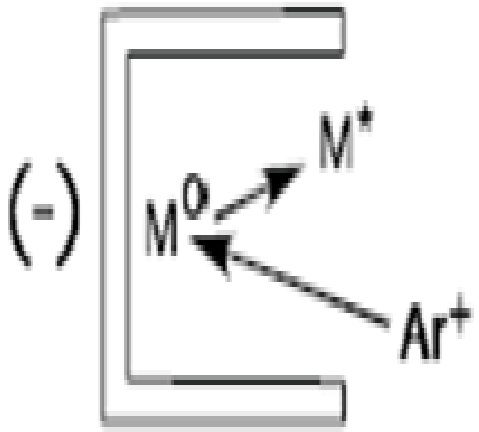
3- Ar^{+} collide with the negatively charged cathode

4-dislodge metal atoms in a process called "sputtering."

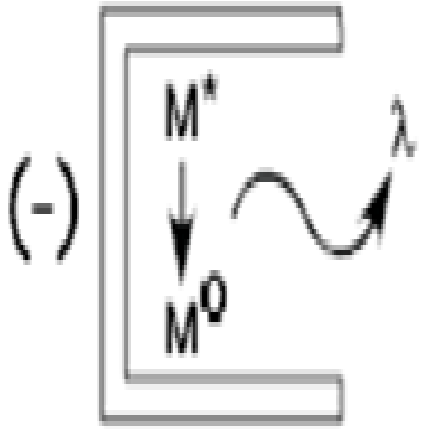
5-Sputtered metal atoms are further excited to emission through impact with the fill gas



1. Sputtering



2. Excitation



3. Emission

- Hollow cathode lamps have a finite lifetime.

With extended use, the sputtering process removes some of the metal atoms from the cathode and these are deposited elsewhere.

- Fill gas is absorbed in the sputtered metal, on the glass walls and also absorbed into the glass from bombardment.
- Lamps for volatile elements age faster due to more rapid sputtering of the cathode.

Multi-element Lamps

- Construction a cathode from **a mixture or alloy of several metals**.
- The resulting "multi-element" lamp can be used as a source for all the metals contained in the cathode.
- Not all metals can be used in combination due to metallurgical properties or spectral limitations.
- As a hollow cathode lamp ages, it may be necessary to increase the lamp current to the maximum current rating to give additional element light emission to equal that originally obtained when the lamp was new

Single-Element or Multi-element

The emission intensity for a particular element in a multielement lamp is not as great as that for the same element in a single-element lamp.

This can result in a poorer signal/noise ratio which can influence the precision of analyses and the detection limit.

- If economics is a problem, one multielement lamp can take the place of several single-element lamps.
- A multielement lamp is adequate for routine analyses that are well above the detection limit.
- If a backup lamp is necessary for a specific determination, a multielement lamp is ideal.
- If an infrequent analytical determination is required for several elements, a multielement lamp can offer considerable savings

Atomizers in absorption techniques

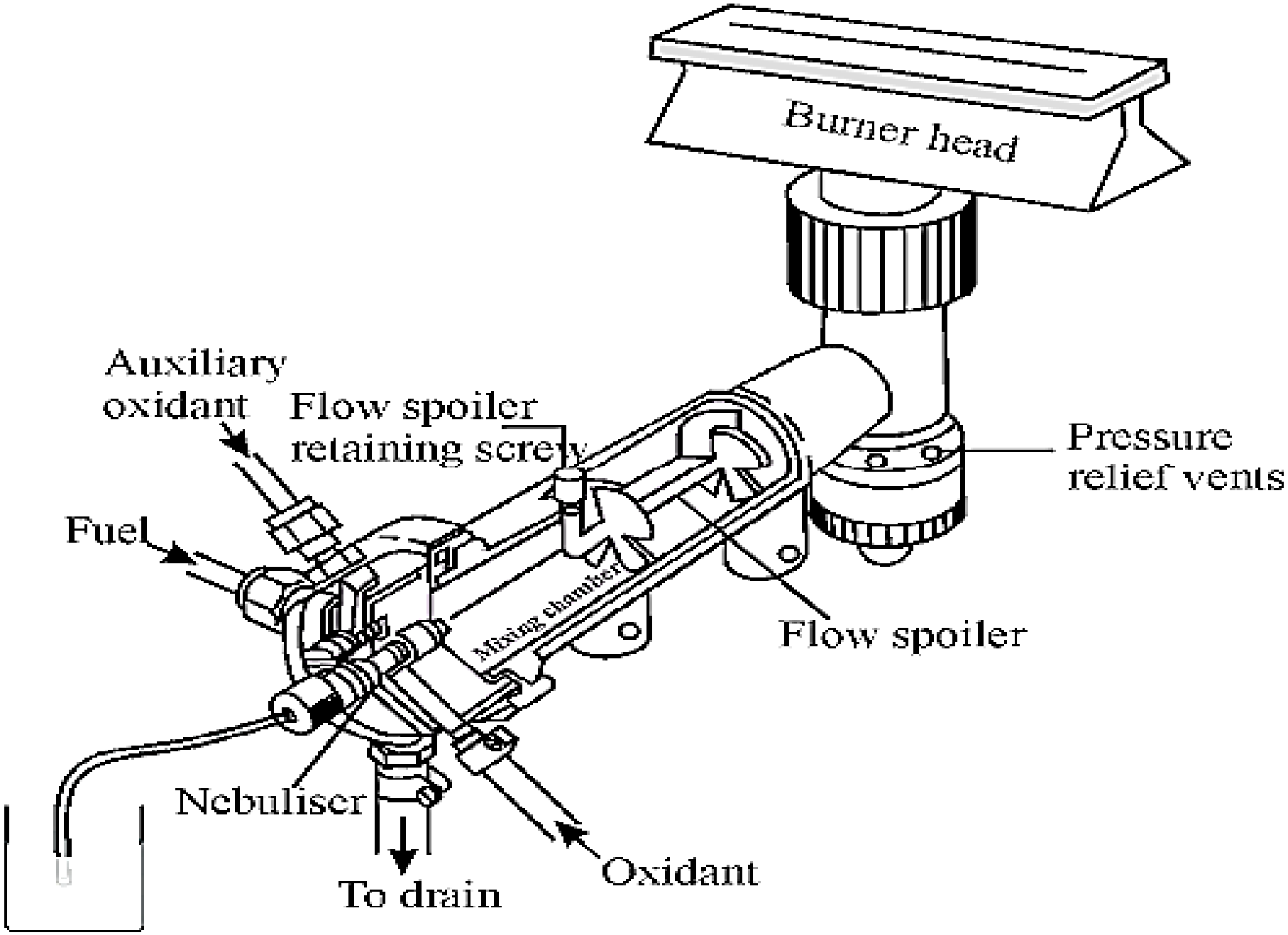
Type	Method of Atomization	Radiation Source
A- Flame	sample solution aspirated into a flame	HCL
B- Non-flame:		
- Electrothermal	sample solution ignited (2000 -3000 ^{o}C)	HCL
- Hydride generation	Vapor hydride generated	HCL
- Cold vapor	Cold vapor generated (Hg)	HCL

Atomizer Burners

Type of atomization burners have been used **is a Pre-mix burner**

The sample is introduced in the form of a fine spray at a controlled rate into the flame of a burner with the help of nebulizer.

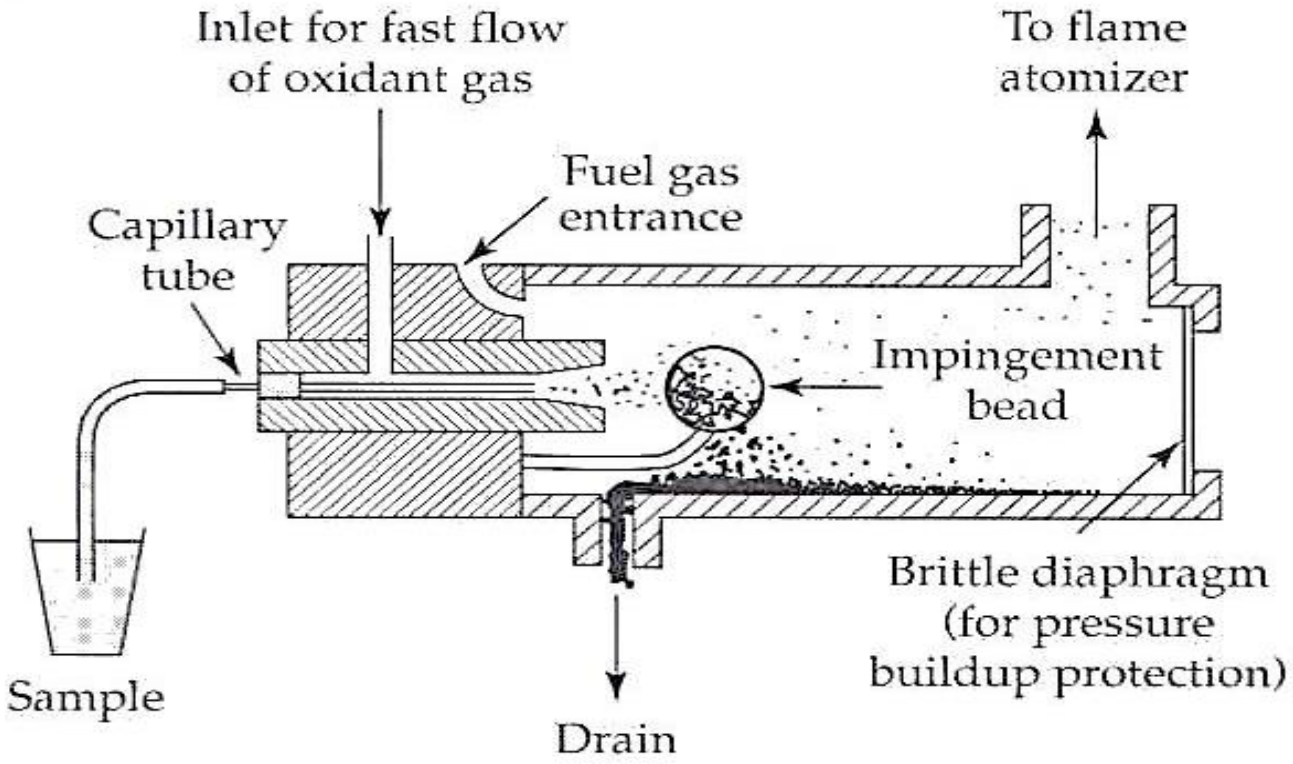
In the burner, the analyte undergoes a number of processes as mentioned earlier.


Burner head
Auxiliary oxidant
Flow spoiler retaining screw
Fuel
Pressure relief vents
Mixing chamber
Flow spoiler
Nebuliser
To drain
Oxidant

Premix (Laminar)burner

- **Fuel and oxidant are thoroughly mixed before enter the inner zone of the flame.**
- **In this type of burner, the solution of the analyte is aspirated with the help of a nebulizer into the mixing chamber in which the fuel gas is also introduced.**
- **The larger drops are stopped by baffles in the mixing chamber and are drained off. Pressure and density fluctuation of the aerosol due to atomization are smoothened in the mixing chamber and mixture of aerosol, fuel gas and oxidant burns to yield stable noiseless flame.**
- **The efficiency of the premix burner is low and only 5% of the sample reaches the burner.**

Liquid samples introduced to atomizer through a nebulizer



Pneumatic nebulizer

Advantage of Premix, Laminar burner

It is quiet to operate and the analytical signal is significantly less noisy than that of total consumption burner .

Disadvantages of Premix, Laminar burner

Most of the sample solution goes down the drain which leads to loss of sensitivity in the determination of a given analyte. Further, special precautions are necessary to avoid a flash back as the fuel and oxidant both are present and well mixed in the mixing chamber before combustion.

Flame atomization

The most common fuel to use is acetylene.

Either air or nitrous oxide are used as oxidants, with N_2O producing a hotter flame.

	Temperature, °C
C_2H_2/Air	2100 - 2400
C_2H_2/N_2O	2600 - 2800

N_2O also tends to produce a noisier flame.

Flame atomization tends to produce stable signals in the ppm range for most metals.

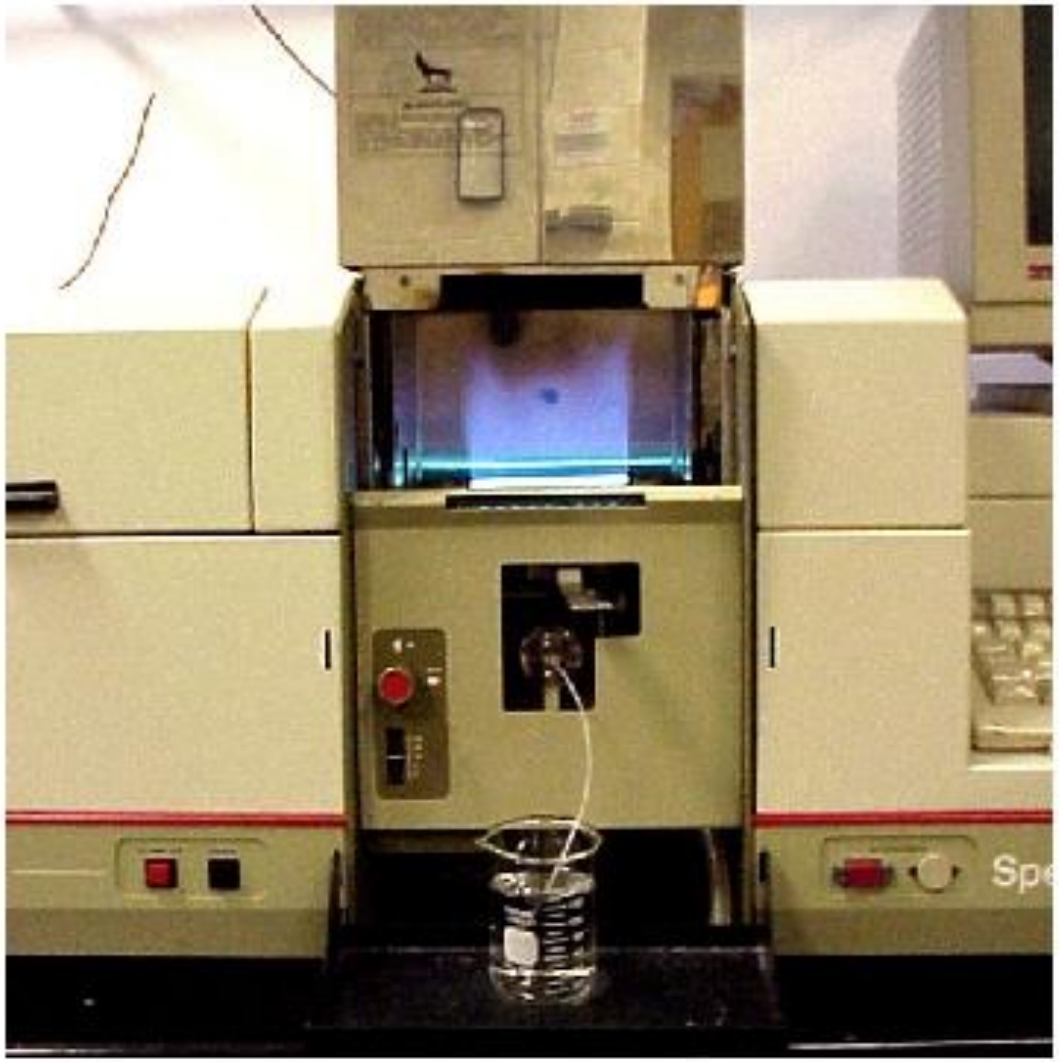
It is a dynamic method

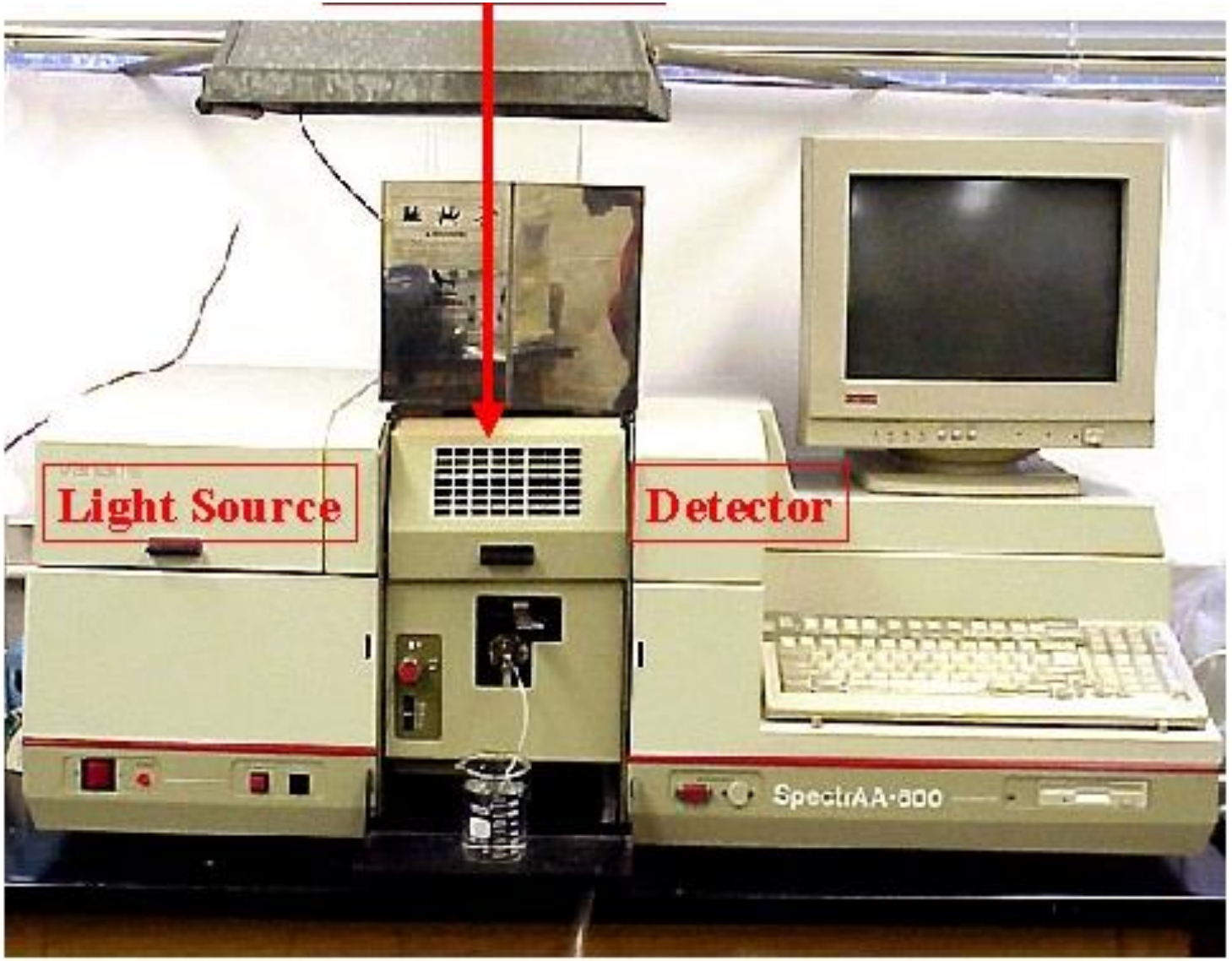
Sample is constantly being consumed.

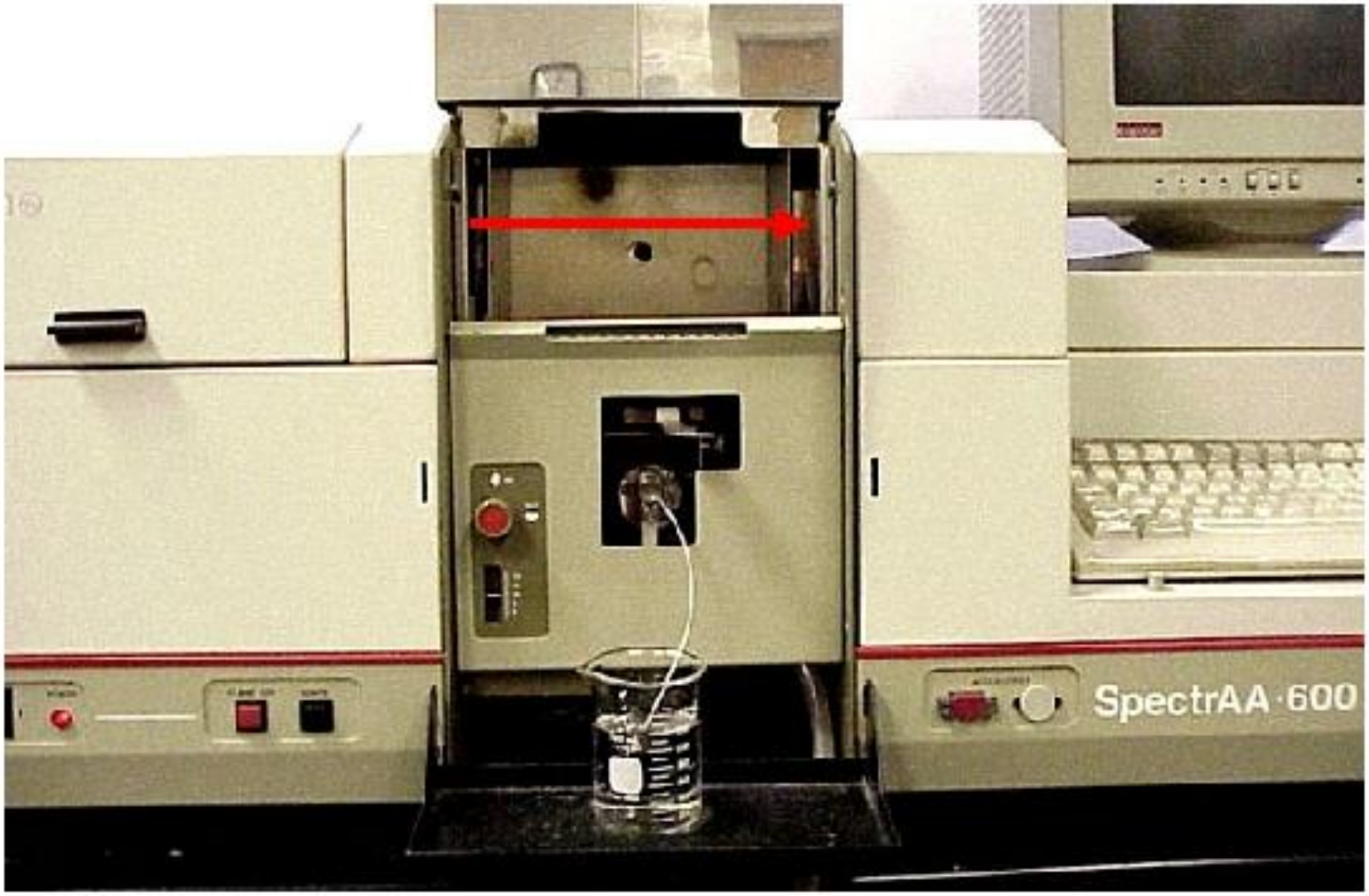
Large sample size (>1 ml).

Your sample must be a fluid.

The detection limits are relatively high since only a small portion of your sample is present in the flame at any given time.




Light Source
Detector
SpectrAA-800


SpectrAA·600

Sample is vaporized in the flame.

Aspirator tube sucks the sample into the flame in the sample compartment.