ATOMIC SPECTROSCOPY BASIC PRINCIPLE AND INSTRUMENTATION

By

Dr. Aveen Faidhalla Jalal

Spectroscopy

- **Atomic**
  - Absorption
  - Emission
- **Molecular**
  - Absorption
  - Emission

Atomic		Molecular	
Atomic Absorption		**UV-Visible**	Fluorescence
	Flame Emission	**IR**	Phosphorescence

Atomic – Transitions:

- Electronic transitions

Line spectrum

Molecular – Transitions:

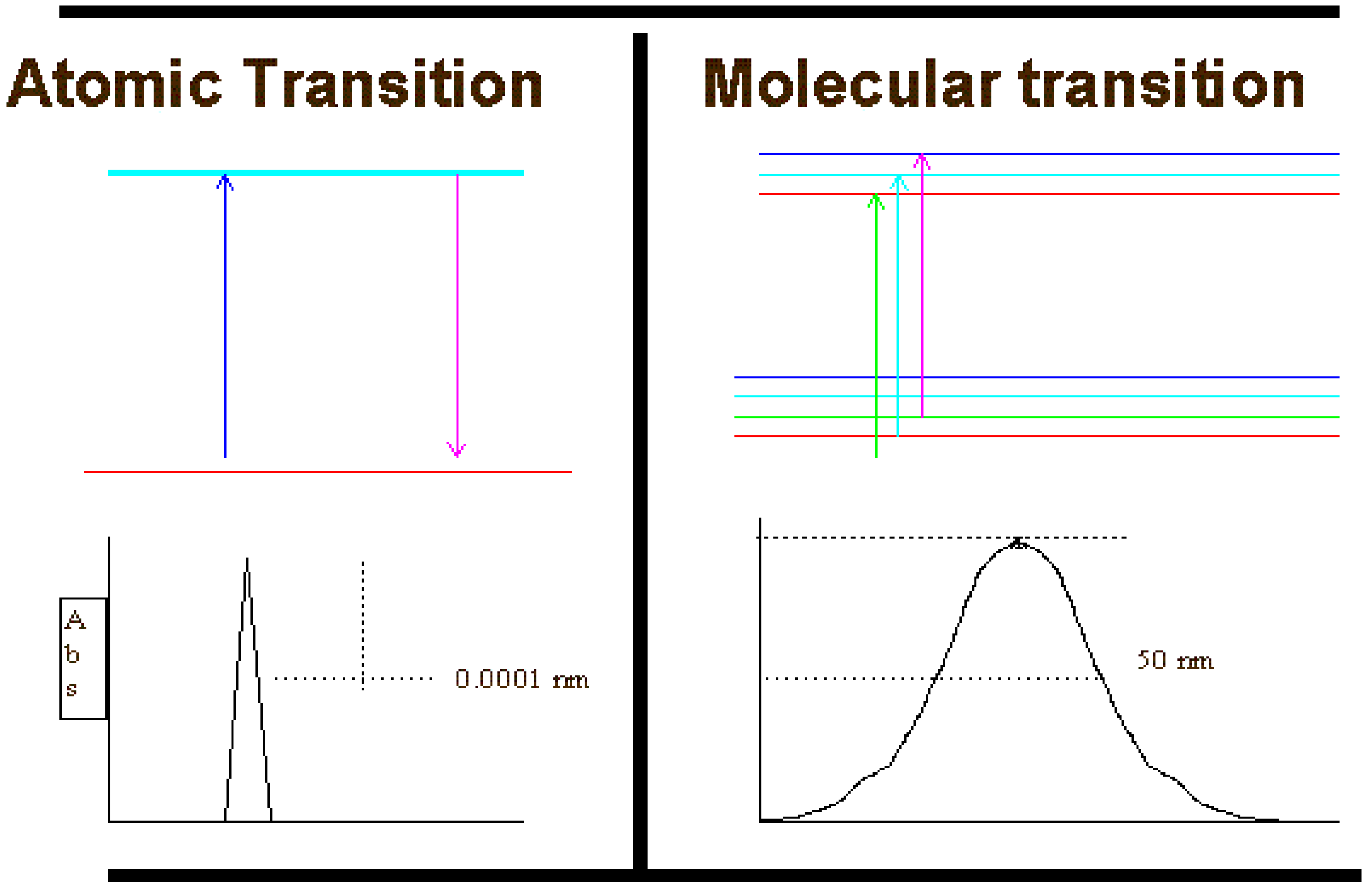
- Electronic,
- Vibrational and
- Rotational transitions

Band spectrum

Atomic Spectroscopy

- Methods that deal with **absorption** and **emission** of EMR by **gaseous atoms**.
- The methods deal mainly with the **free atoms** (***not ions***), and only electronic transitions are possible as there are no rotational and vibrational energy levels
- ***Line spectra*** are observed
- ***Specific spectral lines*** can be used for both **qualitative and quantitative analysis** of elements

Molecular and Atomic Spectra

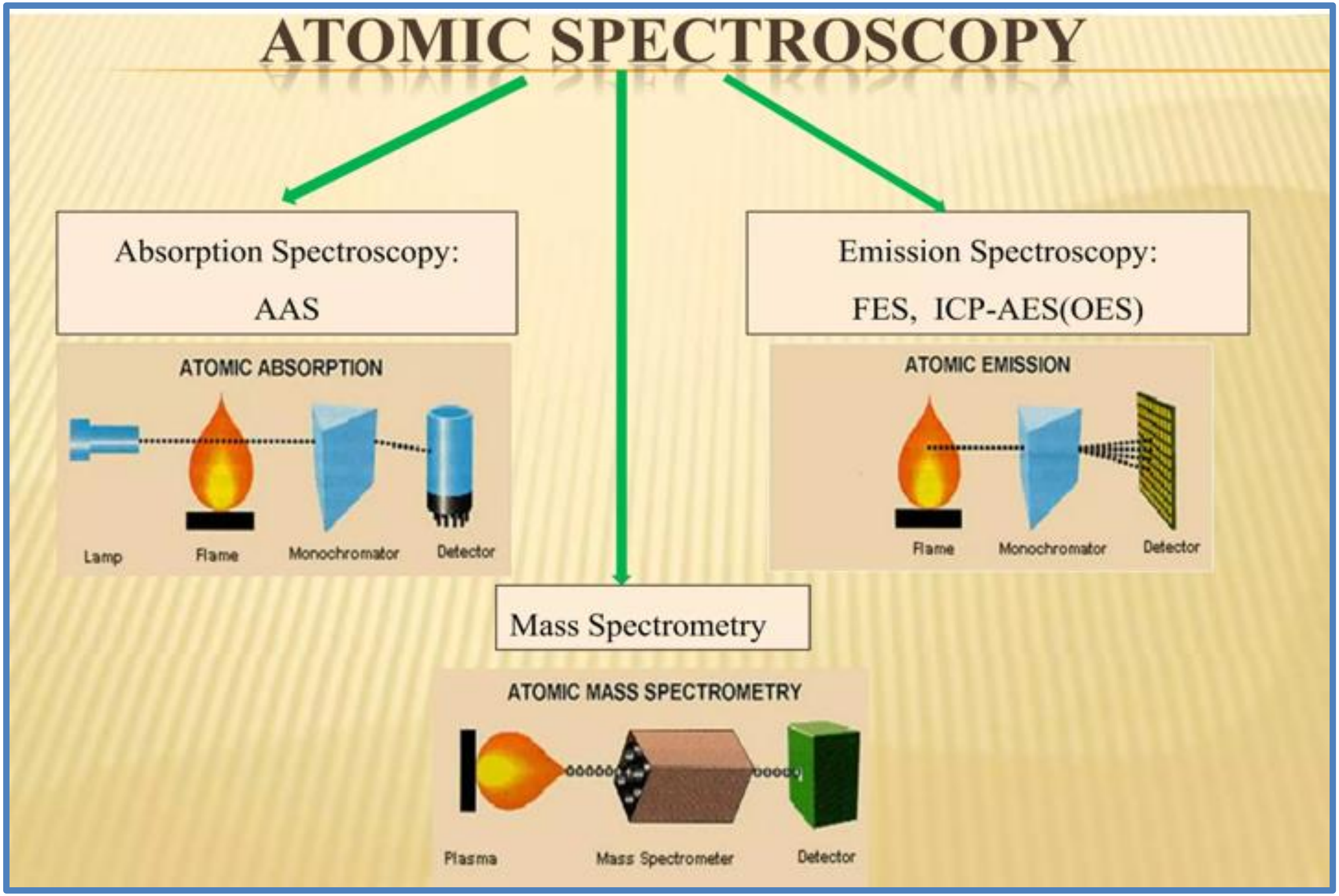


Atomic spectral line

Molecular spectral line

Flame -Atomic Emission Spectrometry (F-AES)

- The flame emission is technique for determining trace quantities of elements, this technique requires **flame.** This flame **emits a specific light** and by measuring this light can determinate the element.
- Quantities of these elements present in the sample determined by measuring the intensity of radiation which is produced by the flame.(**a light source not required**).



ATOMIC SPECTROSCOPY
Absorption Spectroscopy:
AAS
ATOMIC ABSORPTION
Lamp
Flame
Monochromator
Detector
Emission Spectroscopy:
FES, ICP-AES(OES)
ATOMIC EMISSION
Flame
Monochromator
Detector
Mass Spectrometry
ATOMIC MASS SPECTROMETRY
Plasma
Mass Spectrometer
Detector

Flame photometry

- One of the **oldest instruments** is flame photometry.
- Flame emission spectrometry (**FES**) is the ***inexpensive, rapid and simple.*** It is the most ***convenient*** analytical technique for the detection and determinant estimation of: ***metals*** which are **easily moved from the ground state to excited higher energy levels** ***even at low temperature.*** such as :

Lithium, **Sodium**, **Potassium**

Metal	emission light at	color
Lithium	670nm	range-red
Sodium	589nm	orange-yellow

- **The radiation emission intensity depends on the electron excited from the ground stated by the heat.**

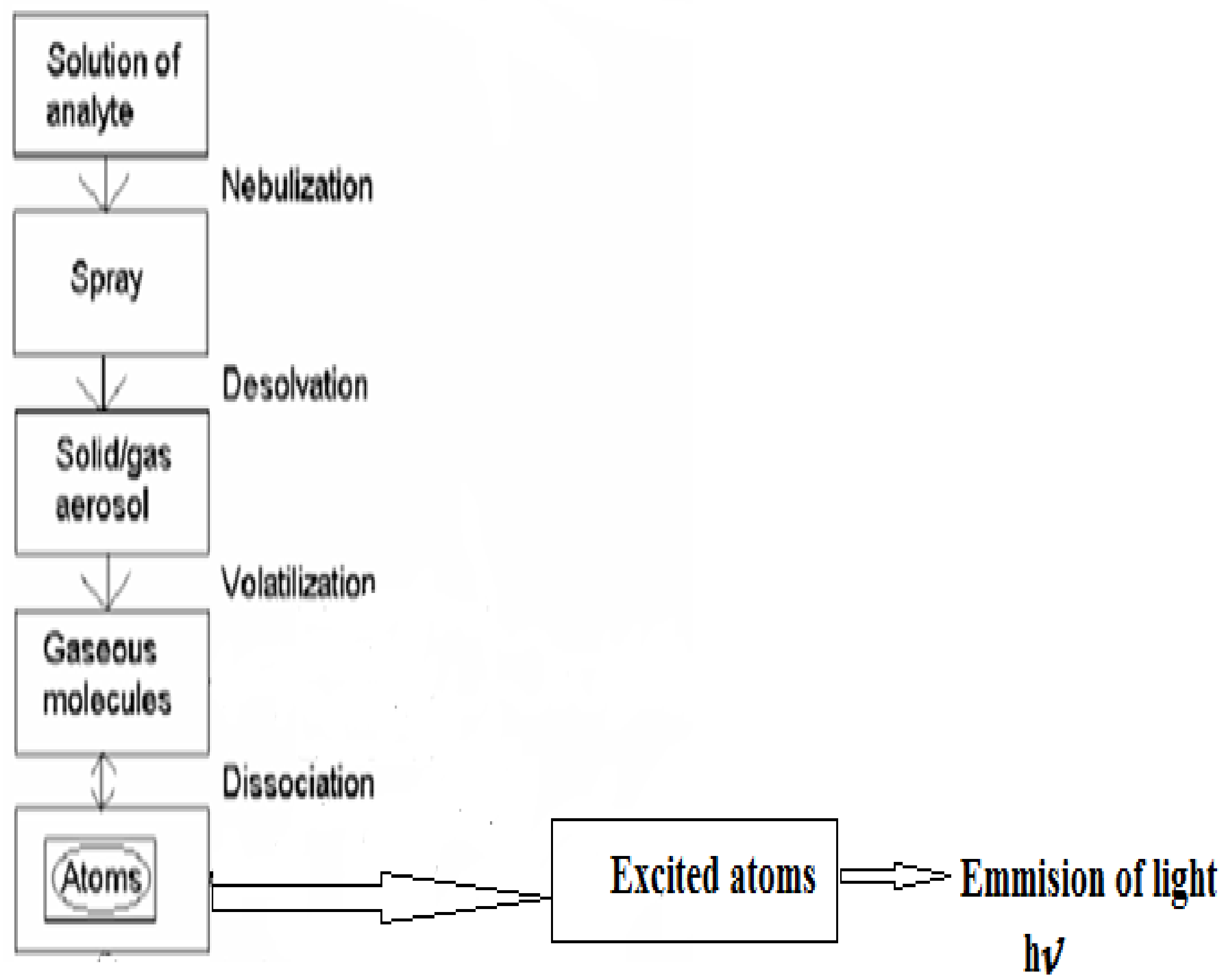
Compound Name/Formula	Flame Color
Magnesium (demo)	Bright White
Barium Chloride (demo)	Yellow
Potassium Chloride (demo)	Yellowish Orange
Lithium Chloride (LiCl)	Red
Sodium Nitrate (NaNO)	Yellowish Orange
Calcium Chloride (CaCl)	Orange
Cupric Nitrate (CuNO)	Green
Strontium Nitrate (SrNO)	Pinkish Red/Hot Pink
Lithium Nitrate (LiNO)	Red
Sodium Chloride (NaCl)	Yellowish Orange
Copper Chloride (CuCl)	Bluish Green
Unkown (UNK)	Orange

- Flame photometry is the most commonly used method for the determination and detection of **alkali and alkaline earth metals**.
- When compared to the **AAS**, **AES** obtained considerably sensitive results, hence AES is considered as the most important analytical technique for both qualification and quantification in all field

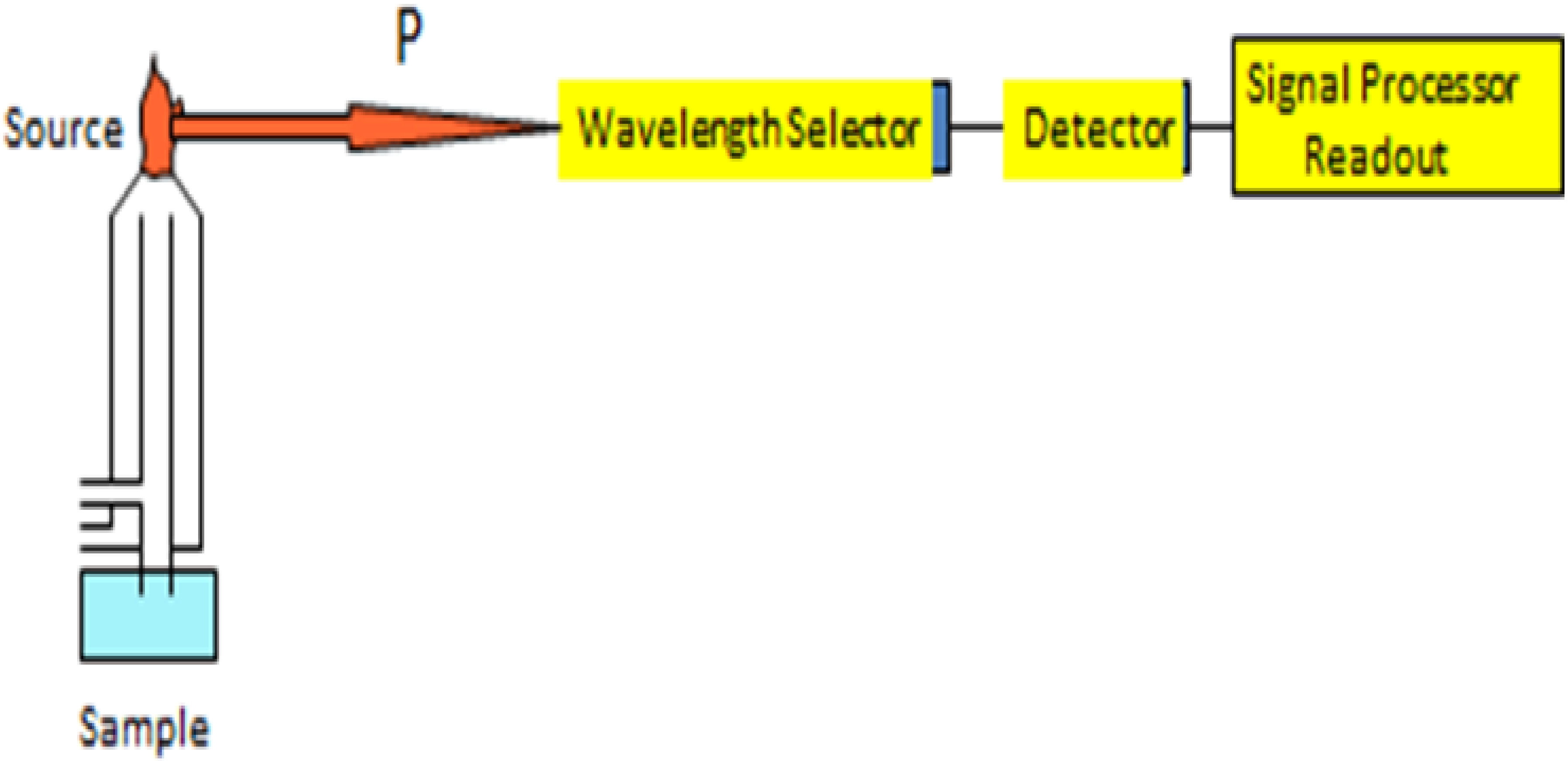
Instrumentation of Flame Photometry

- The fundamental requirements for flame photometer are **Nebulizer** and **Atomizer.**
- Here Nebulization of liquid sample introduced by converting into fine droplets before reaching the flame and atomization of the atom will happen.
- ***Burner*** is the sours of radiation in the flame photometry.
- ***Filter*** is used for detecting which element or atom it allows to pass through the filter by selecting the wavelength, **photo-detector**, amplifier and read out. There are different type for **readout,** computer or meter or digital and for some instrument will get by chart recorder.

Processes that take place in flame or plasma



Instrumentation of Flame Photometry



Nebulization

- Nebulization is the process at which the liquid sample introduced to the burner by converting into fine droplets before reaching the flame.
- In this process Nebulizer (Aspirator) is used for the formation fine liquid droplets.
- The conversion to fine droplets from bigger droplets sample solution is known as nebulization /Aspiration

Types of nebulizers

1. Pneumatic Nebulizers (most common).

This is the simple technique of nebulization in which gas is used at high velocity, called pneumatic nebulization. Nebulization is conversion of a sample to a fine mist of finely divided droplets using a jet of compressed gas.

There are four types of Pneumatic nebulizers:

a- Concentric tube - The liquid sample is sucked through a capillary tube by a high pressure jet of gas flowing around the tip of the capillary (***Bennoulli effect***). This is also referred to aspiration.

The high velocity breaks the sample into a mist and carries it to the atomization region.

b- Cross-flow

The jet stream flows at right angles to the capillary tip. The sample is sometimes pumped through the capillary.

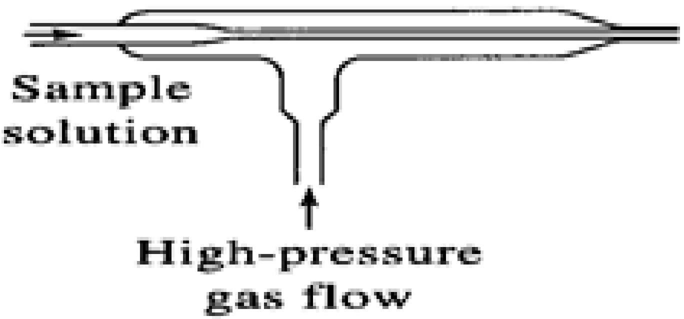
c- Fritted disk

The sample is pumped onto a fritted disk through which the gas jet is flowing. Gives a finer aerosol than the others.

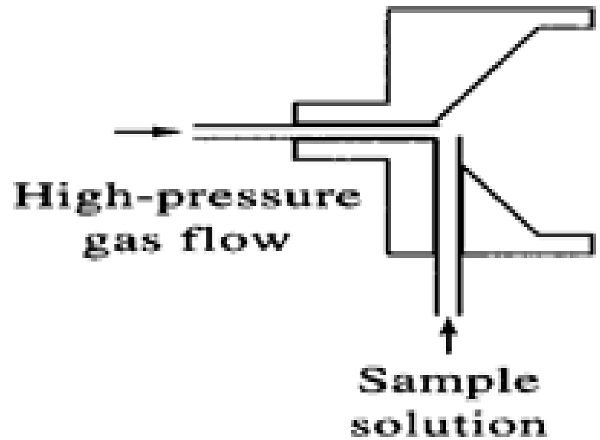
d- Babington

Jet is pumped through a small orifice in a sphere on which a thin film of sample flows. This type is less prone to clogging and used for high salt content samples.

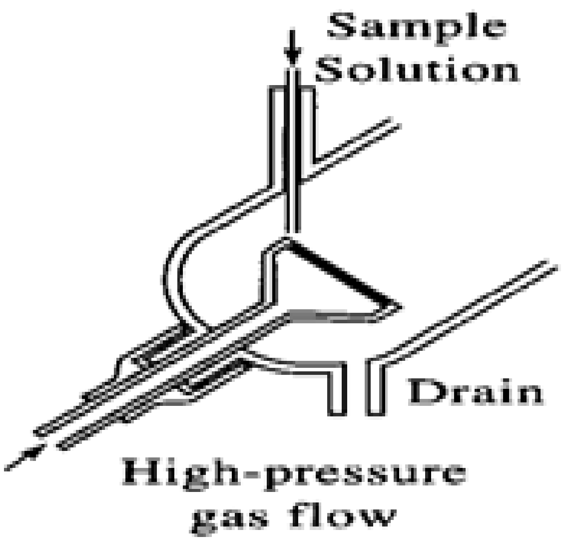
Concentric tube



(a)

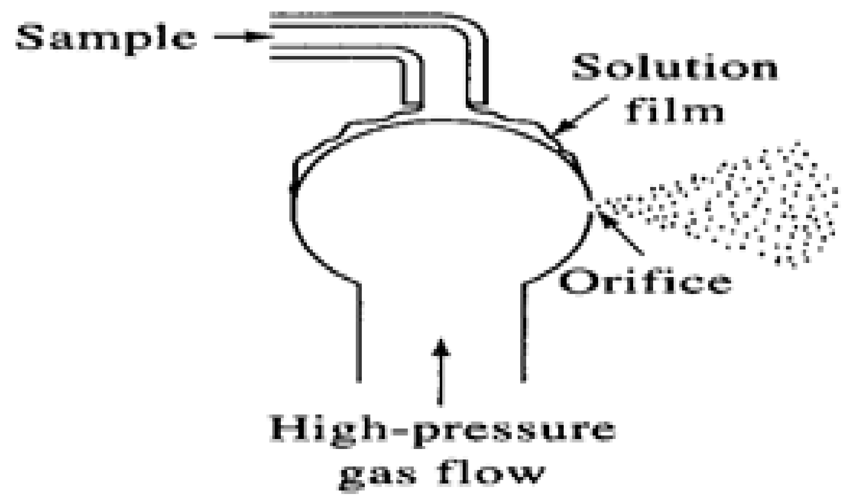


(b) Cross flow



(c)

Fritted disk



(b)

Babington

2- Ultrasonic Nebulizer

The sample is pumped onto the surface of a vibrating piezoelectric crystal. The resulting mist is denser and more homogeneous than pneumatic nebulizers.

3- Electro-thermal Vaporizers (ETV)

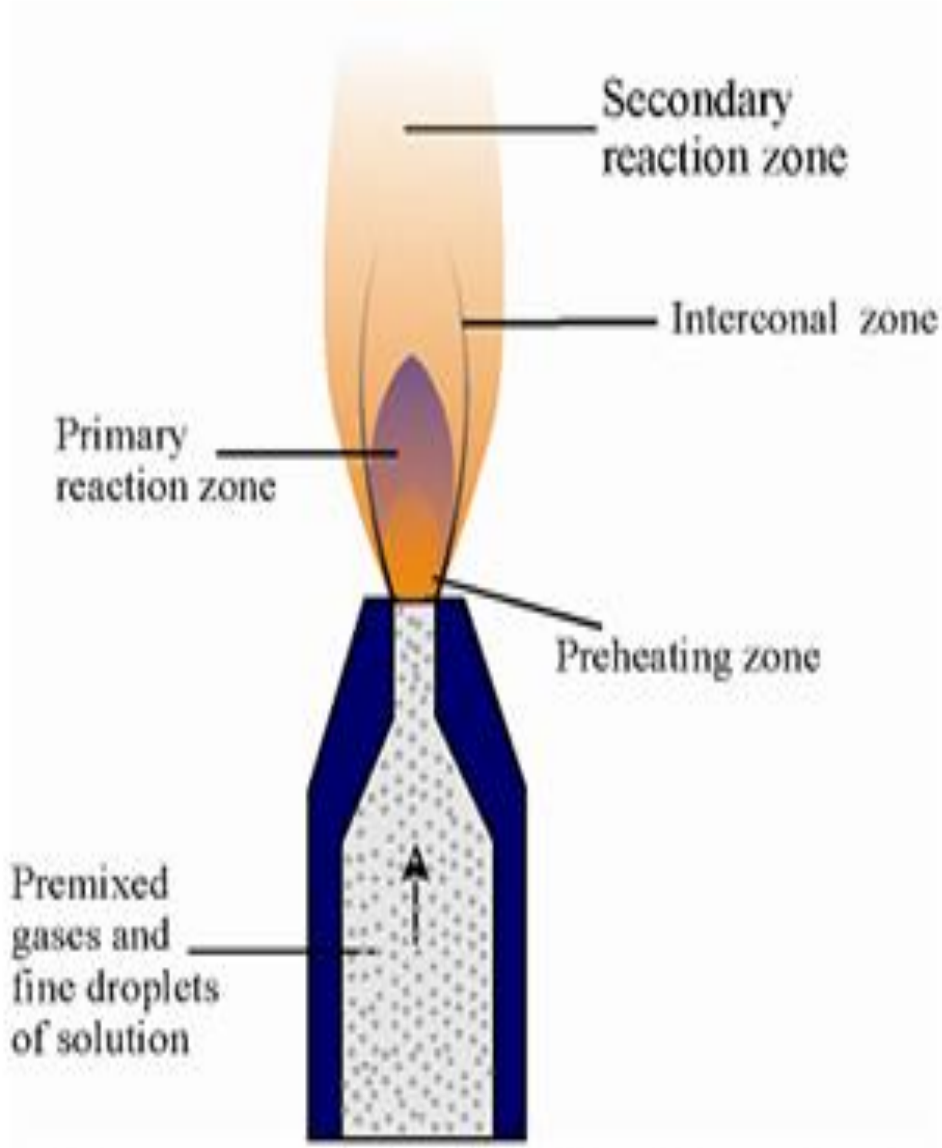
An electro thermal vaporizer contains an evaporator in a closed chamber through which an inert gas carries the vaporized sample into the atomizer.

Atomization:

The whole process of **breakdown of molecules into atoms** is known as **Atomization.**

Determination of the sample can be done by exposing the analyte present in the sample to flame at a high temperature.

The most common fuel used is butane and propane flame (1900^{o}C)(LPG is a by-product of natural gas extraction and crude oil refining).



Schematic structure of a laminar flow flame showing

Fuel	**Oxident**	**Temp. ^{o}C**
Natural gas	Air	1700 - 1900
Natural gas	Oxygen	2700 - 2800
Hydrogen	Air	2000 - 2100
Hydrogen	Oxygen	2550 - 2700
Acetylene	Air	2100 - 2400
Acetylene	Nitrous oxide	2600-2800
Acetylene	Oxygen	3050 - 3150

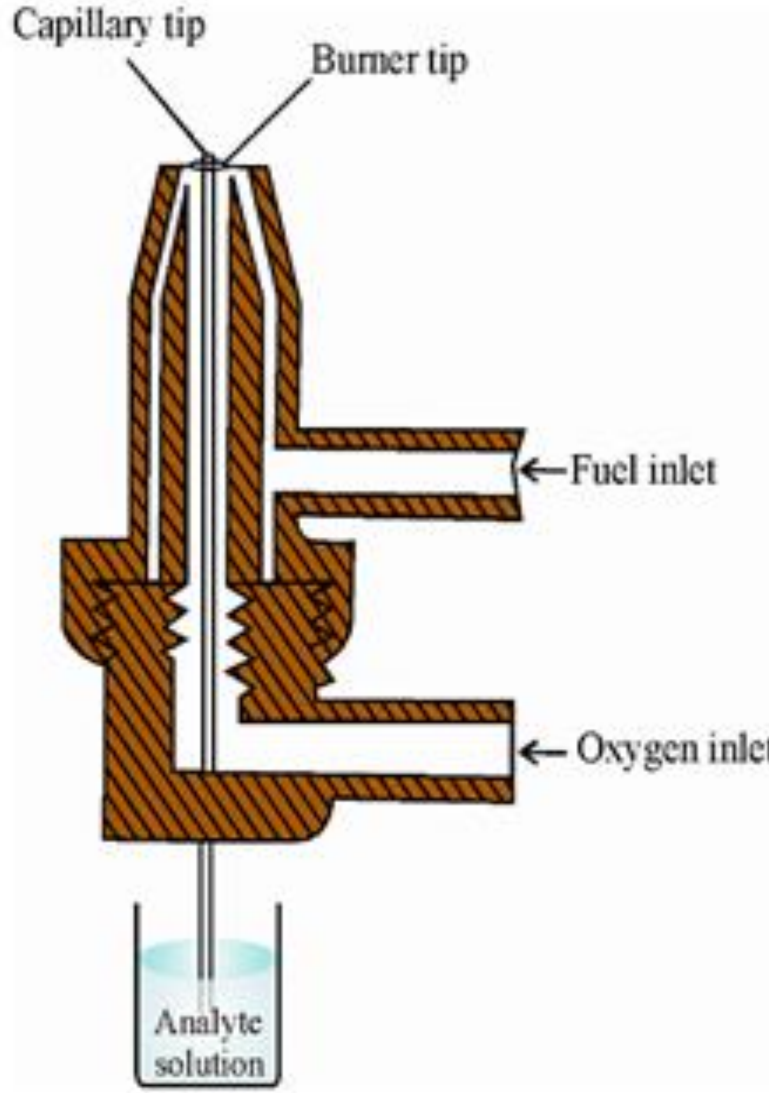
Total consumption burner

A total consumption burner combines the functions of nebulizer and burner.

In this type of burner, the suction created by the compressed oxidant streaming past the inner capillary, introduces the sample directly into the flame even if it included suspended particles or large solvent droplets; hence the name “total consumption burner”.

Here the oxidant and fuel emerge from separate ports and are mixed above the burner orifices through their turbulent motion.

The flame produced by such a burner is **turbulent**. As the aspirated the sample solution as such is put into the flame, **IUPAC recommends the term direct-injection burner** in place of total consumption burner. However, due to its prevalent use the earlier term still continues to be in use.



Advantages of the total consumption burner

- There are **no losses** by condensation of spray; **all the material enters the flame**. For this reason, the **emission** for a given concentration of analyte in solution **is higher** than that from a premix flame (with indirect atomization).
- No fractionation of the sample takes place during aspiration. This **eliminates errors** due to loss of nonvolatile components.
- Combustible sample e.g. **petroleum can be directly aspirated** into the flame without any danger of explosion.

Disadvantages of the total consumption burner

- Droplets of **widely varying sizes** are formed during aspiration. Many of the larger droplets are frequently blown right through the flame without totally evaporating or without pyrolysis of the solute.
- The flame is **more strongly cooled** by heavier load of the liquid.
- The **burner tip can become incrusted with salts** left after evaporation of solvent leading to a change in the aspiration rate of the solvent.
- The **burners are very noisy both physically and electronically** which lead to poor reproducibility of analytical results.

For the above reasons, the total consumption burner is not much used except for explosive flames e.g. hydrogen with other oxidants.

Filters

The essential part of atomic emission spectrometer is monochromator which separates a certain wavelength of light which emitted by element passes through the monochromator.

Availability the different kinds of filters, some filters are allowed along with the chosen wavelength also leaked light at nearest wavelengths.

Practically, **using special filters get excellent results**

Detector:

Detectors work is changing the light signal to electrical signal. The Photomultiplier tube detector is the most commonly used in AES it's possessed high sensitivity and accuracy.

Readout:

Another part of the flame photometry is the readout and it’s the final part of the flame photometry, there are different type of the red out the first digital voltmeter and the second is simple galvanometer and the third is a potentiometer and the fourth computer. It decreases the error by the operator.

- **Flame emission intensity dependent upon** the **number of excited atoms**, is greatly **influenced by temperature variations**.

$$N^*/N \ \alpha \ e^{-(\Delta E/kT)}$$

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

Measured signal and analytical concentration in Atomic Emission

Signal = Intensity of emission = K N_f = K' N_{ex} = K''C

- N_f = number of free atoms in flame
- N_{ex} = number of exiting atoms in flame
- C = concentration of analyte in the sample

- **K, K` & K’’ depend upon**:

1- Rate of aspiration (nebulizer),

2- Efficiency of aspiration (evaporation efficiency),

3- Flow rate of solution,

4- Solution concentration,

5- Flow rate of unburnt gas into flame,

6- Efficiency of atomization

(**Effect of chemical environment**),

and this depends upon:

a- Droplet size,

b- Sample flow rate,

c- Refractory oxide formation,

d- Ratio of fuel/oxygen in flame,

e-Temperature effect (choice of flame)

Application of flame photometry

- Flame atomic emission spectrometry is **rapid, sensitive and low cost** for determination of the sodium ion and potassium ion and lithium-ion in many matrices content because the **alkaline element easily atomized in flame**.

- Alkali metals play an essential role in pharmaceutical and environmental fields.
- The flame photometry has the most important application is determination sodium, potassium in the biological sample and clinical sample such as **determination of sodium in blood**.