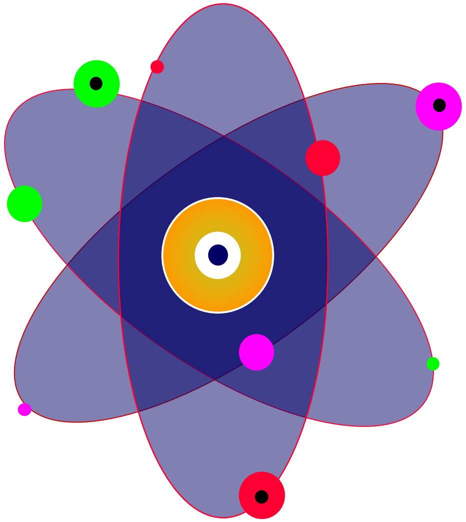
Atomic Spectroscopy

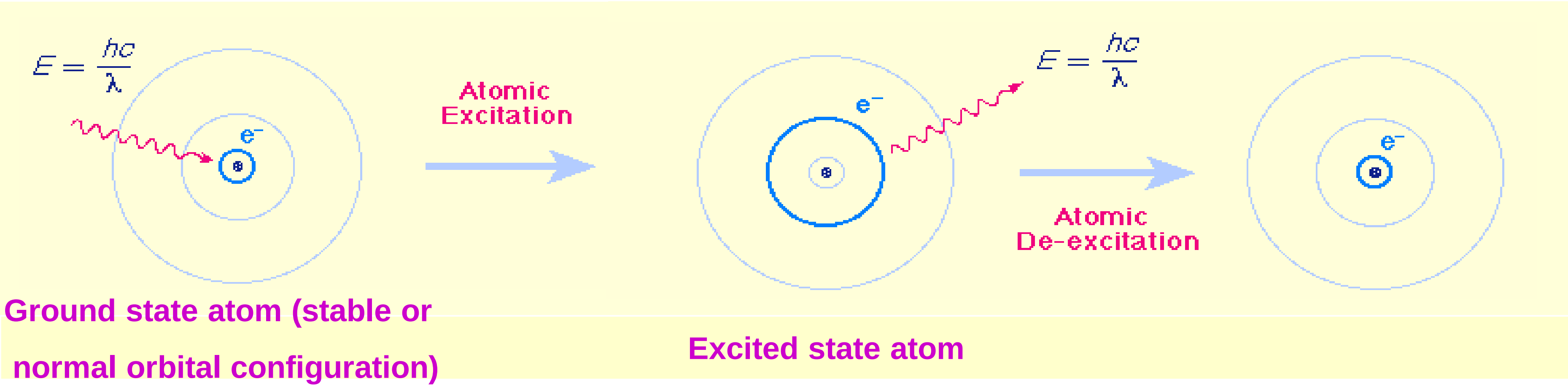


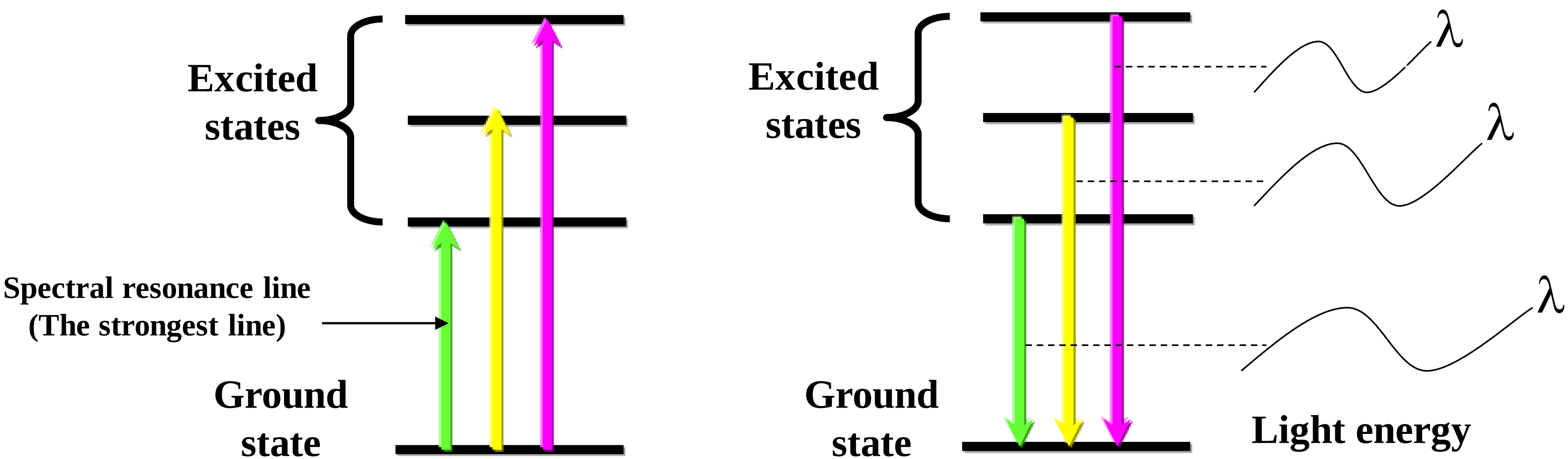
Atomic Spectroscopy Methods

1. Atomic Emission Spectroscopy (Flame Photometry)
2. Atomic Absorption Spectrometry (AAS)

Atomic Spectroscopy

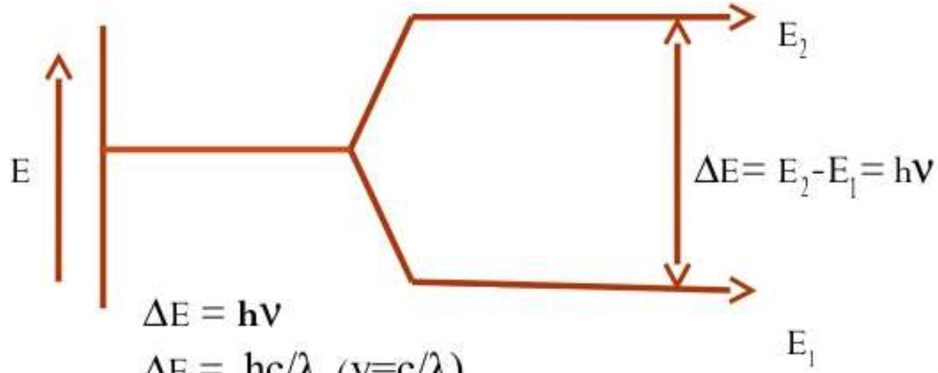
To understand the relationship of these techniques to each other, It is important to understand the atom itself and the atomic process involved in each technique.





Atomic Spectroscopy

Practically, the ratio of the excited to ground state atoms is extremely small. Therefore, The absorption spectrum is usually only associated with transitions from the ground state to higher energy states.



$\Delta E = h\nu$

$\Delta E = hc/\lambda \quad (\nu = c/\lambda)$

ΔE = Energy difference

h = Plank's constant($6.626068 \times 10^{-34}\ m^2kgs^{-1}$)

ν = frequency of emitted light

c = velocity of light

The fraction of free atoms that are thermally exited if governed by a Boltzmann Distribution

Boltzmann equation explain the relationship between the ground and excited state atoms

$$N_1/N_\circ = e^{-\Delta E/KT}$$

N_1: Number of excited atoms, $N_\circ$: Number of ground state atoms, ΔE: excitation energy K: Boltzmann constant and T: Temperature in kelvin

Atomic Spectroscopy

The process of excitation and return to ground state is involved in the two techniques of atomic spectroscopy.

We measure the energy absorbed or emitted and use it for quantification process

Atomic Emission Spectroscopy (AES) (Flame Photometry)

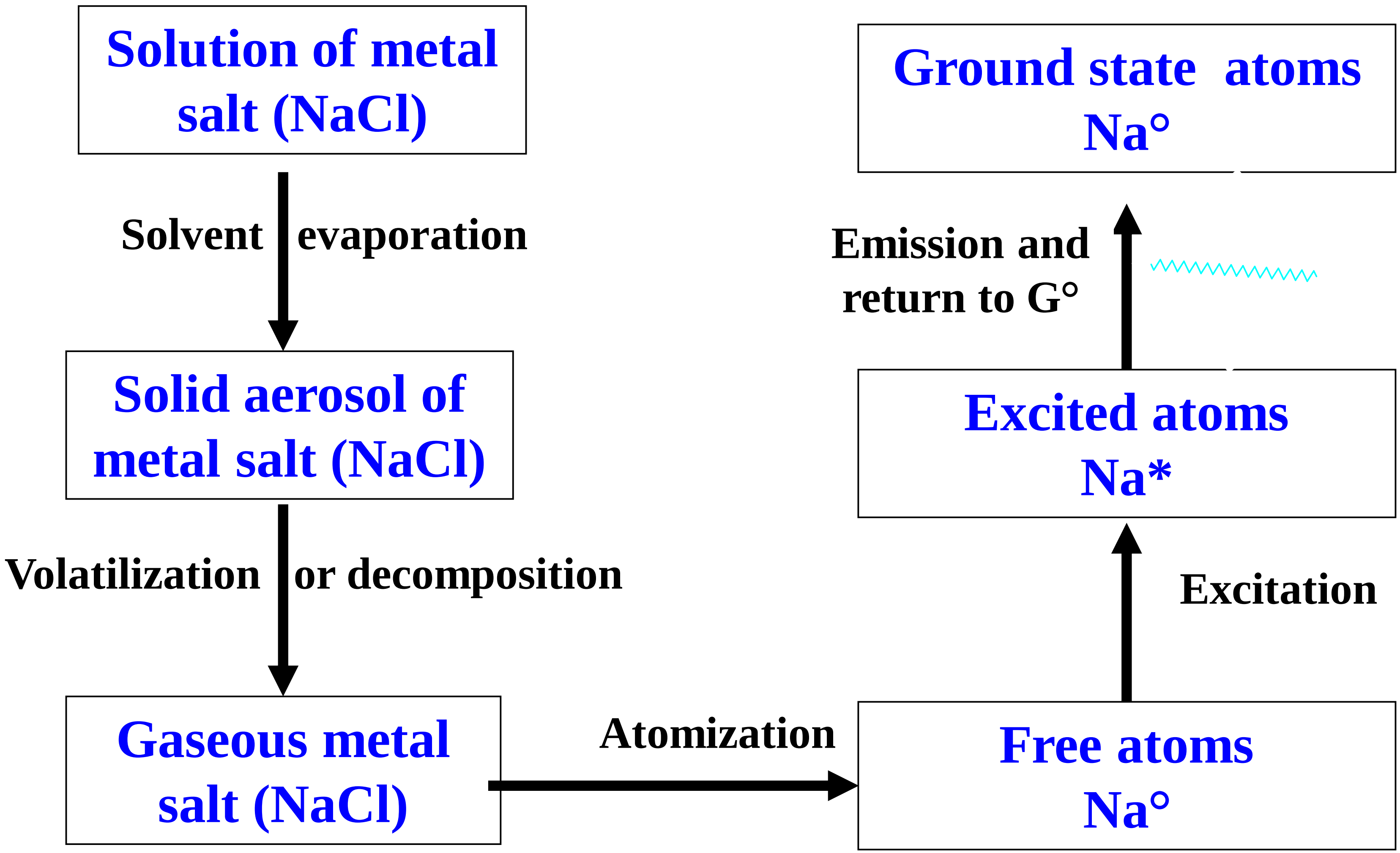
Principle: **Flame photometry is based upon those particles that are electronically excited in the medium.**

Flame : **is the source of excitation energy. (low energy source).**

Uses:

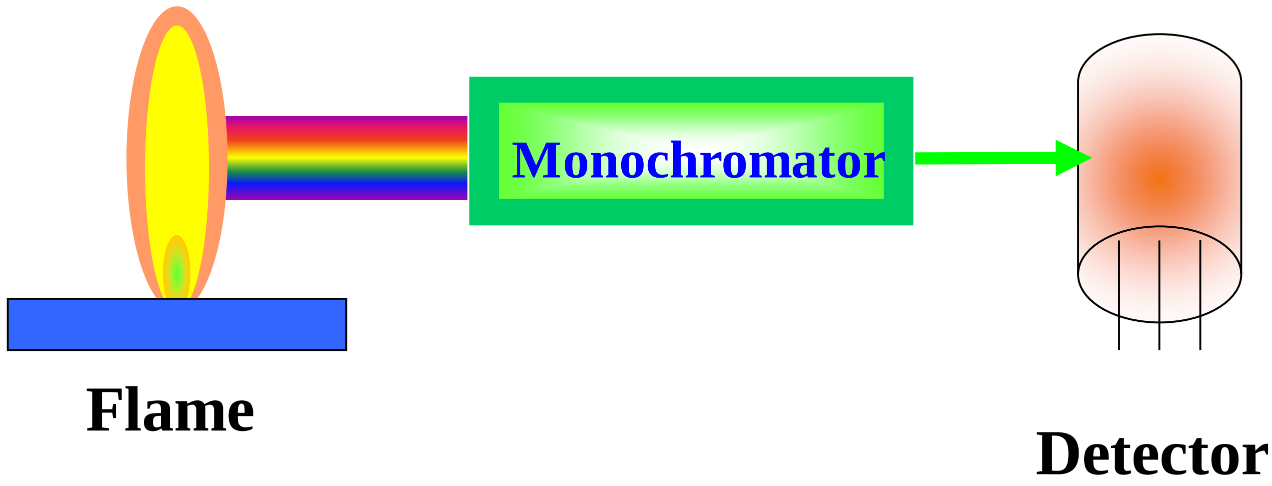
Flame photometry is used mainly for the determination of alkali metals and easily excited elements (Na, K, Li, Ca, etc.) particularly in biological fluids and tissues

Flame Photometry

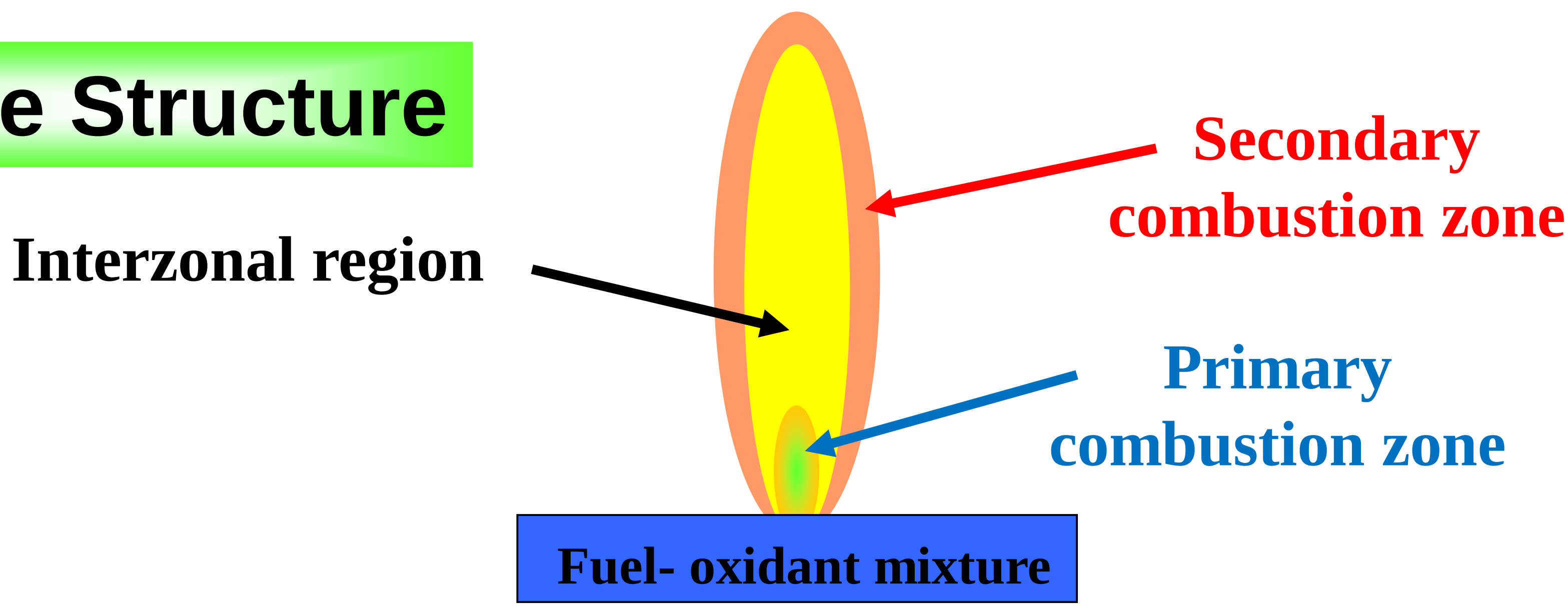


Flame Photometry

Instrument components



Flame Structure



Flame Photometry

Functions of Flame

1. To convert the constituents of liquid sample into the vapor state.

2. To decompose the constituents into atoms or simple molecules:

$$M^+ \quad + \quad e^- \ \text{(from flame)} \quad \rightarrow \quad M \quad + \quad h\nu$$

3. To electronically excite a fraction of the resulting atomic or molecular species

$$M \quad \rightarrow \quad M^*$$

The flame is composed of :

a fuel gas and oxidant gas

Fuel	Oxidant	Max. temp. (^oC)
Propane	Air	1725
Acetylene	Air	2400
Acetylene	Oxygen	3100
Acetylene	Nitrous oxide	3000
Hydrogen	Air	2000
Hydrogen	Oxygen	2700
-hydrogen	Air + argon	1577

Flame Photometry

Factors affecting intensity of flame emission :

1- The concentration of the analyte in solution

2- The rate at which excited atoms are formed in the flame.

3- The rate at which the sample is introduced into the flame.

4- Temperature of the flame.

5- Composition of the flame.

6- The ratio of fuel to oxidant in the flame.

7- Solvent used to dissolve the sample.

The flame temperature is the most important factor. Increase in flame temperature causes an increase in emission intensity. This is controlled by composition of the flame.

High temperature flames should not be used for elements that ionized easily e.g. Na, K, Li or Ce. However, high temperature flames are generally favored for transition elements and alkaline earth metals.

Flame Photometry

Effect of the solvent used to dissolve the sample; if the solvent is water the process is slow and if it is organic solvent the process is fast and emission intensity is increased.

It is therefore very important that calibration curves be prepared using the same solvent.

The stochiometric ratio of fuel to oxidant in the flame must be used, in which both fuel to oxidant are totally consumed.

Flame Photometry

The nebulizer-burner system

To convert the test sample into gaseous atoms

Nebulizer produce an aerosol of the test solution

Burner in which the mixing between fuel and oxidant

Types of burner system

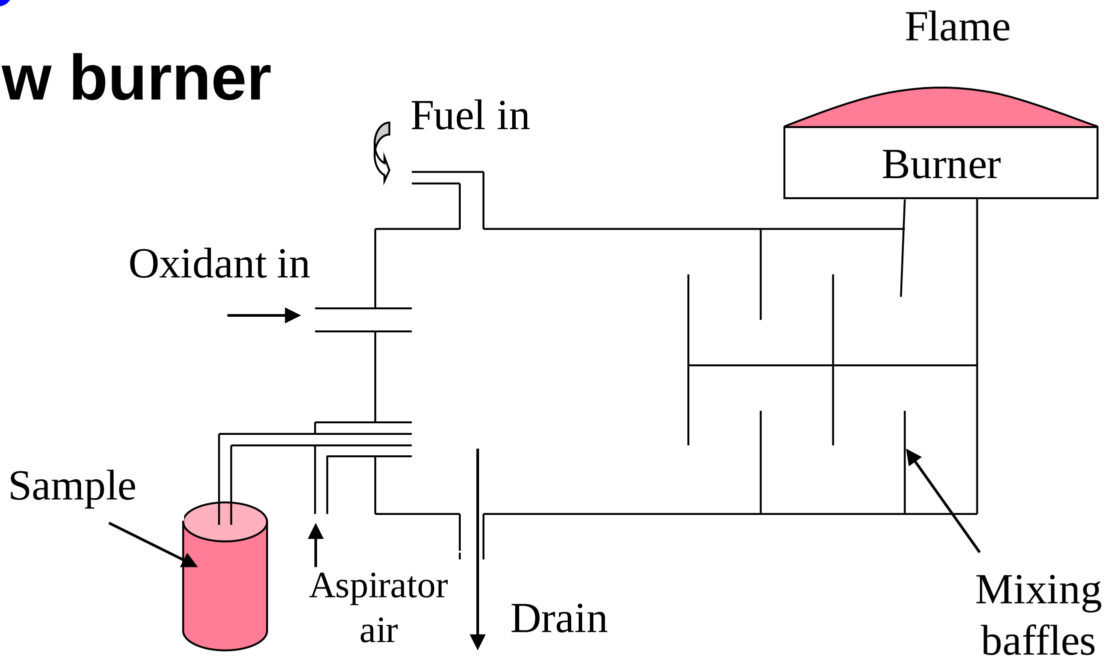
1. Pre-mix or laminar flow burner

Advantages

Homogenous flame

Disadvantages

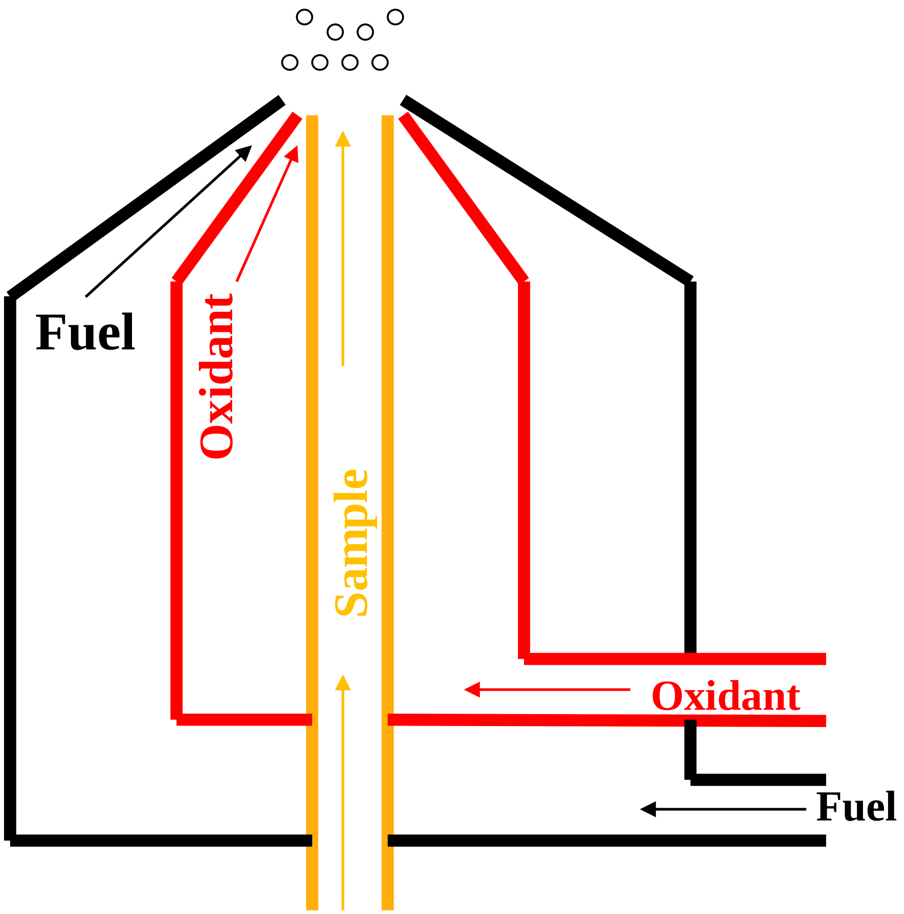
Suffers from explosion hazards



Flame Photometry

2. Total consumption burner

Three concentric tubes, the sample, fuel and oxidant only mix at the tip of burner



Advantages

1. **Simple to manufacture**
2. **Allows a total representative sample to reach the flame**
3. **Free from explosion hazards**

Disadvantages

Aspiration rate varies with different solvents

Flame Photometry

Non Flame Atomizers

For example: Heated Gravite Furnace

Sample evaporation→ time and temp. controlled drying and ashing

Advantages

1. **small samples are analysed**
2. **1000-fold more sensitive than flame**
3. **Oven is adaptable to determination of solid samples**

Disadvantages

1. **Low accuracy** 2. **Low precision**
2. **More ionic interferences due to very high temp.**

Flame Photometry

Monochromators — **As in UV**

Detectors — **Films or photomultipliers**

Analytical technique

1. **<u>Choice of the wavelength</u>:** **of maximum sensitivity and minimum spectral interferences**
2. **<u>Sample preparation</u>:**
   a. It is very important to obtain the sample in a <u>form of solution</u>, where the spectral and chemical interferences are absent

   b. <u>Demineralized distled Water</u> and very pure reagents are to be used because of the high sensitivity of the technique

   c. Because of the instability of the very dilute Solution, it is advisable to <u>dilute the solution just before use</u>.

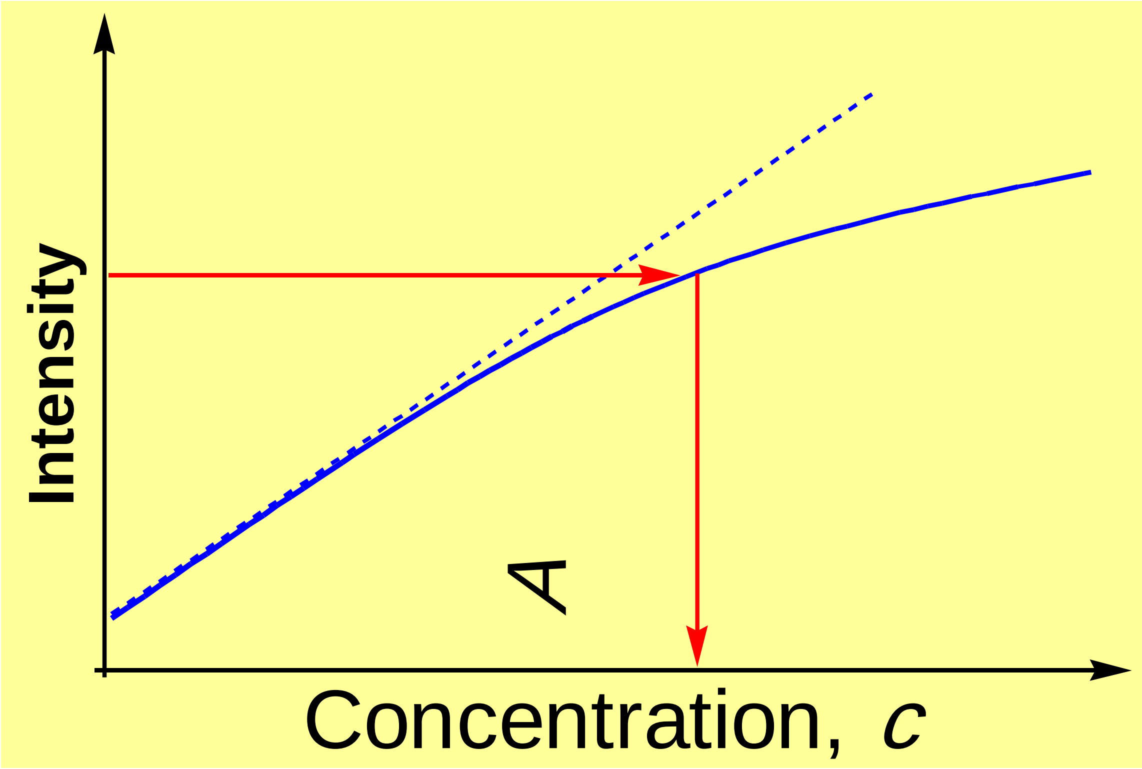
   d. Several elements can be determined in <u>blood, urine, cerebrospinal fluid</u> and other biological fluids by direct aspiration of the sample after dilution with water.

Flame Photometry

Chemical interferences: can often be overcome by simple dilution with a suitable reagent solution e.g. serum is diluted by EDTA solution for the determination of Calcium in order to prevent interference from phosphate.

3. Standard curves

Deviations from linearity may occur



Flame Photometry

3. <u>Qualitative analysis</u>

Flame photometry are useful mostly **for the detection of elements in group I and II of the periodic table**. The presence of certain elements can be detected by the use of a filter or monochromator.

<u>Advantages and disadvantages</u>

The method is **<u>not</u>** as **<u>reliable</u>** as other atomic emission spectroscopic methods, but it is **<u>fast and simple</u>**.

4. <u>Quantitative analysis</u>

To perform quantitative analysis, the sample is introduced into the flame and the intensity of radiation is measured. The concentration of the emitting substance is then calculated from a calibration curve or using standard addition method.

Flame Photometry

Application of flame photometry in pharmaceutical analysis

1. **Metals are major constituents of several pharmaceuticals such as dialysis solutions, lithium carbonate tablets, antacids and multivitamin - mineral tablets.**
2. **The elements Na, K, Li, Mg, Ca, Al and Zn are among the most common elements subjected to pharmaceutical analysis using flame emission technique.**
3. **Sodium and potassium levels in biological fluids are difficult to analyze by titrimetric or colorimetric techniques. Their analysis is very important for control of <u>infusion and dialysis</u> solutions which must be carefully monitored to maintain proper electrolyte balance.**

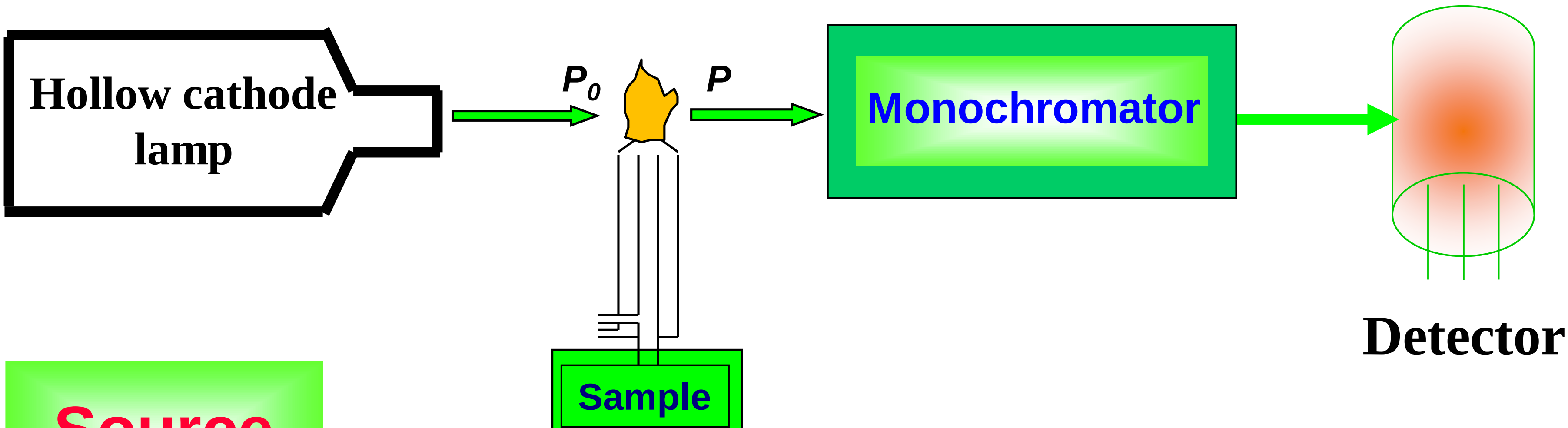
<u>Advantages</u>

1. **Flame emission is the <u>simplest</u> and <u>least expensive</u> technique.**
2. **The analysis may be carried out without prior separation as other components such as dextrose, do not interfere.**

Atomic Absorption Spectroscopy

Atomic Absorption spectroscopy involves the study of the absorption of radiant energy by neutral (ground state) atoms in the gaseous state.

Instrument components



Source Lamps

Hollow Cathod lamp