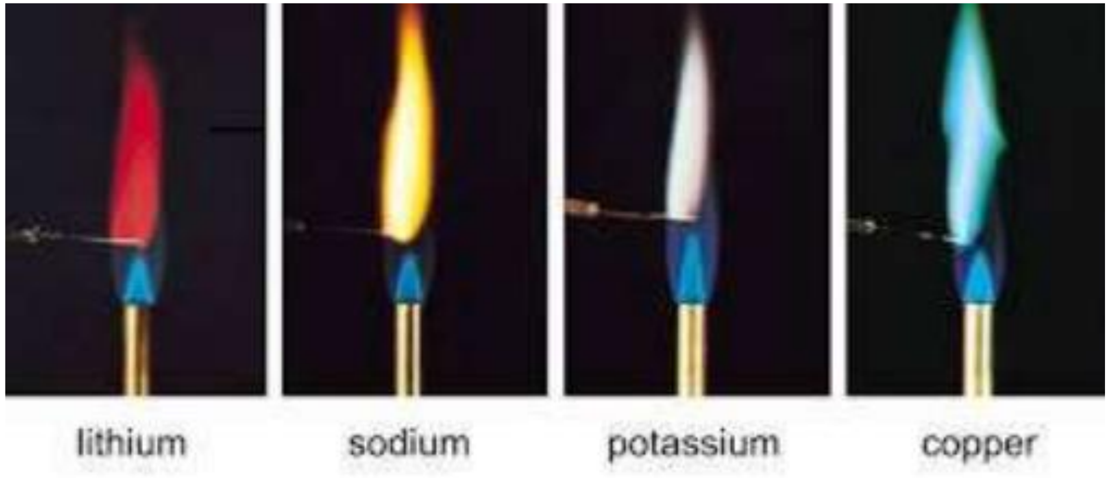
# Flame Emission Spectroscopy (FES)

In flame emission spectroscopy, measurement of  the radiation emitted by the excited atoms is measured and it is co-related to concentration of the sample.

FES is  generally used  for the determination of alkali  and alkaline earth elements. (Na, K, Li, Ca, etc.).

This technique is useful for qualitative as well as quantitative analysis. Alkali and alkaline earth metals gives characteristic colour to the flame.



# Flame Emission Spectroscopy (FES)

Wavelength emitted (flame colour) is used for qualitative analysis, while intensity of emission is related to the concentration.

This technique is mainly used in hospitals to measure the level of Na and K in body fluid and tissues.

# Flame Emission Spectroscopy

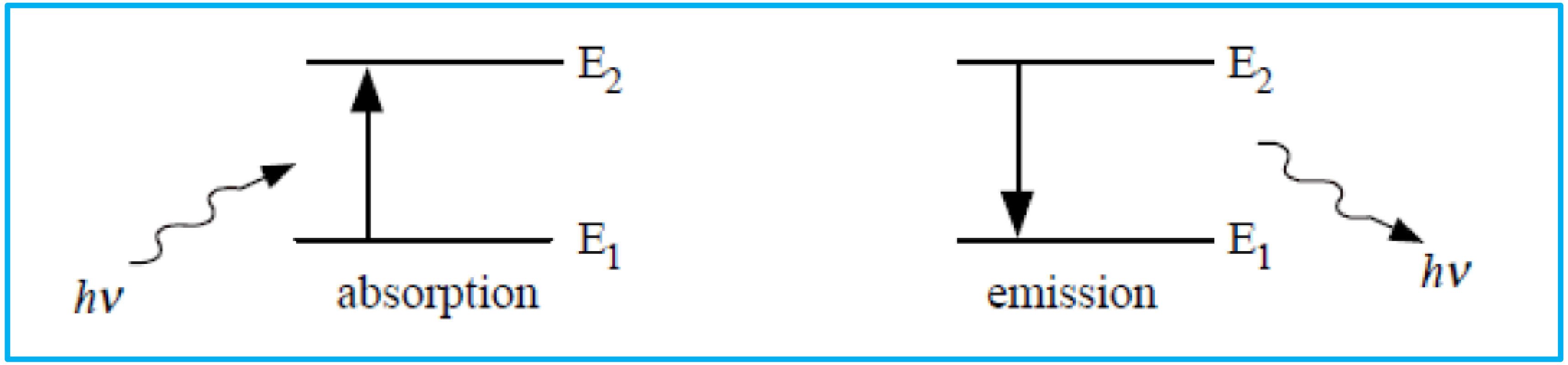
Principle:

Metallic salt solution introduced in flame in the form of mist. The flame evaporate solvent and form residual solid. These solid particles vaporize into gaseous state. These gaseous state molecules dissociate into neutral gaseous atoms or radicals.

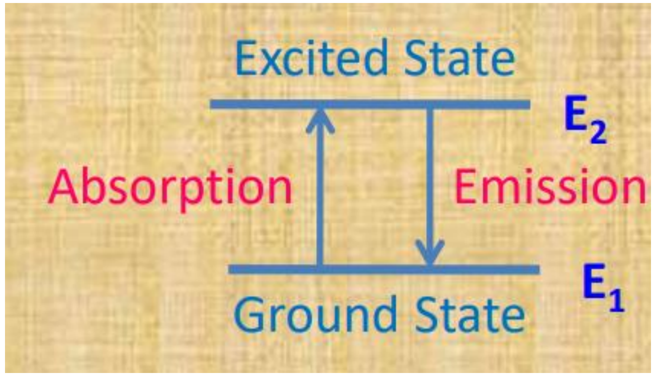
Due to thermal energy, the atoms get excited to a higher energy level.

These excited atoms return to ground state and emit some radiations as a wavelengths .

The emitted wavelengths are specific for specific elements.



# Flame Emission Spectroscopy




Principle:

Frequency of emitted light is calculated as

$h\gamma = E_2 - E_1$ -----------1

h= Plank's constant

$\gamma$ =Frequency of emitted light

$E_2$= Higher energy level (Excited state)
$E_1$=Lower energy level ( Ground State

Now $\gamma = C/\lambda$ -----------2 (C velocity of light and $\lambda$ is frequency of emitted radiation)

Putting value $\gamma$ of in eq.1

$hc/\lambda = E_2 - E_1$

$\lambda = hc/E_2 - E_1$

From the $\lambda$ value , element present in the sample can be find out.

# Flame Emission Spectroscopy

The number of excited atoms N* per cm3 can calculated by using Boltzmann's Equation

$$N^*/N = Ae^{-Ea/KT}$$

N= Number of atoms in ground state

N*= Number of atoms in excited state

A= Constant for particular element

Ea= Difference in energy of two level ( excitation energy)

K= Boltzmann constant

T temperature of flame in kelvin

Thus number of excited state atoms are depend on the flame temperature.

At higher temperature, number of excited atoms are more.

# Flame Emission Spectroscopy

In Flame Emission Spectroscopy the number of excited state atoms depend on the flame temperature. As temperature of flame increases number of atoms in excited state also increases.

Flames used in FES

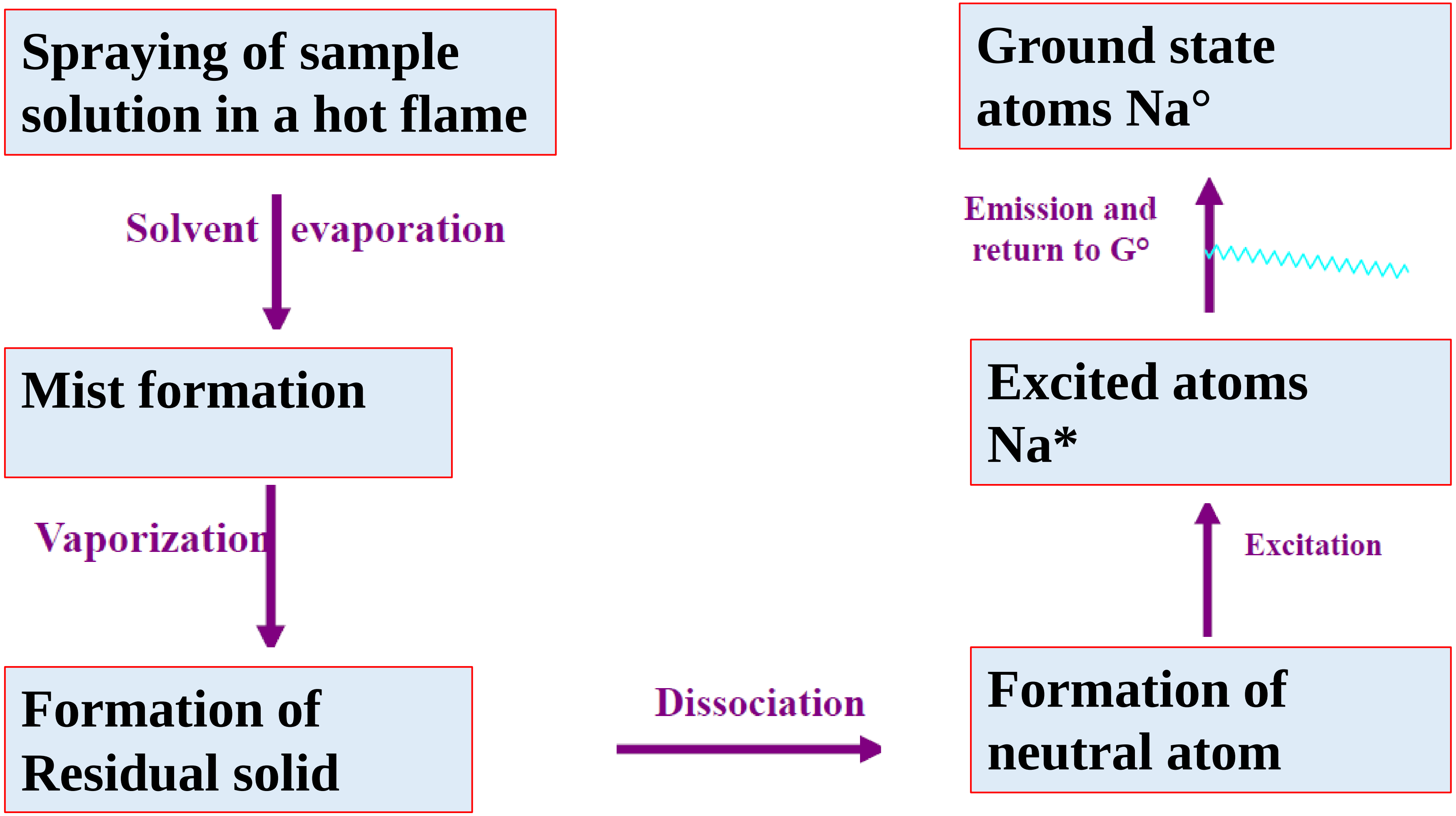
**Types of Flames**

| Fuel / Oxidant | Temperature |
|---|---|
| acetylene / air | 2200 °C |
| acetylene / $O_2$ | 3050 °C |
| Hydrogen /Air | 2100 °C |
| Hydrogen /$O_2$ | 2780 °C |
| Methane/ Air | 2000 °C |
| Methane/$O_2$ | 2700 °C |
| Propane/Air | 1725 °C |
| Propane / $O_2$ | 2800 °C |
| Butane/Air | 1900 °C |
| Butane / $O_2$ | 2900 °C |

Selection of flame depends on the volatilization temperature of the atom of interest.

# Flame Emission Spectroscopy

**Events occur in FES**



# Flame Emission Spectroscopy

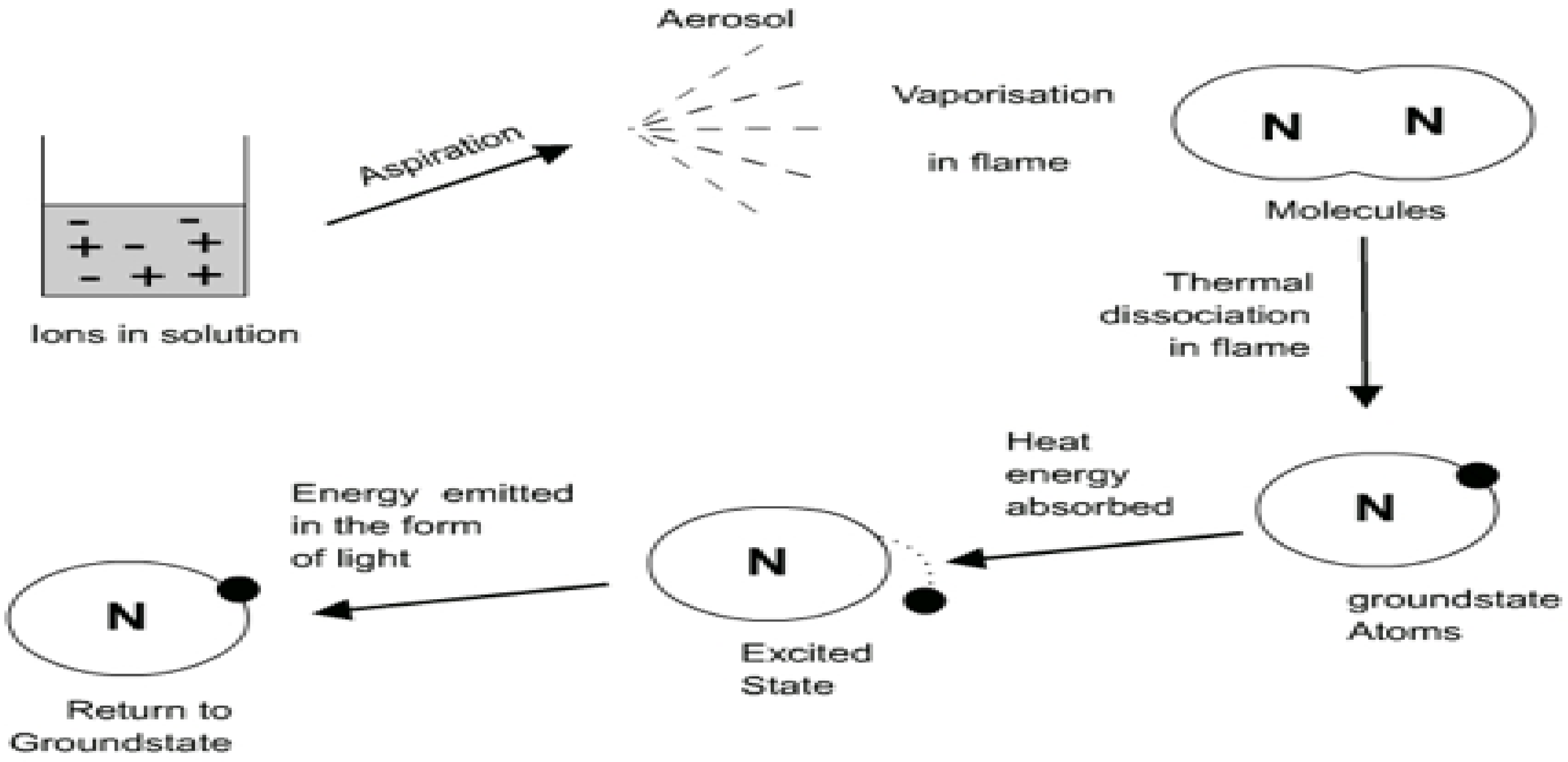



Fig 2 : Brief overview of the process

# Flame Emission Spectroscopy

**Advantages of FES**

1) It is more accurate method
2) It is faster technique
3) Detection sensitivity for alkali and alkaline earth metal is very good
4) Identification of one element in presence of other is possible
5) Easy to carry out

**Disadvantages:**

1) Only limited number of elements can be analyzed
2) Concentration required for analysis should be high
3) Sample in liquid form is necessary
4) There is possibility of spectral interference.

# Flame Emission Spectroscopy

Factors affecting intensity of the flame

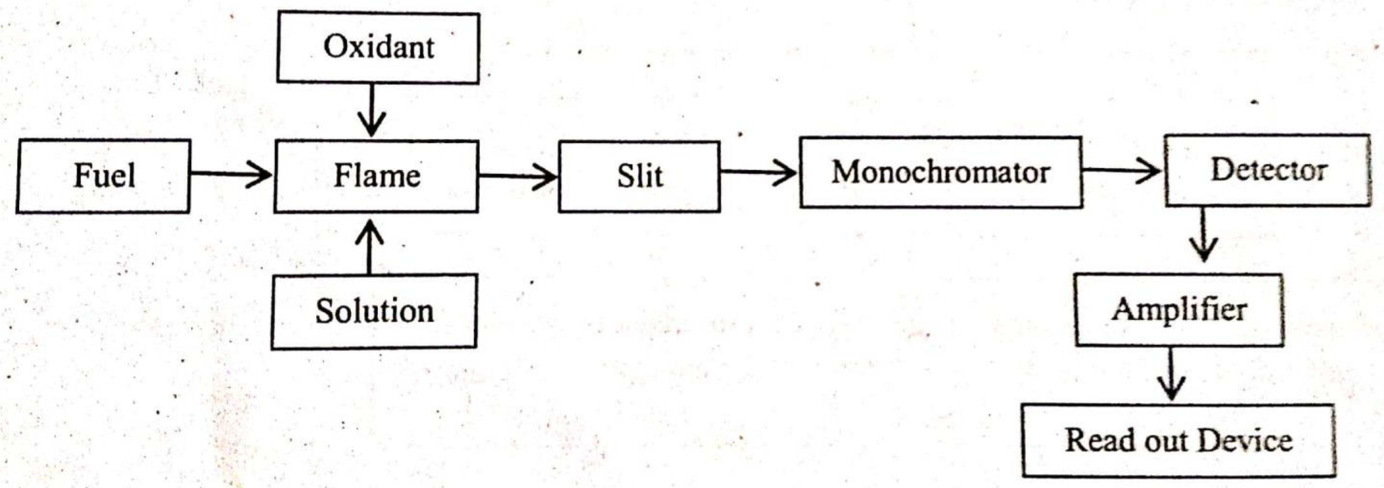
1) Concentration of analyte
2) Rate of formation of excited atoms in flame
3) Rate of introduction of sample in the flame
4) Temperature of the flame
5) Flame composition
6) Solvent used for dissolution

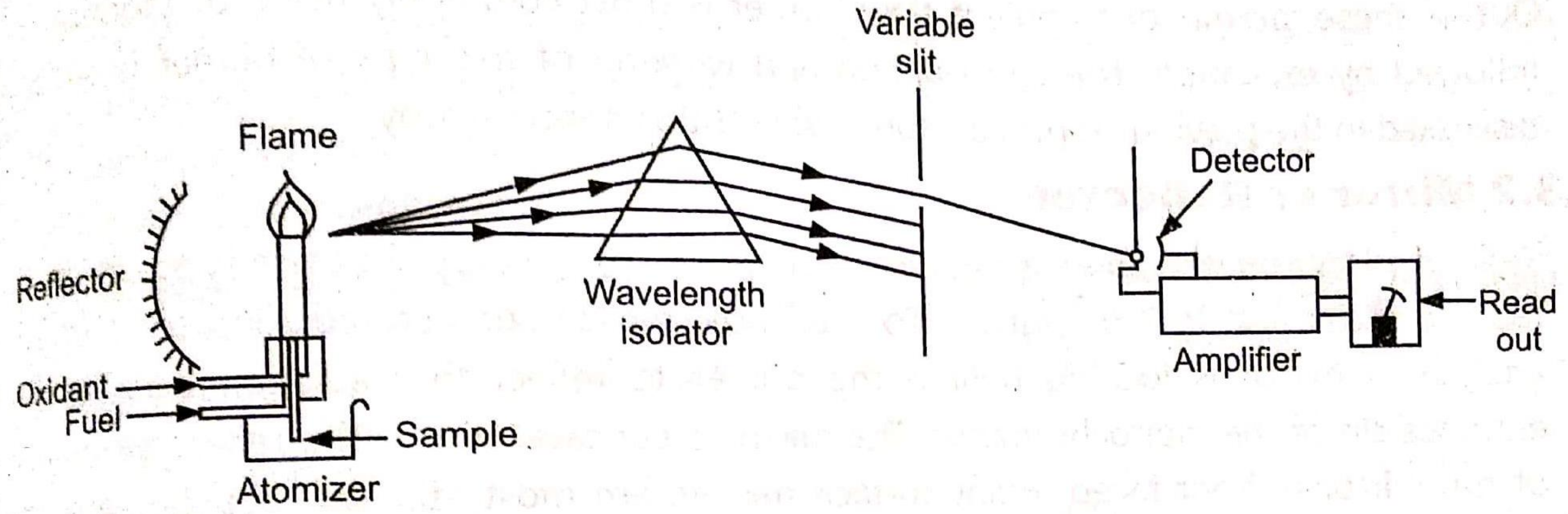
Alkali metals easily undergo ionisation , hence high temperature is not required for analysis of these elements. However for other elements including alkaline earth elements high temperature flame is preferred.

# Flame Emission Spectroscopy

## Instrumentation

1) Burner
2) Mirrors and slit
3) Monochromator
4) Detector
5) Amplifier
6) Read out device



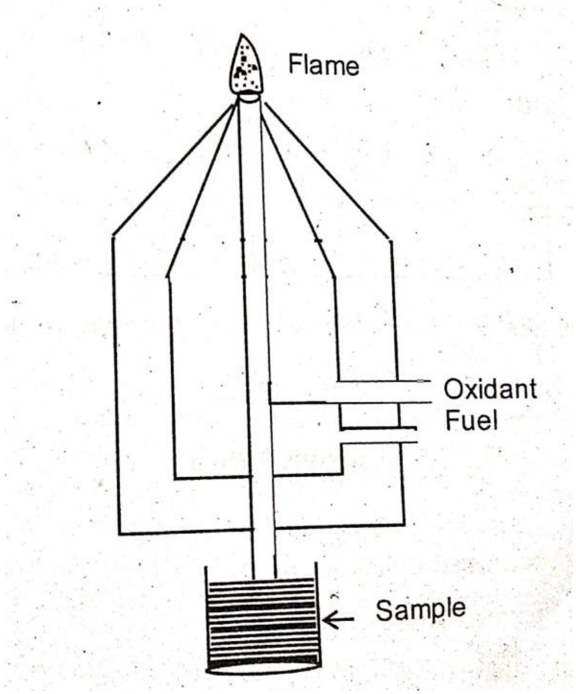
# Flame Emission Spectroscopy

**Instrumentation:**

**1) Burners:**

Types of Burners

**1) Total consumption burner:**




Sample solution, fuel gas and oxidising gas are passed through separate inlet and mixed at the top of the flame.

Sample solution is converted tiny droplets, which on evaporation form residue and residue finally produce ground state atoms.

**Advantages:**

1) High sensitivity 2) No risk of explosion

**Disadvantages:**

1) Clogging is possible 2) Poor reproducibility

3) Noisy operation

4) Rate of sample introduction depends on viscosity of solution

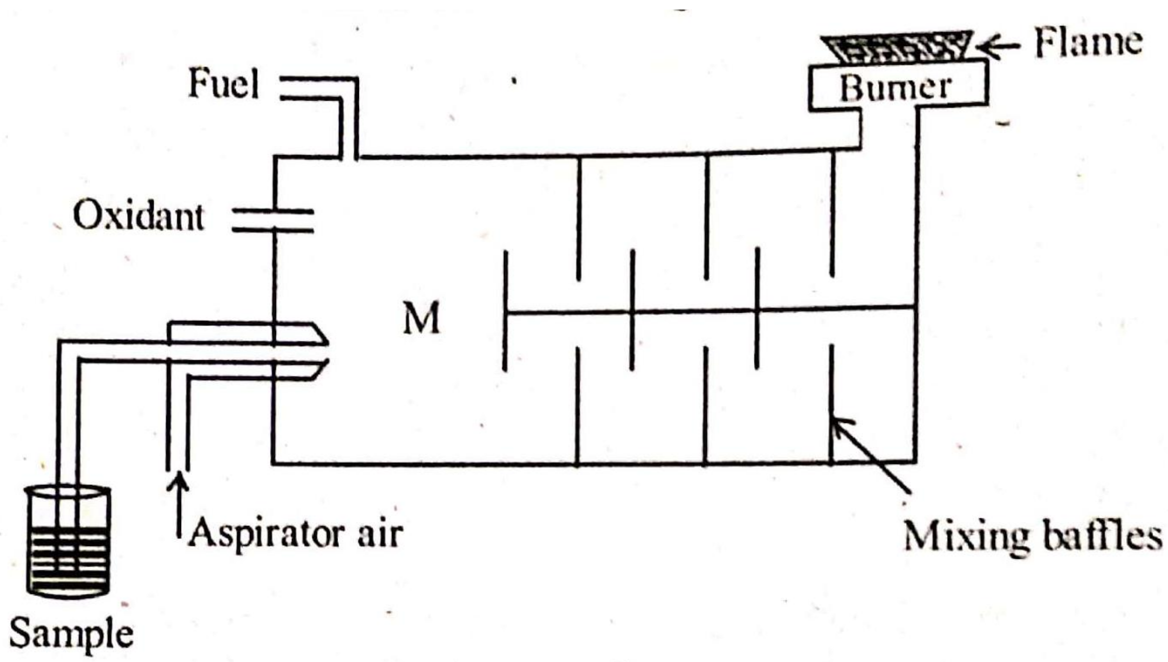
# Flame Emission Spectroscopy

**Instrumentation:**

**1) Burners**

Types of Burners

**2) Laminar flow /Premix burner:**




Sample solution, fuel gas and oxidising gas are mixed in mixing chamber

This mixture is then passed through a series of baffles where thorough mixing and formation of uniform droplets of the sample take place.

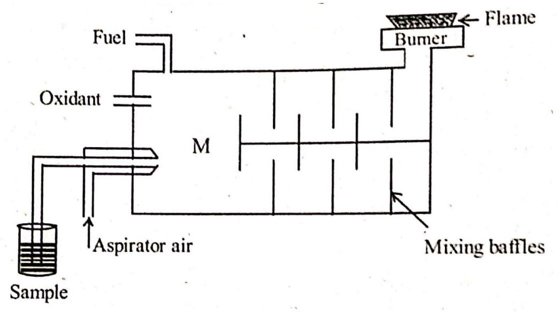
# Flame Emission Spectroscopy

**Instrumentation:**

**1) Burners:**

Types of Burners

**2) Laminar flow /Premix burner:**




**Advantages:**

1) Atomization efficiency is high as droplets are finer
2) Sensitivity is very high sensitivity due to mixing baffles.
3) Good reproducibility
4) Little tendency to clog
5) No noisy operation

**Disadvantages:**

1) Rate of sample introduction is slow
2) Possibility of explosion in mixing chamber.
3) Selective evaporation of mixed solvent can lead to analytical errors.

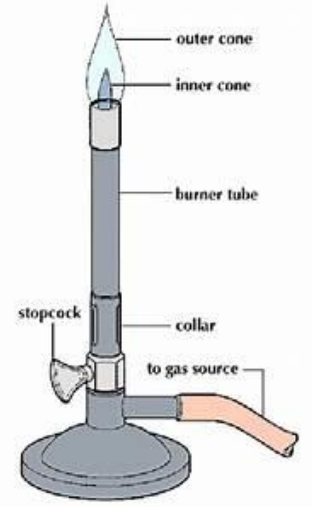
# Flame Emission Spectroscopy

**Instrumentation:**

**1) Burners:**

Types of Burners

**3) Mecker burner:**




This burner was used in earlier days.

It used natural gas as fuel and air as oxidant

Flame temperature is low, hence only used for easily ionizable elements.

**Advantages:**

1) Burner cap can cooled easily.
2) Possibility of flashing back is less.

**Disadvantages:**

1) Only used for alkali metals
2) Flame is not homogeneous
3) Produce relatively low temperature

# Flame Emission Spectroscopy

**Instrumentation:**

## 2) Mirrors:

It is important component in FES placed behind the flame. It collects all radiations emitted by the flame and focus towards the monochromator. Generally concave mirror is used. It creates inverted image of the flame, of equal size, at the location of the flame.

## 3) Slits:

Entrance and exit slits are used to control incoming and outgoing radiation

# Flame Emission Spectroscopy

**Instrumentation:**

**4)Monochromator:**

Monochromator: It is the combination of the components from entrance slit to exit slit. There are two types of monochromators used in FES are Prism or grating. For more accuracy gratings are used and hence cost of instrument increases. In simple FES filter can be used. Overall cost of instrument is based on monochromator. The low cost instruments are useful for routine analysis or simple analysis.

# Flame Emission Spectroscopy

**Instrumentation:**

**4) Monochromator:**

**i) Prism:**
It is triangular shape piece of glass or quartz. It work on refraction phenomenon.

**ii) Diffraction Grating:**

It is dispersing element that can isolate a selected band of wavelength. It is prepared by ruling a large number of parallel equidistance groves upon highly polished metallic surface. Approximately 15,000 to 30,000 groves per square inch are present on diffraction grating, these groves acts as scattering centers.

# Flame Emission Spectroscopy

**Instrumentation:**

**5) Detectors: a) Phototube**

Detector convert the radiation energy into electrical signal. In Flame Emission Spectroscopy, radiation emitted by excited state atoms is detected by using photosensitive detector. In Flame Emission Spectroscopy phototube and photomultiplier tubes are used as a detectors.

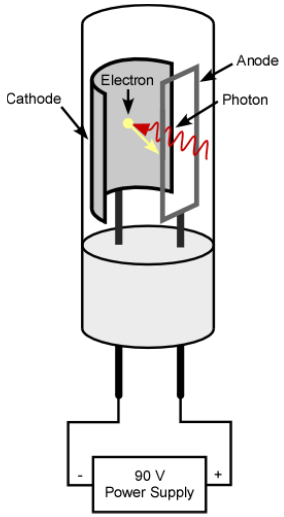


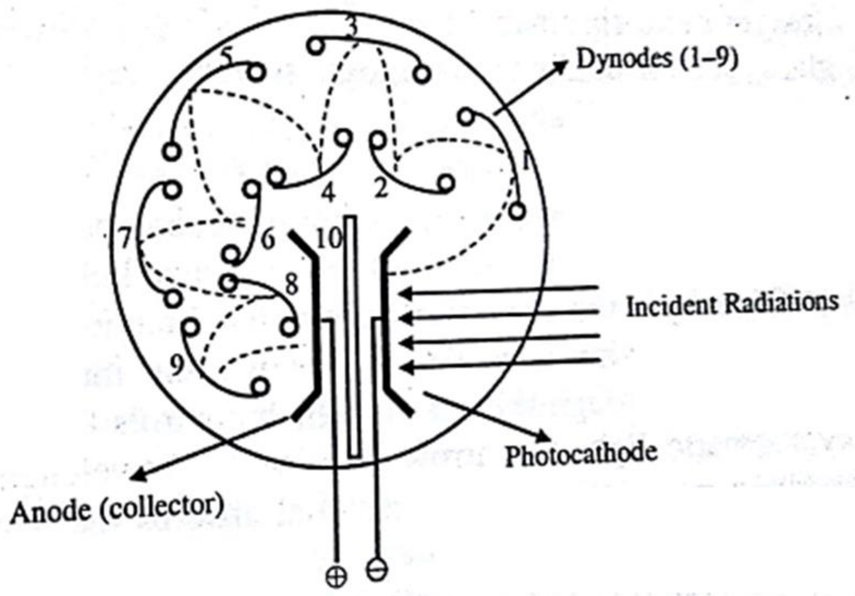

Photo Tube (Image Courtesy : http://people.whitman.edu/)

A phototube consists of an anode and a light-sensitive cathode. These are placed in an evacuated glass or quartz bulb. Approximately 100 volt potential difference is applied across the two electrode. When radiation ( photon) strikes on surface of cathode, ejection of an electrons take place. These ejected electrons strikes on the surface of anode and current start flowing. This low intensity current needs amplification for measurement.

# Flame Emission Spectroscopy

**Instrumentation:**

**5) Detectors: b) Photomultiplier tube**




**Photomultiplier tube**

**Construction:**

It contain photosensitive half cylinder of metal which act as cathode.

Inner surface of cathode is coated with light sensitive material like $Cs_2O$, $Ag_2O$ and $K_2O$.

It consist of 9 dynodes which having coating of cesium metal which emits several electrons (2 to 5).

These electrons are collected by collecting electrode (anode).

# Flame Emission Spectroscopy

**Instrumentation:**

**5) Detectors: b) Photomultiplier tube**

**Working:**

When light strike on cathode surface, it eject electrons due to photoelectric effect.

These electrons strike on the surface of first dynode and ejection of 2 to 5 electrons take place.

These electrons strike on surface of second dynode and ejection of more electron take place.

This process is continued up to 9$^{th}$ dynode. Emitted electrons are collected by collecting electrode and current begin to flow. This current is amplified and measured by read out device.

**Advantages:**

1) It is very fast (response time is $10^{-9}$ second)
2) High sensitivity for U.V. and visible region.

# Flame Emission Spectroscopy

**Instrumentation:**

## 6) Amplifier:

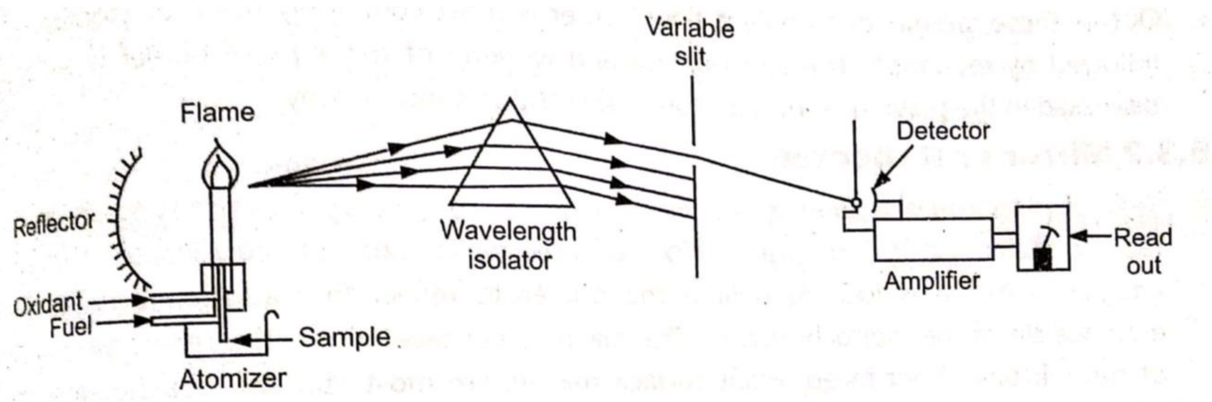
Amplifier is placed in between detector and read out device. It amplifies the signal received from the detector.

## 7) Read out device:

Galvanometer is used as read out device

# Flame Emission Spectroscopy

**Measurement by FES:**




1) Sample is dissolved in suitable solvent.
2) Solution along with fuel and oxidant are aspirated to the flame.
3) Ground state atoms are produced
4) Ground state atoms goes to excited state and return to ground state by emitting radiation.
5) Radiation passed through monochromator and strike on detector.
6) Amplifier amplify detector response and give to read out device.

# Flame Emission Spectroscopy

## Interferences in FES:

**Interference** : Any process which causes error in determination is called interference.

**Interferent** is the substance present in the sample, blank or standard solution which affects the signal of the analyte.

### 1) Spectral Interference:

When emission lines overlap with each other, then this kind of interference is observed.

Emission of an interfering species either overlap or lies so close to the analyte band that resolution by the monochromator become difficult.

This interference arises when flame temperature is very high. At high temperature number of spectral lines are produced.

Spectral interference is very common in FES.

Example: Iron line at 3247.28 $A^0$ overlap with copper line at 3247.54 $A^0$

Aluminium line at 3082.15 $A^0$ overlap with vanadium line at 3082.11 $A^0$

# Flame Emission Spectroscopy

**Interferences in FES:**

**2) Ionization Interference:**

Due to high flame temperature ionization of atoms take place.

FES is used for analysis of alkali and alkaline earth elements. Ionization energy of these elements is low , hence ionization interference is most common in FES

To overcome this effect easily oxidisable elements are added to the solution

Example: During analysis of sodium , potassium is added in the solution. Potassium undergo ionization and electrons are produced in the flame which help to prevent ionization of sodium in.

# Flame Emission Spectroscopy

## Interferences in FES:

### 3) Chemical Interference:

Because of formation of stable compound which cannot undergo decomposed at flame temperature.

Example  Aluminum and magnesium form a thermally stable mixed oxide, thus low results are obtained for magnesium in presence of aluminum..

This process leads to lower number of atoms in the flame for excitation.

Example: Analysis of calcium: If phosphate ions present in the analyte solution, formation of calcium phosphate stable compound is observed.

This interference can be avoided by adding excess of lanthanum salt in the analyte solution. Lanthanum preferentially combines with phosphate ions and calcium will be unaffected.

# Flame Emission Spectroscopy

**Interferences in FES:**

**4) Anion error:**

Anions interfere as components of salt and acid

Example: Chloride and sulphate can cause this type of interference.

**5) Cation –Cation Interference:**

Presence of metal cations of Na and K can cause this type of interference . This decrease the signal intensity.

# Flame Emission Spectroscopy

**Interferences in FES:**

**6) Background Absorption :**

It is caused by absorption of the species other than the atoms at resonance wavelength.

It is wavelength dependent phenomenon and gives a positive error in the analysis.

It can be minimized by using Deuterium arc background correction (continuum source)

# Flame Emission Spectroscopy

**Applications of FES:**

**1) Qualitative analysis:**

Alkali and alkaline earth elements can be detected by this technique. It is fast, simple and accurate technique.

**2) Quantitative analysis:**

For quantitative analysis, liquid sample is introduced into the flame and the intensity of radiation is measured. The quantitative analysis of alkali and alkaline earth elements can be done by using the following method.

a) Standard Addition Method

b) Internal Standard Method

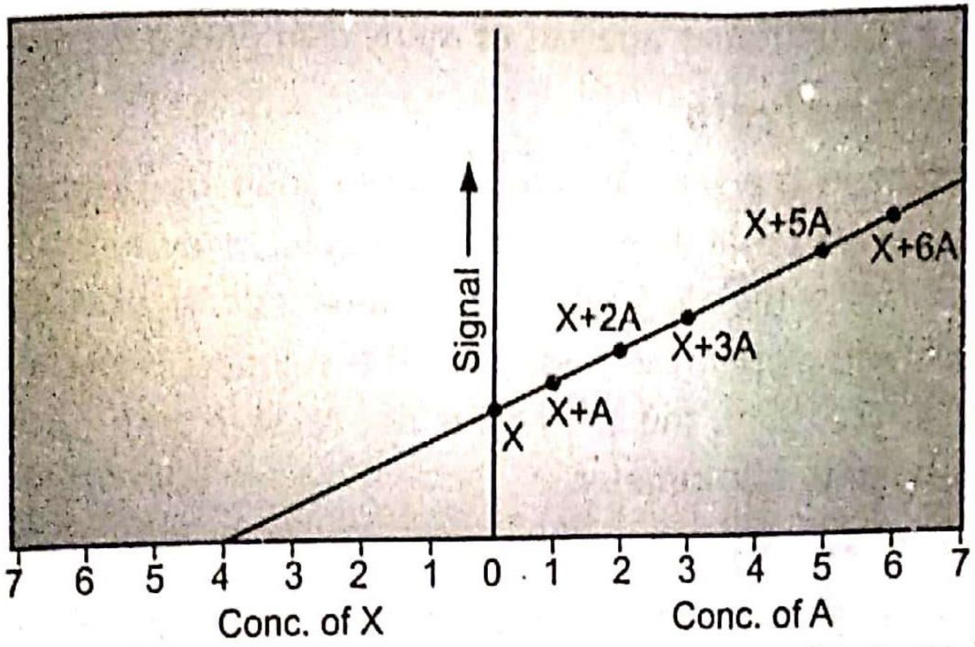
c) Calibration Curve Method

# Flame Emission Spectroscopy

**Applications of FES:**

**2) Quantitative analysis:**

**a) Standard addition method:**




**Plot of signal against concentration of solutions**

1) Signal intensity ( emitted radiation) of unknown sample(X) is measured.

2) Series of solution containing fixed amount of unknown (X) and different amount of standard is prepared.[ (X+A), (X+2A), (X+3A), (X+4A), (X+5A), (X+6A)]

3)Signal intensity of each solution is measured and plot of signal vs concentration (X+A) is plotted.

4) Concentration of unknown solution(X) can determined by the intersection of the curve with the concentration axis.

# Flame Emission Spectroscopy

**Applications of FES:**

**2) Quantitative analysis:**

**b) Internal standard method:**

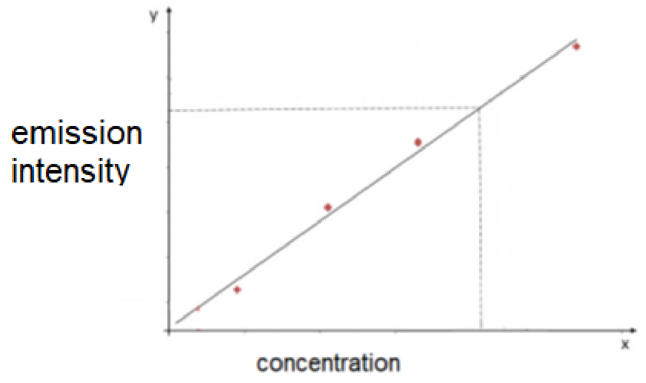
1) Series of standard solution is prepared.
2) Known amount internal standard (ex. Li) is added
3) Signal intensities of all standard solution having internal standard are measured.
4) Signal intensity of unknown solution is measured.
5) Graph of ratio of signal intensity vs concentration is plotted and concentration of unknown solution is determined.

# Flame Emission Spectroscopy

**Applications of FES:**

**2) Quantitative analysis:**

**c) Calibration curve method:**




1) Series of standard solutions of element to be analyzed is prepared
2) Emission intensity of each standard solution is measured.
3) Emission intensity of unknown solution is measured.
4) Calibration curve of emission intensity vs concentration of standard solution is plotted.
5) Concentration of unknown solution is find out by extrapolation method.

# Flame Emission Spectroscopy

**Applications of FES:**

**3) Simultaneous Multielement Analysis:**

**Analysis of m**ore than one element can be done by using FES. By using vidicon detector system multielement analysis is possible.

**4. Miscellaneous Applications:**

**a) Soil and Water Analysis:**

It is used in agriculture field for soil and water analysis. Sodium, magnesium, potassium, calcium, iron content of soil and water can be analyzed by FES.

It is useful for deciding proper fertilizer required for soil.

**b) Food Analysis:** This technique is very useful in analysis of food products. Fresh milk can be studied for there nutritional value. Butter milk, fruit juices, soft drinks and alcoholic beverages can be analyzed by FES.

# Flame Emission Spectroscopy

**Applications of FES:**

**4. Miscellaneous Applications:**

**c) Medicine and Biology:**

Sodium and Potassium level from body fluid can be analyzed by FES

**d) Geology, Industry and other field:.**

Waste water analysis from industry is carried out by using FES.

Analysis of raw material and finished product

Analysis of geological materials such as minerals, ores, clay, petroleum etc.

# Flame Emission Spectroscopy

**Preparation of standard solutions:**

**1. Standard solution of sodium ions:**

2.542 g Sodium chloride is dissolved in 1 liter deionized water in graduated flask.

This solution contains 1.0 mg of sodium ions per mL. This stalk solution is diluted to get solution having 10, 5, 2.5 and 1 μg (microgram) of sodium ions

**2. Standard solution of potassium ions:**

1.909 g Potassium chloride is dissolved in 1 liter deionized water in graduated flask.

This solution contains 1.0 mg of potassium ions per mL. This stalk solution is diluted to get solution having 10, 5, 2.5 and 1 μg (microgram) of sodium ions

# Flame Emission Spectroscopy

**Preparation of standard solutions:**

**3. Standard solution of Lithium ions:**

5.324 g Lithium carbonate is dissolved in 1 liter deionized water in graduated flask.

This solution contains 1.0 mg of lithium ions per mL. This stalk solution is diluted to get solution having 10, 5, 2.5 and 1 µg (microgram) of sodium ions