FLAME PHOTOMETRY

INTRODUCTION

Flame Photometry is a branch of spectroscopy in which the species are examined in the spectrometer are in the form of atoms.

A Flame Photometer is an instrument used in inorganic chemical analysis to determine the concentration of certain metal ions (mainly are sodium, potassium, calcium, lithium)

Flame photometry is based on measurement of intensity of light emitted when a metal is introduced into the flame. -

The wavelength of the colour tells what the metal is

[Qualitative]

The color’s intensity tells us how much element present

[Quantitative]

Flame Photometry is also named as **Flame Emission Spectroscopy** because of the use of a flame to provide the energy of excitation to atoms introduced into the flame.

Classification of Atomic Spectroscopic Methods:

As mentioned earlier, in atomic spectroscopy, the elements present in a sample are converted to gaseous atoms or elementary ions in a process called atomisation. This process can be accomplished in a number of ways, using any of the following.

- Flame
- Electrothermal (or furnace) method
- Inductively coupled argon plasma
- Direct current argon plasma
- Electric arc

Atomic Spectroscopic Methods-I:

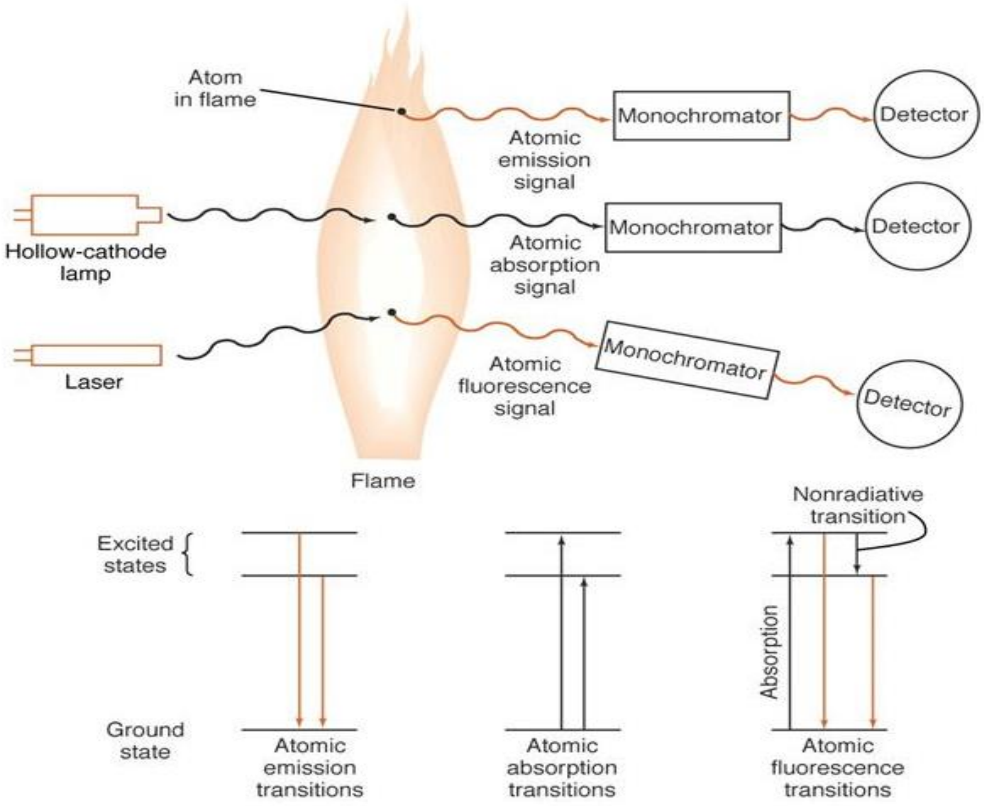
These methods accomplish the atomisation process in different temperature ranges. Once in the vapour phase, the atoms of the elements interact with radiation and provide information about themselves. You would recall from Unit 1 that the interaction of radiation and matter can manifest itself in terms of absorption, emission or fluorescence emission. Accordingly, we have atomic absorption, emission or fluorescence spectroscopies. Let us learn about the basic principle of these methods.

Atomic Absorption Spectrometry (AAS): In this method, the atomic vapours containing free atoms of an element in the ground state are subjected to a UV-VIS radiation source emitting a characteristic frequency of the element present in atomic vapours. The radiation is absorbed and the intensity of the radiation is attenuated. The absorbed radiation causes excitation of electrons from the ground state to an excited level. The extent of absorption is a quantitative measure of the concentration of the atomic vapours of the element in the ground state. It is an electronic excitation and the energy of transitions lies in the to UV-VIS region of the electromagnetic spectrum.

Atomic Emission Spectrometry (AES): In this method, a sample is normally excited by the thermal energy of a flame, argon plasma or an electrical discharge. The atoms in the sample absorb thermal energy, causing the excitation of the outer orbital electrons. As the excited state is short lived, the excited atoms return back to the ground state after a very short lifetime (typically 10–6 to 10–9 s). This is accompanied by the emission of electromagnetic radiation, normally in the form of light in the UV - VIS region. The wavelength of the emitted radiation and its intensity provide the qualitative and quantitative information about the analyte. The atomic emission spectroscopy employing flame as a means of excitation is called flame photometry or flame emission spectroscopy (FES). It is used for the routine determination of metals, mainly of alkali and alkaline earth metals, though other metals can also be analysed.

Atomic Fluorescence Spectrometry (AFS): In AFS, the gaseous atoms are excited to higher energy level by absorption of the electromagnetic radiation and the fluorescence emission from these excited atoms is measured. The main advantage of fluorescence detection compared to absorption measurements is the greater sensitivity achievable because the fluorescence signal has a very low background radiation. A schematic representation of the transitions associated with the phenomenon of atomic absorption, atomic emission and atomic fluorescence emission is given in figure:

Absorption, emission, fluorescence



Schematic representation of absorption, emission, and fluorescence.

- **GENERAL PRINCIPLES**

(simplified version of sequential events:)

Liquid sample conataining salt solution is intriduced into the flame

Solvent is first veporised , leaving the particles of solid salt which are then veporiesd into gaseous state.

The gaseous molecules are dissociated to give free neutral atoms or radicals which can be excited by thermal energy of flame

The unstable excited atoms emit photons while returning to lower energy state.

The measurment of emitted photons-radiation forms the basis of flame photometry.

: Under constant and controlled conditions, the light intensity of the characteristic wavelength produced by each of the atoms is directly proportional to the number of atoms that are emitting energy, which in turn is directly proportional to concentration of the test sample.

A brief overview of the process:

1. The solvent is first evaporated leaving fine divided solid particles.
2. This solid particles move towards the flame, where the gaseous atoms and ions are produced.
3. The ions absorb the energy from the flame and excited to high energy levels.
4. When the atoms return to the ground state radiation of the characteristic element is emitted.
5. The intensity of emitted light is related to the concentration of the element.

The processes occurring during flame photometer analysis are summarized below:

Desolvation: Desolvation involves drying a sample in a solution. The metal particles in the solvent are dehydrated by the flame and thus solvent is evaporated.

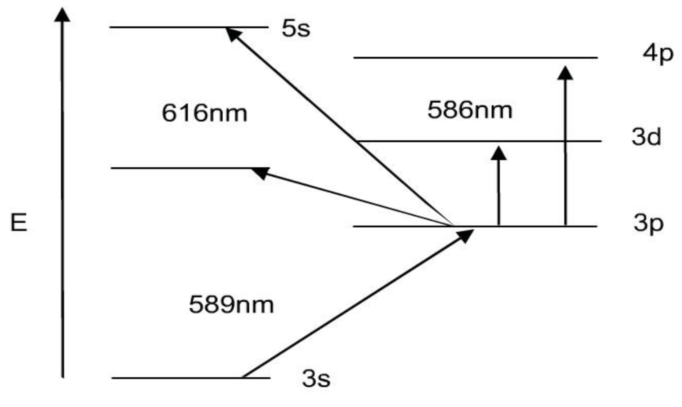
Vaporization: The metal particles in the sample are also dehydrated. This also led to the evaporation of the solvent.

Atomization: Atomization is the separation of all atoms in a chemical substance. The metal ions in the sample are reduced to metal atoms by the flame.

Excitation: The electrostatic force of attraction between the electrons and nucleus of the atom helps them to absorb a particular amount of energy. The atoms then jump to the higher energy state when excited.

Emission: Since the higher energy state is unstable the atoms jump back to the ground state or low energy state to gain stability. This jumping of atoms emits radiation with characteristic wavelength. The radiation is measured by the photo detector.

The energy level diagram of the sodium atom is shown in figure.



Energy level diagram for atomic sodium

Scheibe-Lomakin equation:

Scheibe-Lomakin equation describes intensity of light emitted with the help of following formula:

$\mathbf{I = k \times c^n}$

Where:

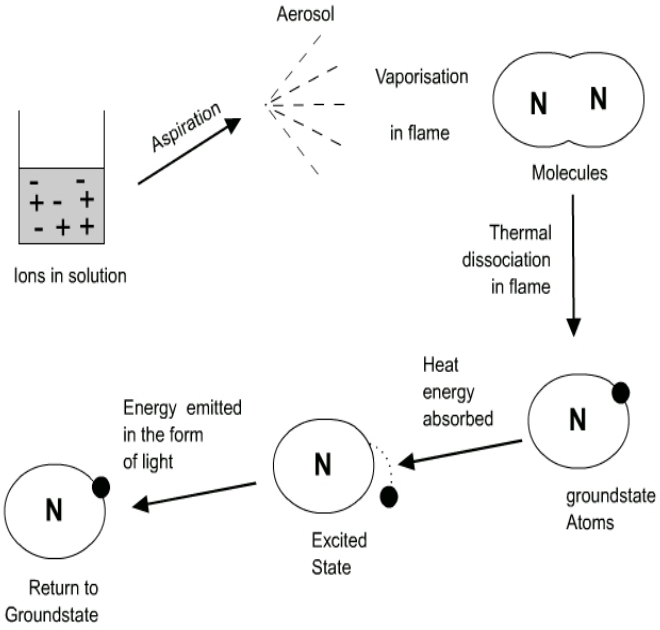
I = Intensity of emitted light

c = Concentration of the element

k = Proportionality constant

At the linear part of the calibration curve $n \sim 1$,

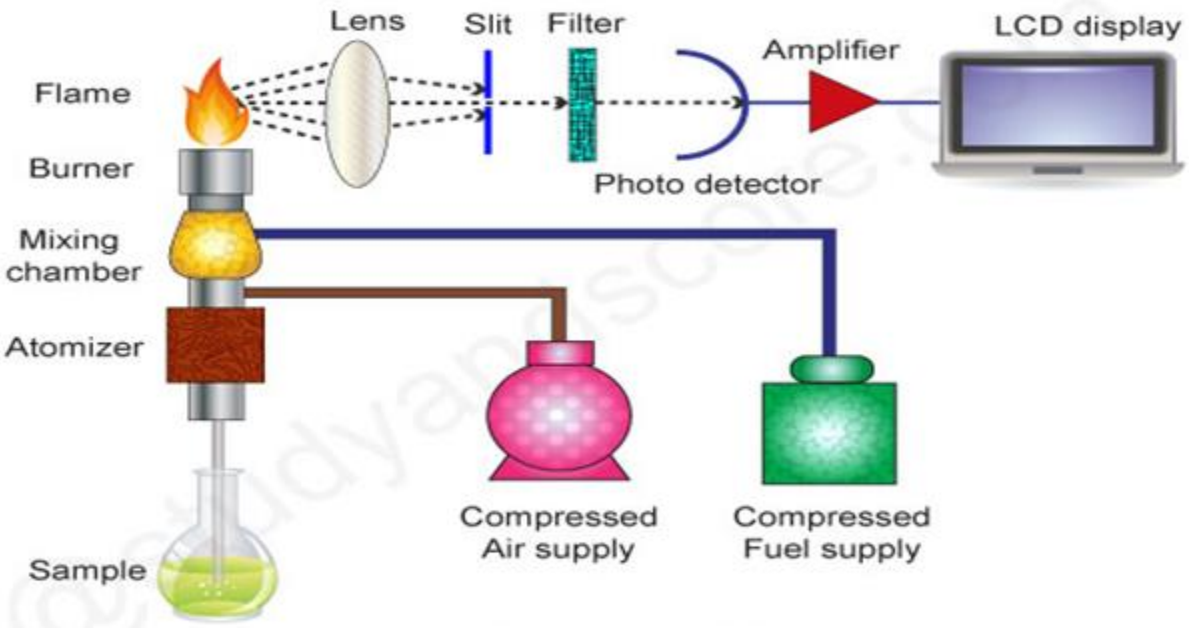
then $I = k \times c$. In other words, the intensity of emitted light is directly related to the concentration of the sample.



Name of the element	Emitted wavelength range (nm)	Observed colour of the flame
Potassium (K)	766	Violet 

Lithium (Li)	670	Red 
Calcium (Ca)	622	Orange 
Sodium (Na)	589	Yellow 
Barium (Ba)	554	Lime green 

- **INSTRUMENTATION**



FLAME PHOTOMETER

The instrument possesses the same basic components as a spectroscopic apparatus has.

However, the major components are:

1. Sample delivery system
2. Source
3. Mirrors
4. Slits
5. Monochromators/Filters
6. Detectors

1. SAMPLE DELIVERY SYSTEM:

There are Three components for introducing the liquid sample.

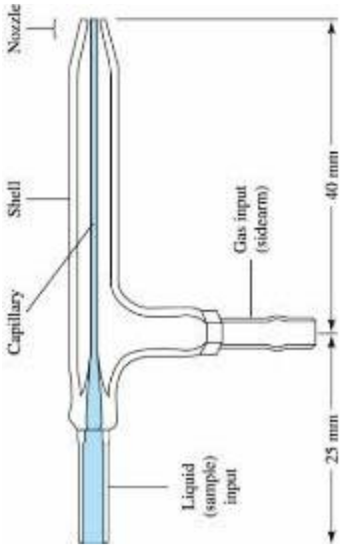
(a) Nebulizer: it breaks up the liquid into small droplets. Nebulization is a conversion of sample to a mist of finely divided droplets using a jet of compressed gas. a flaw carries the sample into atomization region.

Nebuliser is a device used for sample introduction into the flame. The process is called nebulisation and consists of thermal vapourisation and dissociation of aerosol particles at high temperatures producing small particle size with high residence time.

A number of nebulisation methods are available. A few are listed below.

- Pneumatic nebulisation
- Ultrasonic nebulisation
- Electrothermal vapourisation
- Hydride generation (used for certain elements only)

However, we would discuss about the pneumatic nebulisation only. It is the most commonly employed nebulisation method in flame photometers. Pneumatic nebuliser is the most commonly used nebuliser for introducing aqueous/ liquid samples. In this the sample solution is fed or aspirated into the nebuliser which converts liquid into a fine mist, or aerosol which is then fed into the flame. A common type of pneumatic nebuliser is called concentric pneumatic nebuliser, as shown in Fig. 7.9. The concentric pneumatic nebuliser consists of a fine capillary surrounded by concentric tube with a small orifice near one end of the capillary. The capillary is dipped into a solution of the analyte while the outer tube is connected to a high pressure gas supply. The analyte is sucked into the capillary by the high pressure gas stream flowing around the tip of the capillary using the Bernoulli effect. The process is called aspiration. The high velocity gas breaks up the liquid into various sized fine droplets. The other types of the pneumatic nebulisers also work on the same principle.



Concentric type pneumatic nebuliser

(b) Aerosol modifier: it removes large droplets from the stream and allow only smaller droplets.

(c) Flame or Atomizer: it converts the analyte into free atoms.

2. SOURCE/BURNER:

The flame used in in instrument must possess these functions…

-the flame should possess the ability to evaporate the liquid droplets from the sample solution resulting in the formation of solid residues.

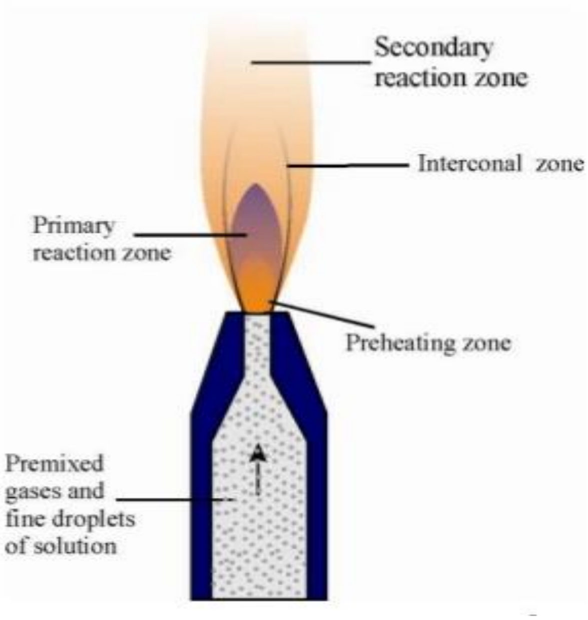
-the flame should decompose the compound in the solid residue, resulting in the formation of atoms.

-it must have capability to excite the atoms and cause them to emit radiant energy (emission intensity should be steady over reasonable periods of time 1-2 min.)

: In flame photometry, several burners and fuel-oxidant combinations have been used to produce the analytical flame. Including Mecker, Lundergarph, Total consumption burner, Premix of Laminar air flow burner, Shielded burners, Nitrous Oxide-Acetylene flames.

- Sequence of Events in Flame:
  1. The water or solvent is evaporated, leaving minute particles of the dry salt.
  2. The dry salt is vaporized or converted into the gaseous state.
  3. A part or all of the gaseous molecules are dissociated to give free neutral atoms/radicles.
  4. Which are thermally excited or even ionized.

Structure of Flames: Flames are not uniform in composition, length or cross section. The structure of a premixed flame, supported as a laminar flow is shown in Figure:



Schematic structure of a laminar flow flame showing various zones

As seen in the figure, the flame may be divided into the following regions or zones.

i) Preheating zones

ii) Primary reaction zone or inner zone

iii) Internal zone

iv) Secondary reaction zone

The first or the innermost region of the flame is the preheating zone where the combustion mixture is heated to the ignition temperature by thermal conduction from the primary reaction zone. The second zone is the primary reaction zone or inner zone. This zone is about 0.1 mm thick at atmospheric pressure and is visible by virtue of its blue green light ascribed to radicals . C2 and CH. There is no thermodynamic equilibrium in this zone and the concentration of ions and free radicals is very high. This region is not used for flame photometry.

Immediately above the primary reaction zone lies the third or interconal zone or the reaction free zone which can extend up to considerable height. The maximum temperature is achieved just above the tip of the inner zone. The higher temperature favours both production of free atoms and maximum excitation for atomic emission spectroscopy. Therefore, this zone is used for flame photometry.

The outermost fourth zone is the secondary reaction zone. Within this zone, the products of the combustion processes are burnt to stable molecular species by the surrounding air.

The shape of an unmixed flame is generally different. The inner zone can still be recognised, but it is very vague and is thickened. A laminar flame makes a strong hissing noise which gets louder when a liquid is atomised into it. We shall now look into the reactions which are taking place when the element is placed in flame.

Reactions in Flames:

The most important reactions occurring in the flame are given below.

i) Dissociation of molecules

$MX \rightarrow M + X, \; Kmx = Pm\,Px/Pmx$

ii) Formation of compounds with flame components

$M + Y \rightarrow MY, \; Kmy = Pm\,Py\,/Pmy$

ii) Formation of compounds with flame components

$M + Y \rightarrow MY, \; Kmy = Pm\,Py\,/Pmy$

iii) Ionisation of atoms

$M \rightarrow M^{+} + e^{-}$, $KP = Pm\ P / Pm$

In these equations, p is the partial pressure of the species indicated in the subscript. The partial pressure of the flame gas components is much larger than the partial pressure of the given element. It is, therefore, considered constant and included into the equilibrium constant.

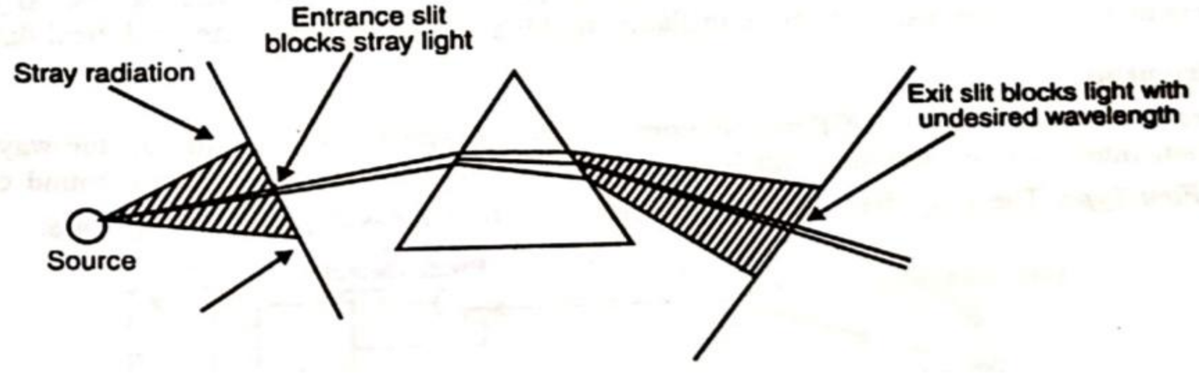
The most important of the flame gas components forming compounds with the elements are oxygen, the hydroxyl radical and hydrogen. The most common compounds formed in flames burning with air or oxygen and metal monoxides. For example, a major fraction of alkaline earth elements is present as monoxides unless very fuel rich flames are used. However, alkali metals practically do not form any oxides.

Hydroxide species are present for some alkali and alkaline earth elements in hydrocarbon flames. Sodium forms practically no hydroxide, while the concentration of LiOH molecules often exceeds the atomic lithium concentration by a factor of 10. None of the alkali metal hydroxides emit spectral bands in the visible or UV region; whereas the spectral bands of alkaline earth monohydroxide can be used for the determination of these elements.

3.MIRRORS:

The radiation from the flame is emitted in all direction in space. In order to maximize the amount of radiation used in the analysis, a mirror is located behind the burner to reflect the radiation back to the entrance slit of the monochromator. This mirror is concave and covers as wide angle from the flame as possible.

4.SLITS: Entrance and exit slits are used before and after the dispersion elements.



The entrance slit cuts out most of the radiation from the surroundings and allows only the radiation from the flame and the mirrored reflection of the flame to enter the optical system. The exit slit is placed after the monochromator and allows only a selected wavelength range to pass through detector.

5.MONOCHROMATORS:

In simple models the monochromator is the prism, but in expensive models, the gratings are used.

Prisms- Quartz is the material most commonly used for making prisms. The reason is that quartz is transparent over the entire region.

Gratings- It employs gratings which is essentially a series of parallel straight lines cut into a plane surface.

(Sometimes optical filter may be used in place of slit and monochromators system. When a filter is kept between the flame and detector, the radiation od desired wavelength from the flame will be entering the detector and be measured. The remaining undesired wavelength will be absorbed by the filter and not measured.)

6.DETECTORS:

The radiation coming from the optical system is allowed to fall on the detector which measure the intensity of radiation falling on it. The detector should be sensitive to radiation of all wavelengths that may be examined. In good flame photometer, the photomultiplier detectors are employed which produce an electrical signal from the radiation falling on them.

- **INTERFERENCES IN FLAME PHOTOMETRY:**

  In determining the amount of particular element present, other elements can also affect the result.

1.Spectral Interference:

(a) first type of spectral interference arises when two elements may exhibit different spectra but their spectra may partly overlap and both are emitting at some particular wavelength. Ex: Iron line at 3247.28 Å overlaps the copper line at 3247.54Å. This canbe overcome by removing interfering element effect by using calibration curves which are prepared from a solution having similar quantities of that interfering element.

(b) The second type occurs if spectral lines of two or more elements are close but their spectra do not overlap. This occurs when filter is used as spectral isolation device, and can be overcome by increasing the resolution of spectral isolation device.

(c) The third type occurs between a spectral line and continuous background. Due to high concentration of salts in the sample, especially in salts of alkali and alkaline earth metals. It can be corrected by scanning technique.

Other spectral line Interference example:

a) Na and K mixtures interfere with each other.

Remedy: 1. Extraction of interefering material.

2. Calibration curve of interfering material.
3. Use of gratings instead of prism / filters.

b) Aluminium interferes with emission line of Ca and Mg
c) Orange band of Ca – 543 – 622 nm interference with Na doublet 589 and 589.6nm and Ba line at 553.6nm

4. Ionization Interference:

In some cases, some of the metal atoms may ionize in high temperature flame. e.g., Sodium ion possesses an emission spectrum of its own, with different frequencies from those of the atomic spectrum of sodium. This can be overcome by adding a large quantity of potassium salt to all the solution-unknown and standard. The addition of K prevents theionization of Na.

5. Cation-Cation Interference:

This decreases the signal intensity of the element present in the sample. Ex= Al interference with Ca and Mg. Also Na and K have interference on one another.

6. Cation-Anion Interference:

Anion such as oxalate, phosphate, sulphate, may affect the intensity of radiation emitted by element. For example, Ca in the presence of phosphate ion apparently forms a stable substance, so the calcium signal is depressed because it will not decompose easily.

5. Oxide Formation Interference:

It arises due to the formation of stable oxide with free metal atoms if oxygen is present in the flame. This can be overcome by either using very high temp flames for dissociation or using oxygen free environment.

- **APPLICATIONS**:

1. Qualitative Analysis:

Flame photometry is used to detect elements of groups l and ll of the periodic table. These are Na, K, Li, Mg, Ca etc. Identification is done by Peak matching technique, where at least 3 peaks of emission spectrum should match when sample and standard spectra are recorded.

Flame photometric methods are widely used for the determination of alkali and the alkaline earth metals in samples that are easily prepared as aqueous solutions. Some of these elements can be detected visually by the colour in the flame, e.g. sodium produces yellow flame. However, this method is not very reliable. The best method is to use flame photometer with a filter or monochromator to separate radiation with the wavelengths characteristic of the different metals from other radiations present. If the radiation of the characteristic wavelength is detected, it will indicate the presence of the metal in the sample.

The method to carry out detection of elements by flame photometry is fast, simple and if carried out with care, quite reliable. However, there are some difficulties. It does not provide information about the molecular structure of the compound present in the sample solution. Nonradiating element such as carbon, hydrogen and halides cannot be detected. These can only be determined under special circumstances.

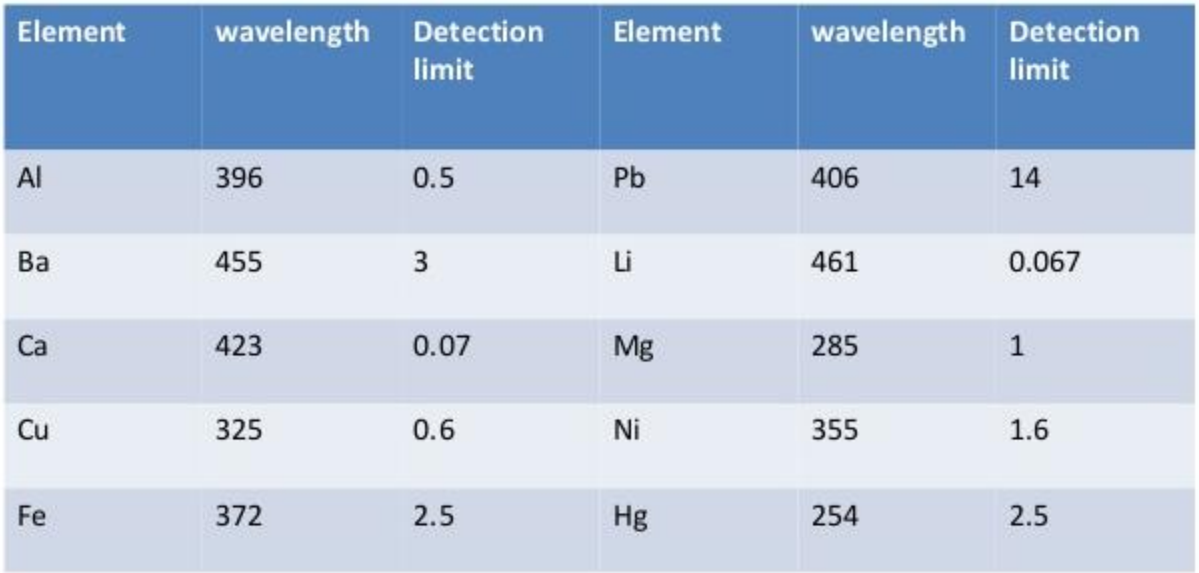
2. Quantitative Analysis:

- Concentration of calcium in serum.
- Concentrationof Na, K, Ca, and K in urine.
- Amount of Ca, Na, K, and Mg in intravenous fluids, ORS.
- Assay of KCl in in syrup.
- Concentration of Lithium in serum for therapeutic drug monitoring.

(The concentration or the amount of elements can be determined by any of the following four methods.)

(a) Direct comparison method
(b) Calibration curve method.
(c) Standard addition method.
(d) Internal standard method.

Table: Elements, their characteristic emission wavelengths and detection limits



Element	wavelength	Detection limit	Element	wavelength	Detection limit
Al	396	0.5	Pb	406	14
Ba	455	3	Li	461	0.067
Ca	423	0.07	Mg	285	1
Cu	325	0.6	Ni	355	1.6
Fe	372	2.5	Hg	254	2.5

3. Also used in determination of alkali and alkaline earth metals.
4. Used in determination of lead in petrol.
5. Used in determination of Ca and Mg in cement.
6. To estimate Na, K, Li, Ca in serum, body fluids, CSF and urine.
7. In soil analysis.
8. In industrial waste, glass, cement and petroleum products.

Advantages of flame photometer

1. The method of analysis is very simple and economical.
2. It is quick, convenient, selective and sensitive analysis.
3. It is both and qualitative and quantitative in nature.
4. Even very low concentrations (parts per million/ppm to parts per billion/ppb range) of metals in the sample can be determined.
5. This method compensates for any unexpected interfering material present in the sample solution.
6. This method can be used to estimate elements which are rarely analysed.

Disadvantages of flame photometer

1. In spite of many advantages, this analysis technique has quite a few disadvantages:
2. The accurate concentration of the metal ion in the solution cannot be measured.
3. It cannot directly detect and determine the presence of inert gases.
4. Though this technique measures the total metal content present in the sample, it does not provide the information about the molecular structure of the metal present in the sample.
5. Only liquid samples may be used. Also sample preparation becomes lengthy in some cases.
6. Flame photometry cannot be used for the direct determination of each and every metal atom. A number of metal atoms cannot be analysed by this method. The elements such as carbon, hydrogen and halides cannot be detected due to their non-radiating nature.

MERITS AND LIMITATIONS OF FLAME PHOTOMETRY:

Qualitative and quantitative determination of several cations, especially for metals that are easily excited to higher energy levels at a relatively low flame temperature. The metals mainly are Na, K, Rb, Cs, Ca, Ba and Cu. The salient features of analysis by flame photometry can be summarised as follows.

Propane-air or natural gas-air mixtures that give good flame with strong heat

and minimal background light emission are used for the atomisation.

- A solvent blank is run for setting zero emission.

- As the concentration intensity relationship is not valid for all concentrations, the solutions are suitably diluted to fall within linear part of the calibration curve.

- The use of solutions of very low concentration of Na+ and K+ solutions are avoided as these may encounter problems of contamination; especially in case of Na+ which leaches slowly from glass and on contact with skin.

- The interference effects of anions and cations can cause errors and need to be suitably accounted for.

- The random flame instability and random dilution errors can be minimised by using an internal standard (lithium).

Let us learn about the merits and limitations of the flame photometry method.

Merits

Flame photometry, coupled with simple read-out devices, provides high sensitivity and high reliability for the determination of elements in the first two groups of the periodic table. Among these elements are sodium, potassium, lithium, calcium, magnesium, strontium and barium. The measurement of these elements is very useful in medicine, agriculture and plant science. The two important merits of flame photometry are as follows.

- The sensitivities of the flame photometry for most alkali and alkaline earth metals lie in the ppm and sub-ppm range.
- Flame photometry is also successful in determining certain transition elements such as copper, iron and manganese.

Limitations

The flame photometric methods like many other techniques have some limitations also. These are given below.

- As natural gas and air flame is employed for excitation the temperature is not high enough to excite transition metals, therefore the method is selective towards detection of alkali and alkaline earth metals.
- The low temperature renders this method susceptible to certain disadvantages, most of them related to interference and the stability of the flame and aspiration conditions. Fuel and oxidant flow rates and purity, aspiration rates, solution viscosity, affect these. It is therefore very important to measure the emission of the standard and unknown solutions under identical conditions.

- The relatively low energy available from the flame leads to relatively low intensity of the radiation from the metal atoms, particularly those that require large amount of energy to become excited. Flame photometry is a means of determining the total metal concentration of a sample; it tells us nothing about the molecular form of the metal in the original sample.

- Only liquid samples can be used. In some cases, lengthy steps are necessary to prepare liquid samples.

Despite the limitations, the flame photometry is extensively used due to its portability, ease of operation, etc.