
UNIT 7 FLAME PHOTOMETRY

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7.1 INTRODUCTION

In this course you have so far learnt about the spectroscopic methods of analysis based on the molecular spectroscopies. In the present and the next few units, you would learn about spectroscopic methods based on atomic spectroscopies. In atomic spectroscopy, the element present in a sample is converted to gaseous atoms or elementary ions in a process called atomisation which may be brought about by any of the available methods. The absorption of the radiation by the vapourised atoms in the ground state, or emission or fluorescence emission of suitably excited state forms the basis of different types of atomic spectroscopies. Collectively, the atomic spectroscopic methods can be used for the qualitative and quantitative determination of about 70 elements in a wide variety of samples of clinical, biological, and environmental origin. These methods are quite quick, convenient, and selective and offer sensitivities in the parts per million (ppm) to parts per billion (ppb) range.

This unit concerns flame photometry which refers to the measurement of the EM radiation in UV-VIS range emitted by the vapourised atoms after they are

electronically excited by the thermal energy of the flame. It is a simple, rapid and inexpensive method for routine analysis of alkali and alkaline earth metals like, sodium, potassium, lithium, calcium and barium in environmental, clinical and biological samples especially in biological fluids and tissues. The convenience, speed and relative freedom from interferences has made flame photometry a method of choice for the determination of these elements, which are otherwise difficult to determine. With the help of more sophisticated instruments, the method has also been applied to the determination of many other elements, with varying degree of success.

We begin the unit with an understanding of the origin and classification of different types of atomic spectroscopic methods. Then we will take up the principle of flame photometry which is followed by the instrumental aspects of flame photometry. In the end we will take up some qualitative and quantitative applications of flame photometry. In the next unit you would learn about atomic fluorescence spectrometry.

Objectives

After studying this unit, you will be able to:

- define atomic spectroscopic methods and classify them,
- explain different characteristics of atomic spectrum and contrast them with that of the molecular spectrum,
- explain the principle of flame photometry,
- draw a schematic diagram illustrating different components of a flame photometer,
- enlist the applications of flame photometry,
- discuss the factors affecting flame photometric determinations, and
- state the merits and limitations of the flame photometric technique.

7.2 ORIGIN AND CLASSIFICATION OF ATOMIC SPECTROSCOPIC METHODS

As a chemist you would have performed a flame test for the identification of some elements especially the alkali and alkaline earth metals in their salts. You would have observed the beautiful colours imparted by the elements to the flame. The colour is a consequence of the emission of radiation by the gaseous atoms / ions in the excited state. The emitted radiation can be analysed in terms of the wavelength and the intensity and can be used for the identification and quantification of the element. This forms the basis of atomic emission or flame emission spectroscopy-one of the types of atomic spectroscopy.

There are three major types of spectrometric methods used for the identification of an element present in matter-solid, liquid or gas, and determination of their concentrations: optical spectrometry, mass spectrometry and x-ray spectrometry. We are dealing with optical spectrometry here.

Atomic spectroscopy is the oldest instrumental method of elemental analysis. The origin of these techniques dates back to the times of Bunsen and Kirchhoff in the mid 19th Century wherein they showed that the optical radiation emitted from flames is characteristic of the elements present in the flame gases or the ones introduced into the burning flame by different means. It was also demonstrated during the same time that the intensities of the radiation, characteristic of different elements, present in the spectra, were dependent on the amount of elemental species present. Thus, the potential of atomic spectroscopy both as qualitative as well as quantitative analysis was established. It was also shown that the wavelength emitted by a given element in the analyte was absorbed by cold vapours (atoms in their ground state) of the same element.

Further developments facilitated by the developments in the area of instrumentation led to the widespread application of atomic spectroscopy. Today, atomic spectroscopic methods or atomic spectrometry is indispensable tools in the hands of analytical chemists. Let us understand the origin of atomic spectroscopy in terms of the transitions amongst different atomic energy levels.

7.2.1 Origin of Atomic Spectrum

You would recall from your earlier knowledge that an atom contains a set of quantised energy levels that can be occupied by the electrons depending on the energy. The energy level with the minimum energy is called **ground state** while the ones of higher energy are referred to as the **excited states**. Further, electron in an energy level can undergo a transition to another level of a higher energy by absorbing a photon of appropriate energy equal to the difference in the energies of the two levels. On the other hand the transition of an electron from a higher energy level to a level of lower energy is accompanied by the **emission** of the difference in energy in the form of a radiation of appropriate wavelength. A spread of the wavelengths of the photons absorbed or emitted versus their intensities is called a **spectrum**. The atomic spectroscopic methods are based on the transitions amongst the quantised electronic energy levels caused by the absorption of radiation by the atoms in ground state or by the emission of radiation by the excited atoms in vapour phase.

You have learnt in details about the molecular spectroscopic methods in Blocks 1 and 2 of this course. In what way do you think that the transitions in the molecular systems are different from that in atomic systems? Try to answer this question in the space given below, before you go further.

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Yes, you are right. In molecular systems the rotational and vibrational motions are also quantised besides the electronic energies. Different types of electromagnetic radiation (microwave, IR, UV-VIS) are required to cause transitions amongst these levels. On the other hand, in case of atomic systems only electronic energies are quantised; the transitions being brought about by UV-VIS radiation.

Let us learn the different ways in which the transitions amongst the atomic energy levels can be exploited for the identification and analytical determination of different elements.

7.2.2 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

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 Fig. 7.1.

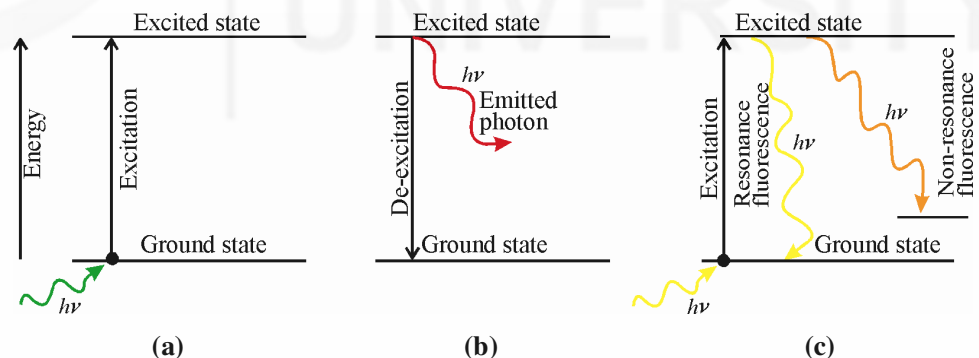


Fig. 7.1: Schematic representation of the transitions in atomic (a) absorption, (b) emission and (c) fluorescence (resonance and nonresonance) emission

As we have a number of methods of atomisation and three different ways viz., absorption, emission and fluorescence emission, of measuring the radiation analyte interaction, there are a number of different types of atomic spectroscopic methods. The

type of atomic spectroscopic method is determined both by the method of atomisation as well as the nature of the interaction. For example, an atomic spectroscopic method using electrothermal atomisation method and studying the fluorescence emission of radiation would be called as **electrothermal atomic fluorescence spectroscopy**.

SAQ 1

Identify the method of atomisation and the type of radiation-analyte interaction used in the following atomic spectroscopic methods.

- i) Flame atomic emission spectrometry (FAES)
- ii) Graphite furnace atomic absorption spectrometry (GFAAS)
- iii) Inductively coupled plasma atomic absorption spectrometry (ICPAAS)
- iv) Flame atomic fluorescence spectrometry (FAFS)

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7.3 CHARACTERISTICS OF ATOMIC SPECTRUM

You would recall from Blocks 1 and 2 on molecular spectroscopic methods that the molecular spectra are generally broad. These consist of a number of closely spaced lines constituting what is called a **band spectrum**. The band nature of the spectrum is due to a number of factors like, the quantisation of the rotational and vibrational motions of the molecules along with the quantisation of electronic energy levels. In addition, the width of the spectrum is also dependent on some of the instrumental parameters.

In contrast to the above, the atomic spectra consist of a number of very sharp lines, characteristic of the atomic species. It implies that these give rise to **line spectra**. The atomic spectra are generally much sharper because in atomic systems, the rotational and the vibrational motion are not quantised and the transitions are observed amongst the electronic energy levels of the absorbing species. A typical atomic spectrum is shown in Fig. 7.2.

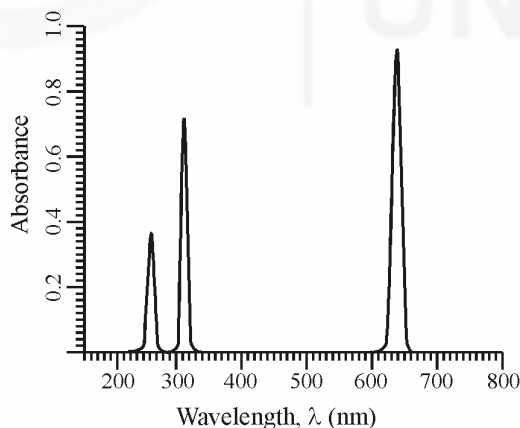


Fig. 7.2: Representation of a typical atomic spectrum

Similar to the molecular spectrum, the signals in an atomic spectrum are also characterised in terms of three parameters. These are given below.

- position
- intensity
- width

Let us learn about these parameters.

7.3.1 Position of the Signal

You know that in spectroscopy, we study about the interaction of radiation and matter. This interaction is manifested in terms of absorption, emission or scattering of the radiation. In case of atomic species, the interaction causes transitions amongst the electronic energy levels. Whereas, you have learnt that in case of molecules, the interaction led to transitions amongst the rotational, vibrational or electronic energy levels or combinations of these. However, like in case of molecular spectra, here also the position of the spectral signals is determined by the difference in the energies of different energy levels. If E_2 and E_1 represent the energy of the higher and lower energy levels concerned, the energy change during the transition from E_2 to E_1 level may be defined as follows.

$$\Delta E = (E_2 - E_1) = h\nu = hc/\lambda$$

$$\text{Or } \lambda = hc/(E_2 - E_1) = \frac{hc}{\Delta E}$$

where, h is the Planck's constant, c is the velocity of light, ν the frequency and λ the wavelength of the emitted radiation. The wavelength of the radiation is characteristic of the atoms of the particular element from which it is emitted. When flame photometry is employed as an analytical tool, the wavelength of the radiation emerging from a flame tells us about the elements that are present in that flame.

7.3.2 Intensity of the Signal

The intensity of a signal depends on the population of the energy level from which the transition is originating and the probability of such a transition. You would recall from Unit 1 that according to the Boltzmann statistical distribution, the population of the ground state i.e., the number of species in the ground state is highest and it keeps on decreasing as we go to higher energy levels. In case of the atoms the population of any excited state relative to that of the ground state is given by the following formula.

$$\frac{N^*}{N_0} = \frac{g^*}{g_0} e^{-\frac{\Delta E}{kT}}$$

$$\text{Or } N^* = N_0 \frac{g^*}{g_0} e^{-\frac{\Delta E}{kT}} \quad \dots (7.1)$$

where,

N^* and N_0 = Number of atoms in excited state and ground state, respectively,

ΔE = Energy difference between ground and excited state (in J),

g^* and g_0 = Statistical factors that depend on the degeneracies of the levels involved,

k = Boltzmann constant ($= 1.28 \times 10^{-23} \text{ J k}^{-1}$), and

T = Absolute temperature.

According to Eq.7.1, after the ground state, the lowest energy excited state will be most populated and the population of the higher excited states would decrease progressively. Eq. 7.1 can be used to determine the population of an excited state with respect to the ground state. Let us illustrate this with the help of an example.

Example 7.1

The characteristic yellow emission of sodium vapours consists of a pair of lines at 589 nm and 589.6 nm. These arise from the emission of radiation by the gaseous sodium atoms in the 3p excited state to 3s ground state. Compute the ratio of the sodium atoms in the excited state to the ground state.

Solution

As per Eq. 7.1 we have,
$$\frac{N^*}{N_0} = \frac{g^*}{g_0} e^{-\frac{\Delta E}{kT}}$$

Therefore, to evaluate the ratio of the atoms in the excited state to that in the ground state we need to know the statistical factors g^* and g_0 and ΔE .

As the 3s and 3p levels have two and six quantum states i.e., the statistical factors are 2 and 6 respectively, the ratio of g^* and g_0 comes out to be $6/2 = 3$

The change in energy, ΔE , can be calculated by using the formula,
$$\Delta E = \frac{hc}{\lambda}$$

$$\Delta E = \frac{6.626 \times 10^{-34} \text{ Js} \times 3.0 \times 10^8 \text{ ms}^{-1}}{589.3 \times 10^{-9} \text{ m}}$$

The wavelength is taken as an average of the two, i.e.,
$$\left(\frac{589.0 + 589.6}{2} \right)$$

$$\Delta E = 3.37 \times 10^{-19} \text{ J}$$

Substituting the value of ΔE in the above equation, we get the following.

$$\frac{N^*}{N_0} = \frac{6}{2} e^{-\frac{-3.37 \times 10^{-19} \text{ J}}{1.38 \times 10^{-23} \text{ JK}^{-1} \times 3000 \text{ K}}}$$

$$\frac{N^*}{N_0} = 3e^{-\frac{-3.37 \times 10^{-19}}{4.14 \times 10^{-20}}} = 3e^{-8.08} = 3.096 \times 10^{-4}$$

You have learnt above that the intensity of a signal depends on the population of the level from which the transition originates and the probability of such a transition. These are the intrinsic parameters of the analyte being determined. In addition to these, the intensity of a signal does depend on an important external parameter, viz., the concentration of the analyte. This, in fact is the basis of quantitative aspect of the spectroscopic methods. Let us see how the intensity depends on the concentration of the analyte for an emission spectrum.

Intensity Concentration Relationship

The intensity of the emitted radiation (P) is proportional to the number of excited atoms N^* .

$$P \propto N^*$$

$$P = a \cdot N^* \text{ (where } a \text{ is the proportionality constant)}$$

The position of the emission line is suggestive of the element while its intensity is a measure of the concentration of the analyte.

Again, from Eq. 7.1, we see that the number of atoms in the excited state, N^* , at a given temperature are proportional to N_0 . Therefore, we can write the following.

$$P = a. N_0 \frac{g^*}{g_0} e^{-\frac{\Delta E}{kT}} \quad (\text{as } N^* = N_0 \frac{g^*}{g_0} e^{-\frac{\Delta E}{kT}})$$

$$P = K. N_0 \quad (K = a. \frac{g^*}{g_0} e^{-\frac{\Delta E}{kT}})$$

$$P = K'. C \quad (\text{as, } N_0 \text{ is directly proportional to metal concentration})$$

Thus, the intensity of the emitted light will be directly proportional to the concentration of the element introduced into the flame.

7.3.3 Spectral Line Width

The lines are generally symmetric around the λ_{\max} , the wavelength at which the intensity of emitted radiation is maximum. The absorbance is also the maximum at the same wavelength. The **line width** is defined as the width of the signal measured at one half the height of the maximum signal. It is expressed as $\Delta\lambda_{1/2}$ and is measured in the units of wavelength. This full width is measured at one half of the maximum (*FWHM*) is also called as **effective line width**. Fig. 7.3 shows the schematic diagram defining the atomic line width. The line width resulting from a transition of an electron between two discrete, single valued energy states is expected to be zero.

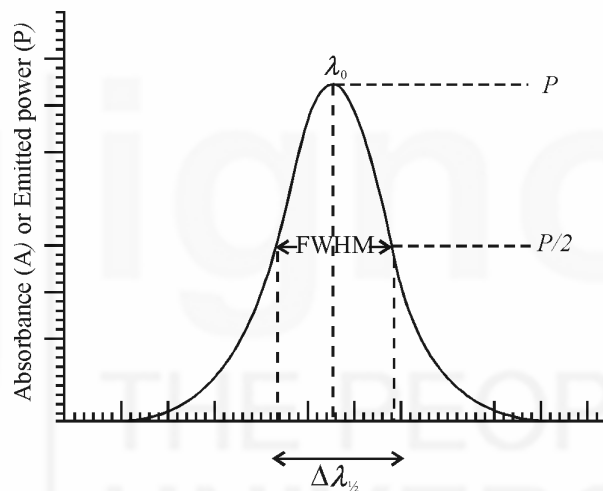


Fig. 7.3: A schematic diagram defining the atomic line width

You may be wondering that if the transitions leading to the atomic spectrum are amongst the discrete energy levels, then how do we get width or broadness in the signal? Your apprehension is quite justified. This 'finite' or the **natural width** of the atomic spectrum results from a number of phenomena. These are given below.

- **Uncertainty or Heisenberg broadening:** This arises due to the uncertainty in the energies of the excited state.
- **Collisional broadening:** It is due to the distortion of the outer energy levels arising as a consequence of the collision with other atoms.
- **Doppler broadening:** It is due to the shift in the frequencies of the emitted photon due to relative motion with respect to the detector.

The details of these phenomena can be obtained from any of the standard text books on spectroscopy. Some of the books are listed at the end of the Block.

Flame photometry is a method used for the determination of elements which can be easily excited for example, alkali and alkaline earth metals. This method is based upon the measurement of intensity of radiation emitted, in the visible region, when a metal atom is introduced into a flame. The wavelength of the radiation (or the colour), emitted tells us what the element is, and the intensity of the radiation tells us how much of the element is present. The International Union of Pure and Applied Chemistry (IUPAC) Committee on Spectroscopic Nomenclature has recommended abbreviation **FAES** (flame atomic emission spectrometry) for this technique.

Let us learn about the processes occurring when a solution of the analyte is put into the flame.

7.4.1 Fate of the Sample in the Flame

In a typical flame photometric experiment, a solution containing the relevant substance to be analysed is aspirated into the burner and dispersed into the flame as a fine spray. This process is called **nebulisation**. In the flame, the solvent evaporates first, leaving finely divided solid particles which move to hottest region of the flame where gaseous atoms and ions are produced. The atoms are excited by absorbing energy available from the flame. As the excited atoms return to a ground state of lower energy, radiation of wavelength, characteristic of the element, is emitted. The intensity of the emitted radiation is then measured, which can be related to the concentration of the element present, which forms the basis of quantitative analysis. The following processes occur in the flame.

- i) **Desolvation:** The sample containing metal particles is dehydrated by the heat of the flame and the solvent is evaporated.
- ii) **Vapourisation:** The heat of the flame vapourises the sample constituents. No chemical change takes place at this stage.
- iii) **Atomisation:** At this stage the metal ions that were in the solvent are reduced to metal atoms. For example, $Mg^{2+}(aq) + 2e \rightarrow Mg(g)$. By heat of the flame and action of the reducing gas (fuel), molecules and ions of the sample species are decomposed and reduced to give atoms.
- iv) **Excitation:** The atoms at this stage are able to absorb energy from the heat of the flame. The amount of energy absorbed depends on the electrostatic forces of attraction between the negatively charged electrons and the positively charged nucleus. This in turn depends upon the number of protons in the nucleus. As electrons absorb energy they move to higher energy levels and are in the excited state.
- v) **Emission of radiation:** Electrons in the excited state are very unstable and move back down to the ground state or a lower energy state quite quickly. As they do so, they emit the energy in the form of radiation of characteristic wavelength, which is measured by a detector. For some metals this radiation corresponds to wavelengths of light in the visible region of the electromagnetic spectrum and is observed as a characteristic colour of the flame. As electrons from different energy levels are able to emit light as they relax, the flame colour observed will be a mixture of all the different wavelengths emitted by the different electrons in the metal atom under investigation. Fig. 7.4 gives a block diagram representing the processes.

Nebulisation serves to increase the surface area of the solution sample, so that the solvent evaporation (desolvation) can proceed more rapidly and the resulting dried solute particles can be volatilised better.

The **five processes** occurring in the flame can be summarised as follows.

- i) $MX(soln.) \rightleftharpoons MX(solid)$
- ii) $MX(solid) \rightleftharpoons MX(vap.)$
- iii) $MX(vap.) \rightleftharpoons M + X$
- iv) $M(ground\ state) \rightleftharpoons M^*(excited\ state)$
- v) $M^* \rightarrow M. + h\nu$

Processes (ii) and (iii) may take place simultaneously and process (iii) may take place partially if the temperature of the flame is too low.

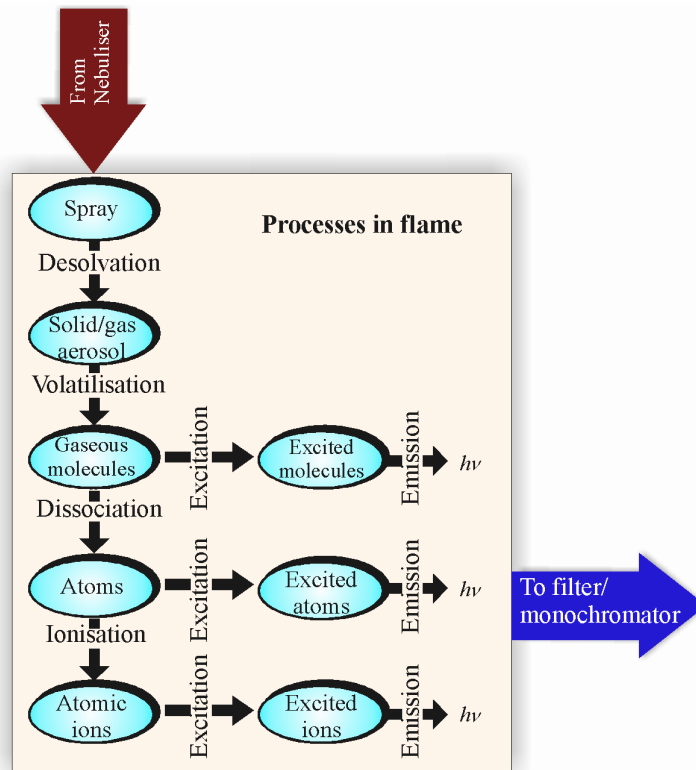


Fig. 7.4: Diagrammatic representation of the processes occurring in flame obtained from any hydrogen flame

The flame emission spectrum of the element sodium can be obtained by placing a solution of sodium chloride in a suitable flame. At the temperature of the flame (2000°C to 3000 °C) the outer electron of the sodium atom is promoted from the ground state $3s$ orbital to excited p orbitals ($3p, 4p, 5p$). The relaxation of the excited electron gives rise to the characteristic emission spectrum of the sodium atom. The emission spectrum of the sodium atom is relatively simple and consists of about 40 signals or lines; the most prominent emission signals being in the region of 285 nm, 330 nm and 590 nm. Fig.7.5 shows a portion of the flame emission spectrum for sodium atom; the excitation being done by an oxyhydrogen flame.

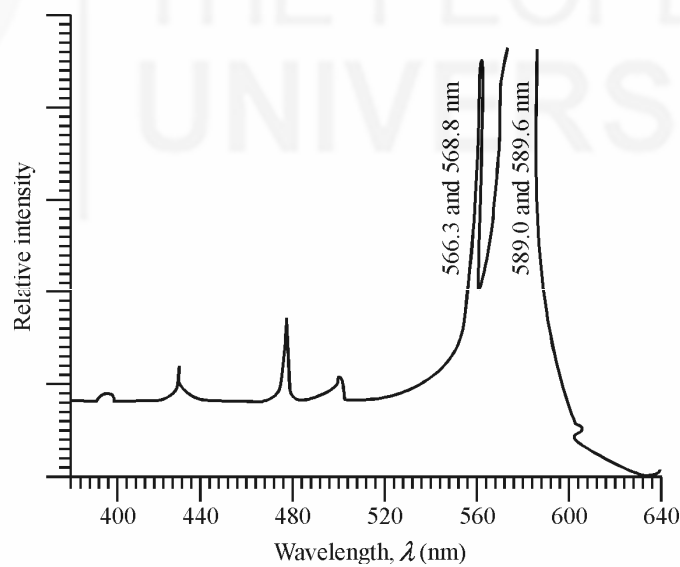


Fig. 7.5: Truncated flame emission spectrum for sodium atom obtained from oxyhydrogen flame

You would observe an intense signal at 589 nm in the emission of the sodium atom. This in fact consists of a pair of lines at 589 and 589.6 nm, which could not be resolved due to instrumental limitations. This pair of lines originates from the relaxation of the excited electron in $3p$ to the $3s$ level and is responsible for the characteristic yellow glow of the sodium light.

The origin of the signals can be rationalised in terms of the energy level diagram, as given in Fig. 7.6.

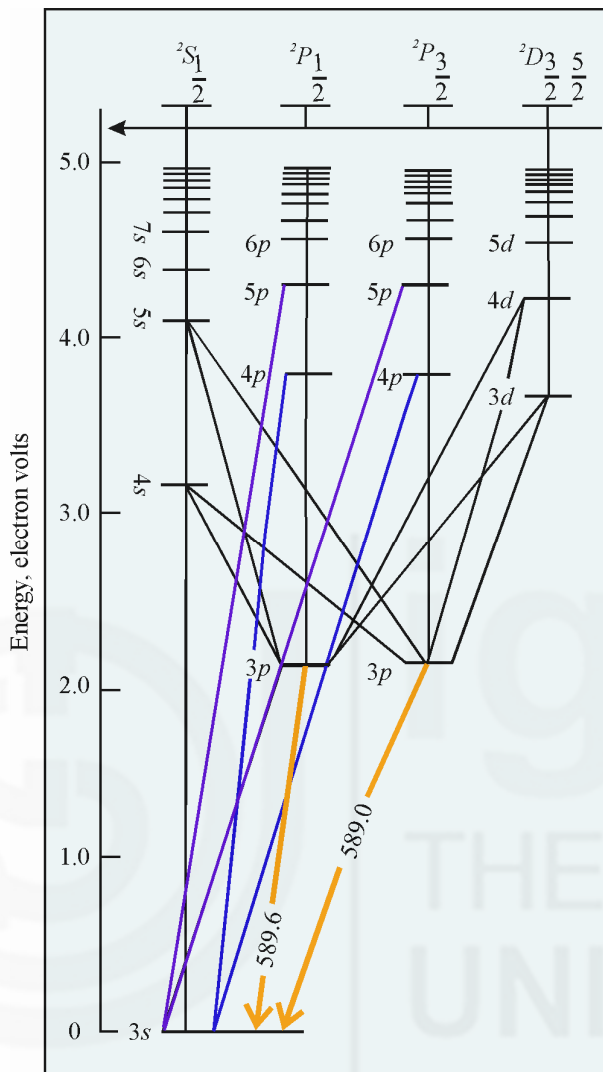


Fig. 7.6: The energy level diagram for sodium atom

As you have learnt above, in case of atomic emission spectroscopy, the intensity of emission signal depends upon the number of atoms in the excited state. In case of Na the ground state is $2S_{1/2}$ ($3s$) and the excited states are $2P_{3/2}$, $2P_{1/2}$ ($3p$), $2D_{5/2}$, $2D_{3/2}$ ($3d$), $2S_{1/2}$ ($4s$); $2P_{3/2}$, $2P_{1/2}$ ($4p$), etc. The intensity of the emission when the excited atoms return to the ground state will be maximum from the first excited state, if this transition is allowed ($\Delta s = 0$, $\Delta l = \pm 1$). As in case of sodium, $2P_{3/2}$ and $2P_{1/2}$ states would be most populated and transition from this state to ground state is allowed (as it meets the selection rule given above, i.e., ($\Delta s = 0$, $\Delta l = \pm 1$)); the intensity of emission from this state would be maximum. The fraction of atoms in the excited states (corresponding to the prominent spectral line) of different elements at various temperatures is presented in Table 7.1. The data shows that nearly all the atoms are present in the ground state.

You would have learnt in your earlier classes that the different atomic energy levels in multi-electron atoms are identified by the atomic term symbols like, $2S_{1/2}$, $2P_{3/2}$, $2P_{1/2}$, etc.

Table 7.1: Fraction of atoms in the excited states of different elements at various temperatures

Element	Emission Line (λ nm)	Temperature °Kelvin		
		2000	3000	4000
Sodium	589	1×10^{-5}	6×10^{-4}	4×10^{-3}
Potassium	767	1.7×10^{-4}	3.8×10^{-3}	1.8×10^{-2}
Lithium	670	4.4×10^{-5}	1.5×10^{-5}	9.4×10^{-3}
Calcium	422	1×10^{-7}	4×10^{-7}	6×10^{-4}
Magnesium	285	3.4×10^{-11}	1.5×10^{-7}	1×10^{-5}

The number of atoms in the excited state increases very rapidly with increase in temperature as shown in Table 7.1. Therefore, flames with higher temperatures will increase the number of excited atoms and make the method more sensitive. Higher temperatures are also required for decomposition of the compound having high lattice energies into atoms. However, higher temperatures may also cause ionisation of the atoms that may cause interference in the determination. We will take up this issue later in this unit (Sec. 7.7.5). Therefore, we need to optimise the temperature of the flame to be used.

We have so far learnt about the origin and classification of atomic spectroscopic methods, the characteristics of atomic spectrum and the principle of flame photometry. As flame has a crucial role to play in flame photometry, let us now learn about the flame and its characteristics before taking up the instrumentation required for the measurement of atomic spectra.

SAQ 2

What is the basis of qualitative and quantitative analysis by flame photometry?

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7.5 FLAME AND ITS CHARACTERISTICS

A flame can be described as a steady state gas phase reaction which takes place with emission of light. It is produced by burning a mixture of fuel and air or oxidant in a burner. In flame photometry a variety of fuels can be used and generally air, oxygen or nitrous oxide (N_2O) is used as the oxidant. The flame temperature depends on **fuel-oxidant ratio**. Combination of a given fuel gas with air produces lower temperatures as compared to when O_2 is used as oxidant. Alkali and alkaline earth metals are easily excited at low temperatures obtained by using air. However, for heavy metals O_2 or N_2O are employed as oxidants. The requisite temperature for analysis can be obtained by varying the fuel-oxidant ratio. Table 7.2 lists some common fuels and oxidants along with range of temperature attainable by using them.

The maximum operating temperature is determined by the identity of fuel and oxidant whereas, the exact temperature is fixed by the ratio of fuel and oxidant.

Table 7.2: Fuel-oxidant mixtures and the attainable temperature

Fuels	Oxidants		
	Air	Oxygen	Nitrous oxide
Propene	2250	3070	---
Acetylene	2470	3320	3220
Hydrogen	2370	3050	---

The most commonly employed flames in flame photometry can be grouped into two types:

1. Flames in which the fuel and oxidant as air or oxygen are well mixed before combustion, these are called **pre-mix or laminar flames** as they exhibit laminar flow.
2. Flames in which the fuel gas and the oxidant are first mixed in the flame itself. They are called **unpremix or turbulent flames** since they exhibit turbulence.

These flames are obtained by using suitable burners about which you would learn in subsection 7.6.2.

For now, let us learn about the structure and the reactions taking place in the different regions of the flame.

7.5.1 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 Fig. 7.7.

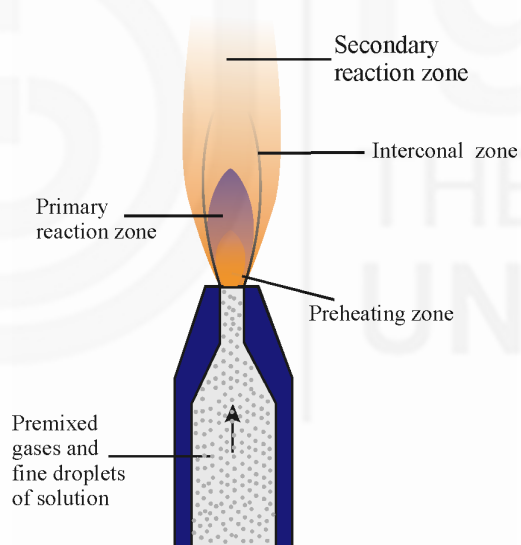


Fig. 7.7: Schematic structure of a laminar flow flame showing various zones

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 $\cdot\text{C}_2$ and $\cdot\text{CH}$. 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.

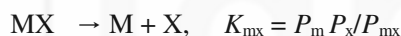
The outermost fourth zone is the **secondary reaction zone**. Within this zone, the products of the combustion processes are burnt to stable molecular species by the surrounding air.

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.

7.5.2 Reactions in Flames

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

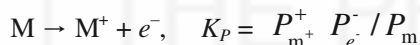
i) Dissociation of molecules



ii) Formation of compounds with flame components



iii) Ionisation of atoms



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.

List the different zones of a laminar flow flame. Which of these zones is used in flame photometry?

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7.6 INSTRUMENTATION FOR FLAME PHOTOMETRY

You know by now that in flame photometry the sample is introduced into a flame wherein it undergoes a number of processes leading to the formation of excited atomic species which emit radiation. The radiation is then measured and suitably analysed. The instrument used for the purpose is called **flame photometer** and it consists of the following basic components.

Flame atomiser: It converts the sample into excited atomic species and consists of the following.

- **Nebuliser and mixing chamber:** It is a means of transporting a homogeneous solution into the flame at a steady rate.
- **Atomiser burner:** Here the fuel and oxidant burn to give a flame that can be maintained in a constant form and at a constant temperature.

Monochromator (or filter): It isolates the light of the wavelength to be measured from that of extraneous emissions.

Detector: It helps in measuring the intensity of radiation emitted by the flame.

Amplifier and Readout Device: It is used to amplify the signal and provides a suitable output.

The schematic diagram showing the layout of various components of a flame photometer is given in Fig. 7.8.

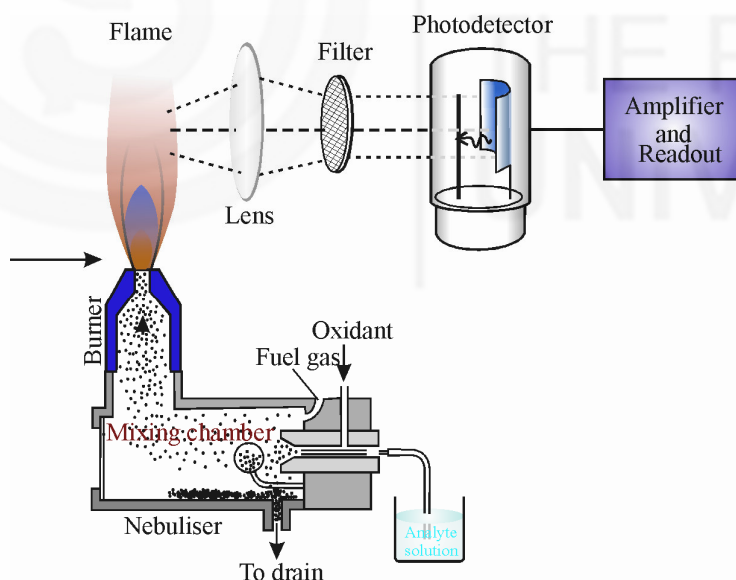


Fig. 7.8: Schematic diagram showing the layout of various components of a flame photometer

Let us learn about the different components of a flame photometer.

7.6.1 Flame Atomiser

The role of atomiser is to generate the vapours of analyte which get excited by the thermal energy of the flame and then emit characteristic radiation that is measured. The flame atomiser assembly consists of two components. The prior is a nebuliser where the sample in the form of a solution is drawn in and converted into a fine mist or an aerosol. It is then passed onto the second component i.e. the burner along with air or oxygen and a fuel gas. In the flame a number of processes (Section 7.4) occur that convert the analyte into excited species. Let us learn about the nebulisers used in flame photometers. You would learn about the burners in the next subsection.

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.

The other types of pneumatic nebulisers are; the cross flow nebuliser, fritted nebuliser and the Babington nebulizer.

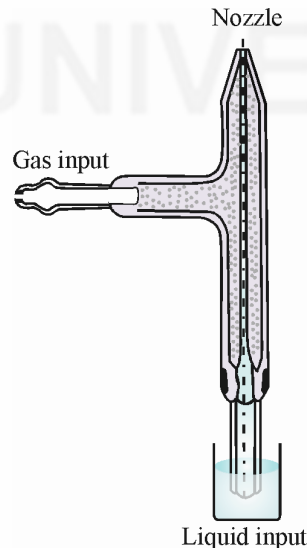


Fig. 7.9: Concentric type pneumatic nebuliser

7.6.2 Atomiser Burners

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 nebuliser. In the burner, the analyte undergoes a number of processes as mentioned earlier. Two types of atomisation burners have been used in flame photometry which are given below and explained in the following paragraphs..

- a) Pre-mix or Lundegarh burner
- b) Total consumption burner

a) Premix or Lundegarh burner

In the premix burner, fuel and oxidant are thoroughly mixed inside the burner housing before they leave the burner ports and enter the primary-combustion or inner zone of the flame. In this type of burner, the solution of the analyte is aspirated with the help of a nebuliser from the sample container 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 atomisation are smoothed in the mixing chamber and mixture of aerosol, fuel gas and oxidant burns to yield stable noiseless flame.

The premix type of burner usually produces an approximately laminar flame, and is commonly combined with a separate unit for nebulising the sample.

The solvent of the smaller droplets evaporates partly first in mixing chamber, then in the conduit of the burner and finally in the flame. Only drops of a certain size can reach the burner and are completely burnt. Thus, the efficiency of the premix burner is low and only 5% of the sample reaches the burner. The efficiency of this burner has been improved by putting an impact bead immediately after the nebuliser. The impact bead has the effect of breaking up large droplets as they come out from the nebuliser, thereby increasing the number of smaller droplets and the efficiency of nebulisation. The schematic diagram of a premix burner is given in Fig. 7.10.

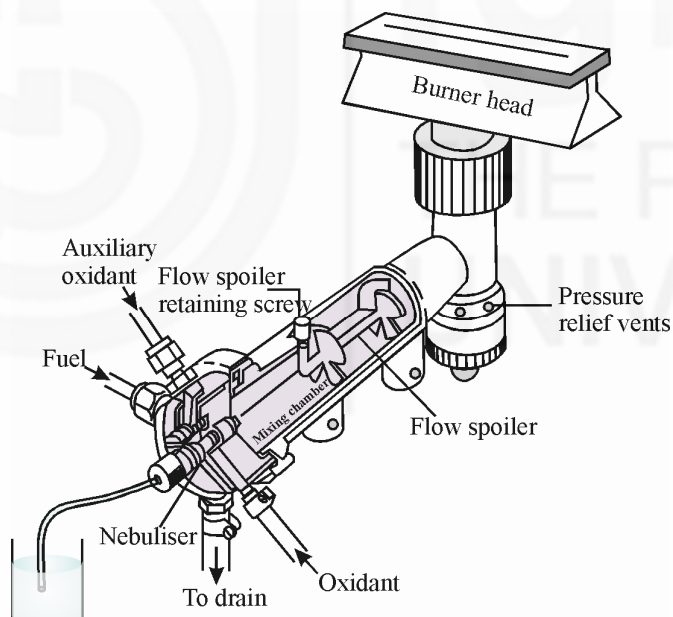


Fig. 7.10: Schematic diagram of a premix burner

Premix burners are called **Bunsen**, **Méker**, or **slot burners** depending on whether they have one large hole, a number of small holes, or a slot as outlet port(s) for the gas mixture, respectively. In case the burner contains several parallel slots it is called a **multislot burner** (e.g. a **three-slot burner**). The small diameter of the holes in the Méker burner or the narrowness of the slot in

the slot burner usually prevents the unwanted **flash back** of the flame into the burner housing.

The **advantage** with the premix burner is that it is quiet to operate and the analytical signal is significantly less noisy than that of total consumption burner (described below). However, it also has certain **disadvantages** like; 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.

b) Total consumption burner

A total consumption burner combines the functions of nebuliser 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. A schematic diagram of total consumption burner is given in Fig 7.11.

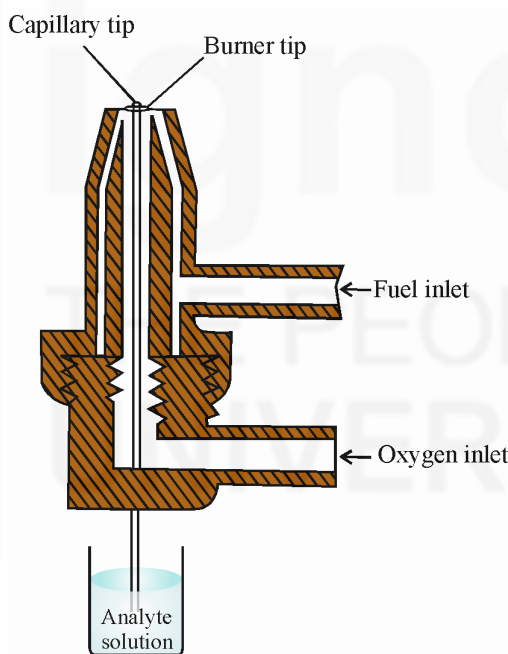


Fig. 7.11: Schematic diagram of a total consumption burner

The total consumption burner has the following advantages.

- 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 atomisation).
- 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.

However, the total consumption burner suffers from the following disadvantages.

- 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 incrustated 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.

7.6.3 Monochromator

You have learnt about monochromators in Unit 2 on UV-VIS spectrophotometry. Generally a grating or a prism monochromator is employed. The role of the monochromator is to disperse the radiation coming from the flame and falling on it. The dispersed radiation from the exit slit of the monochromator goes to the detector. In case a low temperatures flame is used, the spectral lines from only a few elements are emitted. In such a case, for most routine analyses, a filter can be used as a monochromator to isolate a particular spectral line. Filters are generally made from materials which are transparent in a small selective wavelength region. The filter chosen is one which has a wavelength range in which it is transparent to emission from the element of interest. In such a case, a condenser lens system is employed to collect the emitted light and send the rays through the filter as an approximately collimated (parallel) beam to reach the detector. Filters have been designed for use in the determination of lithium, sodium, potassium, calcium and other elements.

It is common to use a filter or a monochromator to allow for easy detection. While a simple, inexpensive flame photometer with filters can be used for routine determination of some of the alkali and alkaline earth metals, a more sophisticated instrument with high resolution employing a monochromator is required for other elements.

7.6.4 Detector

The function of a detector is to measure the intensity of radiation falling on it. Photoemissive cells or photomultiplier tubes are commonly employed for the purpose. These detectors are also used in UV-VIS spectrophotometers. You have learnt about these in Unit 2. You are advised to have a relook at subsection 2.4.3 to recall the functioning of different types of detectors.

7.6.5 Amplifier and Readout Device

The output from the detector is suitably amplified and displayed on a readout device like a meter or a digital display. The sensitivity of the amplifier can be changed so as to be able to analyse samples of varying concentrations. Nowadays the instruments have microprocessor controlled electronics that provides outputs compatible with the printers and computers thereby minimising the possibility of operator error in transferring data.

SAQ 4

Why is the sensitivity of a determination using pre-mix burner less than that on employing a total consumption burner?

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7.7 APPLICATIONS OF FLAME PHOTOMETRY

You have learnt earlier in the unit that flame photometry is suitable for qualitative and quantitative determination of several cations, especially for metals that are easily excited to higher energy levels at a relatively low flame temperature. Let us take up some important qualitative and quantitative applications of flame photometry.

7.7.1 Qualitative Applications

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.

7.7.2 Quantitative Applications

Flame photometry was developed by Lundegarth to determine the concentration of various soil components. The concentration of various alkali and alkaline earth metals is important in determining the suitability of the soil for cultivation. Very often an analysis of shed leaves of the plant for K^+ and Ca^{2+} is carried out. This gives an idea of the concentration of these ions in the soil which can be taken up by the plant. For agricultural purposes, an analysis of a proper mixture of surface soil and subsoil is carried out to determine the fertilizer requirement of the soil. In all these analysis, the soil or the ash is evaporated to dryness with conc. hydrochloric acid and the residue is treated with water or dilute hydrochloric acid to get these ions into aqueous solutions.

In clinical chemistry, it is very important to determine the concentration of sodium and potassium ions in body fluids since their ratio controls the action of muscles including the heart. Since these ions form few insoluble compounds and exhibit essentially no acidic or basic properties, they cannot be determined readily by conventional wet chemical techniques and are usually measured instrumentally. Flame photometry is the usual technique employed in determining these ions. This is achieved by diluting the blood serum and aspiration into the flame.

Very often internal standard lithium is added to take care of matrix effects. For example, in calcium analysis, La(III) or EDTA must be added to the solution to avoid interference due to phosphate. Food and drinks are usually analysed by ashing and leaching out the ash with mineral acid to leach out these elements. Soft drinks, fruit juices and alcoholic beverages can sometimes be analysed by using flame photometry.

Analysis of water from various sources is carried out to determine its suitability for drinking, washing, agricultural and industrial purposes. Analysis of effluent water from different industries is carried out to suggest the possible methods of treatment of this waste water.

The applications enumerated above show the importance of quantitative determinations of simple ions in wide range of samples. Such determinations are one

of the most useful applications of flame photometry. Table 7.3 lists some of the elements that can be determined by flame photometry and their detection limits.

Table 7.3: Elements, their characteristic emission wavelengths and detection limits

Element	Wavelength λ (nm)	Detection limit (μg)	Element	Wavelength λ (nm)	Detection Limit (μg)
Al	396	0.5	Cu	325	0.6
	484	0.5			
Sb	253	1.0	Fe	372	2.5
		2.7			
As	2350	2.2	Pb	406	14
Ba	455	3	Li	671	0.067
	554	1			
Bi	223	6.4	Mg	285	1.0
				383	1.6
Ca	423	0.07	Hg	254	2.5
	554	0.16	Ni	355	1.6
	662	0.6	Pd	363	0.1

Let us learn about the methodology for quantitative determination using flame photometry.

7.7.3 Methodology of Quantitative Analysis

As you would have understood by now that the general procedure in flame photometric determination involves preparation of the sample solution in a suitable solvent and aspirating it into the flame and measuring the intensity of the emitted radiation at the characteristic wavelength of the element. From the radiation intensity measured, the concentration of the element in the sample is then determined. You have learnt in Sec. 7.3 that the energy emitted by the excited atoms in the flame can be related to the number of atoms contained in the sample.

However, flame photometry is not an absolute method; it is empirical and is sensitive to experimental conditions. For example, the signal intensity from a flame is dependent on the flame temperature, the rate of flow of liquid into the flame, the pressure and rate of flow of fuel gases, and many other variables which affect the character of the flame or atomisation of the sample. Therefore, we can obtain reliable results only by performing repeated checks of reproducibility and the effects of altering conditions. It is therefore, essential that the relation between the intensity of the emitted radiation and the concentration of the associated element must be established. In other words we need to prepare a **calibration curve** as shown in Fig. 7.12.

The calibration curve is prepared by measuring the intensity of emission for a series of solutions of different concentrations prepared by using a standard solution and plotting a graph between emission intensity versus concentration of the ionic species of the element of interest. The concentration of the element in the unknown sample can then be found out from the standard plot as is done in visible spectrophotometry. Further, it is very important to measure the emission from the standard and unknown solutions under conditions that are as nearly identical as possible.

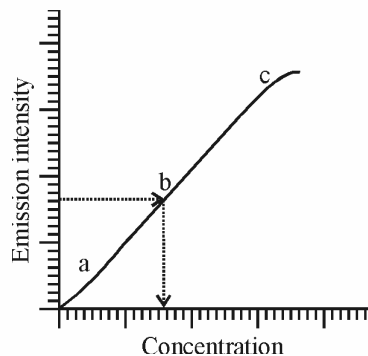


Fig. 7.12: Calibration plot: Emission intensity versus Concentration of the analyte

The standard calibration plot is usually linear over wide range but a deviation is generally observed at both low and high concentration ends. Let us have a close look at a typical calibration plot as given in Fig. 7.12. As you can see, three different regions of the calibration plot are distinctly visible. The explanation for these regions is given below.

- i) The region marked 'a' in the figure is depicted at very low concentration range. In this very low concentration range, emission falls below expected value due to ionisation as some atoms are converted to ions. For example, for potassium the ionisation is as given below.



Such ionisation is however, insignificant at higher concentration.

- ii) The region marked 'b' is the **linear region**, which can be used for quantitative measurements.
- iii) The region marked 'c' is depicted at a high concentration. In this concentration range **negative deviation** is observed due to self absorption. Photons emitted by the excited atoms are partly absorbed by ground state atoms in flame.

Thus, the calibration curve method helps in finding the concentration of unknown samples. However, for some samples, it is difficult to prepare standards which are sufficiently similar. This may occur when the samples contain high and variable concentrations of matrix materials, or when the samples contain solids whose effect on absorption is hard to duplicate. In such cases we need to resort to any of the following two methods.

- Standard addition method
- Internal standard method

Let us understand the two methods in detail.

Standard Addition Method

You have learnt about this method in the context of UV-VIS spectrometry in Unit 1. You would recall that in this method, known amount of a standard solution is added to identical aliquots of the sample and the absorbance is measured. The first reading is the absorbance of sample alone and the second reading is absorbance of sample containing analyte plus, a known amount of analyte and so on. Similarly, in flame photometric determinations, increasing amounts of a standard solution of the salt of the element to be determined is added to a series of solutions of the sample. The intensity of emission for all these solutions is then measured. A curve of intensity vs. concentration of the added element is obtained and extrapolated to zero value of intensity to give concentration of the element in the sample. Let us take an example of the standard addition method.

Example 7.2

In the determination of sodium in an unknown solution, the following series of solutions were prepared. Each solution contained 10 cm³ of the unknown solution to which increasing volumes of 25 ppm sodium (as sodium chloride) salt solution is added and the total volume is made up to 25 cm³. The emission readings of all these solutions are given below. Determine the concentration of sodium in the unknown solution.

Volume of 25 ppm Na ⁺ (added as NaCl)	0.0	2.0	4.0	6.0
Emission reading	30	50	70	90

Solution

A curve of emission reading versus the concentration of added sodium ion (in ppm) is given in Fig. 7.13.

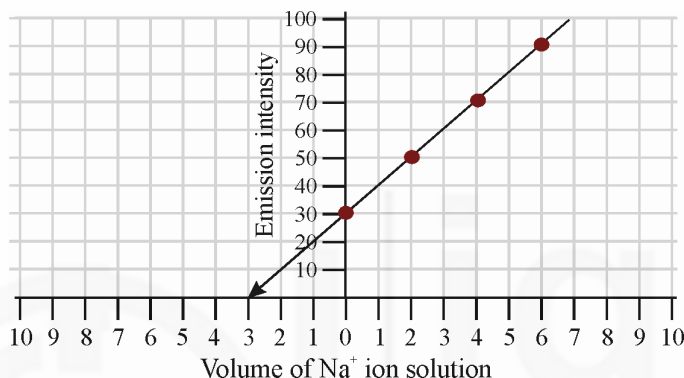


Fig. 7.13: Schematic calibration plot of Emission vs. Concentration in the determination of sodium by standard addition method

On extrapolating the curve to zero emission intensity, it meets the x-axis on the negative side of the concentration axis. The concentration of sodium is found to be 3.0 ppm. Since the given (unknown) solution is diluted from 10 ml to 25 ml in the final solution, the concentration of sodium is $3 \times 25/10 = 7.5$ ppm.

Internal Standard Method

In this method, a constant amount of another metal which is not present in the sample is added to both the unknown sample and a series of standard solutions of the element to be determined. This is called **internal standard**, for example, lithium is added in the determination of sodium metal. Since both the element and the internal standard are in the same solution, the emission readings at the wavelengths of both the internal standard and the element to be determined are simultaneously determined. The intensity ratio for the two elements is then plotted against concentration of the standard solution. From the observed ratio for the sample, the concentration of the element in it can be determined. Let us take an example to understand it.

Example 7.3

The following data were obtained in the flame photometric determination of sodium by internal standard method. 10 ppm of lithium was added to the series of standard solutions of sodium and the sample. The ratios of intensity of emission at the wavelengths of sodium and the lithium are given in Table 7.4.

Table 7.4: The ratio of intensity of emission at the wavelength of Na and Li during flame photometric determination by internal standard method

Solution number	Concentration of Li, ppm (fixed)	Concentration of Na, ppm (varying)	Intensity ratio of sodium to lithium
0	10.0	0.0	0.0
1	10.0	2.0	15.8
2	10.0	4.0	31.4
3	10.0	6.0	45.4
4	10.0	8.0	58.1
5	10.0	10.0	70.2
Sample	10.0	Unknown	43.0

Solution

The plot of the intensity ratios versus the concentration of the standard solutions of sodium is given in Fig. 7.14.

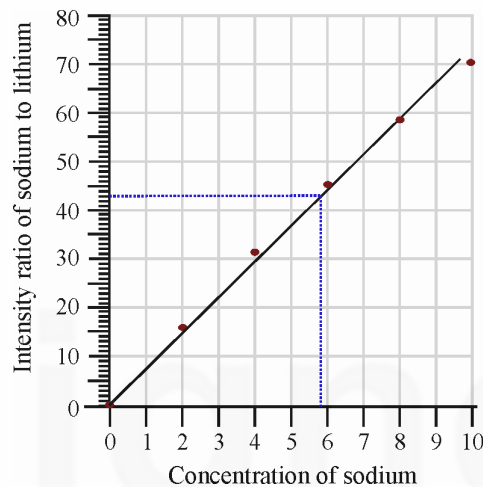


Fig. 7.14: Schematic calibration plot of Intensity ratios versus the Concentration during flame photometric determination of sodium by internal standard method

As the intensity ratio for the solution of unknown concentration is 43, we can determine the unknown concentration with the help of the graph plotted above. The observed ratio for the given sample corresponds to a concentration of 5.7 ppm of sodium.

7.7.4 Other Applications

A relatively new application of flame emission spectroscopy is called **simultaneous multi-element analysis**. A number of methods have been suggested for carrying out simultaneous multi-element analysis. By using a suitable detection system and monochromator, the resolution of 2.0 nm can be achieved and simultaneous determination of upto ten elements have been carried out by this method. In addition to the determination of metals, flame photometry can also be applied to nonmetal analysis by utilising the infrared region of the spectrum using flame infrared emission technique.

SAQ 5

What are the different methods for quantitative analysis?

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7.8 INTERFERENCES IN QUANTITATIVE DETERMINATIONS

As mentioned above, the success of the quantitative determination depends on how accurately the intensity of the emitted radiation represents the concentration of the analyte. It has been found that number of factors besides the analyte, affect the intensity of the emitted radiation. The analytical signals measured often include contributions from constituents other than the analyte. The constituents are called the **matrix constituents**. The contributions are known as **interferences** and are found to influence the outcome of the analytical procedure. These can be corrected by subtracting their contributions to the signal. The contribution of the interferent can be calculated from the magnitude of the interference and the concentration of the interferent. The interferences encountered can be classified as follows.

- Spectral interferences
- Ionised interferences
- Chemical interferences

Let us learn about different types of interferences encountered in quantitative determinations by flame photometry.

7.8.1 Spectral Interferences

These refer to the interferences that affect the spectral intensity or resolution. There are several types of spectral interferences which are explained below.

- The **first type** of interference arises when two elements exhibit spectra, which partially overlap, and both emit radiation at some particular wavelength. The detector cannot distinguish between the sources of radiation and records the total signal, thus resulting in incorrect answer. Such interferences are more common at high flame temperatures because numerous spectral lines are produced at high temperatures. For example, the Fe line at 324.73 nm overlaps with the Cu line at 324.75 nm. Such interference can be overcome either by taking measurements at an alternative wavelength which has no overlap, if available, or by removing the interfering element by extraction. Alternatively, one may make a calibration curve, which is prepared from a solution having similar quantities of the interfering element.
- The **second type** of spectral interference deals with spectral lines of two or more elements which are close but their spectra do not overlap. This type of interference becomes a problem when a filter is used as the device to isolate spectral lines. A filter may allow spectral lines separated by 5.0-10.0 nm to pass through, thus resulting in an error in the analysis. Such interferences can be reduced by increasing the resolution of the spectral isolation system. However, the interference cannot be eliminated entirely due to the finite width of the spectral isolation system and the finite slit width in such systems.
- A **third type** of spectral interference occurs due to the presence of continuous background which arises due to high concentration of salts in the sample, especially of alkali and alkaline earth metals. Some organic solvents also produce a continuous background. This type of interference can be corrected by using suitable scanning technique.

7.8.2 Ionisation Interferences

In some cases, high temperature flame may cause ionisation of some of the metal atoms, e.g., in case of sodium, it can be given as follows.



The Na^+ ion possesses an emission spectrum of its own with frequencies, which are different from those of atomic spectrum of the Na atom. This reduces the radiant power of atomic emission. This interference can be eliminated by adding a large quantity of a potassium salt to the standards as well as sample solutions. The addition of potassium salt suppresses the ionisation of sodium, as the potassium atom itself undergoes ionisation due to low ionisation energy. Thus, the sodium atom emission is enhanced. This type of interference is restricted to alkali metals.

7.8.3 Chemical Interferences

The chemical interferences arise out of the reaction between different interferents and the analyte. These are of different types. Some of these are given below.

- **Cation-anion interference**

The presence of certain anions, such as oxalate, phosphate, sulphate and aluminate, in a solution may affect the intensity of radiation emitted by an element, resulting in serious analytical error. For example, calcium in the presence of phosphate ion forms a stable substance, as $\text{Ca}_3(\text{PO}_4)_2$ which does not decompose easily, resulting in the production of lesser atoms. Thus, the calcium signal is depressed. Another similar example is that of determination of barium in presence of sulphate forming insoluble BaSO_4 . This type of interference can be removed either by extraction of the anion or by using calibration curves prepared from standard solutions containing same concentrations of the anion as found in the sample.

- **Cation-cation interference**

In many cases, mutual interferences of cations have been observed, resulting in reduced signal intensity of the element being determined. These interferences are neither spectral nor ionic in nature and the mechanism of such interferences is not well understood. Thus, for example, aluminum interferes with calcium and magnesium. Also, sodium and potassium show cation-cation interference on one another.

- **Interference due to oxide formation**

This type of interference arises due to the formation of stable metal oxide if oxygen is present in the flame, resulting in reduced signal intensity. The alkaline earth metals are subject to this type of interference. This type of interference can be eliminated by either using very high flame temperature to dissociate the oxides or by using oxygen-deficient environment to produce excited atoms.

7.8.4 Other Factors

A number of other factors affect the intensity of light emission from a given sample solution. For example, the organic solvents in a sample may also influence the intensity of the emission line by changing the viscosity and surface tension of the liquid, which in turn alter the rate at which the sample is aspirated into the flame. They also affect the flame temperature through their contribution to the heat of combustion. An increase in the line intensity is usually observed.

SAQ 6

An element A is to be determined in an analyte by flame photometry. The analyte also contains element B which emits radiation with wavelength overlapping that of element A, thus causing interference. What alternatives would you suggest to overcome the problem of this type of interference?

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7.9 MERITS AND LIMITATIONS OF FLAME PHOTOMETRY

You have learnt that flame photometry is suitable for 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.

The status of the flame photometer is similar to that of the colorimeter (which uses filters) compared to the spectrophotometer (which uses a monochromator).

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. Let us summarise what have we learnt in this unit.

7.10 SUMMARY

Atomic spectroscopy is the oldest instrumental method of elemental analysis. The origin of these techniques dates back to the times of Bunsen and Kirchhoff in the mid-19th century wherein they showed that the optical radiation emitted from flames is characteristic of the elements present in the flame and the intensities of the emitted radiation were dependent on the amount of elemental species present.

The atomic spectroscopic methods are based on the transitions amongst the quantised electronic energy levels caused by the absorption of radiation by the atoms in vapour phase or by the emission of radiation by the excited atoms. As the transitions manifest in terms of absorption, emission or fluorescence emission. Accordingly, we have atomic absorption, emission or fluorescence spectroscopies. The type of atomic spectroscopic method is determined both by the method of atomisation as well as the nature of the analyte radiation interaction. In contrast to the molecular spectra, the atomic spectra consist of a number of sharp absorption lines, characteristic of the atomic species. The signals in an atomic spectrum are also characterised in terms of the position, intensity and the band width.

Flame photometry is a method for the determination of elements which can be easily excited and is based upon the measurement of intensity of radiation emitted, in the visible region, when a metal is introduced into a flame. The wavelength of the emitted radiation, tells us what the element is, and the intensity of the radiation tells us how much of the element is present. The sensitivity of the flame photometric method depends on the number of excited atoms, which in turn depends on the flame temperature. The flame temperature is a function of the type of fuel and oxidant used.

In a typical flame photometric experiment, a solution of the analyte is aspirated into the burner and dispersed into the flame as a fine spray in a process called nebulisation. A number of processes occur in the flame to generate the gaseous atoms and ions in the excited state. The intensity of the emitted radiation is then measured for the qualitative and quantitative determination of the analyte.

A flame can be described as a steady state gas phase reaction which takes place with emission of light. These are produced by burning a mixture of fuel and air or oxidant in a burner. The maximum operating temperature of the flame is determined by the identity of fuel and oxidant whereas the exact temperature is fixed by the ratio of fuel and oxidant. Either pre-mix (or laminar) or unpremix (or turbulent) flames are used in flame photometry. In the former, the fuel and oxidant are well mixed before combustion, whereas in later these are mixed in the flame itself.

The instrument used in flame photometry is called flame photometer; it consists of a flame atomiser, flame burner, monochromator, detector, amplifier and readout device. A simple inexpensive flame photometer employing glass filters, is sufficient for routine analysis of alkali and alkaline earth metals though more expensive sophisticated instrument using monochromator may be required for analysis of other elements.

The quantitative analysis can be carried out using standard calibration curve, by standard addition or internal addition method. The method is subject to various interferences such as spectral, ionisation, and chemical interferences.

The major applications of flame photometry include qualitative and quantitative analysis especially of Group I metals (Li, Na, K) and Group II metals (Mg, Ca, Sr, Ba). It is very useful in routine determination of these metals in medicinal, biological, agricultural and industrial fields. Merits of the technique include high sensitivity and reliability, inexpensive instrumentation and advantages in analysis of alkali and alkaline earth metals. On the other hand, the method is chiefly restricted to these elements, liquid samples, and is subject to different types of interferences, and gives no information on chemical form of the element present.

7.11 TERMINAL QUESTIONS

1. Discuss briefly the principle underlying the quantitative analysis by flame photometry.
2. Why flame photometry is also called atomic flame emission spectrometry?
3. What are the different kinds of interferences possible in quantitative analysis by flame photometry?
4. List major components of a flame photometer and draw a block diagram of the equipment.
5. What are the advantages of flame photometry?
6. Enlist the limitations of flame photometry.
7. What are the applications of flame photometry?
8. Explain the necessity of using the linear region of the calibration plot for quantitative analysis in the space provided.
9. List different types of spectral interferences that may affect the accuracy of flame photometric determinations.

7.12 ANSWERS

Self Assessment Questions

1. The method of atomisation and the type of radiation-analyte interaction used in the given atomic spectroscopic methods are as follows.

S.No	Method of atomisation	Radiation-analyte interaction
i)	Flame	Emission
ii)	Graphite Furnace	Absorption
iii)	Inductively Coupled Plasma	Absorption
iv)	Flame	Fluorescence

2. The flame photometric method is based on the principle that when an analyte containing element of interest is introduced into a flame, it is converted into gaseous atoms which are excited to higher energy level by absorbing energy from flame. As the excited atoms return to ground state, radiations of characteristic wavelength are emitted. The wavelength of the radiation emitted is characteristic of the element present and hence tells us what the element is. This forms the basis of the qualitative analysis by flame photometry. The intensity of the radiation emitted tells us how much of the element is present. This, therefore, is the basis of quantitative analysis using flame photometry.

3. The regions of a premix flame are:

- Preheating zone
- Primary reaction zone
- Interconal zone
- Secondary reaction zone

The secondary reaction zone is used in flame photometry.

4. In the premix burner, a large fraction of the solvent from the aspirated solution evaporates before it reaches the flame. Only 5% of the sample reaches the burner, therefore, efficiency of the pre mix burner is low. Whereas, in case of total combustion burner, the sample is introduced directly into the flame.

5. The different methods for quantitative analysis by flame photometry are as follows.

- i) Standard calibration curve method
- ii) Standard addition method
- iii) Internal standard method

6. If the element A also emits radiation of another characteristic wavelength which does not overlap with those of element B, this alternative characteristic wavelength can be used for quantitative measurements. Another option is to use a calibration curve prepared from a solution having similar quantities of the interfering element B.

Terminal Questions

1. In flame photometry, the thermal energy from flame is utilised to convert the analyte into gaseous atoms and then to excite them to higher energy level. As the excited atoms return to a state of lower energy, radiation of wavelength characteristic of the element is emitted. The intensity of the emitted radiation is related to the concentration of the element present, forming the basis of the quantitative analysis by flame photometry.

2. As we measure the emission spectrum of the atoms that were excited using the thermal energy of flame, the technique is called flame atomic emission spectroscopy (FAES).

3. The different kinds of interferences encountered in analysis by flame photometry are:

- Spectral interferences
- Ionisation interferences
- Chemical interferences

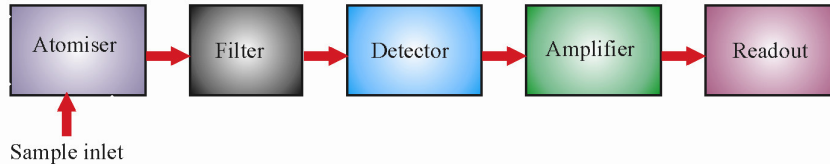
In addition, some other factors, such as viscosity, and surface tension of the solvent also affect the intensity of light emission, thus contributing to erroneous results of analysis.

4. The major basic components of instrumentation for flame photometry are:

- Flame atomiser (consisting of nebuliser and burner)
- Monochromator
- Detector

- Amplifier and Readout device

The block diagram of the instrumentation involved in flame photometry is given below:



A block diagram showing different components of a flame photometer

- The following are the major advantages of flame photometry.
 - It provides high sensitivity and high reliability for the determination of elements like, sodium, potassium, lithium, calcium, magnesium, strontium, and barium. These determinations are useful in medicine, agriculture and environmental science.
 - It is also successful in determining certain transition elements such as copper, iron and manganese.
 - By making wavelength scan of the emission spectrum, it is possible to do qualitative analysis by employing flame photometer, but the application is severely limited.
- The limitations of the method include the following.
 - The low temperature of the natural gas and air flame limits the method to easily ionized metals. The method is selective though restricted towards easily excitable alkali and alkaline earth metals.
 - The low flame temperatures render this method susceptible to certain disadvantages, most of them related to interference and the stability of the flame and aspiration conditions.
 - 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.
- Some common applications of flame photometry are given below.
 - Flame photometry can be used to detect the presence of the elements of Group I and II of the periodic table, e.g. Na, K, Li, Mg, Ca, Sr and Ba.
 - Flame photometry is very important in the analysis of biological fluids and tissues, in which elements like sodium, potassium, aluminium, calcium, cobalt and iron are detected and determined. It has also been used for analysis of soil, natural and industrial waters, glass, cement.
 - Flame photometry can also be applied to nonmetal analysis by utilising the infrared region of the spectrum using flame infrared emission technique.
 - By using a suitable, detection system and a monochromator, simultaneous determination of upto ten elements (including elements other than alkali and alkaline metals) can be carried out.
- When a quantitative analysis using a standard calibration curve is carried out, a calibration plot of emission intensity vs concentration of the ionic species of

interest is plotted. Such a curve shows deviations at the low and high concentration ends.

9. The following types of spectral interferences may affect the accuracy of flame photometric determinations:
- The first type of interference arises when two elements exhibit spectra, which partially overlap, and both emit radiation at some particular wavelength.
 - The second type of spectral interference deals with spectral lines of two or more elements which are close but their spectra do not overlap.
 - A third type of spectral interference occurs due to the presence of continuous background which arises due to high concentration of salts in the sample.

