

BCHET-141
ANALYTICAL METHODS IN
CHEMISTRY

Block

4**SPECTROSCOPIC METHODS OF ANALYSIS**

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BLOCK 4: SPECTROSCOPIC METHODS OF ANALYSIS

In the previous block of this course, you have learnt about thermal and electroanalytical methods. In this last block of the course, you would learn about spectroscopic methods of analysis. Spectroscopic methods of analysis are based on the consequences of the interaction of radiation with matter. The interaction may lead to the absorption, emission or scattering of radiation. In this block you would learn about the concepts based on the nature of radiation and the type of interaction involved in its interaction with matter. The block is divided into five units.

Unit 11, titled '**Electromagnetic Radiation**', deals mainly with the electromagnetic radiation in terms of its nature, characteristics, and properties. It also covers the ways in which different types of electromagnetic radiation interact with matter and the types of spectra that result because of the interaction.

Unit 12, titled '**UV-Visible Spectrometry**', deals with the theory behind UV-VIS spectrometry in terms of the origin and principles that form the basis of the analytical applications. It also gives an account of the instrumentation and the qualitative and quantitative applications of UV-VIS spectrometry.

Unit 13 deals with the consequences of the interaction of infrared radiation with the molecules and is titled '**Infrared Spectrometry**'. It deals with the theory, instrumentation, and analytical applications of the IR spectrometry.

Unit 14, titled '**Flame Atomic Absorption Spectrometry**', deals with the atomic spectroscopic method arising out of the absorption of radiation by atomised analyte element in the ground state; the atomisation being achieved thermally by a flame. It covers the conceptual background, instrumentation, and applications of the technique along with the possible interferences and their management.

Unit 15, titled '**Flame Atomic Emission Spectrometry(Flame Photometry)**', deals with the atomic spectroscopic method arising out of the emission of radiation by atoms excited by the thermal energy of the flame. It covers conceptual background, spectral characteristics, instrumentation required for the measurement of the spectra and applications of the technique along with the possible interferences and their management.

Expected Learning Outcomes

After studying this block, you should be able to:

- ❖ describe the wave and particle nature of electromagnetic radiation and define the parameters that characterise electromagnetic radiation;
- ❖ discuss different types of interactions of electromagnetic radiation with atoms and molecules;

- ❖ explain the origin and the characteristics of UV-VIS, Infrared, FAAS and FAES spectra;
- ❖ explain the Lambert's and Beer's laws and list the factors leading to deviation from Beer-Lambert's law;
- ❖ describe the essential components of UV-VIS, Infrared, FAAS and FAES spectrometers;
- ❖ explain the principles of different types of spectrometers used in UV-VIS, Infrared, FAA and FAE spectrometric methods;
- ❖ describe different types of vibrational modes and identify IR active and inactive modes of vibration for small molecules;
- ❖ interpret the IR spectra of simple organic molecules to ascertain their functional groups.
- ❖ describe the structure and characteristics of a flame and explain the fate of the analyte sample introduced into the flame;
- ❖ explain the principles of FAAS and FAES spectrophotometric methods;
- ❖ outline the quantitative methodologies for UV-VIS, FAA, and FAE spectrometric methods;
- ❖ discuss the interferences observed in FAA and FAE spectrometric determinations, and
- ❖ enlist the applications of UV-VIS, IR, FAA, and FAE spectrometric methods

UNIT 11

ELECTROMAGNETIC RADIATION

Structure

11.1 Introduction

Expected Learning Outcomes

11.2 What is Electromagnetic Radiation?

Wave Mechanical Model of Electromagnetic Radiation

Quantum Model of Electromagnetic Radiation

11.3 Modes of Interaction of Radiation and Matter

Absorption of Radiation

Emission of Radiation

Scattering of Radiation

11.4 Nature of Spectrum

Atomic Spectra

Molecular Spectra

Line Spectra versus Band Spectra

11.5 Summary

11.6 Terminal Questions

11.7 Answers

11.1 INTRODUCTION

You would surely have seen a beautiful rainbow showing seven different colours during the rainy season. You know that this colorful spectrum is due to the separation or dispersion of the white light into its constituent parts by the rain drops. The rainbow spectrum is just a minute part of a much larger continuum of the radiations that come from the sun. These are called electromagnetic radiations and the continuum of the electromagnetic radiations is called the electromagnetic spectrum.

In the first unit of this block on 'spectroscopic methods of analysis', you would learn about the electromagnetic radiation and origin and nature of spectra. We would begin the unit with a discussion on the nature, characteristics, and properties of electromagnetic (EM) radiation. In this context we would explain the wave model and particle models of EM radiation and discuss about different parameters that characterise a radiation. Since spectroscopy is the study of interaction of electromagnetic radiation with matter, we would recall the quantum mechanical nature of matter before discussing the different ways in which electromagnetic radiation interacts with matter and gives a spectrum.

Thereafter we would take up a discussion on the nature of spectra that are obtained because of the interaction of radiation and matter.

In the next unit you would learn about ultraviolet-visible spectroscopy—a consequence of interaction of electromagnetic radiation in the ultraviolet-visible range with the matter.

Expected Learning Outcomes

After studying about and performing this experiment, you should be able to

- ❖ describe the wave nature of electromagnetic radiation;
- ❖ define the parameters that characterise wave form of electromagnetic radiation;
- ❖ give interrelations between different characteristics of EM radiation and solve problems based on them;
- ❖ describe the particle nature of electromagnetic radiation;
- ❖ explain the quantum mechanical nature of matter (atoms and molecules);
- ❖ discuss different types of interactions of electromagnetic radiation with atoms and molecules;
- ❖ describe the nature of spectrum in atomic and molecular systems; and
- ❖ explain the origin of line spectrum and band spectrum.

11.2 WHAT IS ELECTROMAGNETIC RADIATION?

You feel hot while sitting close to a fire. You would say it is obvious, what is so special about it? Fine! But have you ever wondered what makes you feel hot or in other words how does the energy as heat reach you from the source?

This is in the form of **electromagnetic (EM) radiation**. Heat energy reaches us in the form of infra-red radiations which is a type of electromagnetic radiation. Let us learn about EM radiation in general.

An electromagnetic radiation may be defined as *the radiant energy which is transmitted through space at enormous velocities*. It exists in various forms; the visible light and radiant heat being the easily recognised forms which we experience in day-to-day life. The EM radiation, unlike sound, does not require a medium for transmission and pass readily through vacuum and in vacuum, the velocity of EM radiation is $3 \times 10^8 \text{ m s}^{-1}$. The study of different ways in which EM radiation can interact with matter is of great importance. To understand these interactions, it is therefore necessary to have knowledge of the characteristics of EM radiation. The properties of an electromagnetic radiation could be explained in terms of classical wave model (classical model) and particle model (quantum model).

Let us learn about these models of EM radiation and the properties associated with them. We begin with wave model.

11.2.1 Wave Model of Electromagnetic Radiation

You would recall from your school chemistry and physics that according to the wave model, the electromagnetic radiation is like a sinusoidal wave, i.e., a wave varying like a sine function. You would also recall that according to the Maxwell's theory, an electromagnetic wave can be visualised as oscillatory electric and magnetic fields travelling in the planes perpendicular to each other and to the direction of propagation (Fig. 11.1). This gives rise to its name viz., electromagnetic radiation.

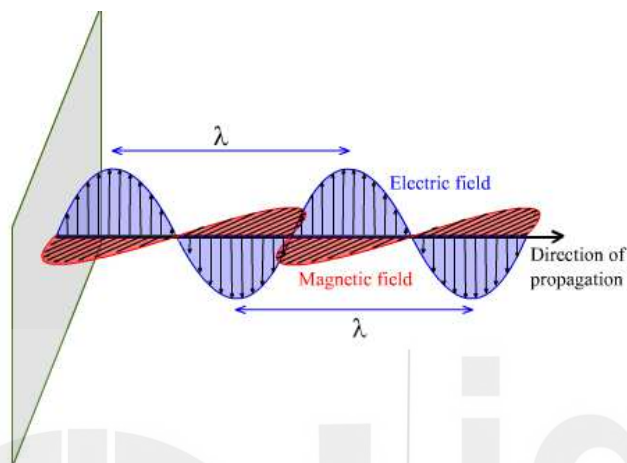


Fig. 11.1: An EM radiation showing oscillatory electric and magnetic fields.

Characteristic Parameters of Electromagnetic Radiation

The electromagnetic wave is characterised in terms of several parameters. These are as follows:

Amplitude: It refers to the maximum height to which the wave oscillates and equals the height of the crests or depths of the troughs. It is a measure of the radiant power of the radiation. The **radiant power** refers to the energy of the radiation striking at a given area per unit time. It is denoted as P and is related to the square of the amplitude. It is important to know that a closely related term, **intensity** of the radiation is defined as the radiant power per unit solid angle. However, sometimes these terms are used interchangeably.

Wavelength: It is the linear distance between two consecutive wave-crests or wave-troughs or the distance of complete cycle of the wave as shown in Fig. 11.1. It is represented by Greek letter **lambda** (λ) and expressed in terms of meter (m), centimeter (cm), micrometer (μm), nanometer (nm) or Angstrom ($\text{\AA}$) units. The wavelength of electromagnetic radiation varies from a few Angstroms to several meters.

$1 \text{ cm} = 10^{-2} \text{ m}$
$1 \mu\text{m} = 10^{-6} \text{ m}$
$1 \text{ nm} = 10^{-9} \text{ m}$
$1 \text{\AA} = 10^{-10} \text{ m}$

Frequency: It is defined as the number of wave crests or wave troughs that pass-through a given point per second. It is represented by Greek letter **nu** (ν) and expressed in terms of second inverse or per second (s^{-1}) or Hertz (Hz).

The relationship between wavelength and frequency is given as:

$$\nu = \frac{c}{\lambda} \quad \dots(11.1)$$

Where, the wavelength λ is in meters, the frequency ν is in reciprocal seconds, s^{-1} and the velocity of light, $c = 3 \times 10^8 \text{ ms}^{-1}$.

Wave number: It equals the number of waves per centimetre or per unit distance. It is denoted as **nu bar**($\bar{\nu}$) and is equal to the reciprocal of the wavelength expressed in meters (m). The SI unit of $\bar{\nu}$ is meter inverse (m^{-1}) though cm^{-1} is also commonly employed, where the wavelength is expressed in the units of cm. The wavenumber and wavelength are related as:

$$\bar{\nu} = \frac{1}{\lambda} \quad \dots(11.2)$$

Velocity: It is defined as the linear distance travelled by the wave in one second. The velocity in meters per second can be obtained by multiplying frequency in second inverse by wavelength in meters.

$$c = \nu (\text{s}^{-1}) \lambda \quad \dots(11.3)$$

The velocity of EM radiation depends on the medium. It has maximum value in vacuum and equals $3.00 \times 10^8 \text{ ms}^{-1}$.

Energy: The energy of the electromagnetic radiation depends on its wavelength(or frequency). The relationship is as under.

$$E = h\nu = \frac{hc}{\lambda} \quad \dots(11.4)$$

where, h is the Planck's constant and has a value of $6.626 \times 10^{-34} \text{ J s}$; ν is the frequency, c is the velocity of light and λ is the wavelength.

Table 1.1: Characteristics of EM radiation, their relationship with wavelength and common units of measurement

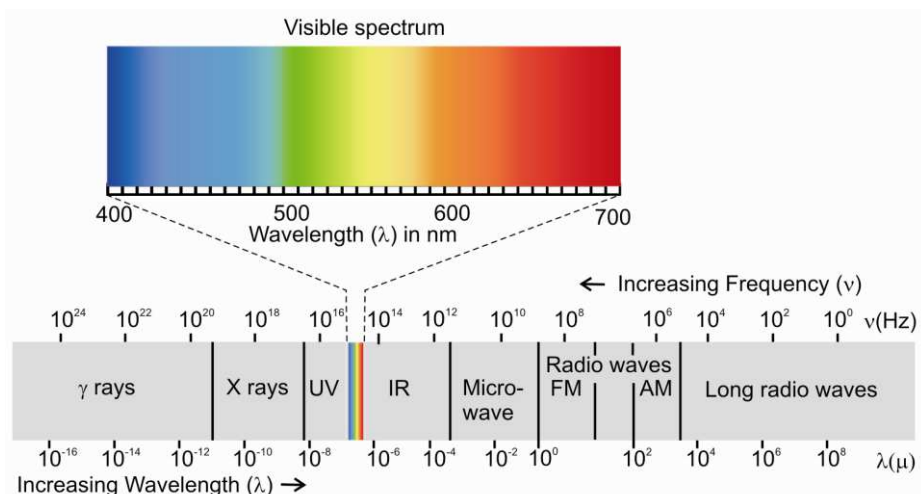
Characteristic of EM Radiation	Relationship with Wavelength	Common Units
Wavelength	λ	m, μm , nm
Wave number	$\bar{\nu} = \frac{1}{\lambda}$	m^{-1} , cm^{-1}
Frequency	$\nu = \frac{c}{\lambda}$	s^{-1} (Hz)
Velocity	$c = \nu\lambda$	m s^{-1}
Energy	$E = \frac{hc}{\lambda}$	Joule (J)

As you can make out that the energy is directly related to the frequency and inversely related to the wavelength of the radiation. In other words, a high frequency radiation will have a higher energy while a longer wavelength radiation will be of low energy. Table 1.1 summarises the important characteristics of the EM radiation, their relationship with wavelength and the common units of their measurement.

The Electromagnetic Spectrum

Depending on the wavelengths, electromagnetic radiation is of many types and constitutes what is called an **electromagnetic spectrum**. The EM

spectrum is divided into different regions like γ -rays, x-rays, ultraviolet, visible, infrared, microwave, and radio waves, etc. as shown Fig. 11.2.



Deuterium lamp is commonly employed as the source of UV radiations.

Fig.11.2: Electromagnetic spectrum showing different regions.

The visible region of the spectrum which the human eye can sense is very tiny, as compared to the other spectral regions. Since the range of electromagnetic spectrum is quite large, it is expressed in logarithmic or exponential scale. The sources of radiation mostly give EM radiation spread over a range. In other words, the EM radiation emitted by the source contains several radiations having a range of slightly different wavelengths. Such a radiation is called **polychromatic radiation** signifying that it consists of many radiations of different wavelengths. For example, a hot deuterium lamp emits radiations in the wavelength range of approximately 190-380 nm. We can generate or separate out radiation of a single wavelength from the polychromatic radiation by using a suitable device called **monochromator**. The radiation so obtained is called a **monochromatic radiation** i.e., consisting of a single wavelength. You would learn about monochromators in the next unit.

Having learnt about the wave model of electromagnetic radiation let us take up quantum model. However, before that answer the following simple question to assess your understanding.

SAQ 1

How is an electromagnetic radiation different from sound waves?

11.2.2 Quantum Model of Electromagnetic Radiation

The wave model of electromagnetic radiation described above was successful in explaining many observed phenomena. However, it could not explain some of the experimental observations like in case of black body radiation and the photoelectric effect. You have learnt about these experiments in BCHCT-131 course. Therefore, a new model for the electromagnetic radiation was required. This is called the **quantum model** (also called **particle model**) of radiation. In the quantum or particle model, the radiant energy is considered

The quantum of light was later called a **photon**.

as a stream of discrete particles or packets of energy called **quanta** (singular, quantum) whose energy is proportional to its frequency. The energy and frequency are related as,

$$E = h\nu \quad \dots(11.5)$$

Alternatively, the energy of the quantum can be related to the wavelength or wavenumber as follows

$$E = h \frac{c}{\lambda} \text{ or } E = hc\bar{\nu} \quad \dots(11.6)$$

Let us take an example to understand the application of the relationship between the energy and other characteristics of the radiation.

Example 1: A microwave radiation has a frequency of 12 gigahertz.

- What would be the energy of the photon corresponding to this radiation?
- Calculate the wavelength of the radiation.

$$(h = 6.626 \times 10^{-34} \text{ J s} \text{ and } 1 \text{ gigahertz} = 10^9 \text{ Hz})$$

Solution:

- The energy of radiation is related to the frequency as, $E = h\nu$

Substituting the values of frequency and Planck's constant, we get

$$E = 6.626 \times 10^{-34} \text{ Js} \times 1.2 \times 10^{10} \text{ s}^{-1} = 7.95 \times 10^{-24} \text{ J}$$

$$\therefore \text{The energy of the photon having a frequency of 12 gigahertz} \\ = 7.95 \times 10^{-24} \text{ J}$$

- We know that $E = h \frac{c}{\lambda}$

$$\text{we can rearrange the equation to get } \lambda = \frac{hc}{E}$$

Substituting the values of E , h , and c we get

$$\lambda = \frac{6.626 \times 10^{-34} \text{ Js} \times 3.0 \times 10^8 \text{ ms}^{-1}}{7.95 \times 10^{-24} \text{ J}} = 400 \text{ nm}$$

$$\therefore \text{The wavelength of the radiation} = 400 \text{ nm}$$

Having learnt about the wave and particle models of electromagnetic radiation answer the following simple question to assess your understanding.

SAQ 2

The green light has a wavelength of 535 nm. Calculate the energy of a photon of green light.

Note correction: the formula was incorrect in the printed version.

11.3 MODES OF INTERACTION OF RADIATION AND MATTER

We have defined spectroscopy as the study of interaction of electromagnetic radiation with matter. As a result of this interaction, we get a **spectrum**.

Therefore, to understand the origin of spectra, we need to understand the interaction of radiation with matter. In turn, to understand the nature and mechanism of interaction of radiation with matter we would first like you to recall what you have learnt about nature of matter in earlier classes. You would recall from your understanding of the quantum mechanical description of the electronic structures of atoms and molecules, that these have unique set of quantised electronic energy states available to them. These arise from the motion of electrons around the nucleus. The electrons in atoms and molecules are present in the allowed or permissible energy states only.

However, in case of molecules, the rotation and vibration motions are also quantised, in addition to these electronic energy states. The allowed energy level with the least energy is termed as the **ground state** while the rest are called **excited states**. The energy levels for a molecule can be schematically shown as given in Fig. 11.3.

There are several vibrational energy levels in an electronic state and a large number of rotational energy levels are there in a vibrational energy level.

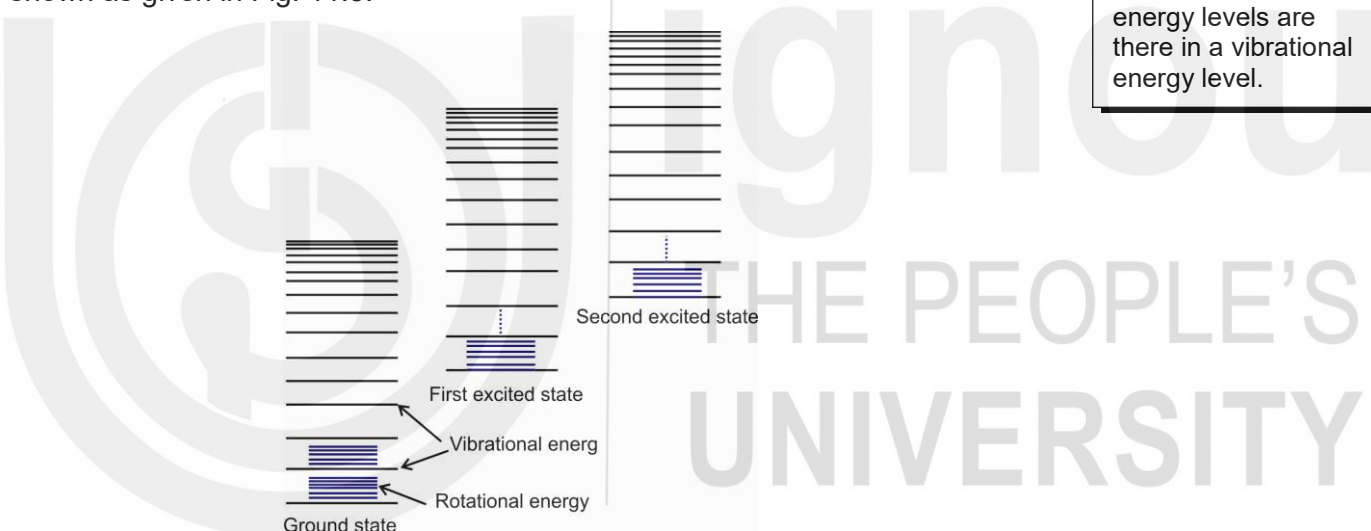


Fig. 11.3: Schematic diagram showing energy levels for a molecule.

The transitions amongst these energy states may be brought about by absorption of a photon of suitable energy or these transitions may lead to release of such a photon. In simple words we can say that the system may go from the lower energy state, E_1 , to higher energy state, E_2 by absorbing a photon of energy equal to the difference of the energies of the two states i.e.,

$$\Delta E = E_2 - E_1 = h\nu \quad \dots(11.7)$$

where, h is the **Planck's constant** and has the value of 6.626×10^{-34} J s (joules second), ν is the frequency of electromagnetic radiation which is causing the energy changes. Alternatively, a system initially in the higher energy state E_2 can go to the lower energy state E_1 by emitting a photon of the energy equal to the difference in energies. A yet another possibility is of the radiation getting scattered during its interaction with matter. The three phenomena occurring due to interaction of radiation with matter viz. absorption, emission and scattering are explained in the following subsections.

11.3.1 Absorption of Radiation

Let us see what happens when a polychromatic radiation is made to fall upon a sample containing atoms or molecules. One simple possibility is that it gets transmitted unaffected through the sample. The other possibility is the radiation coming out of the sample is devoid of the certain frequencies. In the latter case the missing frequencies are said to be absorbed by the sample. Only those photons are absorbed whose energy matches with the difference in energy of any two energy states of the sample provided the transition amongst these levels is allowed. For example, when white light containing the whole range of frequencies in the visible range is made to fall on a sample containing gaseous sodium atoms in the ground state, yellow light of wavelength 589 nm is absorbed. This causes the transition of electron from 3s level to 3p level as shown in Fig. 11.4.

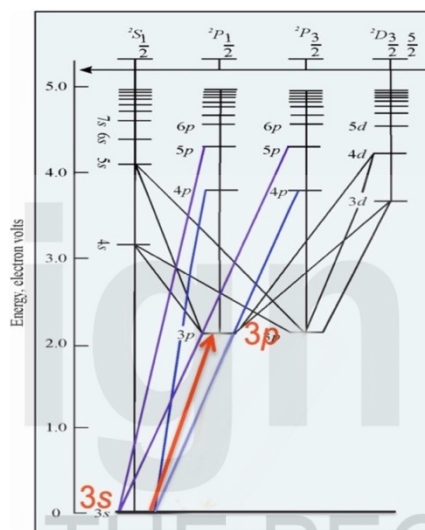


Fig. 11.4: Schematic representation of absorption of radiation causing transitions in electronic energy levels of sodium atom.

This kind of absorption of EM radiation by gaseous atomic species in their ground state forms the basis of an important spectroscopic method called '**atomic absorption spectrometry**', about which you would learn in Unit 14 of this course.

In case of molecules, the situation is different. As mentioned above, that in case of molecules, besides the electronic energies, the rotational and vibration energies are also quantised. Therefore, in case of molecules, different types of absorption are possible. For example, the radiation in the microwave region (see Fig. 11. 2) is very small and its interaction with molecular species can cause transitions only in the rotational energy levels, Fig.11.5 (a)

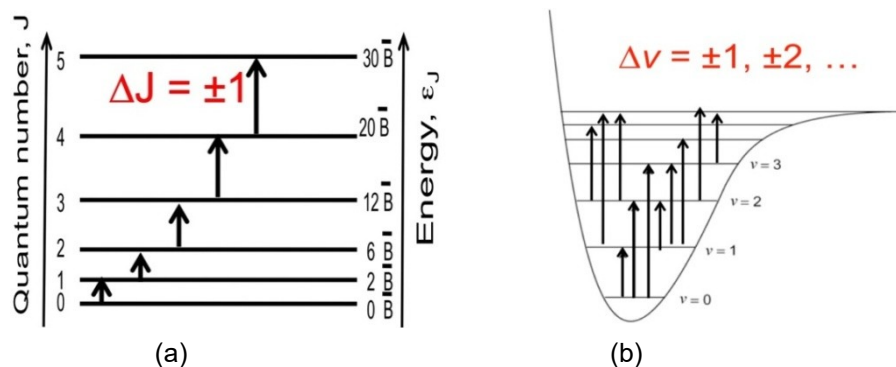


Fig. 11.5: Schematic representation of absorption of radiation causing (a) transitions in rotational energy levels (b) transitions in vibrational energy levels of the molecule.

Similarly, the radiation in the infra-red region (see Fig. 11. 2) is small but larger than that of the microwave radiation, and its interaction with molecular species can cause transition in the vibrational energy levels; Fig.11.5 (b). These are accompanied by that in the rotational energy levels and forms the basis of **IR spectroscopy** about which you would learn in Unit 13.

The energy of EM radiation in UV-VIS range is still larger and is of the order of the difference in the electronic energy levels of the molecules. Therefore, absorption of EM radiation in the UV-VIS region causes the transitions amongst the electronic energy levels and forms the basis for **UV-VIS spectrometry** about which you would learn in the next unit of this course.

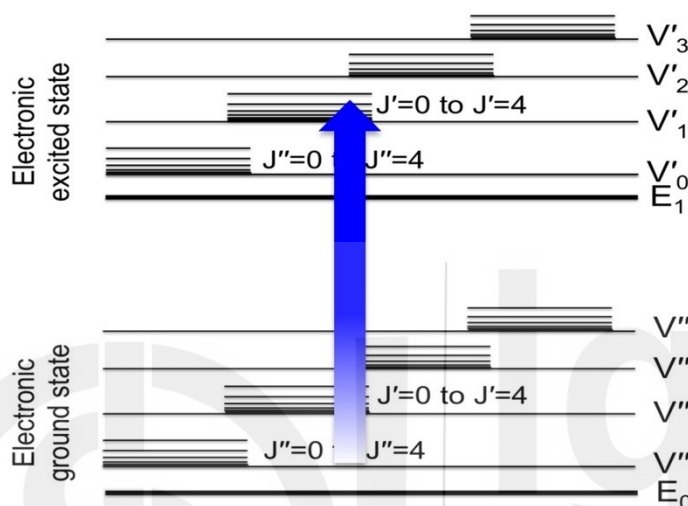


Fig. 11.6: Schematic representation of absorption of radiation causing (a) transitions in electronic energy levels, accompanied by the vibrational and rotational energy levels of the molecule.

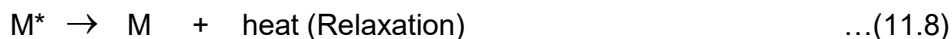
The electronic transitions in the molecules are accompanied by the transitions amongst the vibrational and rotational energy levels also. This means that in the initial state the molecule could be in a certain vibrational and rotational energy level of the ground state and on absorption of radiation, there may be a change in the vibrational and rotational energy levels also along with the electronic energy level, Fig.11.6.

We have seen that on absorption of radiation by an atomic or molecular species we get the species in the excited state. In addition to the absorption of radiation, the atoms and molecules can be excited by providing the required energy in other ways. Some of these are

- Bombardment with electrons or other elementary particles
- Exposure to high potential alternating current
- Using spark, arc, or a flame

The concentration of the excited species so obtained is quite small and its lifetime is very short. These excited species generally relax (come down to ground energy level) by losing energy to the other atoms or molecules. This mode of relaxation is called **non-radiative relaxation** and occurs in the time frame of about 10^{-6} to 10^{-9} s. The excess energy is transferred in a series of small steps to the neighboring species as their kinetic energy and is

manifested in the form of heat. Because of this, the temperature of the system increases slightly.



In addition to the non-radiative relaxation, the excited species, irrespective of the mode of their excitation, can relax by emitting a radiation. This is referred to as **radiative relaxation**. Let us learn about different types of radiative relaxation mechanisms and the spectra which arises due to them.

11.3.2 Emission of Radiation

During the festive season or at the times of celebrations, you must have enjoyed the beautiful display of colours by fireworks in the sky. This splendid show is a result of relaxation of excited species from higher energy to the ground level releasing the excess energy in the form of light and heat. The colours we see are electromagnetic radiations in the visible range. The radiation emitted by an excited species is represented in terms of an **emission spectrum**.

You have learnt above that the absorption of radiation by atoms and molecules generates excited species. Like absorption of radiation, the radiative relaxation of atoms and molecules is also different. You would surely have performed flame test in your school chemistry laboratory. You would recall that in such a test we place a sample of the salt being analysed into the flame and observe the development of colour (if any) in the flame. A sodium salt imparts a golden yellow colour to the flame. This is due to the emission of characteristic radiation (radiative relaxation) by the sodium atom that got excited by absorbing energy from the flame. The characteristic colour is due to the emission of visible radiation having a wavelength of about 589 nm, Fig.11.7.

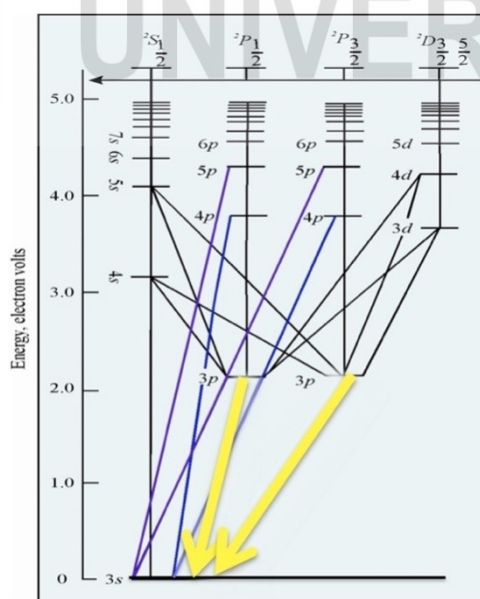


Fig. 11.7: Schematic representation of emission of radiation by sodium atom in excited state.

In case of molecules in the electronically excited state, generally non radiative relaxation precedes the radiative emission. This means that the electron in the

excited state does not relax down to the ground state straightway by emission of a radiation.

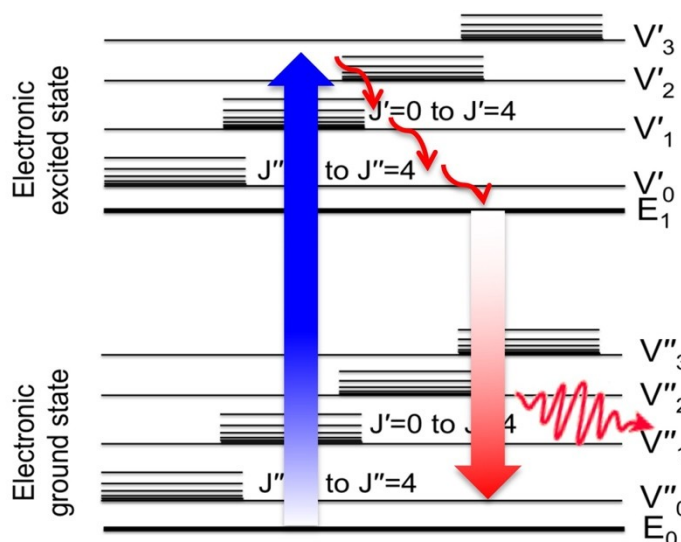


Fig. 11.8: Schematic representation of emission of radiation by a molecule in electronically excited state.

Instead, it loses part of its energy to the neighbouring species and comes down to the vibrational ground state of the excited electronic energy level. Thereafter, it can undergo electronic relaxation by emitting a photon as shown in Fig.11.8. This type of radiative relaxation, in fact, is the basis of the phenomenon of **fluorescence** and **phosphorescence**. Similar mechanism is responsible for closely related phenomenon of **chemiluminescence** and **bioluminescence** (in firefly), Fig. 11.9. In these cases, the excitation occurs due to a chemical and biochemical reaction respectively.

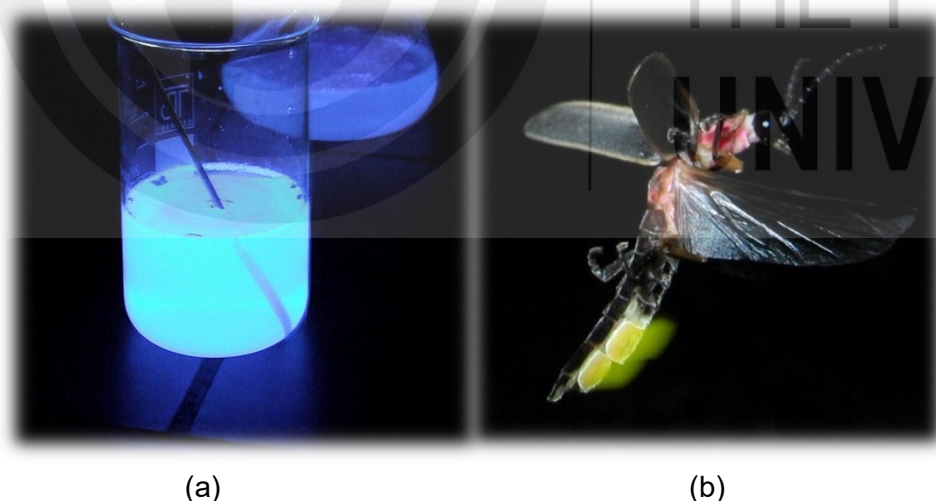


Fig. 11.9: Representative images of the phenomenon of (a) chemiluminescence and (b) bioluminescence.

11.3.3 Scattering of Radiation

There is a yet another way of interaction between the radiation and matter. It is called **scattering**. The radiation having wavelength comparable to the interacting species gets scattered. The scattered radiation is generally measured in the direction perpendicular to the incident direction. If a monochromatic radiation is used, then it is observed that most of the scattered radiation is of the same frequency as the incident frequency. This is called

Rayleigh scattering is a consequence of elastic scattering in which there is no exchange of energy between the radiation and matter.

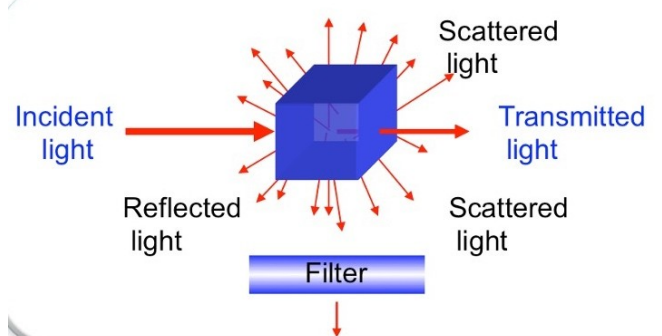


Fig. 11.9: Schematic representation of consequences of radiation falling on a sample.

However, it has been found that in certain cases the radiation may interact with matter in such a way that it involves certain amount of energy exchange. Consequently, the scattered radiation has frequencies greater or smaller than that of the incident radiation. The presence of radiation of different wavelengths in the scattered radiation is called **Raman Effect** and such a scattering is called **Raman scattering**. This phenomenon of inelastic scattering is the basis of Raman spectroscopy—an important analytical tool.

Having learnt about different modes of interaction of radiation and matter, let us now learn about the nature of spectra that are obtained because of such interactions. However, before that answer the following simple question to assess your understanding.

SAQ 3

What are different ways in which an excited state of atoms or molecules can be obtained?

11.4 NATURE OF SPECTRA

You have learnt above that there are three ways in which the radiation and matter interact i.e., absorption, emission and scattering of radiation. Also, you have observed that the consequence of such an interaction is different in case of atoms and molecules. Let us learn what kind of spectra are observed due to these interactions in case of atoms and molecules.

11.4.1 Atomic Spectra

Most of the sources of radiation generate polychromatic radiation i.e., there are many radiations spread over a range of wavelengths. For example, a tungsten lamp gives out radiation spread over the whole range of visible spectrum. This can be shown by passing the radiation from such a source through a prism or any suitable dispersion device, it gives a **continuous spectrum** of EM radiation in the visible range, Fig. 11.10 (a). This implies that passing the light emitted by a tungsten lamp through a sample is equivalent of passing all these radiations simultaneously through the sample.

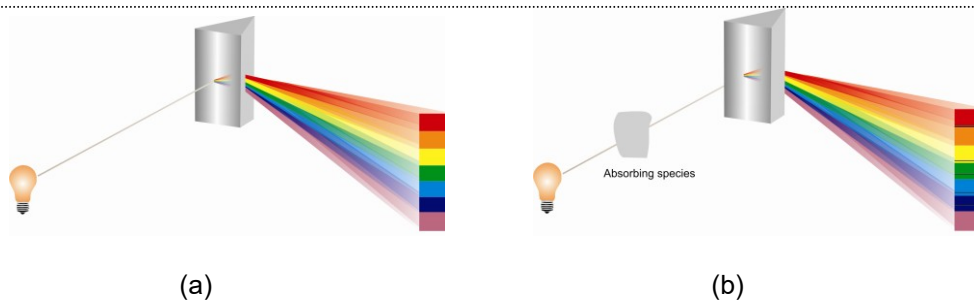


Fig. 11.10: (a) Dispersion of a polychromatic radiation through a prism to give a continuous spectrum (b): Schematic representation of the set up for getting an absorption spectrum.

When such a radiation is passed through a sample containing gaseous atoms in ground state before being dispersed as in Fig. 11.10 (b), and certain frequencies are found to be missing. These are said to be absorbed by the sample and the spectrum so obtained is called an **atomic absorption spectrum**.

You have learnt above that absorption of radiation in the UV-VIS region of spectrum causes transitions amongst the electronic energy levels. Since the difference in the electronic energy levels is unique for each species, knowledge of the wavelengths absorbed by a given species may provide information about the species being studied. Let us consider the simple case of absorption by gaseous sodium atom. It exhibits two sharp absorption peaks in the yellow region of visible spectrum (589 nm and 589.6 nm) as shown in Fig. 11.11 (a), consequent on excitation of 3s electron to two of the 3p states.

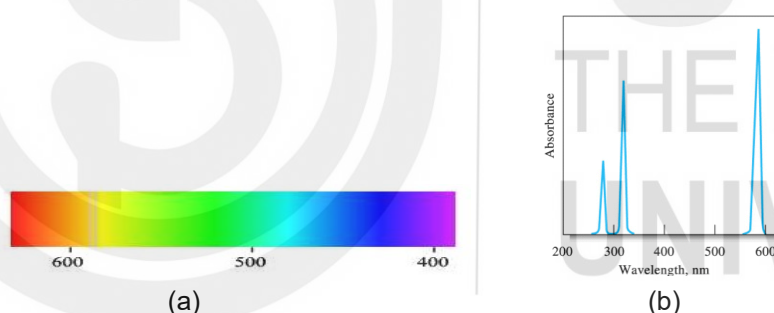


Fig. 11.11: Absorption spectrum of sodium vapours (a) in the visible range (b) in UV-VIS region.

On the other hand, absorption by gaseous sodium atoms in the UV region results in signals at 330 nm and 285 nm due to the excitation of 3s electron to 4p and 5p orbital respectively. Thus, you may note that the absorption characteristics of a given species are described in terms of the **absorption spectrum**, which is a plot of the extent of absorption by the species as a function of wavelength or frequency or wave number of the radiation absorbed. The nature of spectrum obtained depends on the nature of the absorbing species.

Thus, when atoms in the gaseous state absorb ultraviolet or visible radiation, they result in a spectrum consisting of several very sharp absorption lines, characteristic of the atomic species. Such a spectrum is called a **line spectrum**. Atomic absorption spectra of alkali and alkaline earth metals are quite simple. On the other hand, the transition elements give rise to many lines, yet each element has its own characteristic absorption lines and is

The atomic absorption spectrum is composed of a series of sharp and well defined lines characteristic of each element.

useful for qualitative and quantitative studies. You would learn about atomic absorption spectroscopy in detail in Unit 14 of this course.

Now a question comes up is that what kind of spectrum is observed when the excited atomic species relax? If we pass the radiation emitted from an excited atomic sample through a prism, we will observe a spectrum containing a number of lines, Fig. 11.12.

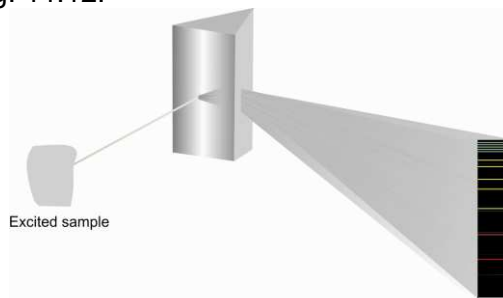


Fig. 11.12: A schematic emission spectrum.

The line spectrum is a result of relaxation of atoms or ions and generally consists of a series of well-defined lines characteristic of the species involved. You may be wondering that the atomic absorption and emission spectra both are line spectra then how do we differentiate between them? You may note that as shown in Fig. 11.11(a) in case of the atomic absorption all the radiation of the source (minus the absorbed ones) are observed. On the other hand, in case of atomic emission only the emitted radiations are observed.

As regards the third mode of interaction, viz., scattering you may recall that scattering is observed when the wavelength of the radiation is comparable to the species with which it interacts. The radiation having wavelengths comparable to the atomic sizes falls in the x-ray region of the EM spectrum and these do get scattered. However, this kind of scattering of x-rays gives rise to the phenomenon of Small Angle X-Ray Scattering (SARS) and x-ray diffraction and is beyond the scope of this course.

11.4.2 Molecular Spectra

You would recall from above that in case of molecular species the electronic, vibrational as well as rotational energies are quantised. In such a case, again as discussed above, the type of transition would depend on the type of EM radiation interacting with a molecular sample. Let us see what kind of spectra do we get in such cases?

In case of the interaction of microwave radiation with simple molecules we get rotational spectrum as the energy of the radiation is barely sufficient to cause transitions amongst rotational energy levels. The vibrational or electronic energy levels are not perturbed. A schematic rotational spectrum of a simple diatomic molecule is given in Fig. 11.13. It consists of a series of equally spaced lines.

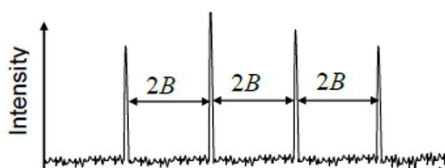


Fig. 11.13: A schematic representation of rotational spectrum of a diatomic molecule.

In case of the interaction of radiation in the Infra-red region, that can cause transitions amongst the vibrational energy levels the spectrum is quite complicated. In this case the rotational transitions accompany the vibrational transitions.

Besides, this, the selection rule and the possibilities of combination and difference bands etc., are also responsible for the complexity of the IR spectrum. You would learn in detail about the IR spectroscopy in Unit 13 of this course. For now, a sample IR spectrum is given in Fig. 11.14. It is an absorption spectrum though on the y-axis, % transmittance is plotted as an indication of intensity. A higher percentage of transmittance indicates lower absorption and vice-versa.

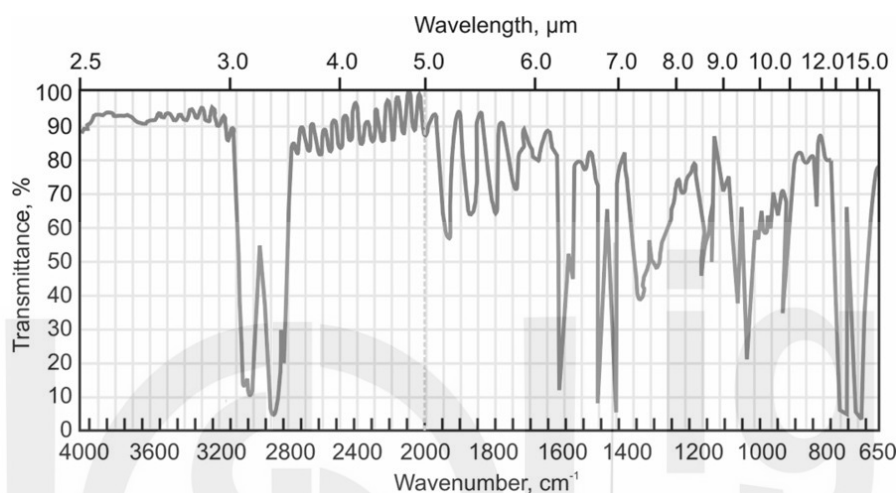


Fig. 11.14: A sample IR spectrum showing the complexity.

Moving further, the absorption of EM radiation in the UV-VIS region by the molecular species causes transitions amongst the electronic energy levels. As stated above, these transitions are accompanied by the vibrational as well as rotational transitions also. The nature of spectrum depends on the state of the sample e.g., whether the absorbing species is in the gaseous phase or in solution. Representative UV spectra in vapour phase and in solution are given in Fig. 11.15. You can note the vibrational fine structure in the electronic spectrum in vapour phase.

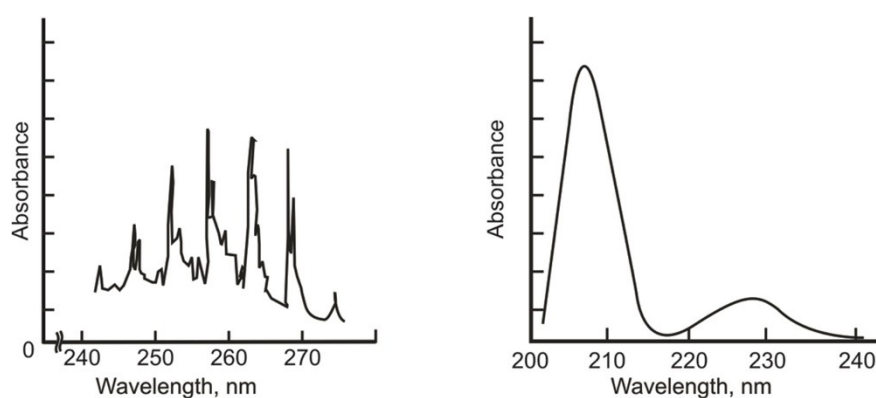


Fig. 11.15: Representative UV spectra (a) in vapour phase and (b) in solution phase.

Sometimes the sample does not absorb radiation of a given type under ordinary conditions but on placing the sample in a magnetic field it does. This

phenomenon is of immense analytical applications and is the origin of probably the most exploited molecular structure determination technique i.e., **nuclear magnetic resonance (NMR)**. Another important technique of **electron spin resonance (ESR)** also needs magnetic field. Let us learn about the magnetic field induced absorption.

The elementary particles such as electrons and nucleons are associated with magnetic properties. When subjected to external strong magnetic field, the interactions between the internal and external magnetic fields give rise to additional quantised energy levels. The difference in the energies of these levels is small and transitions amongst these energy levels are brought about by absorption of the radiation of longer wavelength ranges. The transitions amongst the energy levels generated due to the interaction of the nuclear magnetic moment with the applied magnetic field are studied using radio-waves in the range of 30 to 500 MHz and give rise to **Nuclear Magnetic Resonance (NMR) spectroscopy**. The energy separation of the levels created by interaction between the electron magnetic moment with the applied external field is even smaller. These are studied under **Electron Spin Resonance (ESR) Spectroscopy** by using microwaves of a frequency of about 9500 MHz. Representative NMR and ESR spectra are given in Fig. 11.16.

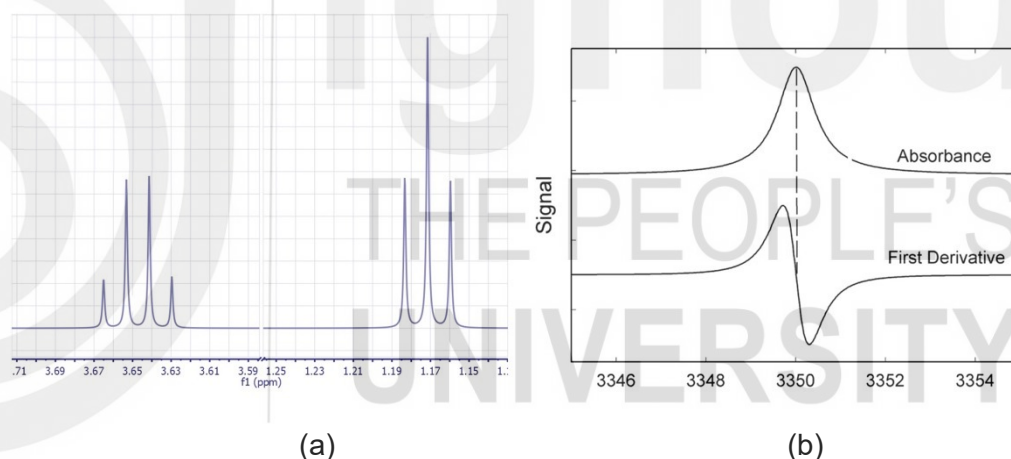


Fig. 11.16: Representative (a) NMR and (b) ESR spectra.

As regards the emission spectra of excited molecular systems, you have learnt above that the molecules generally undergo non radiative relaxations before emitting radiation. In such cases we get fluorescence spectrum, a representative spectrum is given in Fig. 11.17.

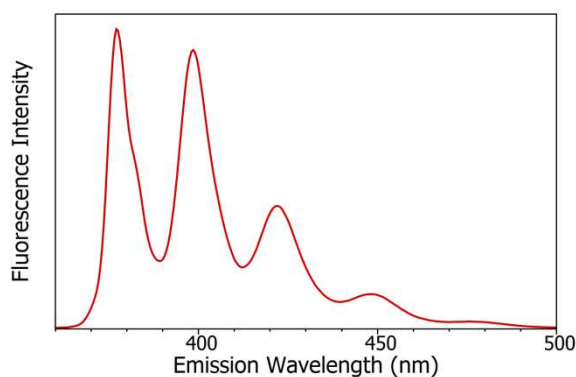


Fig. 11.17: Representative fluorescence spectrum showing different bands

Typically, the fluorescence emission is observed at a wavelength greater than that used for excitation. This is so because part of the absorbed energy is lost as heat during non-radiative relaxation.

In case of molecules, scattering as a mode of interaction is possible and is observed in certain cases. The spectra in such a case consists of a large signal (Rayleigh line) corresponding to the frequency of the incident radiation that has undergone elastic scattering. In addition, the spectrum has a series of signals on either side of Rayleigh line. These are the consequence of inelastic scattering where there has been an energy exchange between the radiation and molecule. The location of these signals is determined by the vibrational and / or rotational energies of the molecules. A representative Raman spectrum is given in Fig. 11.18.

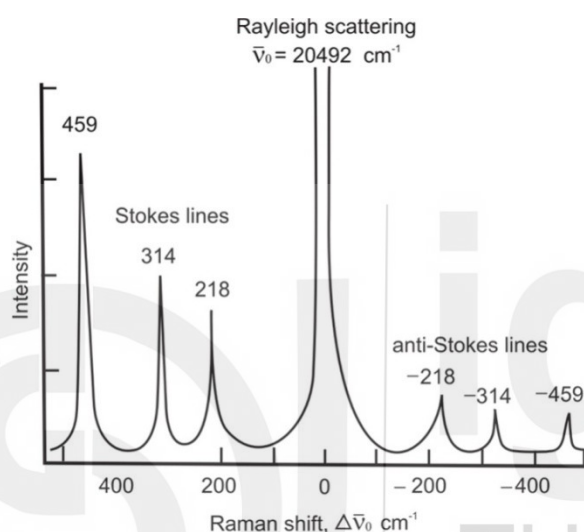


Fig. 11.18: Raman spectrum for CCl_4 using 488 nm laser source showing the Rayleigh line and the Raman (Stokes and anti-Stokes lines).

11.4.3 Line Spectra versus Band Spectra

You may have observed that the atomic spectra (absorption as well as emission) consist of discrete lines whereas the molecular spectra consist of several groups of lines that are closely spaced and not resolved. The atomic spectra are called **line spectra** whereas molecular spectra are called **band spectra**. Now the question comes up is that why atomic spectra are line spectra whereas the molecular spectra are band spectra? Let us try to understand.

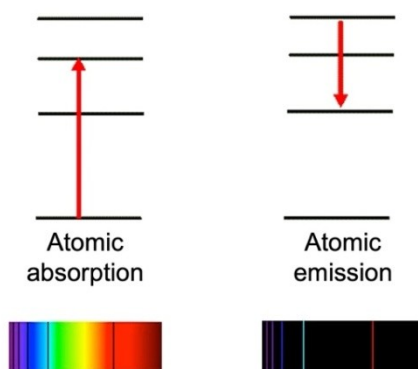


Fig. 11.19: Schematic representation of transitions amongst the atomic energy levels giving rise to line spectrum.

You would recall from above that in case of atoms only the electronic energy is quantised, i.e., there are discrete energy levels in the atom outside the nucleus. When absorption of radiation takes place the electron present in the lower energy level is excited to a higher energy level by absorbing a photon of energy equal to the difference in the energies of the two levels. As the energies of these levels are discrete the photons of specific energies only are absorbed giving rise to discrete lines in the spectrum, Fig. 11.19.

On the other hand, the absorption by molecules is more complex than by atoms, as there are many energy states possible in case of molecules. You would recall that in case of molecules the vibrational and rotational energies are also quantised in addition to the electronic energies. A molecular energy level in fact has three components and its energy can be given by the following expression.

$$E = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}} \quad \dots(11.9)$$

Since each electronic energy level is associated with several vibrational levels and each of the vibrational level is associated with several of the rotational energy levels (please see Fig. 11.3 again), the transitions caused by UV-VIS radiation have associated vibrational and rotational transitions. The electronic transition from a given vibrational energy level (say v_0) of the ground electronic energy level to the excited electronic energy level may take the molecule into any of its vibrational energy levels as shown in Fig. 11.20 (a). Similarly, for the transitions occurring from vibrational energy level v_1 of the ground electronic energy level to the excited electronic energy level also. In all these transitions, the difference in the energies of electronic energy levels is same but the difference in the energies of the vibrational levels is different.

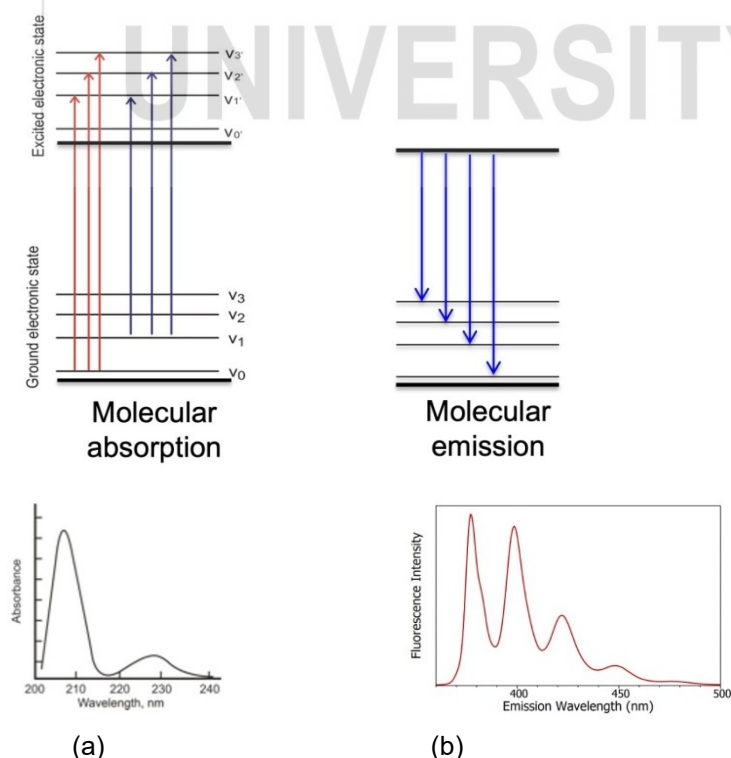


Fig. 11.20: Schematic representation of transitions amongst the molecular energy levels giving rise to (a) absorption and (b) emission band spectrum.

This implies that the molecule will absorb several radiations whose wavelengths are very close. Therefore, we get a band spectrum. In the same way we can explain the spectra observed in the infra-red spectrum. Here, the transitions caused by radiations in the IR region have an associated rotational component. Similarly, we can explain the band nature of molecular emission spectrum also. In such a case during radiative relaxation, the molecule will emit several radiations whose wavelengths are very close, and we get a band spectrum, Fig. 11.20 (b).

Let us sum up what have we learnt in this unit. However, before that answer the following simple question to assess your understanding.

SAQ 4

What is the difference between elastic scattering and inelastic scattering?

11.5 SUMMARY

In the first unit of this block on 'spectroscopic methods of analysis', we began with a discussion on the nature of electromagnetic radiation. In this context we talked about the wave and particle models of EM radiation. The wave description of EM radiation visualises an electromagnetic wave as oscillatory electric and magnetic fields travelling in the planes perpendicular to each other and to the direction of propagation. It is characterised by several parameters like, amplitude, wavelength, frequency, wavenumber, velocity, energy etc. On the other hand, according to the quantum or particle model, the radiant energy is considered as stream of discrete particles or packets of energy called as quanta, whose energy is proportional to its frequency.

Having discussed the nature and characteristics of EM radiation we moved on to discuss about the modes of interaction of radiation and matter. To facilitate the discussion, we recapitulated the quantum mechanical description of atoms and molecules. The atomic electronic energies are quantised whereas in case of molecules the electronic, vibrational, and rotational energies are quantised. We discussed about the transitions involved during absorption, emission and scattering of radiation by atoms and molecules.

Discussion on the modes of interaction of radiation and matter led us to the discussion on the nature of spectra obtained in case of atomic and molecular systems. Herein we discussed the nature of spectra obtained in different cases. Towards the end of the unit we explained the origin of line spectra and band spectra.

11.6 TERMINAL QUESTIONS

1. Name the phenomena which could not be explained by wave model of EM radiation.
2. What is an electromagnetic radiation? List any three characteristics of electromagnetic radiation.

3. An EM radiation has a wavelength of 3500 Å. Express it in terms of micrometers and nanometers.
4. Calculate the frequency and wave number for the EM radiation having a wavelength of 10 m.
5. Compute and compare the energies of the photon corresponding to the FM radio frequencies of your region.
6. Atomic spectrum consists of sharp lines whereas molecular spectrum contains broad bands. Explain.
7. Name the type of transitions involved in the UV-Visible, IR, and Microwave spectroscopic techniques?

11.7 ANSWERS

Self-Assessment Questions

1. The electromagnetic radiations do not need a medium for transmission; these can transmit through vacuum. However, for sound waves a medium is necessary for transmission.

2. We know that $E = h\nu = \frac{hc}{\lambda}$

$$h = 6.626 \times 10^{-34} \text{ J s}$$

$$c = 3.0 \times 10^8 \text{ m s}^{-1}$$

$$\lambda = 535 \times 10^{-9} \text{ m}$$

Substituting the values, we get

$$E = \frac{6.626 \times 10^{-34} \text{ J s} \times 3.0 \times 10^8 \text{ m s}^{-1}}{5.35 \times 10^{-7} \text{ m}} = 3.72 \times 10^{-19} \text{ J}$$

3. An atom or molecule can be excited by any of the following ways:
 - Absorption of radiation
 - Bombardment with electrons or other elementary particles
 - Exposure to high potential alternating current
 - By using spark, arc, or a flame
4. Elastic scattering refers to the scattering of radiation without any exchange of energy with matter. The scattered radiation has same frequency as that of the incident radiation. On the other hand, in case of inelastic scattering there is an exchange of energy and the scattered radiation has a frequency greater than or less than that of the incident radiation.

Terminal Questions

1. The wave model of electromagnetic radiations could not explain the phenomenon of black body radiation and photoelectric effect.

2. Electromagnetic radiation is a kind of energy which is transmitted through space in the form of electric and magnetic fields. It travels with the speed of light and does not need any medium to travel. The different characteristics of electromagnetic radiation are

- Amplitude
- Wavelength
- Frequency
- Wave number
- Velocity

3. We know that $1\text{Å} = 1 \times 10^{-10}\text{ m}$

So, $3500\text{ Å} = 3500 \times 10^{-10}\text{ m}$

We can write it as $= 0.35 \times 10^4 \times 10^{-10}\text{ m} = 0.35 \times 10^{-6}\text{ m} = 0.35\text{ }\mu\text{m}$

Similarly, we can write

$$3500\text{ Å} = 350 \times 10 \times 10^{-10}\text{ m} = 350 \times 10^{-9}\text{ m} = 350\text{ nm}$$

4. We know that $\nu = \frac{c}{\lambda}$ and $c = 3.0 \times 10^8\text{ ms}^{-1}$

We are given wavelength $= 10\text{ m}$

Substituting the values, we get

$$\nu = \frac{3.0 \times 10^8\text{ m s}^{-1}}{10\text{ m}} = 3.0 \times 10^7\text{ s}^{-1} = 3.0 \times 10^7\text{ Hz}$$

Further, as wavenumber and wavelength are related as, $\bar{\nu} = \frac{1}{\lambda}$

Substituting the values of the wavelength we get, wavenumber

$$\bar{\nu} = \frac{1}{10\text{ m}} = 0.1\text{ m}^{-1}$$

5. Energy and frequency are related as $E = h\nu$

The frequencies of the FM radio stations range from about 90 to 108 MHz; let us take the frequencies of two FM stations as ν_1 and ν_2 MHz, respectively

The energies of the photons corresponding to the radio frequencies of the two stations would be $h\nu_1$ and $h\nu_2$ respectively and can be calculated by substituting the values of h and the frequency.

The ratios of the energies can be calculated as $\frac{E_2}{E_1} = \frac{h\nu_2}{h\nu_1} = \frac{\nu_2}{\nu_1}$

You may substitute the values corresponding to the FM radio frequencies of your region and compute the ratio.

6. In case of atomic spectrum, the transitions occur from one electronic energy level to the other and result in sharp lines or line spectra. On the other hand, in case of molecules the vibration and rotation energies are also quantised, and each electronic energy level is associated with several vibrational levels and each of the vibrational level is associated with several of the rotational energy levels.

Thus, the electronic transitions in the molecules have associated vibrational and rotational transitions and radiations over a range of wavelengths are absorbed (or emitted). Therefore, the molecular absorption spectra have broad bands.

7. UV-Visible : electronic
IR : vibrational
Microwave : rotational



UNIT 12

UV-VIS SPECTROMETRY

Structure

12.1 Introduction	Monochromators
Expected Learning Outcomes	Sample Handling
12.2 Origin and Characteristics of UV-VIS Spectrum	Detectors
Origin of UV-VIS spectrum	Signal Processing and Output Devices
Characteristics of UV-VIS Spectrum	12.5 Types of UV-Visible Spectrometers
Absorbing Species	Single Beam Spectrometers
12.3 Principle of UV-VIS Spectrometry	Double Beam Spectrometers
Lambert's Law	12.6 Analytical Applications of UV-Visible Spectrometry
Beer's Law	Qualitative Applications
Deviations from Beer-Lambert's Law	Quantitative Applications
12.4 Instrumentation for UV-VIS Spectrometry	12.7 Summary
Radiation Sources	12.8 Terminal Questions
Wavelength Selectors	12.9 Answers

12.1 INTRODUCTION

In the previous unit you have learnt about the electromagnetic radiation in terms of its nature, characteristics, and properties. You have also learnt that the interaction of radiation with matter brings about transitions among some of the quantised energy levels of the matter and study of such an interaction is called spectroscopy. Further, the interaction of radiation with matter may take place in terms of its absorption, emission or scattering. In this unit you would learn about the ultraviolet-visible (UV-VIS) spectrometry. This concerns the measurement of the consequences of interaction of EM radiations in the UV and/or visible region with the absorbing species like, atoms, molecules, or ions.

We will begin the unit by explaining the origin and characteristic features of the UV-VIS spectrum. Herein we would also take up different types of species that absorb UV-VIS radiation and the transitions taking place in them. Then we will discuss the fundamental principles that form the basis of the analytical applications of UV-VIS spectrometry. Herein we would take up Beer Lambert's law and outline its importance. We would also discuss about the methodology of quantitative analysis using UV-VIS spectrometry. It will be followed by an account of the essential components of a UV-VIS spectrometer and their functions. Thereafter, we will discuss the qualitative and quantitative applications of UV-VIS spectrometry in diverse areas.

In the next unit you will learn about the study of infrared spectrometry which concerns the interaction of electromagnetic radiation in the infrared region with matter.

Expected Learning Outcomes

After studying about and performing this experiment, you should be able to

- ❖ explain the origin and the characteristics of UV-VIS spectrum;
- ❖ outline different types of species absorbing in the UV-VIS region;
- ❖ explain the Lambert's and Beer's laws;
- ❖ list the factors leading to deviation from Beer-Lambert's law;
- ❖ describe the essential components of UV-VIS instruments and state their role;
- ❖ explain the principles of different types of UV-VIS instruments;
- ❖ elaborate the methodology of quantitative applications of UV-VIS spectrometry; and
- ❖ state different applications of UV-VIS spectrometry.

12.2 ORIGIN AND CHARACTERISTICS OF UV-VIS SPECTRUM

UV-VIS spectrum results from the interaction of electromagnetic radiation in the UV-VIS region with molecules, ions, or complexes. It forms the basis of analysis of different substances such as, inorganic, organic and biochemicals. These determinations find applications in research, industry, clinical laboratories and in the chemical analysis of environmental samples. It is therefore important to learn about the origin of the UV-VIS spectrum and its characteristics. Let us try to understand the origin of the UV-VIS spectrum.

12.2.1 Origin of UV-VIS Spectrum

In the previous unit you have learnt that the absorption of EM radiation by a species causes the transitions amongst the electronic energy levels, and these are accompanied by vibrational and rotational excitations also. This results into a spectrum that consists of several closely spaced lines (Fig 12.1(a)),

constituting what is called a **band spectrum**. However, in the solution phase, the absorbing species are surrounded by solvent molecules and undergo constant collisions with them. These collisions and the interactions among the absorbing species and the solvent molecules cause the energies of the quantum states to spread out. Therefore, the sample absorbs photons spread over a range of wavelength. Thereby, the spectrum acquires the shape of a smooth and continuous absorption band in the solution phase. A typical UV-VIS spectrum in the solution phase is depicted in Fig. 12.1 (b).

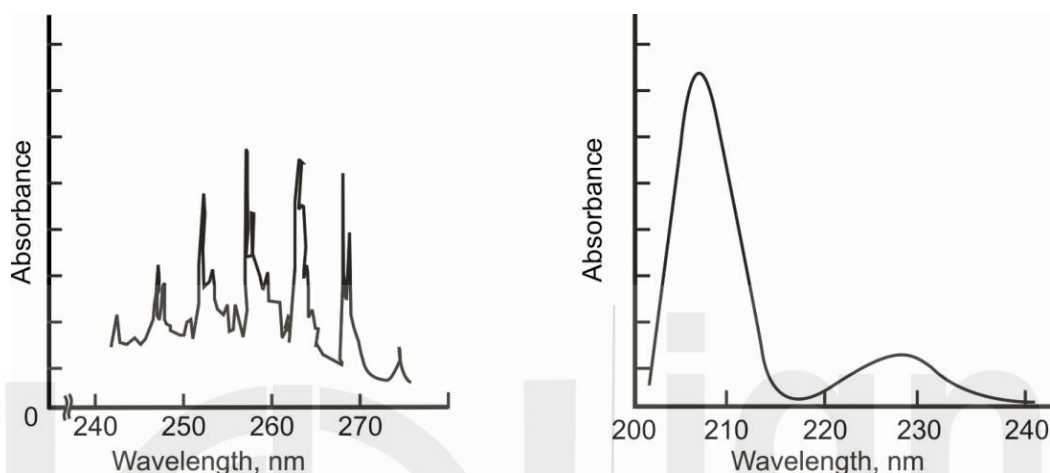


Fig. 12.1: Representative UV spectrum: a) in vapour phase and b) in solution phase.

12.2.2 Characteristics of UV-VIS Spectrum

To obtain a UV-VIS spectrum the sample is irradiated with the electromagnetic radiation varied over a range of wavelength. A monochromatic radiation i.e., a radiation of a single wavelength is employed at a time. This process is called **scanning**. The amount of the radiation absorbed at each wavelength is measured and plotted against the wavelength to obtain the spectrum. Thus, a typical UV spectrum is a plot of wavelength or frequency versus the intensity of absorption. Have a look at Fig. 12.1 (b) again. The abscissa (x-axis) indicates the wavelengths absorbed and therefore, is marked in wavelength though sometimes frequency may also be used. The ordinate (y-axis) on the other hand represents the intensity of absorption and is generally represented in terms of absorbance (explained later). The UV spectra of substances are characterised by three parameters, namely, the **position** of the maximum of the absorption band called λ_{max} , the **intensity** of the bands and the **width** of the band. The λ_{max} refers to the wavelength of the most absorbed radiation and is a measure of the difference in the electronic energy levels involved in the transition. The intensity is indicative of the **probability of the transition** i.e., whether the transition is allowed or not and if yes, to what extent?. It is also a measure of the concentration of the absorbing species. The relationship between the intensity of absorption and the concentration is explained later. The width of the spectral band depends partly on the instrumental factors and partly on the intrinsic nature of the absorbing species. Let us learn about different types of species that absorb UV-VIS radiation.

12.2.3 Absorbing Species

As discussed above, the UV-VIS spectra arise due to electronic transitions in the absorbing species. The electronic transitions do not occur in all the species when a radiation in UV region is passed through the sample. Let us learn about the species in which these transitions are observed and the nature of the transitions involved.

Organic Molecules

You would recall from your earlier knowledge of bonding in organic molecules that the constituent atoms in organic molecules are bonded through σ and π bonds. In addition, these may have nonbonding electrons on the atoms like, N, O, S, and halogens etc. There are several transitions possible involving the bonding and the nonbonding electrons. The generalised molecular orbital energy level diagram and possible transitions for organic molecules is given in Fig. 12.2.

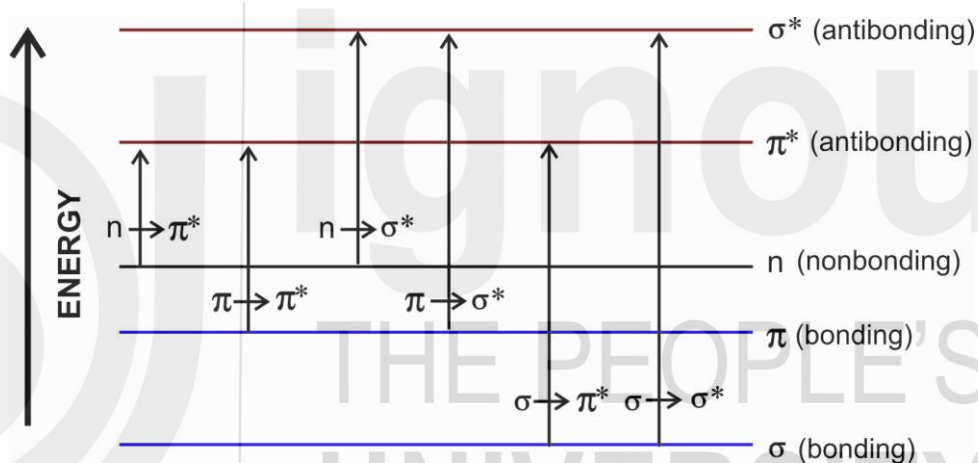


Fig. 12.2: Generalised molecular orbital energy level diagram for organic molecules and possible transitions amongst them.

As a rule, the transitions occur from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) in a molecule. In most of the organic molecules, the bonding and sometimes the nonbonding orbitals also are filled, and the antibonding orbitals are empty. Of the six possible transitions indicated in the figure, only the two of the lowest energy ones ($n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$) can be achieved by the energies available in the 200 to 800 nm region.

Thus, only those molecules are likely to absorb radiation in the 200 to 800 nm region which contain π -electrons and may also have atoms with non-bonding electrons. Such groups of atoms in a molecule, that absorb radiation in the UV-VIS region are referred to as **chromophores**. Chromophore in Greek means, "colour bearing". However, the term chromophore is now not limited to colours only but is used in a general way for groups which are responsible for causing an absorption of electromagnetic radiation between about 175 to 800 nm. A list of some simple chromophoric groups and the type of transitions occurring in them is given in Table 12.1.

Table 2.1: Absorption characteristics of some common chromophoric groups

Chromophore	Example	$\lambda_{\max}$	Type of Transition
$>C = C<$	$C_6H_{13}CH = CH_2$	177	$\pi \rightarrow \pi^*$
$-C \equiv C-$	$C_5H_{11}C \equiv C - CH_3$	178	$\pi \rightarrow \pi^*$
$>C = O$	CH_3COCH_3	186	$n \rightarrow \sigma^*$
	CH_3CHO	280	$n \rightarrow \pi^*$
$-COOH$	CH_3COOH	180	$n \rightarrow \sigma^*$
		293	$n \rightarrow \pi^*$
$-CONH_2$	CH_3CONH_2	204	$n \rightarrow \pi^*$
$-N = N-$	$CH_3N=NCH_3$	214	$n \rightarrow \pi^*$
$-NO_2$	CH_3NO_2	339	$n \rightarrow \pi^*$
$-N = O$	C_4H_9NO	280	$n \rightarrow \pi^*$
		300	-
		665	$n \rightarrow \pi^*$

Inorganic Species

Many inorganic salts containing atoms with electrons in *d*-orbitals give weak absorption bands in the visible range. The ions and the complexes of the elements of the first two transition series belong to this group and are coloured. The colour of these species is due to transitions amongst *d*-orbitals. The complex formation of these ions with solvent molecules or with other ligands lifts the degeneracy of the five *d* orbitals. Therefore, these split into groups having different energies. The electronic transitions from the lower energy *d* orbitals to higher energy *d* orbitals are responsible for the observed colour. These transitions are called ***d-d* transitions**. The blue colour of the aqueous solutions of copper sulphate and the violet colour of potassium permanganate are some of the examples. The ions of the lanthanides and actinides are also coloured, however, these involve ***f-f* transitions**.

Charge Transfer Complexes

Many a times a given compound that is transparent in the UV region starts absorbing after interacting with another species. This happens if the species has an electron **donor** group and the interacting species has an electron **acceptor** group. When the two species bind to each other, the resulting species is intensely coloured. This is due to the formation of a complex between the two species. Such a complex is called **charge transfer complex**. For example, the blood red color of the complex ion, thiocyanatoiron(III) ion, $Fe(SCN)^{2+}$ is due to the formation of a charge transfer complex. The radiation absorbed by this product or complex causes the transfer of an electron from an orbital on the donor to an orbital of the acceptor.

Having learnt about origin and characteristics of UV-VIS spectrum and the species that absorb radiation in the UV-VIS region, let us now learn about the principle of spectrometric determinations. However, before that why don't you assess your understanding by answering the following simple question?

SAQ 1

List different types of species that may absorb in the UV-VIS region of the spectrum and indicate the type of transitions involved in them.

The transmitted radiation has information about the nature and the amount of the absorbing species.

12.3 PRINCIPLE OF UV-VIS SPECTROMETRY

In a typical absorption spectral measurement, a monochromatic radiation is made to fall on a sample taken in suitable container called **cuvette**. In such a situation a part of the radiation is reflected, a part is absorbed, and a part is transmitted. The intensity of original radiation, P_o is equal to the sum of the intensities of reflected (P_r), absorbed (P_a) and transmitted (P_t) radiation.

$$P_o = P_r + P_a + P_t \quad \dots (12.1)$$

The effect of reflection can be compensated by passing equal intensities of beams through the solution and through the solvent contained in the same or similar container and comparing the transmitted radiations. We can then write the above equation as follows:

$$P_o = P_a + P_t \quad \dots (12.2)$$

The intensity of the transmitted light is measured and is found to depend on the thickness of the absorbing medium and the concentration, besides the intensity of the incident radiation. This dependence forms the basis of spectrometric determinations and is given in terms of two fundamental laws. Let us discuss these laws one by one.

2.3.1 Lambert's Law

Lambert (1760) and Bouguer independently studied the decrease in the intensity of radiation when it passes through a substance and made the following observations:

- i) The amount of monochromatic radiation absorbed by a substance is proportional to the intensity of the incident radiation i.e., the ratio of the intensity of the transmitted and incident radiation is constant.
- ii) The intensity of the transmitted radiation decreases exponentially when the thickness of the substance, through which the radiation is passing, increases linearly.

These observations, called Lambert's law can be translated into a mathematical expression as described below.

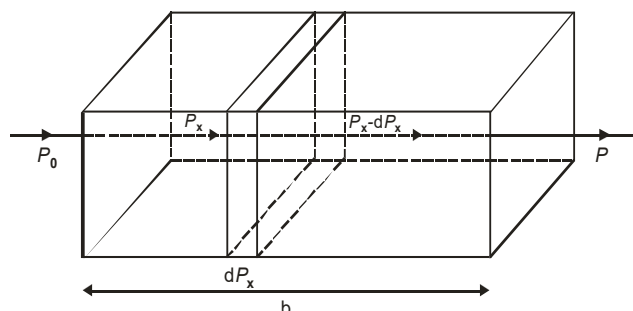


Fig. 12.3: Illustration for establishing the Lambert's Law.

In Fig.12.3, if P_o represents the radiant power of incident radiation and P represents the radiant power of transmitted radiation after passing through a slab of thickness b . If we consider a small slab of thickness dx within this slab, then the change in radiant power (dP_x), is proportional to the radiant power of incident radiation (P_x) multiplied by the change in thickness (dx) of the slab through which the radiation is passed. That is,

$$dP_x \propto P_x dx$$

$$\text{or } dP_x = -kP_x dx \quad \dots(12.3)$$

where k is the proportionality constant, and the negative sign indicates that radiant power of radiation decreases with absorption. Eq. 12.3 can be rearranged to Eq. 12.4.

$$\frac{dP_x}{P_x} = -k dx \quad \dots(12.4)$$

Integrating Eq. 12.4 within the limits of P_o to P for intensity and 0 to b for the thickness we get,

$$\int_{P_o}^P \frac{dP_x}{P_x} = -k \int_0^b dx \quad \dots (12.5)$$

$$\ln \frac{P}{P_o} = -kb \quad \dots (12.6)$$

Eq. 12.6 is the mathematical expression for Bouguer-Lambert law or Lambert's law. Changing this equation to logarithms to base 10 and rearranging we get,

$$\log \frac{P_o}{P} = \frac{k}{2.303} b = k' b \quad \dots (12.7)$$

Note that the ratio P/P_o has been inverted to remove the negative sign. Lambert's law applies to any homogeneous non-scattering medium, regardless of whether it is gas, liquid, solid, or solution.

12.2.2 Beer's Law

In 1852, Beer and Bernard independently studied the dependence of intensity of transmitted radiation on the concentration of the solution. It was found that the relation between intensity of the transmitted radiation and concentration was the like that found by Lambert for the intensity of the transmitted radiation and the thickness of the absorbing medium. Mathematically, the Beer's observations can be expressed as follows.

Consider a monochromatic radiation of intensity P_x passing through any thickness of solution of a single absorbing substance of concentration c . If c is changed by a small amount dc , to $c + dc$, the change in transmitted power dP_x is proportional to the incident intensity P_x and dc . We can express it as follows.

$$\begin{aligned} dP_x &\propto P_x dc \\ dP_x &= -k'' P_x dc \end{aligned} \quad \dots(12.8)$$

where k'' is the proportionality constant and the negative sign indicates that radiant power decreases with absorption. This equation can be rearranged to:

$$\frac{dP_x}{P_x} = -k'' dc \quad \dots(12.9)$$

On integration within the limits of P_0 to P for intensity and 0 to c for concentration we get,

$$\int_{P_0}^P \frac{dP_x}{P_x} = -k'' \int_0^c dc \quad \dots (12.10)$$

$$\text{or} \quad \ln \frac{P}{P_0} = -k'' c \quad \dots (12.11)$$

$$\text{or} \quad \log_{10} \frac{P_0}{P} = \frac{k''}{2.303} c \quad \dots (12.12)$$

Eq. 12.12 is the mathematical expression for Beer's law. The Lambert's and Beer's laws are combined and are expressed as per Eq. 12.13.

$$\log \frac{P_0}{P} = abc \quad \dots (12.13)$$

Absorbance is defined as the logarithm of the ratio of the intensities of the incident and transmitted radiations.

In this expression, 'a' is a constant (combining two constants k' , k'' and the numerical factor) and is called **absorptivity** (earlier called extinction coefficient) whose value depends on unit of concentration used and is a function of wavelength of the monochromatic light used. The concentration is generally expressed in terms of g per dm^3 and b in cm. Therefore, it has units of $\text{cm}^{-1} \text{g}^{-1} \text{dm}^3$.

Eq. 12.16: use 'a' if concentration is expressed in g/L and path length in cm and 'ε' if the concentration is in mol dm^{-3} and b in cm.

However, if the concentration is expressed as mol dm^{-3} and b in cm then it is called **molar absorptivity** (earlier called molar extinction coefficient) and expressed as ϵ . Its units are $\text{cm}^{-1} \text{mol}^{-1} \text{dm}^3$. The modified expression for the Beer-Lambert's law becomes,

$$\log \frac{P_0}{P} = \epsilon bc \quad \dots(12.14)$$

The term $\log P_0/P$ is called **absorbance** and is represented as 'A'.

$$A = \log \frac{P_0}{P} \quad \dots (12.15)$$

The expression for Beer-Lambert's law then becomes,

$$\log \frac{P_0}{P} = A = abc \text{ or } \epsilon bc \quad \dots(12.16)$$

You may note here that though transmittance and absorbance are equivalent expressions which can be interconverted, it is the absorbance which is directly proportional to the absorbed fraction of the radiation.

The absorbance, A is related to another important term called **transmittance** which is defined as the fraction of the incident radiation transmitted by the absorbing medium. Mathematically,

$$\text{Transmittance, } T = \frac{P}{P_0} \quad \dots(12.17)$$

It is generally expressed as a percentage and is expressed as %T.

$$\%T = \frac{P}{P_0} \times 100\% \quad \dots (12.18)$$

It is related to absorbance as,

$$A = -\log T \quad \dots (12.19)$$

In typical measurements the radiant power transmitted by a solution is measured and compared with that transmitted by the solvent (also called a blank). The ratio of transmitted powers through solution and that through blank or solvent is called as transmittance. It is desirable that you get acquainted with the expressions of the Beer-Lambert's law and learn to use them. Let us take an example to illustrate the application of this law.

Example 12.1: The molar absorptivity of a substance is $2.0 \times 10^4 \text{ cm}^{-1} \text{ mol}^{-1} \text{ dm}^3$. Calculate the transmittance through a cuvette of path length 5.0 cm containing $2.0 \times 10^{-6} \text{ mol dm}^{-3}$ solution of the substance.

Solution: As per the Lambert-Beer's law,

$$\text{Absorbance, } A = \epsilon c b$$

Given:

$$\epsilon = 2.0 \times 10^4 \text{ cm}^{-1} \text{ mol}^{-1} \text{ dm}^3, c = 2.0 \times 10^{-6} \text{ mol dm}^{-3} \text{ and } b = 5.0 \text{ cm}$$

Substituting the values we get,

$$A = 2.0 \times 10^4 \times 2.0 \times 10^{-6} \times 5.0 = 0.2$$

$$\Rightarrow \log 1/T = 0.2$$

$$\therefore A = \log 1/T$$

Taking antilog on both sides, we get

$$1/T = 1.585$$

$$\therefore T = 0.63$$

As per the Beer's law discussed above, there is a direct proportionality between the absorbance and concentration. A plot of absorbance versus concentration is expected to be a straight line passing through origin. However, this is not always true; there are certain limitations. The law does not hold for all species under every condition. Many a times instead of a straight line, a curvature in the plot may be observed as shown in Fig. 12.4. The upward curvature, curve (a), is known as **positive deviation** and the downward curvature, curve (c), as **negative deviation**.

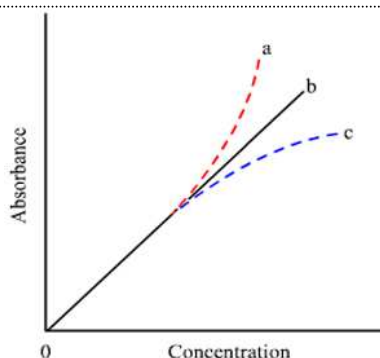


Fig. 12.4: Beer-Lambert law plots; the curvatures show deviations from the law.

Some of the factors responsible for the deviation from Beer's law are as follows.

- Presence of Electrolytes
- Hydrogen Ion Concentration
- Complexation, Association or Dissociation
- Non-monochromatic Nature of the Radiation
- Concentration of the Analyte
- Temperature

Therefore, in any quantitative determination based on Lamber-Beer's law these factors should be controlled to get dependable results. Let us now take up the instrumental aspects of UV-VIS spectrometry. However, before that answer the following simple questions to assess your understanding.

SAQ 2

In a spectrophotometer set at the $\lambda_{\max}$ of a sample the value of P_0 (with the solvent) was found to be 85.4 using cuvettes of 2.00 cm path length. The value of P for a solution of the sample having a concentration of $1 \times 10^{-4}\text{M}$ was measured in the same cuvette and was found to be 20.3. Calculate the molar absorptivity of the sample.

SAQ 3

A substance has a molar absorptivity of $14,000 \text{ cm}^{-1} \text{ mol}^{-1} \text{ dm}^3$ at the wavelength of its maximum absorption. Calculate the concentration of the substance whose solution in a cuvette of path length 1 cm has an absorbance of 0.85.

12.4 INSTRUMENTATION FOR UV-VIS SPECTROMETRY

Today a wide range of instruments are available for making molecular absorption measurements in the UV-visible range. These vary from simple and

inexpensive machines for routine work to highly sophisticated devices that can be used for specialised work and of course the routine jobs also. However, the basic components of these instruments remain the same. The five essential components of UV-VIS instruments are as follows

- A stable radiation source
- Wavelength selector
- Sample holder
- Radiation detector or transducer, and
- Signal processing and output device

The general layout of the essential components in a UV-VIS spectrometer is given in Fig. 12.5.

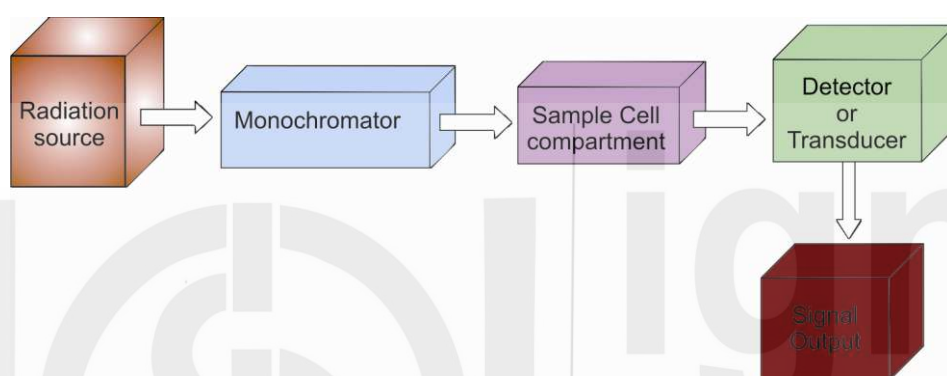


Fig. 12.5: General layout of the essential components in a UV-VIS spectrometer.

Let us learn about these components one by one.

12.4.1 Radiation Sources

A spectrophotometric radiation source must provide a stable high energy output over a broad range of wavelengths. There is no inexpensive source available that may provide stable output over the entire UV-visible range (~190 nm to ~780 nm). The radiation sources commonly used for the UV and visible range are described below.

For measurements in the UV region, electric discharge sources like hydrogen or a deuterium lamp are used. A hydrogen lamp is commonly used in the UV spectrophotometers and gives radiation in the wavelength region of 160-375 nm. The radiant power of the hydrogen lamp is low, and these are replaced by deuterium lamps, but it increases the cost of the instrument. On the other hand, for measurements in the visible range modern instruments use a tungsten filament lamp as the radiation source. This consists of a thin, coiled tungsten wire that is sealed in an evacuated glass bulb. This gives radiations in the range of 350-2200 nm.

12.4.2 Wavelength Selectors

In spectrophotometric measurements we need to use a narrow (preferably monochromatic) band of wavelengths of radiation. Less expensive instruments use a filter to isolate the radiation and provide a broad band of the

wavelengths. In many applications we need to continuously vary the wavelength over a defined range. This can be achieved by using monochromators. Most modern instruments use monochromators that employ a prism or diffraction grating as the dispersing medium.

Absorption Filters

In low-cost instruments catering to measurements in the visible range, coloured glass filters are used to cut off undesirable wavelengths. A typical filter is a coloured piece of glass, which absorbs light of certain wavelength and allows that of the other to pass through. You know that white light is made up of seven different colours; the acronym is **VIBGYOR** for violet, indigo, blue, green, yellow, orange and red. These seven colours add up to give white light back. To select a suitable filter for a measurement of absorbance of a solution, we need to recall complementary colours. The colour of the filter should be complementary to colour of the solution to be measured.

12.4.3 Monochromators

Monochromators are devices that can selectively provide radiation of a desired wavelength out of the range of wavelengths emitted by the source. These are of two types: the prism and grating monochromators. We will take up only prism monochromators here.

Prism Monochromators

You know that a prism disperses sunlight into seven different colours. This occurs due to the refraction of the light when it passes through the prism. The radiations of different colours having different wavelengths are refracted to different extent due to the difference in the refractive index of glass for different wavelengths. Shorter wavelengths are refracted more than longer wavelengths as depicted in Fig.12.6 (a).

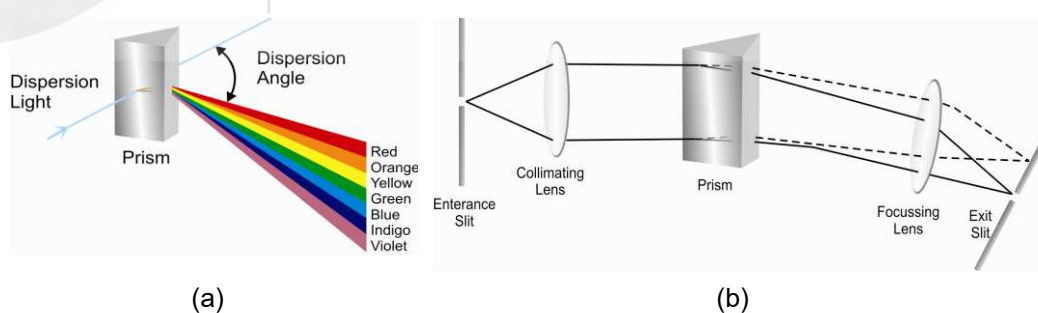


Fig. 12.6: a) Dispersion of radiation by prism b) Schematic diagram of the prism monochromator.

If a prism is rotated, radiation of different wavelengths, coming out after refracting through it, can be made to pass through an exit slit. In a **prism monochromator**, shown in Fig.12.6 (b), a fine beam of the radiation from the source is obtained by passing through an entrance slit. This is then collimated on the prism with the help of a lens. The refracted beams are then focused on an exit slit. The prism is then rotated in a predetermined way to provide the desired wavelength from the exit slit.

Sample Handling

The UV-VIS absorption spectra are usually determined either in vapour phase or in solution. To take the UV spectrum of the sample, it is taken in a cell called **cuvette** which is transparent to the wavelength of light passing through it. A variety of quartz cuvettes are available for the spectral determination in the vapour phase. These are of varying path lengths and are equipped with inlet and outlets. For measurements on solutions in the visible region the cuvettes made of glass can also be used. However, since glass absorbs the ultraviolet radiations, these cannot be used in the UV region. Therefore, most of the spectrophotometers employ quartz cuvettes (Fig 12.7), as these can be used for both visible and UV region. Usually, square cuvettes having internal path length 1.0 cm are used, though cuvettes of much smaller path lengths say of 0.1 mm or 0.05 mm are also available.

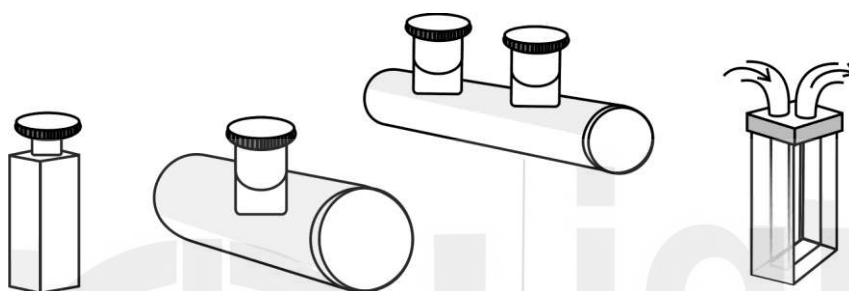


Fig. 12.7: Quartz cuvettes for measurements in solution and in vapour phase.

The sample whose spectrum is to be measured is dissolved in a solvent that is transparent in the UV region. It means that it does not absorb in this region. Hexane, 95% ethanol, methanol and 1,4 dioxane are commonly employed as solvents. Now a days 'spectral grade' solvents are available which have high purity and have negligible absorption in the region of absorption by the sample.

In a typical measurement of a UV spectrum, the solution of the sample is taken in a suitable cuvette and the spectrum is run in the desired range of the wavelengths. The absorption by the solvent, if any, is compensated by running the spectrum for the solvent alone in the same or identical cuvette and subtracting it from the spectrum of the solution. This gives the spectrum only due to the absorption species under investigation. In double beam spectrometers (discussed later), the sample and the solvent are scanned simultaneously.

12.4.4 Detectors

The detectors are used to convert a light signal to an electrical signal which can be suitably measured and transformed into an output. The detectors used in most of the UV-VIS instruments generate a signal, which is linear in transmittance i.e., they respond linearly to radiant power falling on them. The transmittance values can be changed logarithmically into absorbance units by an electrical or mechanical arrangement in the signal read out device. There are three types of detectors which are used in modern spectrophotometers. These are phototube, photomultiplier (PM) tube and diode array detector. We would describe the working of only phototube as a detector.

Phototube

A phototube consists of a photoemissive cathode and an anode in an evacuated tube with a quartz window as shown in Fig.12.8. These two electrodes are subjected to high voltage (about 100 V) difference. When a photon enters the tube and strikes the cathode, an electron is ejected and is attracted to the anode resulting in a flow of current which can be amplified and measured. The response of the photoemissive material is wavelength dependent and different phototubes are available for different regions of the spectrum.

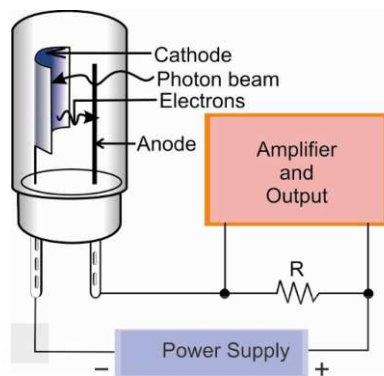


Fig.12.8: Schematic of a phototube detector.

Signal Processing and Output Devices

The electrical signal from the transducer (detector) is suitably amplified or processed before it is sent to the recorder to give an output. The subtraction of the solvent spectrum from that of the solution is done electronically. The output plot between the wavelength and the intensity of absorption is the resultant of the subtraction process and is characteristic of the absorbing species.

Having learnt about different components of UV-VIS instruments and their importance; you are now equipped to learn about the types of instruments commonly used. However, before proceeding further, answer the following simple question to assess your understanding.

SAQ 4

Why do we need to take UV spectra in quartz cuvettes?

12.5 TYPES OF UV-VISIBLE SPECTROMETERS

Having learnt the basics of the different components of UV-Visible spectrometers let us now see how these individual components are arranged in a spectrometer. Two types of spectrometers are commonly used. Let us learn about their set ups.

12.5.1 Single Beam Spectrometers

As the name suggests, these instruments use a single beam of radiation. The same beam is used for reading the absorption of the sample as well as that of

the reference (or solvent). The schematic diagram of a typical single beam UV-Visible spectrometer is given in Fig.12.9. The radiation from the source is passed through a filter or a suitable monochromator to get a band or a monochromatic radiation. It is then passed through the sample (or the reference) and the transmitted radiation is detected by the photodetector. The signal so obtained is sent as a read out or is recorded.

The instruments using filters and photoelectric detectors are called photometers.

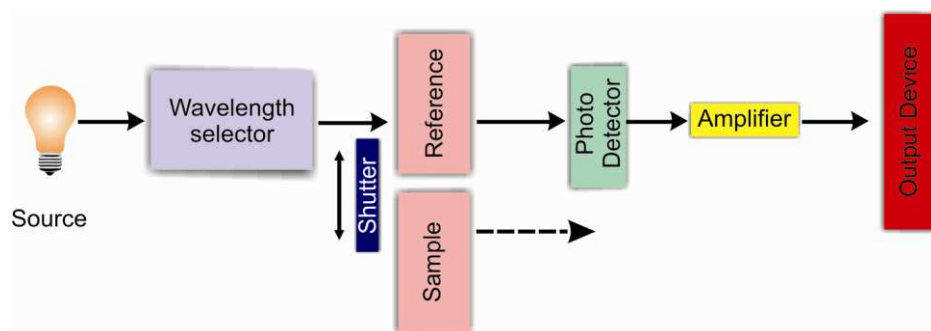


Fig.12.9: Schematic diagram for a single beam UV-VIS spectrometer.

Typically, two operations must be performed – first, the cuvette is filled with the reference solution and the absorbance reading at a given wavelength or the spectrum over the desired range is recorded. Second, the cuvette is taken out and rinsed and filled with sample solution and the process is repeated. The spectrum of the sample is obtained by subtracting the spectrum of the reference from that of the sample solution.

12.5.2 Double Beam Spectrometers

In a double beam spectrometer, the radiation coming from the monochromator is split into two beams with the help of a beam splitter. These are passed simultaneously through the reference and the sample cell. The transmitted radiations are detected by the detectors and the difference in the signal at all the wavelengths is suitably amplified and sent for the output. The general arrangement of a double beam spectrometer is shown in Fig. 12.10.

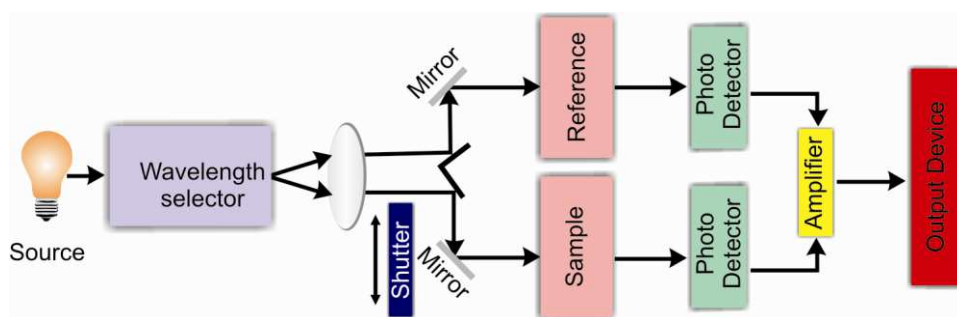


Fig.12.10: Schematic diagram for a double beam spectrometer.

It was mentioned earlier that UV-VIS spectrometry can be used for qualitative and quantitative determinations of the analyte. The quantitative determinations are based on the relationship between the absorption of radiation and concentration of the analyte. Let us learn about this relationship and other applications.

12.6 ANALYTICAL APPLICATIONS OF UV-VISIBLE SPECTROMETRY

UV-VIS spectrometry provides a technique that may be used to detect one or more components in a solution and measure the concentration of these species. The primary advantage of this technique is that even traces of substances can be determined in a simple way which is not possible with classical analytical methods like gravimetric and volumetric procedures. In addition, UV spectrometry is also used for obtaining structural information of substances; particularly the organic compounds and it may as well help in establishing the identity of a molecule. We will discuss some of qualitative and quantitative applications of UV-VIS spectrometry.

12.6.1 Qualitative Applications

In terms of qualitative analysis of the analyte, the UV-VIS spectrometry is quite useful. However, in the context of the determination of structural details of molecules it is of a secondary importance. The information obtained from it needs to be supplemented by that from other spectroscopic methods. This is because of simple and broad nature of the spectra. Nonetheless, it can still provide information about the presence or absence and the nature of the chromophore in the molecule. For example, the presence of one or more signals in the 200-400 nm region of the spectrum is a clear indication of the presence of unsaturation in the molecule. Let us take up some qualitative applications of UV-VIS spectroscopy

Identification of molecules

Though lack of fine structure in the UV-visible spectrum does not allow unambiguous identification of the molecule, yet sometimes the nature of spectrum can be quite useful in distinguishing two molecules having similar colour.

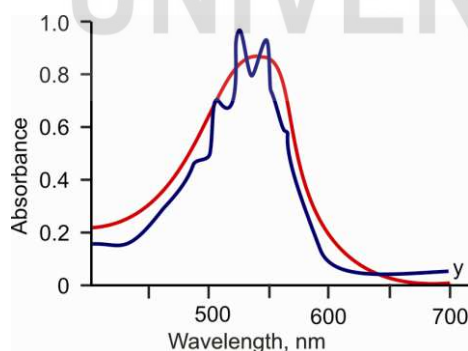


Fig. 12.11: Absorption spectra of two distinctly different compounds but with similar colour.

For example, Fig. 12.11 gives the visible spectra of two purple coloured species of distinctly different structures. One of the spectra happens to be of an azo dye and the other is of permanganate solution. The shapes of the absorption curves help in distinguishing them; the smooth curve with a single maximum is for the dye. Another way in which UV spectrum can be used for identification of molecules is by overlaying the spectra. For example, the Fig. 12.12 gives the UV spectra for the three different batches of a common drug.

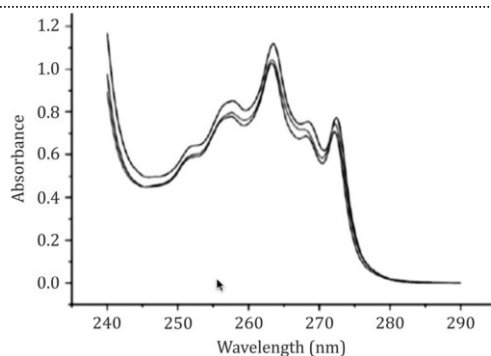


Fig. 12.12: Overlaying spectra of three different batches of a drug .

Ascertaining geometrical isomers

UV spectroscopy can be used for ascertaining the geometrical isomers of a given compound. In general, the cis isomers suffer from distortion and are forced to be non-coplanar. As a result, the cis isomer absorbs at lower wavelength region as compared to the trans counterpart. Also, the intensity of the signal in case of cis isomer is lesser. For example, the cis and trans isomers of Stilbene show λ_{max} at 283 nm ($\epsilon = 12300$) and 294 nm ($\epsilon = 25000$) respectively.



Determination of Composition of Metal Complexes Using Job's Method

Many a times, two or more species interact to form a complex which cannot be isolated as a stable compound. In such a case, the composition of the complex must be determined by indirect method. In one of these methods called **Job's method of continuous variation** a series of solutions of the metal, M and the ligand, L is prepared in which the mole-ratio of the metal ion and the ligand is varied from 0 to 1 at constant total concentration $C = C_L + C_M$. The concentration of the complex formed is determined spectrometrically. Now, if the absorbance of each of the series of solutions is plotted against the mole fraction of the ligand in them, the maximum absorbance will occur at a mole fraction corresponding to the composition of the complex. In case of 1:1 complex we would get the maxima corresponding to the mole fraction of 0.5. For 1:2, and 1:3 complexes the mole fraction corresponding to the maxima would be 0.67 and 0.75 respectively. Fig. 12.13 gives the plot for a complex of ML_3 type.

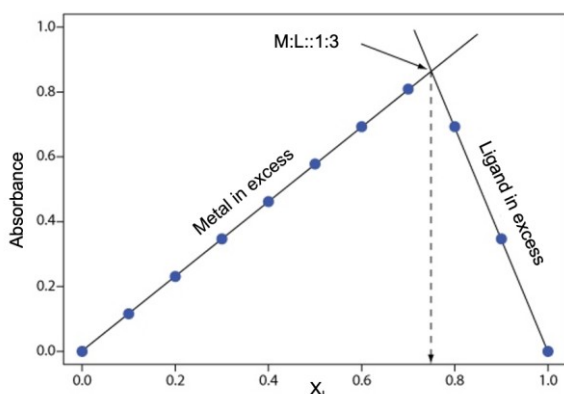


Fig. 12.13: Job's graph for a complex of ML_3 type

Keto-enol tautomerism

The direction of equilibrium in case of keto-enol tautomerism can also be established with the help of UV spectroscopy. In other words, UV spectroscopy can be used for identifying the predominant (stable) tautomer.

For example, in case of tautomeric forms of 2-hydroxy pyridine and pyridone-2, the latter is expected to absorb at higher wavelength because it is a α, β unsaturated ketone. Experimentally, the equilibrium mixture has larger component of species absorbing at higher wavelength therefore we can conclude that the equilibrium lies towards the keto form.

Quantitative Applications

UV-VISspectrometry is probably the most useful tool available for quantitative determinations in diverse areas. It is due its versatility, accuracy, and sensitivity. It can be used for direct determination of many organic, inorganic, and biochemical species accurately at low concentrations; viz., 10^{-4} to 10^{-5} or even lower. In addition to these, the convenience of conducting the determination and its reasonable selectivity make it a method of choice for quantitative determinations. Another significant feature of this technique is that it may also be used for the quantitative determination of analyte which do not absorb in the UV-VISregion. It is achieved by making them react with a reagent that gives a product which absorbs in the UV-VIS region. Let us learn about the methodology used for such determinations.

Quantitative Determination Methodology

The methodology followed for the quantitative determinations have certain essential steps. These are,

- Forming an absorbing species
- Selection of the measurement wavelength
- Controlling factors influencing absorbance
- Validation of Beer and Lambert's law

Let us briefly discuss these steps one by one.

Forming an Absorbing Species

There are only a few analytes that have a strong absorption in the UV or Visible region and can be subjected to direct determinations. However, for most of the analytes we must form an absorbing species by reacting them with a suitable reagent. In any case, the absorbance of the solution should be stable and should not change with minor variations in the pH, temperature, and the ionic strength of the solution. Further, the reagent should be selective towards the analyte and its reaction with the analyte should be quantitative i.e., 100%.

Selection of the Measurement Wavelength

In the absence of interfering substances, the measurements are made at the wavelength of the maxima ($\lambda_{\max}$) of the largest peak in the spectrum. At this wavelength the absorbance is most sensitive to the concentration. However, in

systems where the reagent, metal and products all absorb light, it may so happen that at $\lambda_{\max}$ there is not much of difference in the absorbance value for pure reagent and the metal complex. In such cases we need to identify such a wavelength at which there is large difference in the absorbance values of pure reagent and the complex.

Controlling Factors Influencing Absorbance

As stated earlier, several factors can affect the absorption spectrum of the analyte. These include solvent polarity, pH, temperature, ionic strength, and interferences from other absorbing species. It is, therefore, essential for a reliable quantitative determination that the conditions of the determination are so chosen that there is minimal effect of these factors. A detailed analysis of the effect of these factors and their control is beyond the scope of this course.

Validation of Beer and Lambert's law

Let us rewrite the expression for the Beer and Lambert's law as

$$\log P_0 / P = A = abc \text{ or } \epsilon bc$$

According to this expression, if we know the values of a (or ϵ) and b then we can determine the concentration directly from the absorbance value. However, generally the value of ϵ is not known accurately for the species being determined under the conditions of the determination. Quite often even the validity of the Beer and Lambert's law expression is questionable. Therefore, in most of the methods, a curve is obtained by measuring the absorbance values for a series of standard solutions of the analyte being determined at a fixed wavelength. These solutions should be under similar solution conditions and in the range of the concentration of the analyte. For the law to be valid, the plot of absorbance, A versus the concentration, c for the standard solutions should be a straight line passing through origin. Such a curve is known as **calibration curve** and is handy in determination of concentration of unknown solutions from a measurement of absorbance value. For example, the unknown concentration of a solution of iron can be determined by using a calibration curve obtained by plotting the absorbance values of a series of standard solutions of iron measured at 562 nm depicted in Fig. 12.14 (a).

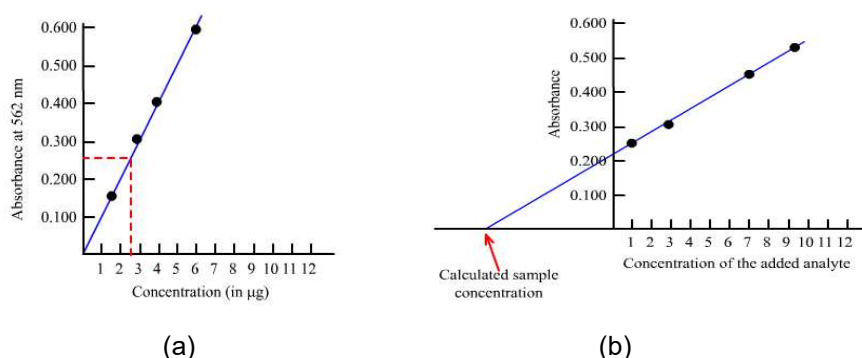


Fig.12.14: Calibration curve: a) Standard solution method (b) Standard addition method.

Sometimes, it may so happen that all the constituents in the sample may not be known; so, a standard solution with the same chemical composition as the sample being analysed cannot be prepared. In such a case, a method called **standard addition method** is used which eliminates any error arising from

molar absorptivities (ϵ) being different in the standard solution from that in the sample solution.

In this method known amounts of the standard 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. The readings so obtained are then plotted to obtain the calibration curve. If the Beer's law is obeyed, i.e., a straight line is obtained; the unknown concentration of the solution can then be obtained by the extrapolation of the calibration curve as shown in Fig. 12.14 (b).

Estimation of Metal Ions from Aqueous Solution

UV-VIS spectrophotometry can be used for direct determination of many organic, inorganic, and biochemical species accurately at low concentrations; viz., 10^{-4} to 10^{-5} M or even lower. As given above, a significant feature of UV-VIS spectrometry is that it can also be used for the quantitative determination of analyte which do not absorb in the UV-VIS region. It is achieved by making them react with a reagent that gives a product which strongly absorbs in the region. For example, in the determination of iron (II) in aqueous solutions, a tricyclic nitrogen heterocyclic compound, 1, 10-phenanthroline ($C_{12}H_8N_2$, ortho-phenanthroline or o-Phen) is used as the ligand that reacts with iron, to form strongly coloured complexes. With ferrous ions (Fe^{2+}), it reacts in a ratio of 1:3 to form an orange red coloured complex $[(C_{12}H_8N_2)_3Fe]^{2+}$ in aqueous medium as per the following equation.



The molar absorption coefficient (ϵ) of the ferrous complex, so obtained is $11,100 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at the wavelength of maximum absorbance, $\lambda_{\text{max}} = 508 \text{ nm}$. The large value is indicative of strong absorption by the complex and forms the basis of the quantitative determination of iron (II). The absorbance of the coloured complex is measured at 508 nm using a spectrometer.

Let us sum up what have we discussed in this unit. However, before that answer the following simple question to assess your understanding.

SAQ 5

What is the advantage of the standard addition technique as compared to a calibration curve method?

12.7 SUMMARY

This unit on ultraviolet-visible (UV-VIS) spectrometry concerns the measurement of the consequences of interaction of EM radiations in the UV and/or visible region with the absorbing species like, atoms, molecules, or ions. We began the unit by explaining the origin and the features of the UV-VIS spectrum. Herein, we discussed about different types of species that absorb radiation in the UV-VIS region and the transitions occurring in them because of

these absorptions. Thereafter, we briefly explained the characteristics of the spectrum, i.e., the position, intensity, and the width of the signal.

This was followed by the fundamental principles (or the basic laws of spectroscopy) that form the basis of the analytical applications of UV-VIS spectrometry. In this context we defined Lambert's law, Beer's laws and the Beer-Lambert's law. We derived the mathematical expressions also for these laws. Thereafter, we took up the instrumental aspects of UV-VIS spectroscopy. In this context we first listed and explained the essential components of the UV-VIS spectrometers and their principles. Then we explained the working of single beam and double beam spectrophotometers. Towards the end of the unit, we explained different qualitative and quantitative applications of UV-VIS spectrometry in diverse areas.

12.8 TERMINAL QUESTIONS

1. The UV-VIS spectra in the solution phase have band structure whereas in the vapour phase we get sharp lines. Explain.
2. Outline the factors that may cause deviations from Beer and Lambert's law.
3. The absorbance of a solution of ferrous 1,10-phenanthroline complex containing 1.00 microgram of iron (II) in 10 cm³ of solution was measured at 508 nm in 1 cm cuvette. It was found to be 0.0200. Calculate the molar absorptivity of the complex.
4. What are monochromators? Describe the functioning of prism monochromator.
5. Enlist the essential steps of quantitative determination methodology.

12.9 ANSWERS

Self-Assessment Questions

1. Different types of species absorbing in the UV-VIS region and type of transition occurring in them are as follows

Species	Type of Transition
Organic molecules	$n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$
Inorganic molecules	$d-d$ or $f-f$ transitions
Charge Transfer complexes	Donor HOMO to acceptor LUMO

2. $P_o = 85.4$ $b = 2.00 \text{ cm}$
 $P = 20.3$ $c = 1 \times 10^{-4} \text{ M}$ $\epsilon = ?$
 $A = \log P_o/P = A = \log 85.4/20.3 = 0.624$

Since $A = \epsilon bc$; $\epsilon = A/b.c$

Substantially the value $\epsilon = \frac{0.624}{2.0 \text{ cm} \times 1 \times 10^{-4} \text{ M}}$

$\Rightarrow 3120 \text{ cm}^{-1} \text{ mol}^{-1} \text{ dm}^3$

3. $\epsilon = 14000 \text{ cm}^{-1} \text{ mol}^{-1} \text{ dm}^3$

$c = ? b = 1 \text{ cm} \quad A = 0.85$

$A = \epsilon bc = A/ \epsilon .b$

$c = 0.85/14000 \times b$

$= 6.07 \times 10^{-5} \text{ M}$

4. To take the UV absorption spectra, the analyte is taken in a quartz cuvette because it is transparent to the electromagnetic radiations of the UV range. As glass absorbs the ultraviolet radiations, these cannot be used for the purpose.
5. The standard addition method allows the determination of the concentration of the species in such solution also in which the other constituents are not fully known.

Terminal questions

1. The UV-VIS spectra arise because of the interaction of the radiation with absorbing species causing a transition amongst their electronic energy levels accompanied by vibrational transitions. In case of gaseous samples, the spectrum consists of several closely spaced discrete lines that resemble a band, and the resulting spectrum is called a band spectrum.

In the solution phase the energies of the quantum states of the molecules are somewhat spread out due to constant collisions with the surrounding solvent molecules. Therefore, the sample absorbs photons spread over a range of wavelength and the spectrum acquires the shape of a smooth and continuous absorption peak.

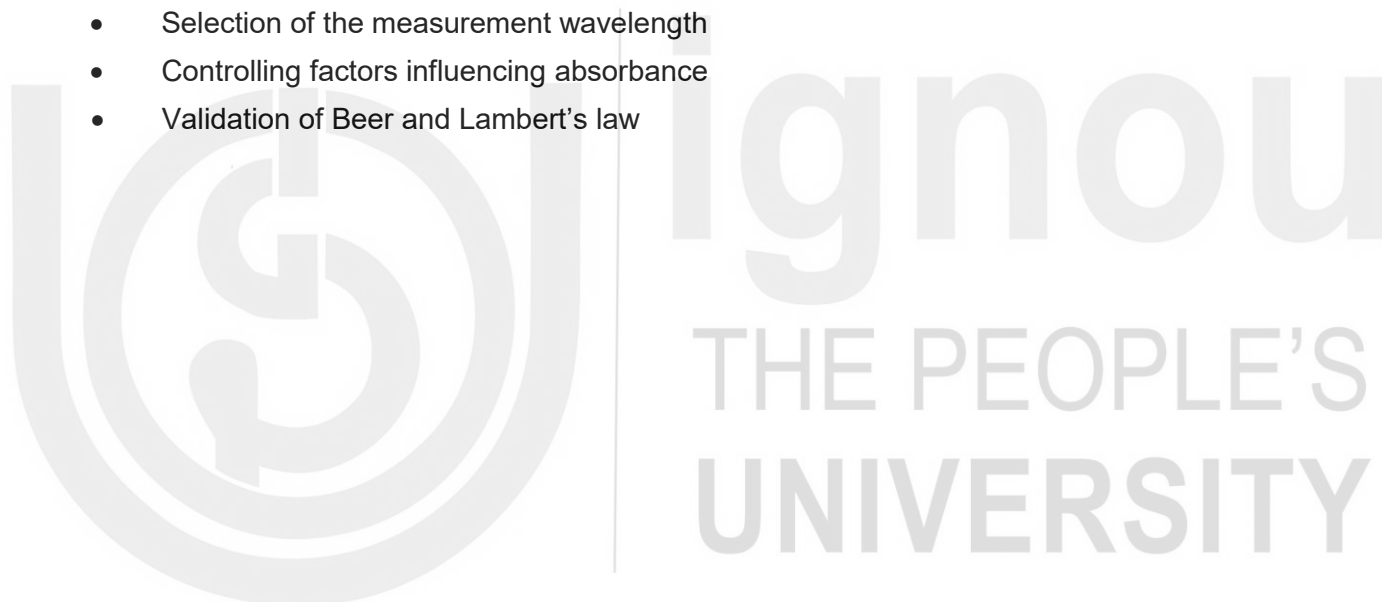
2. Some of the factors responsible for the deviation from Beer and Lambert's law are as follows.
 - Presence of electrolytes
 - Hydrogen ion concentration
 - Complexation, association, or dissociation
 - Non monochromatic nature of the radiation
 - Concentration of the analyte
 - Temperature
3. The atomic weight of iron is 56, therefore the molar concentration of the solution containing 1.00 microgram of iron (II) present in 10 mL of solution will be

$$\frac{1 \times 10^{-6} \text{ g}}{56} \times \frac{1000 \text{ mL}}{10 \text{ mL}} = 1.786 \times 10^{-6} \text{ mol per dm}^3.$$

$$\epsilon = A / b.c \quad \Rightarrow \quad \frac{0.02}{1.786 \text{ mol dm}^{-3} \times 1 \text{ cm}}$$

$$= 1.12 \times 10^4 \text{ dm}^{-3} \text{ mol}^{-1} \text{ cm}^{-1}$$

4. A monochromator is a device that can selectively provide radiation of a desired wavelength out of the range of wavelengths emitted by the source. In a prism monochromator, a fine beam of the radiation from the source is obtained by passing through an entrance slit. This is then collimated on the prism with the help of a lens. The refracted beams are then focused on an exit slit. The prism is then rotated in a predetermined way to provide the desired wavelength from the exit slit.
5. The essential steps of the quantitative determination methodology are,
- Forming an absorbing species
 - Selection of the measurement wavelength
 - Controlling factors influencing absorbance
 - Validation of Beer and Lambert's law



INFRARED SPECTROMETRY |

Structure

13.1 Introduction	Basic Components of IR Instruments
Expected Learning Outcomes	Types of IR Instruments
13.2 Origin and Characteristics of IR Spectrum	13.4 Applications of IR Spectrometry
Vibrations of Diatomic Molecules	Quantitative Applications
Vibrations of Polyatomic Molecules	Qualitative Applications
Nature of IR Spectra of Polyatomic Molecules	Interpreting IR Spectra
Characteristics of IR Spectrum	Strategy for Interpretation
13.3 Instrumentation for IR Spectrometry	13.5 Summary
	13.6 Terminal Questions
	13.7 Answers

13.1 INTRODUCTION

In the previous unit, you have studied about the UV-VIS spectrometry –an important analytical tool that involves the measurement of the consequence of interaction of electromagnetic radiation in the UV and/or visible regions with the molecules, ions, or complexes. In this unit, we take up the study of infrared (IR)spectrometry-another common spectroscopic technique used by organic and inorganic chemists for structure elucidation and quantitative determinations. The IR spectrometry involves the measurement of the amount of IR radiation absorbed or emitted by a sample as a function of the wavelength and its correlation with the structure and amount of the species being analysed. IR spectrometry finds applications in quite diverse areas like drugs and pharmaceuticals, chemical industry, polymer industry, etc.

We shall begin the unit by understanding the origin and characteristics of IR spectrum. It will be followed by a brief account of the essential components of an IR spectrometer and different types of IR spectrometers with their principles, advantages, and disadvantages. Thereafter, we shall take up quantitative and qualitative applications of IR spectrometry followed by outlining a strategy for the interpretation of IR spectra of simple molecules.

In the next unit, we shall take up the study of flame atomic absorption spectroscopy.

Expected Learning Outcomes

After studying about and performing this experiment, you should be able to

- ❖ explain the origin of IR spectrum;
- ❖ calculate the vibrational degrees of freedom for different polyatomic molecules;
- ❖ describe different types of vibrational modes of simple molecules;
- ❖ identify the IR active and inactive modes of vibration for small molecules;
- ❖ explain the reasons for the complex nature of IR spectrum;
- ❖ describe briefly the components of IR instruments;
- ❖ explain the principles of different types of IR instruments;
- ❖ outline the advantages of FT-IR instruments over the dispersive IR instruments;
- ❖ outline different applications of IR spectrometry; and
- ❖ interpret the IR spectra of simple organic molecules to ascertain their functional groups.

13.2 ORIGIN AND CHARACTERISTICS OF IR SPECTRUM

You know that the bond between two atoms in a molecule is not rigid. It has elasticity and therefore the atoms in the molecule do not remain fixed in their positions. They are in a constant state of motion around their mean position i.e., the bond keeps expanding and contracting constantly. The molecule is said to be undergoing vibrational motion. The quantum mechanical treatment of the molecular vibrational motion shows that it is quantised i.e., it can take up only certain (discrete) energies. You have learnt about quantisation of energy in BCHCT-131 course. The EM radiation in the infra- red region causes transitions amongst these quantised energy levels giving rise to an IR spectrum. As the excitation among the quantised vibrational energy levels of the molecules is involved, the IR spectroscopy is also known as **vibrational spectroscopy**. Let us learn about the vibration motion of the molecules and the origin of IR spectrum. We begin with diatomic molecules.

13.2.1 Vibrations of Diatomic Molecules

To begin with, we can visualise a vibrating diatomic molecule, AB as a simple harmonic oscillator; Fig.13.1. The two atoms A and B (shown as red balls) are assumed to be joined by a bond (shown as a spring) of length r_{eq} and molecule is oscillating around its mean position, r_{eq} . That is, the bond length continuously increases and decreases.

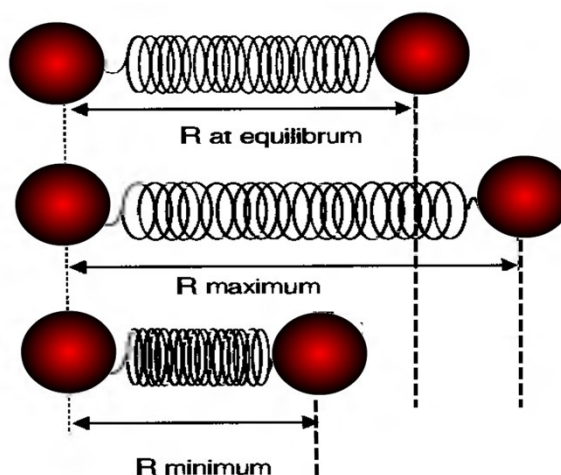


Fig. 3.1: Representation of a harmonic oscillator.

The frequency of vibration of a bond in a molecule is called vibrational frequency. The vibrational frequency of a diatomic molecule is given by the following formula.

$$\omega_{osc} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \text{ Hz} ; \quad \mu = \frac{m_1 m_2}{m_1 + m_2} \quad \dots (13.1)$$

Where, k is the force constant (a measure of strength of the bond) and μ is the reduced mass. The quantised energy levels for a harmonic oscillator are given in Fig.13.2(a). The real molecules are not like harmonic oscillators; these have some element of anharmonicity i.e., they don't expand and contract evenly around the equilibrium position. In such a case the energy levels get modified as shown in Fig.13.2(b). You may note that for anharmonic oscillator, the difference in energy levels keeps on decreasing as we go to a higher energy level (larger values of v) whereas for harmonic oscillator, the difference in the energy levels is constant.

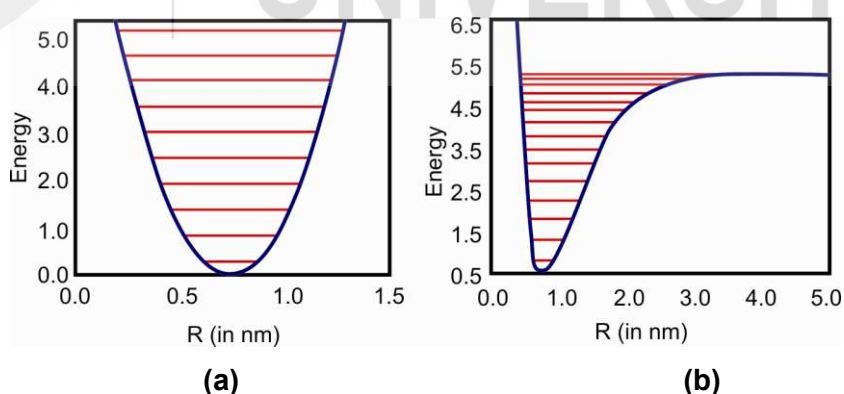


Fig.13.2: The potential energy curves for a) harmonic and b) anharmonic oscillator.

Necessary Condition for Observing IR Spectrum

The presence of quantised energy levels in a molecule does not ensure transitions amongst them when the radiation of appropriate wavelength is made to fall on it. For the oscillating electrical field of the EM radiation to interact with the vibrating molecule, there is an essential requirement. It is essential that during the vibration the molecule has a fluctuating or oscillating

dipole moment. This condition is called **necessary condition** for the interaction between the molecule and the radiation. In the absence of such a fluctuating dipole moment the radiation cannot interact with the vibrating molecule, and we say that the vibration in the molecule is **IR inactive**. For example, a homonuclear diatomic molecule like H_2 would not give an IR spectrum because it does not have a dipole moment and it does not generate a fluctuating dipole moment during the vibration. On the other hand, HBr gas has a permanent dipole moment whose magnitude varies as the molecule vibrates. Therefore, it does absorb in the IR region of EM radiation i.e., the molecule is **IR active**. A diatomic molecule can show only one possible mode of vibration. However, the larger (polyatomic) molecules may have many different modes of vibration. Let us learn about these modes of vibration.

13.2.2 Vibrations of Polyatomic Molecules

A diatomic molecule has only one possible way of executing vibrational motion because there is only one bond, and the molecule is linear. A molecule containing more than two atoms has more than one bond and these bonds may be at angle with respect to each other. For example, water is a triatomic molecule having two O—H bonds at an angle of about 104.5° . Such a molecule can vibrate in more than one possible way, like both the bonds of the molecule may vibrate symmetrically i.e., in unison or they may be showing an asymmetric vibration, or the vibration may involve a change in the bond angle (Fig 3.4). How do we ascertain the possible number of such modes of vibration for a larger molecule? The discussion that follows will help to give an answer.

The translation motional of the molecule refers to the simultaneous movement of all the atoms of the molecule in the same direction.

For a molecule containing N atoms we need to specify $3N$ coordinates (three for each atom) to completely describe the molecule. This fixes all the bond lengths and angles for the molecule. We may say that the molecule has $3N$ degrees of freedom. You are aware that the molecule shows translational, rotational, and vibrational motions. Since the molecule can move around anywhere in the three-dimensional space, the position of the molecule can be specified in terms of the three coordinates. That is, we need three degrees of freedom to account for or to describe the translation motion. So, we are left with $(3N-3)$ degrees of freedom for rotational and vibrational motion.

The number of rotational modes depends on the geometry of the molecule. A linear molecule can rotate around only two of the three axes. If the molecule lies along the "x" axis, then it can rotate only around the "y" or "z" axis. If we try to rotate the molecule around the "x" axis, then the positions of the atoms do not change. We therefore say that a linear molecule can have only two rotational degrees of freedom along with its three translational modes. However, a non-linear molecule may rotate around each of the three axes i.e., it has three rotational degrees of freedom. So, we are left with $(3N-5)$ degrees of freedom for a linear molecule and $(3N-6)$ degrees of freedom for a non-linear molecule.

For a linear molecule containing N atoms, the total vibrational modes are $3N - 5$ and for a non-linear molecule of the same size, the total number of vibrational modes is $3N - 6$.

These are the vibrational modes of the molecule. A linear molecule of N atoms would have $(3N-5)$ and a nonlinear molecule of N atoms would have $(3N-6)$ vibrational modes. For example, the linear molecule like CO_2 will have $3(3)-5$

$= 9 - 5 = 4$ vibrational modes whereas, water – a nonlinear triatomic molecule – would have only $3(3) - 6 = 9 - 6 = 3$ vibrational modes.

Types of Vibrations

There are two types of vibration for a polyatomic molecule. These are **stretching vibrations** and **bending vibrations**. Let us try to understand these vibration types.

The linear and nonlinear molecules have $(N - 1)$ stretching vibrations.

- i) **Stretching vibrations:** In stretching vibrations, the atoms move along the bond axis so that the bond length increases or decreases at regular intervals. The stretching vibrations again are of two types- **symmetric** and **antisymmetric stretching**. In symmetric stretching of a triatomic molecule, both the bonds connected to a common atom either elongate or contract simultaneously. In case of antisymmetric stretching, if one bond is lengthened, the other bond is shortened or vice-versa. The stretching vibrations linear and nonlinear triatomic molecule of the AB_2 type are shown in Fig.3.3.

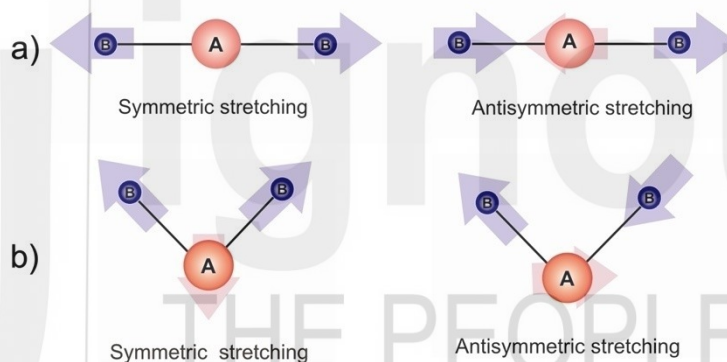


Fig. 3.3: Stretching modes of vibrations of a) linear and b) nonlinear triatomic molecule, of AB_2 type.

In general, there are $(2N - 4)$ and $(2N - 5)$ bending vibrations for linear and nonlinear molecules respectively.

- ii) **Bending vibrations:** The bending vibrations are said to occur when there is a change in the bond angle between bonds connected to a common atom. A linear triatomic molecule has two bending vibrations whereas a nonlinear triatomic molecule has only one bending vibration as shown in Fig.3.4.

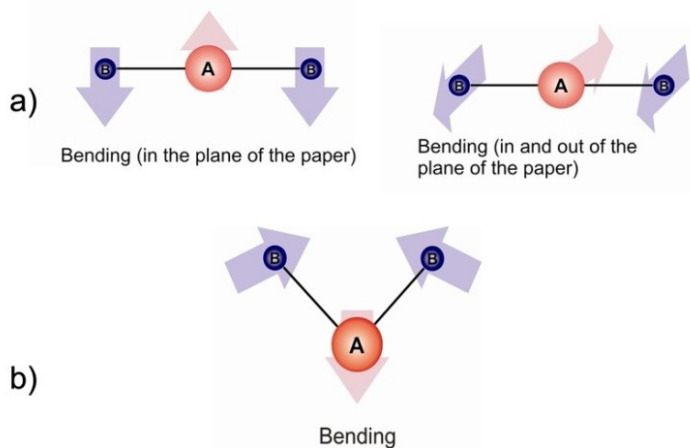


Fig. 3.5: Bending modes of vibrations of a) linear and b) nonlinear triatomic molecule, of AB_2 type.

You have learnt above that a vibrating molecule has several quantised vibrational energy levels. Therefore, there could be many transitions possible amongst them. Now a question arises that, of these, which transitions would we observe? For this we need to know about an important rule called the selection rule.

Selection Rule for the IR Spectroscopy

The selection rule for a spectroscopy refers to the condition that tells us about the transitions that are possible (or allowed) amongst the quantised energy levels. The selection rule for the IR spectroscopy is, $\Delta v = \pm 1, \pm 2, \pm 3 \dots$ etc. That is, the vibrational quantum number can change by any number. In other words, the molecule may go over from any vibrational level to any other vibrational energy level. This implies that there would be many transitions and the resulting spectrum would be quite complex. However, the actual IR spectrum for a diatomic molecule is not so complex. The pure vibration spectrum of a diatomic molecule consists of mainly three signals: an intense signal, a weak signal and a very weak signal.

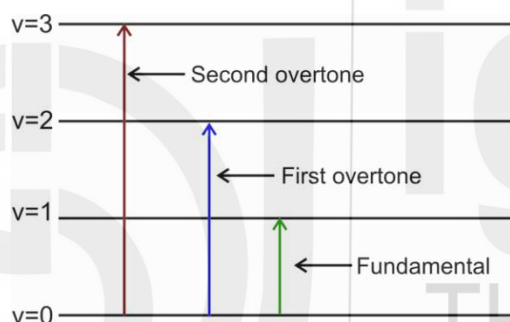


Fig. 13.5: The transitions corresponding to the fundamental vibration and the overtones.

The intense signal is called **fundamental band** and is observed for the transition from ground state ($v = 0$) to the first ($v = 1$) excited vibrational level. The second is a weak signal called **first overtone** is observed at roughly double the frequency of the fundamental band; it is due to the transitions from ground state ($v=0$) to the second ($v = 2$) excited vibrational level. The third and the weakest signal is signal is called the second overtone and is observed at roughly triple the frequency of the fundamental band. This is due to the transitions from ground state ($v = 0$) to the third ($v = 3$) excited vibrational level. The origin of fundamental and overtones for a diatomic molecule is schematically shown in Fig. 13.5. Now, what would be the nature of spectrum in a polyatomic molecule? Let us try to extend our understanding of the vibrational behaviour of a diatomic molecule to polyatomic molecules.

13.2.3 Nature of IR Spectra of Polyatomic Molecules

You would agree that the vibration spectrum of a polyatomic molecule with several bonds is expected to be quite complex. Indeed, the IR spectrum for a molecule of a reasonable size is quite complex and it is almost impossible (and mostly not desirable) to interpret all the signals obtained. However, with a little understanding of the possible vibration modes, their IR activity (or inactivity) and the concept of characteristic group frequencies we can use the

observed signals in the IR spectrum for the determination of the structure of organic molecules. Let us try to have that understanding.

In the light of the discussion above, we can say that the infrared spectrum of a polyatomic molecule would consist of an absorption band at each of the $(3N-6)$ or $(3N-5)$ fundamental frequencies for nonlinear and linear molecules, respectively along with the corresponding overtones. However, in the experimentally observed spectrum, we may also have weak bands due to addition of two fundamentals vibrations or difference of two fundamental bands. Such bands are called **combination bands** and **difference bands** respectively. More so, sometimes a fundamental band and an overtone of another band may have frequencies very close to each other, these may resonate leading to the appearance of signals at frequencies higher and lower relative to the original frequencies. This phenomenon is called **Fermi resonance**.

As the number of atoms in a molecule increases, the spectrum becomes quite complex. Let us take example of a molecule say n-decane, $C_{10}H_{22}$, having 32 atoms. The number of fundamental vibrational modes would be $3(32) - 6 = 96 - 6 = 90$. Along with the corresponding overtones and combination bands the spectrum is expected to have a few hundred signals.

The infrared spectrum of a compound consists of strong fundamental absorptions and weak overtones, combination band and Fermi resonance bands.

$$\bar{\nu} \text{ (in cm}^{-1}\text{)} = \frac{1}{\lambda \text{ (in } \mu\text{m)}} \times 10^4$$

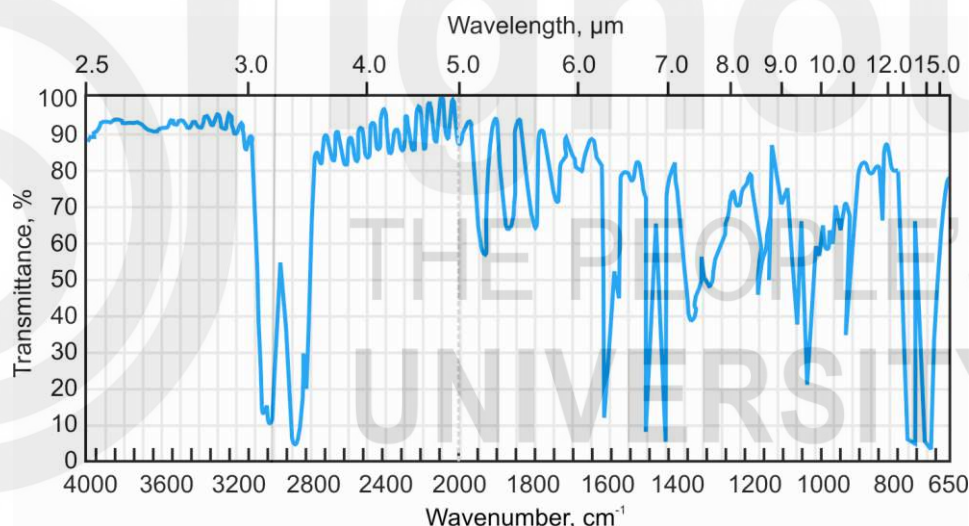


Fig. 13.6: A representative IR spectrum.

However, the actual spectrum has much fewer of them. This is so because all the vibrations may not be IR active. You would recall that for a vibration mode to be IR active it must be associated with a change in the dipole moment. Other reasons for not observing so many signals could be that either they are too weak or are outside the range of the instrument. A representative IR spectrum is given in Fig. 13.6. As you can see the ordinate (Y-axis) represents percent transmittance whereas the abscissa (X-axis) is either wavenumber or wavelength.

13.2.4 Characteristics of IR Spectrum

The positions of IR absorption signals are presented on the x-axis as either wavenumbers (ν) or wavelengths (λ). However, the wavenumber unit (in cm^{-1} , reciprocal centimeter, or centimeter inverse) is preferred over wavelength (in μm , micrometers). This is so because an increase in the wavenumber

You may recall from unit 11 that Wavenumber is the inverse of wavelength.

$$\bar{\nu} = \frac{1}{\lambda}$$

Generally, it is expressed in terms of cm^{-1} and obtained by taking the inverse of the wavelength in cm.

corresponds to an increase in energy (and frequency) whereas the wavelength is related inversely to the energy. You may note that the position of the IR signal in cm^{-1} is commonly (though incorrectly) referred to as the frequency. The frequency by itself is normally not used due to its inconvenient size. You must also take note of the change in the scale of x-axis at 2000 cm^{-1} ; it is more compact at higher values.

The intensity of the signal (on y-axis) is given in terms of % transmittance. It tells about how strongly the IR radiation of a given wavenumber is absorbed. You have learnt in the previous unit that the transmittance, T , is the ratio of radiant power transmitted by the sample (P) to the radiant power incident on the sample (P_0). It ranges from 0 to 100% T . 100% transmittance means no absorption whereas 0% transmittance means complete absorption of the incident IR radiation. The signals in the IR spectrum are called **bands**. A larger band corresponds to a lower value of transmittance and suggests a larger absorption of the radiation. Generally, the IR bands are marked as s, m, and w; these refer to strong, moderate, and weak absorptions.

Transmittance,

$$T = \frac{P}{P_0}$$

$$\% T = \frac{P}{P_0} \times 100\%$$

Having learnt about the origin and the characteristics of IR spectrum let us now learn about the components of the instruments used for recording the IR spectrum. However, before going ahead why don't you answer the following simple questions to assess your understanding.

SAQ 1

What is the necessary condition to observe an IR spectrum?

SAQ 2

Calculate the number of vibrational degrees of freedom for methane, CH_4 . How many of these would be bending modes?

SAQ 3

Why is the IR spectrum preferably shown in wavenumber units?

13.3 INSTRUMENTATION FOR IR SPECTROMETRY

Like UV-VIS spectrometry, IR spectrometry is also a type of absorption spectroscopy. Herein the extent of absorption of different radiation in the IR region by the sample is studied as a function of the wavenumber of the radiation. Let us first learn about the basic components of IR instruments.

13.3.1 Basic Components of IR Instruments

The basic components of IR instruments are also like that of the UV-VIS spectrometers, discussed in the previous unit.

The essential components of an IR instrument are as follows.

- A. A stable and powerful source of radiation
- B. Sampling device
- C. Monochromator or frequency modulator
- D. Transducers or detectors,
- E. Signal processing and output device

Let us learn about these components in brief.

A. Sources of IR Radiation

The commonly employed IR source is generally an electrically heated inert solid that emits a continuum of radiation. The sources commonly employed in the IR spectrophotometers and their description is as under

Nernst Glower or filament lamp: It is a cylindrical rod made up of a mixture of zirconium, yttrium, and erbium oxides (diameter of 1–2mm and length of about 20mm). It is electrically connected through platinum wire and heated by the passage of an electrical current to a temperature of about 1200 to 2200 K.

Globar: It is a silicon carbide rod (diameter of 5mm and length of about 50mm) which is electrically heated to about 1500 K. The electrical contacts have a risk of arcing therefore water cooling of the contacts is used. The spectral output is comparable with the Nernst glower, except at short wavelengths (less than 5 μm) where its output becomes larger.

Incandescent nichrome wire: It is a tightly wound coil of nichrome (Ni-Cr) wire, electrically heated to 1100 K. It produces a lower intensity of radiation than the Nernst or Globar sources but has a longer working life.

Carbon dioxide lasers: The tunable carbon dioxide lasers produce closely spaced discrete lines in a limited range of IR radiation (900 to 1100 cm^{-1}). Though the tunable laser has limited range, but it provides a much larger intensity of all the lines in the range. The laser can be tuned to any of these lines and can be used for the quantitative determination of different species like, ammonia, benzene, and nitrogen dioxide etc.

In addition, some IR sources like, mercury arc and tungsten filament lamp are also used.

B. Sampling Devices

The handling of sample for the measurement of IR spectra is not simple. Firstly, glass or quartz cannot be used as a material for making cuvettes to be used in the infrared region. It is so because glass absorbs strongly at most of the frequencies in this region. Secondly, analysing an analyte as a solution is also not easy because most of the solvents of the organic compounds themselves absorb in many regions of the IR spectrum. In fact, there is no solvent that is transparent in the whole IR range.

In the absence of glass, the salts like NaCl and KBr which are transparent in the IR region are used for the construction of the cuvettes. These cuvettes are called **IR windows**. The NaCl windows are commonly used for routine work in

Alternatively, a rhodium wire heater sealed in a ceramic cylinder may be used as an incandescent wire source.

Carbon dioxide lasers find application as a source in selective monitoring of atmospheric pollutants.

the region $4000\text{--}650\text{ cm}^{-1}$ as these are cheaper than KBr windows. However, for measurements below 650 cm^{-1} the KBr windows are used because NaCl starts absorbing in this region.

The sampling techniques depend upon the phase (solid, liquid or gas) of the sample being analysed. We would take up the sampling of solids here. There are two techniques for handling a solid sample. These are as follows:

Mull technique: In this technique called Nujol mull technique, the solid sample is finely ground to a paste in a small amount of mineral oil hexachlorobutadiene (nujol). It forms a fine suspension or mull of the sample in the oil. The mull is pressed between two NaCl or KBr plates to give a thin film of the sample. The two plates are then clamped in a holder with open windows on both sides and the assembly is kept in the path of the infrared beam.

KBr Pelleting: in this technique, a small amount of sample ($\sim 1\text{--}2\text{ mg}$) is mixed and ground with about hundred times its mass of potassium bromide. The mixture is transferred to an evacuable die (Fig. 13.7), to remove the moisture and then a high pressure is applied to yield a transparent pellet. It is put in a suitable holder and the whole assembly is placed in the line of the infrared beam.



Fig. 13.8: Die assembly for making KBr pellets.

C. Monochromators and Frequency Modulators

You have learnt in the previous unit that a monochromator is an optical device that transmits a selectable wavelength of radiation chosen from a wider range of wavelengths available at the input. There are two types of IR instruments (discussed later) and these use different ways to get monochromatic radiation. In dispersive IR spectrometers we use rotating prisms or diffraction gratings as the monochromators. The monochromator is placed after the sample. You would recall that the monochromator is placed before the sample in UV-VIS spectrometry.

A monochromator is an optical device that transmits a selectable wavelength of radiation chosen from a wider range of wavelengths available at the input.

Most of the modern IR instruments are FT-IR instruments. In these instruments the radiation is not dispersed before or after passing through the sample. Instead, the response of the sample to all the wavelengths in the range is measured simultaneously and the signal so obtained is modulated and collected in time domain. This is then Fourier transformed to get the desirable frequency domain signal.

D. Transducers or Detectors

There are three categories of transducers employed for detecting IR radiation. Let us learn about these in brief.

Thermal Transducers: in this type of transducers, the response depends on the thermal effects. There are two types of thermal transducers—the thermocouples and bolometers.

The thermocouples consist of a pair of junctions of different metals; for example, two pieces of bismuth fused to either end of a piece of antimony. The infrared radiations are made to fall at one junction called hot junction, the other junction called cold junction is kept at a constant temperature. The difference in temperature causes an electrical potential difference between the two joints and its value would depend on the difference in temperature between the junctions. The potential difference, thus, would depend on the amount of radiation falling on the hot junction and therefore is a measure of the radiation.

The **bolometers** on the other hand are a kind of resistance thermometer. These are prepared using thin strips of platinum or nickel. You know that in general the resistance of a metallic conductor changes with temperature; these materials show quite large changes in the resistance on changing the temperature. When infrared radiations fall on a bolometer, its temperature changes and causes a corresponding change in its resistance. The resistance so measured indicates the amount of the radiation falling on the bolometer.

Some bolometers are prepared from semiconductors and are called thermistors.

The pyroelectric material undergoes electric polarisation when an electric field is applied across it. The polarization persists even on removing the field and the degree of polarisation depends on the temperature.

Pyroelectric Detectors: these are temperature dependent capacitors made from a single crystalline wafer of a pyroelectric material, such as triglycerine sulphate. The heating effect of incident IR radiation causes a change in the capacitance of the capacitor which in turn can be measured in the external circuit as current. Pyroelectric detectors have a quick response time to be able to respond to the signal. Therefore, they are used in most of the commercially available FT-IR instruments.

Photoelectric Transducers: these comprise of a film of semiconducting material deposited on a glass surface which is sealed in an evacuated envelope. Absorption of IR radiation by them causes the electrical resistance of the semiconductor to decrease which can be measured. These transducers have better response characteristics than pyroelectric transducers, and find use in FT-IR hyphenated instruments especially GC- FT-IR etc.

E. Signal Processing and Output Devices

The electrical signal from the transducer is suitably amplified or processed before it is sent to the recorder to give an output. In dispersive IR instruments, as discussed later, an optical null system is employed to achieve the equal intensities of the sample and reference beams. On the other hand, in FT-IR instruments, the interferogram obtained in the time domain is mathematically processed by the computer to generate its Fourier transform i.e., the signal in frequency domain. This is then further processed to get the recorder output.

We are sure that having read about different components of IR instruments and their importance, you are equipped to learn about the IR spectrometers. However, before that answer the following simple question to assess your understanding.

SAQ 4

Why is it difficult to take IR spectra in solution phase?

SAQ 5

Why can't we use glass cell holders for IR spectrometry?

13.3.2 Types of IR Instruments

There are three types of IR instruments that are employed for recording IR spectra. These are,

- A. Dispersive infrared spectrometers
- B. Fourier-transform infrared(FT-IR) spectrometers
- C. Non-dispersive infrared spectrometers

We would briefly discuss about the first two of these

A. Dispersive Infra-Red Spectrometers

These instruments though are slightly outdated but are still employed, for qualitative work, due to economic reasons. The general set up of a dispersive IR instrument is like that of the double beam UV - Visible instrument. However, the sample is located between the source and the monochromator. This arrangement helps in getting rid of the scattered radiation from the cell compartment. A schematic diagram of the double beam dispersive instrument is given in Fig. 13.8.

As these instruments employ dispersion of radiation, these are called dispersive IR spectrometers.

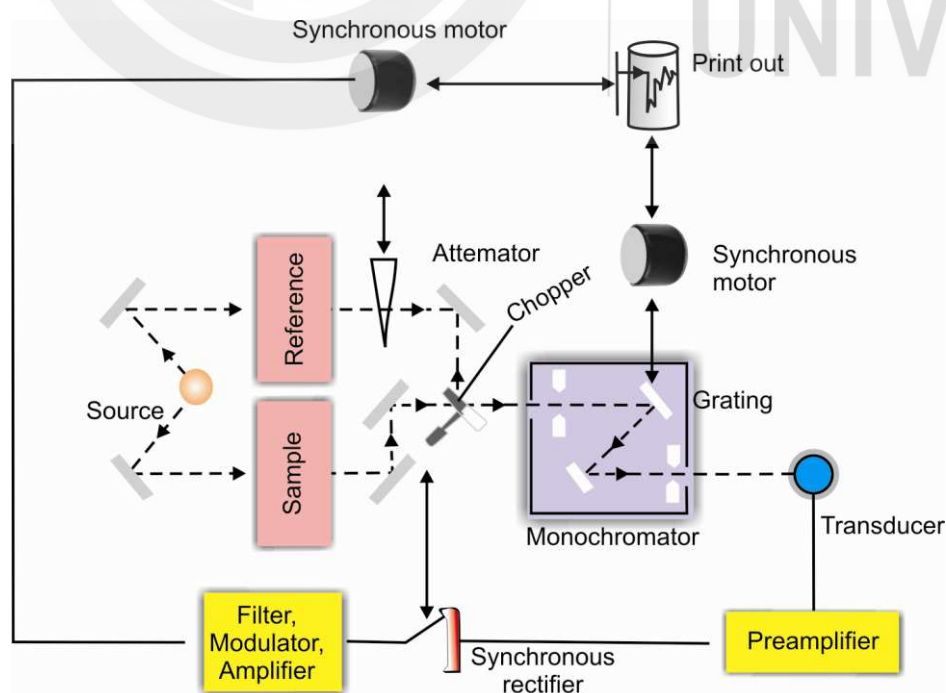


Fig. 13.8: A schematic diagram showing different components and the optic path of a dispersive IR spectrometer.

The radiation produced from an IR source is made to fall on a beam splitter which splits the beam into two equivalent half beams. These beams are focused by separate concave mirror systems on the sample and the reference (normally the solvent) cells. The beam emerging from the reference cell is made to fall on the chopper through an attenuator while the radiation from the sample is sent directly on to the chopper. The chopper alternately allows the reference beam or the sample beam to enter the monochromator. These beams after dispersion by the monochromator are made to fall on the detector. The signals originating from the detector are then suitably processed and sent to the recorder for an output.

B. Fourier Transform IR Spectrometers

In contrast to the dispersive IR spectrometers, where the signal from the sample is dispersed and the response at each wavelength (or wave number) is measured individually, the FT instruments collect the response at all the wavelengths simultaneously.

Michelson interferometer is employed for the modulation of the signal; the output from the interferometer is an interferogram.

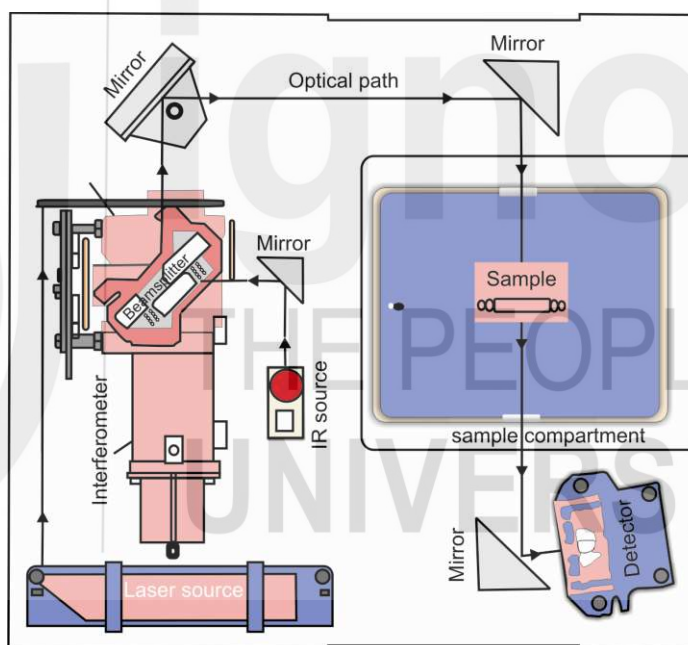


Fig. 13.9: A Schematic diagram showing different components and the optic path of a FT-IR spectrometer.

In these multiplex instruments the monochromator is replaced by an interferometer and the response of the sample to the whole range of IR radiation is suitably modulated and collected in the time domain. These are then decoded using the Fourier transformation. Therefore, it is named the Fourier transform infra-red spectrometer (FT-IR). The basic instrument design for an FT-IR instrument is quite simple. A schematic diagram showing different components is given in Fig.13.9.

The IR radiation from the source is first directed into an interferometer from where it is passed through the sample compartment and then it reaches to the detector. An important aspect of FT-IR is that most bench top FT-IR spectrometers are single-beam instruments and do not obtain transmittance or absorbance IR spectra in real time. A typical operating procedure is as follows:

Steps in getting an FT-IR spectrum of the sample with interferometer

In the first step, an interferogram is recorded without any sample in the beam and saved in computer memory. This interferogram is characteristic of the experimental set up and consists of the response of the spectrometer in terms of the performance of source, interferometer, and the detector. This is called background spectrum. The interferogram is recorded again; this time with a sample introduced into the beam and stored in computer memory. It contains signals from the sample and the background air or solvent. The first interferogram is subtracted from the second with the help of a computer. The resulting difference interferogram is then Fourier transformed to give the spectrum. In the process of taking the difference between the two interferograms the absorption due to atmospheric gases is also removed.

The FT-IR instruments are far superior to the dispersive instruments. The advantages of FT-IR instruments are

Advantages of FT-IR Spectrometers

- As the absorption at all wavelengths is recorded at the same time, this saves lot of experimental time. This is called the **multiplex advantage**. These are much faster, and a given spectrum can be taken in less than a second. This provides for taking multiple scans for low concentration samples and then averaging them. This leads to a spectrum with a better signal to noise (S/N) ratio as compared to a dispersive instrument.
- FT-IR spectrometers give better frequency resolution and reproducibility.
- As there are no narrow slits in an FT-IR spectrometer, the energy output is much greater than in a dispersive instrument. This is referred to as the **Jacquinot advantage**. This also leads to a higher signal to noise ratio (S/N ratio) than the dispersive infrared spectrometers.
- Due to its simple mechanical design with only one moving part (the moving mirror in interferometer), there is less wearing out of the components and hence better reliability of the spectrometer.

Having learnt about the basic components used in IR instruments and the types of instruments used in IR spectrometry let us take up the applications of IR spectrometry. However, before that answer the following simple question to assess your understanding.

SAQ 6

Outline the steps involved in taking a FT-IR spectrum

13.4 APPLICATIONS OF INFRARED SPECTROMETRY

IR spectroscopy is widely used in both research and industry as a simple and reliable technique for measurement, quality control and monitoring of dynamic

processes. The intensity and position of the signals in infra-red spectrum allow the identification of structural elements like typical functional groups, hydrogen bonding, etc. in the sample. As mentioned above, IR spectrometry finds applications in quite diverse areas like drugs and pharmaceuticals, chemical industry, polymer industry, etc. Let us take up qualitative and quantitative aspects of applications of IR spectrometry.

13.4.1 Quantitative Applications

In the previous unit you have learnt that how UV-VIS spectrometry can be used for quantitative determinations. However, in case of IR spectrometry the quantitative use is subject to several practical and instrumental problems. Some of these are as follows:

- Narrowness of the IR bands
- Low intensity of the source and low sensitivity of the transducer
- Non availability of the matched cells for the sample and reference
- Interference by solvents and IR absorbing air contaminants

In the light of these factors the quantitative application of IR requires a thorough planning of the experiment and a skilled execution of the procedure to obtain the spectrum.

13.4.2 Qualitative Applications

The most important qualitative application of the IR spectrometry is in the determination of the structures of organic and biochemical species. It is achieved in an empirical method wherein the signals in the IR spectra are identified with the help of correlation tables (briefly discussed below). Besides structure determination, we shall discuss some other qualitative applications of IR spectrometry.

Structure Elucidation of Organic Molecules by IR Spectra

This is probably the most important application of IR spectroscopy. The IR spectrum of the compound is analysed to decipher the presence of the likely functional groups in the molecule. This information supplemented with other spectroscopic data helps in deciding the structure of the molecule being analysed. This aspect of the interpretation of IR spectrum is dealt with in detail in the next subsection.

Checking the Authenticity of a Compound

A common application of IR spectra is the comparative analysis of the spectra of an unknown compound with the spectra of the likely compounds. For this purpose, the IR spectra may be considered analogous to a fingerprint of an individual. Like, there are no two individuals with the same set of fingerprints there are no two molecules with identical IR spectra, more so in the fingerprint region. To decipher the identity of a molecule we need to run a co-IR. Here, the IR traces of the test molecule and the corresponding authentic sample or its spectrum from the available catalogues on the same chart are seen and matched. If the two compounds are identical then the signals in their IR spectra would match in terms of their positions and the relative intensities.

Monitoring the Progress of a Reaction

Another useful application of IR spectrometry is to monitor the progress of a reaction by monitoring the disappearance (or appearance) of a characteristic IR absorption signal. For example, the oxidation of a secondary alcohol to a ketone can be monitored in terms of the disappearance of the O-H signal in the IR spectrum of the reaction mixture or by the appearance of the carbonyl signal of the ketone being produced. The rate of such reactions can also be measured by taking the time dependent spectra and using the Beer-Lambert Law.

13.4.3 Interpretation IR Spectra

The region of IR spectrum generally ranges from $4000\text{--}600\text{ cm}^{-1}$ and the infrared spectrum can be broadly divided into three regions as given below.

- i) The region spanning the high frequency range from $3600\text{ to }1300\text{ cm}^{-1}$ is called the **functional group region** and includes the stretching vibrations or group frequencies of common functional groups. The absorptions in this region provide information about the presence of characteristic functional groups, such as --OH , --NH , C=O , --SH and --C=C-- etc. The absence of absorption in the assigned ranges for different functional groups can usually be used as evidence for the absence of such groups in the molecule. However, this feature should be used with care as sometimes the signals may be too broad to be noticed and may mislead.

It may not be possible to conclusively assign a signal to the functional group because many functional groups may have absorptions in a frequency range. However, as the functional groups often give rise to different characteristic signals; the spectral interpretations should not be confined to one or two bands; the whole spectrum should be thoroughly examined. The characteristic frequencies of some important functional groups are summarised in a correlation chart given in Table 13.1.

- ii) The region that includes all frequencies in the range of 1300 cm^{-1} to 900 cm^{-1} is called **the fingerprint region** and includes molecular vibrations, characteristic of the entire molecule or large fragments of the molecule. The absorption pattern in this region is frequently quite complex. However, this region is useful for confirming the identity of a particular molecule by comparing with the spectral absorptions of its authentic sample.

The two regions put together are important in the determination of the identity of a molecule. It is almost impossible to assign all the possible frequencies observed in the IR spectrum. However, identification of the characteristic features in the functional group region that includes stretching vibrations, of typical functional groups found in organic molecules, is quite important.

- iii) The region below 900 cm^{-1} is referred to as the **low frequency region**. This region is particularly significant in ascertaining the substitution pattern in aromatic moieties.

Table 13.1: Characteristic IR frequencies of some functional groups

Functional group name	Structure (IR absorbing bond in bold)	IR frequency range (cm ⁻¹)	Functional group name	Structure (IR absorbing bond in bold)	IR frequency range (cm ⁻¹)
Alkane (C-H)	$\text{R}_3\text{C}-\text{H}$ (R= H or C)	3000-2800	Alkyne (C $\equiv$ C)	$\text{RC}\equiv\text{CR}$ (R=H or C)	2260-2100
Alcohol (O-H)	$\text{RO}-\text{H}$	3600-3200 (broad band)	Nitrile (C $\equiv$ N)	$\text{RC}\equiv\text{N}$ (R=C)	2260-2200
Amines, Amide (N-H)	$\begin{array}{c} \text{R} \\ \diagdown \\ \text{N}-\text{H} \\ \diagup \\ \text{R} \end{array}$ -----	3500-3300 (One band) 3500-3300 (two bands), 1650-1560 (bending)	Alkene (C=C)	$\text{R}_2\text{C}=\text{CR}_2$ (R=H or C)	1600-1680
Carboxylic acid (O-H)	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C} \\ \diagup \quad \diagdown \\ \text{O}-\text{H} \end{array}$	3200-2500 (broad band)	Benzene ring (C=C)	 (C=C ring "breathing")	1450-1600 2 to 3 bands
Aldehydes or Ketones (C=O)	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{R} \end{array}$	1750-1705	Alcohol or Ether (C-O)	--- (R=H or C)	1300-1000
Carboxylic acid (C=O)	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{OH} \end{array}$ (R=H or C)	1790-1680	Alkyne (C-H)	$\text{RC}\equiv\text{C}-\text{H}$ (R=C)	3300
Amide (C=O)	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{NR}_2 \end{array}$ (R=H or C)	1850-1800 and 1790-1730	Acid chloride (C=O)	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{Cl} \end{array}$ (R=H or C)	1815-1790
Acid anhydride (C=O)	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{R}-\text{C} \quad \text{C}-\text{R} \\ \diagup \quad \diagdown \\ \text{O} \end{array}$ (R=H or C)	1850-1800 and 1790-1740 (two bands)	Nitro Compound (NO ₂)	$\begin{array}{c} \oplus \quad \text{O} \\ \diagdown \quad \parallel \\ \text{R}-\text{N} \quad \text{O} \\ \diagup \quad \diagdown \\ \text{O} \quad \ominus \end{array}$ (R = C)	1660-1500 (asymmetric stretch) 1390-1260 (symmetric stretch)

In addition to the presence (or even the absence) of a particular functional group, the analysis of IR spectrum also gives the following information:

- Presence of hydrogen bonding in the molecule (3200-3600 cm⁻¹)
- Geometry (cis or trans) in case of alkenes

Over the years, a lot of data on the fundamental absorption frequencies of different molecules and the possible structure-spectrum correlations has been published. These spectral compilations are important for understanding the structures-spectral relationships of the associated molecular vibrations in wide range of molecules. This information can be obtained from many texts available on spectroscopy or from the open-source material available on the internet.

Strategy for the Interpretation of IR Spectra

There is no unique strategy to determine the structural aspects of the molecule based on their spectra. However, there are some suggestive guidelines based on empirical relationships between structure and spectra. We are giving you one such approach. You may follow the following strategy to determine the functional group of an organic compound.

As a first step we determine the nature of carbon skeleton in the molecule, i.e., whether the molecule is aliphatic or aromatic.

A. Nature of carbon skeleton (aliphatic / aromatic)

- i) **C–H stretching:** The =C–H stretch in aromatics is observed at $3100\text{--}3000\text{ cm}^{-1}$ whereas the –C–H stretching frequencies for saturated aliphatic hydrocarbons is below 3000 cm^{-1}
- ii) **C–C ring stretching vibrations:** The aromatic hydrocarbons show C–C ring stretching vibrations in the regions $1610\text{--}1585\text{ cm}^{-1}$ and $1500\text{--}1400\text{ cm}^{-1}$.
- iii) **Out of plane C–H bending vibrations:** these are observed in the region $900\text{--}675\text{ cm}^{-1}$ and provide information about the substitution pattern of aromatic compounds.

Thus, a weak absorption in the region $3080\text{--}3030\text{ cm}^{-1}$ accompanied by medium absorption in the ring vibrations region indicates the presence of an aromatic ring. A signal around 1605 cm^{-1} is quite a good indicator of an aromatic molecule; occasionally it splits into a doublet. The out of plane bending vibrations are also very significant. A lack of strong absorption band in the $900\text{--}650\text{ cm}^{-1}$ region generally indicates a non-aromatic structure.

Having established the aliphatic/ aromatic nature of the molecule the next step is to look for the characteristic frequencies of different functional groups. As the possible functional group in a molecule depends on its elemental composition, the suggested guidelines are categorized according to the elemental composition. We first take up hydrocarbons-i.e., the molecules containing only C and H atoms.

Important

sp^3 C–H stretching:
 $2850\text{ to }3000\text{ cm}^{-1}$
 sp^2 C–H stretching:
 $> 3000\text{ cm}^{-1}$
 sp C–H stretching:
 $\sim 3300\text{ cm}^{-1}$.

B. Molecules containing only C and H i.e., hydrocarbons

For hydrocarbon the first step would be to look for the carbon skeleton as described above.

Look for **C–H stretching** whether it is in the region $3000\text{--}2850\text{ cm}^{-1}$ or above 3000 cm^{-1} ? The absorption above 3000 cm^{-1} indicates a double or a triple bond. The following are other important signals to look for in a hydrocarbon to ascertain its nature.

- i) The C=C bond usually gives rise to a moderate band in the region $1680\text{--}1640\text{ cm}^{-1}$
- ii) The –C≡C– stretch appears as a weak band from $2260\text{--}2100\text{ cm}^{-1}$

- iii) The bending vibrations of the =C-H group are observed in the $1000\text{-}650\text{ cm}^{-1}$ region
- iv) The terminal $\text{-C}\equiv\text{C-H}$ stretch is observed as a strong, narrow band in the range $3330\text{-}3270\text{ cm}^{-1}$
- v) The $\text{-C}\equiv\text{C-H}$ bending vibration is observed in $700\text{-}600\text{ cm}^{-1}$ range
- vi) If a band observed at 1380 cm^{-1} happens to be a doublet, it may be due to the presence of more than one methyl group on the same carbon atom

Next, we take up the molecules containing C, H and O or N atoms.

C. Molecules containing C, H and O or N

Look for a strong absorption in the region, $1820\text{-}1660\text{ cm}^{-1}$ for a C=O group.

If carbonyl group is present, then we have several possibilities; look for the following

- i) Two weak absorptions near 2850 and 2750 cm^{-1} on the lower wave number side of the CH absorptions.

These are due to O=C-H stretching vibrations. The band near 2830 cm^{-1} usually overlaps with other C-H stretching vibration bands however, the presence of a moderate band near 2720 cm^{-1} is very likely to be helpful in determining whether a compound is an **aldehyde**. It often appears as a shoulder-type peak.

- ii) Broad band in the region $3300\text{-}2500\text{ cm}^{-1}$, centered at about 3000 cm^{-1} .

This arises due to the stretching vibration of O-H group of **carboxylic acids**. The broad nature of the band is because carboxylic acids usually exist as hydrogen-bonded dimers.

- iii) Two or more strong absorption bands in the region $1300\text{-}1000\text{ cm}^{-1}$

These are due to the C-O stretching vibrations in **esters**.

- iv) If the above three are absent, then the molecule could be a **ketone**

Similarly, if C=O absorption is absent, look for the following

- i) The N-H stretching vibrations of **amines** in the region $3300\text{-}3000\text{ cm}^{-1}$

These are observed to be weaker and sharper than those observed for the O-H stretching vibrations of alcohols which appear in the same region. The presence of two bands is suggestive of a primary amine whereas a single band is indicative of a secondary amine.

- ii) The corresponding C-N stretching vibrations of aliphatic amines are observed as medium or weak bands in the region $1250\text{-}1020\text{ cm}^{-1}$. The same for aromatic amines are usually observed as strong band in the region $1335\text{-}1250\text{ cm}^{-1}$.

- iii) Nitrile ($\text{C}\equiv\text{N}$) shows a medium, sharp absorption band in the range $2260\text{--}2220\text{ cm}^{-1}$. The isomeric isocyanate's strong bands are observed in the range $2275\text{--}2240\text{ cm}^{-1}$.

Now, we consider the molecules containing C, H, O, and N atoms.

D. Molecules containing C, H, O, and N atoms

For the molecules having this elemental composition, two most common functional groups are amide and nitro. Their absorptions can be looked for in the following regions.

- i) **Amide:** The amides show a characteristic absorption band for the carbonyl group in the region, $1700\text{--}1640\text{ cm}^{-1}$. It is also referred to as the **Amide I band**.

In addition, the N–H stretching vibrations are observed in the $3500\text{--}3100\text{ cm}^{-1}$. The primary amides show two N–H stretching bands whereas the secondary amides give rise to only one such band.

- ii) **Nitro:** In nitroalkanes the N–O stretching vibrations occur in the range of $1550\text{--}1365\text{ cm}^{-1}$; the band at higher value being the stronger of the two. On the other hand, for the nitro group attached to an aromatic ring, the N–O stretching bands are observed in the ranges of $1550\text{--}1475\text{ cm}^{-1}$ and $1360\text{--}1290\text{ cm}^{-1}$.

You would use this strategy to interpret the IR spectra of some simple molecules in the BCHET-142 course.

Let us now sum up what we have discussed in this unit. However, before that answer the following simple questions to assess your understanding.

SAQ 6

What do you understand by the fingerprint region of an IR spectrum? What is its significance?

SAQ 7

What is meant by functional group region of an IR spectrum? How is it useful in deciphering the structure of an organic molecule?

13.5 SUMMARY

We began this unit on IR spectrometry by understanding the origin and characteristics of IR spectrum. Herein, you have learnt that Infra-red spectrometry is one of the common spectroscopic techniques used for qualitative and quantitative determination of different species. The IR spectrum is a consequence of absorption of IR radiation by the molecules causing transitions amongst their quantised vibrational energy levels. It is essential that the molecule has a fluctuating or oscillating dipole moment during a vibration for it to absorb IR radiation. A typical IR spectrum consists of many signals (called bands), the position of these signals indicates the vibration frequencies

of the molecule whereas the intensity indicates the extent to which a given radiation is absorbed. The IR spectrum for a molecule of a reasonable size is quite complex and it is not desirable to interpret all the signals obtained.

Then we discussed about the essential components of an IR spectrometer and different types of IR spectrometers in terms of their principles, advantages, and disadvantages. In this context you have learnt that the basic components of an IR instrument include a stable source of radiation, a suitable sampling device, a monochromator or frequency modulator, a transducer and signal processing and output device. In IR spectrometry, glass or quartz cannot be used as a material for making cuvettes as it strongly absorbs the IR radiation. Therefore, IR windows made from the salts like NaCl and KBr which are transparent in the IR region are used for the purpose. Further, since most of the common solvents absorb in many regions of the IR spectrum, it becomes difficult to run spectra of the solutions.

There are three types of IR instruments. These are dispersive, FT and non-dispersive IR instruments. The dispersive IR instruments are somewhat outdated but can be used for qualitative work as these are quite inexpensive. In contrast to the dispersive IR spectrometers, the FT instruments collect the response at all the wavelengths simultaneously. In these instruments the monochromator is replaced by an interferometer and response of the sample is suitably modulated and collected in time domain which is then decoded using the Fourier transformation. The FT spectrometers have certain advantages over dispersive instruments like it saves time and gives a better signal to noise (S/N) ratio, better frequency resolution reproducibility and a higher sensitivity, etc.

Towards the end of the unit, we discussed about the applications of IR spectrometry. Herein, we have discussed different qualitative and quantitative applications of IR spectrometry in general before taking up the interpretation of IR spectrum for structure elucidation.

13.6 TERMINAL QUESTIONS

1. Will the asymmetric stretching mode of H_2O molecule be IR active?
2. Compute the number of normal modes of vibration for benzene.
3. Draw the vibrational modes of CO_2 molecule using Fig.13.4 and comment on their IR activity.
4. What are the reasons for the complex nature of IR spectra for polyatomic molecules?
5. Briefly describe the sampling techniques for solid samples.
6. What are transducers?
7. List the essential components of an FT-IR spectrometer. What is the role of interferometer?
8. Enumerate the advantages of FT-IR spectrometer over its dispersive counterpart.

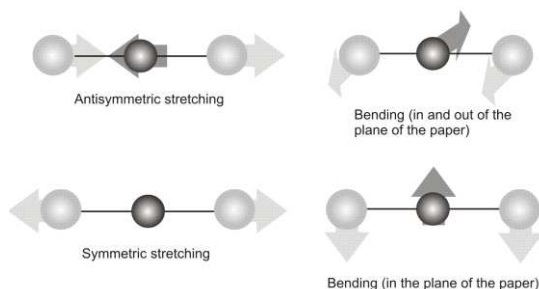
13.7 ANSWERS

Self-Assessment Questions

1. The necessary condition to observe IR spectrum for a molecule is that it must possess an oscillatory dipole moment during vibration.
2. For methane, $N=5$, As the molecule is nonlinear the total vibrational degrees of freedom would be $3N - 6 = (3 \times 5) - 6 = 9$. Similarly, the number of bending modes would be, $2N - 5 = (2 \times 5) - 5 = 5$.
3. The wavenumber unit is preferred for the IR spectrum because an increase in it corresponds to an increase in energy.
4. It is difficult to take the IR spectrum of a substance in solution because most of the solvents of the organic compounds themselves absorb in many regions of the IR spectrum and therefore interfere in the spectrum of the compound.
5. Glass or quartz cannot be used as a material for making cells for taking IR spectra because it strongly absorbs at most of the frequencies in the IR region.
6. The fingerprint region in an IR spectrum refers to all the frequencies below 1300 cm^{-1} . The signals in this region arise from molecular vibrations characteristic of the entire molecule or large fragments of the molecule. There are no two molecules with identical IR spectra, more so in the fingerprint region.
7. It can be used to check the authenticity of a compound. If the two compounds are identical then the signals in their IR spectra would match in terms of their positions and the relative intensities.
8. The region spanning from 3600 to 1200 cm^{-1} is called the functional group region. It arises from stretching vibrations of typical functional groups found in organic molecules. Assigning the bands in this region help in identifying the functional groups present in the molecule; these in turn help in deciphering the structure of the organic molecule.

Terminal Questions

1. YES, the asymmetric stretching mode of H_2O molecule will be IR active.
2. Since benzene is not a linear molecule and has twelve atoms in it, the number of vibrational modes will be $[(3 \times 12) - 5 = 31]$.
3. The vibration modes of carbon dioxide can be drawn as follows:



Out of these all the modes other than the symmetric stretching mode will be IR active.

4. The IR spectra of polyatomic molecules are complex because of several reasons. First, the infrared spectrum of a polyatomic molecule would consist of an absorption band at each of the $(3N-6)$ or $(3N-5)$ fundamental frequencies for nonlinear and linear molecules, respectively. In addition, the overtones, the combination bands, and the difference bands of these fundamental modes are also observed.
5. The sampling of the solids is done by preparing a dispersion of the solid in a liquid or a solid matrix. Accordingly, there are two methods. In the Nujol mull technique, the sample is finely ground to a paste in a small amount of mineral oil (nujol) the mull is then pressed between two NaCl/KBr plates to give a thin film of the sample. In KBr pelleting, a small amount of sample ($\sim 1-2$ mg) is mixed and ground with about hundred times its mass of potassium bromide and is transferred to an evacuable die to remove the moisture and then a high pressure is applied to yield a transparent pellet. The film or the pellet is then placed in the path of IR radiation.
6. Transducers are the specialized materials that respond to the IR radiation in terms of a temperature change or development of current or voltage.
7. The essential components of a FT-IR spectrometer are
 - Source
 - Interferometer
 - Sample assembly
 - Transducer or detector
 - Signal processing and output device

The function of the interferometer is to modulate the signal.
8. Some of the advantages of the FT-IR instruments over the dispersive instruments are as follows:
 - It is much faster because the absorption at all wavelengths is recorded at the same time and a given spectrum can be taken in less than a second.
 - These give better frequency resolution and reproducibility.
 - The energy output is much greater which leads to a higher S/N ratio.
 - FT-IR spectrometers do not need external calibration.
 - These have simple mechanical design which makes it more reliable.

UNIT 14

FLAME ATOMIC ABSORPTION SPECTROPHOTOMETRY

Structure

14.1 Introduction	Components of Flame Atomic Absorption Spectrometer
Objectives	Types of Flame Atomic Absorption Spectrophotometers
14.2 Origin and Characteristics of Atomic Spectrum	Sample Handling in Atomic Absorption Spectrophotometry
Origin of Atomic Spectrum	14.6 Interferences in Flame Atomic Absorption Spectrophotometry
Characteristics of Atomic Spectrum	14.7 Applications of Flame Atomic Absorption Spectrophotometry
14.3 Flame and its Structure	14.8 Summary
Structure of Premixed Flame	14.9 Terminal Questions
14.4 Principle of Flame Atomic Absorption Spectrophotometry	14.10 Answers
Concentration Dependence of Absorption	
14.5 Instrumentation for Flame Atomic Absorption Spectrophotometry	

14.1 INTRODUCTION

In this block you have so far learnt about electromagnetic radiation and two spectroscopic methods based on molecular spectroscopies. In the present and the next unit, 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. The absorption of the radiation by the vapourised atoms in the ground state, or emission or fluorescence emission of suitably excited state of the atoms forms the basis of different types of atomic spectroscopies. In flame atomic absorption spectrophotometry, we measure the absorption of radiation by the atomised element in the ground state. The wavelength(s) of the radiation absorbed, and the extent of the absorption form the basis of the qualitative and quantitative determinations respectively. The flame atomic

absorption method is quite rapid and precise and is applicable to about 67 elements.

We will begin the unit with an explanation of the origin of atomic spectra and their characteristics. Then we would take up the description of structure and characteristics of flames. This will be followed by the principle behind flame atomic absorption spectrophotometry as an important analytical technique. Then we will take up the instrumentation and sample handling procedures required for measurement the spectrum. Thereafter, an account of the possible interferences in atomic absorption spectrophotometry and their removal will be followed by qualitative and quantitative applications of flame atomic absorption spectrophotometry.

In the next unit you would learn about flame atomic emission spectrometry and its applications in diverse areas.

Expected Learning Outcomes

After studying this unit, you will be able to:

- ❖ explain the origin, type, and characteristics of atomic spectra;
- ❖ differentiate between the atomic and molecular spectra;
- ❖ describe the structure and characteristics of a flame;
- ❖ explain the principle of flame atomic absorption spectrophotometry;
- ❖ outline the quantitative methodology of the flame atomic absorption spectrophotometry;
- ❖ draw a schematic diagram illustrating different components of a flame atomic absorption spectrophotometer,
- ❖ describe the functioning of pneumatic nebuliser used in atomic spectrophotometry,
- ❖ outline the importance of sample handling in flame atomic absorption spectrophotometry,
- ❖ discuss the interferences observed in flame atomic absorption spectrophotometric determinations, and
- ❖ state the merits and limitations of the flame atomic absorption spectrophotometric technique.

14.2 ORIGIN AND CHARACTERISTICS OF ATOMIC SPECTRA

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. In mid 19th Century Bunsen and Kirchhoff 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. It was also demonstrated that the intensities of the emitted radiation, was dependent on the amounts of elemental species present. Therefore, the wavelength and the intensity of the emitted radiation can be used for the identification and quantification of the elements in a sample.

Similarly, it was also shown that cold vapours (atoms in their ground state) of an element absorb characteristic wavelength of radiation. This led to the establishment of atomic spectroscopy as an instrumental method of elemental analysis. Let us understand the origin of atomic spectrum in terms of the transitions amongst different atomic energy levels.

14.2.1 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, an 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 of the levels in the form of a radiation of appropriate wavelength. A spread of the wavelengths of the radiation absorbed or emitted by an atom versus their intensities is called an **atomic spectrum**.

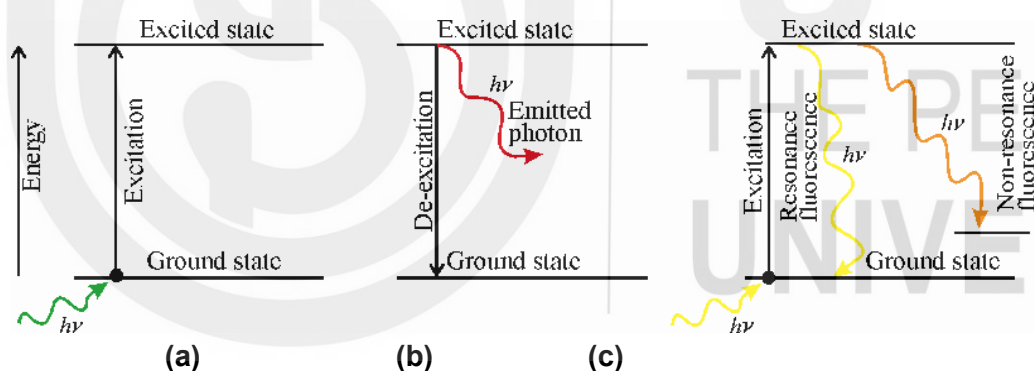


Fig. 14.1: Schematic representation of the transitions in atomic (a) absorption, (b) emission and (c) fluorescence emission spectroscopy.

You would recall from Unit 11 that the interaction of radiation and matter can manifest itself in terms of absorption, emission, or fluorescence emission. Accordingly, we have three different atomic spectroscopic methods viz., atomic absorption, atomic emission, and atomic fluorescence respectively. A schematic representation of the transitions associated with the phenomenon of atomic absorption, atomic emission and atomic fluorescence emission is given in Fig. 14.1. 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. A part of the radiation is absorbed, and the intensity of the radiation decreases. 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 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 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.

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.

14.2.2 Characteristics of Atomic Spectrum

You have learnt in detail about two molecular spectroscopic methods in the previous two units 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.

Yes, you are right. In molecular systems the rotational and vibrational motions are also quantised besides the electronic energies whereas, in case of atomic systems only electronic energies are quantised.

You would recall from the previous two units that the molecular spectra are generally broad. These consist of several closely spaced lines constituting what is called a **band spectrum**. In contrast, the atomic spectrum consists of very sharp lines, characteristic of the atomic species. That is, the atomic spectra are **line spectra**. A typical atomic spectrum is shown in Fig.14.2.

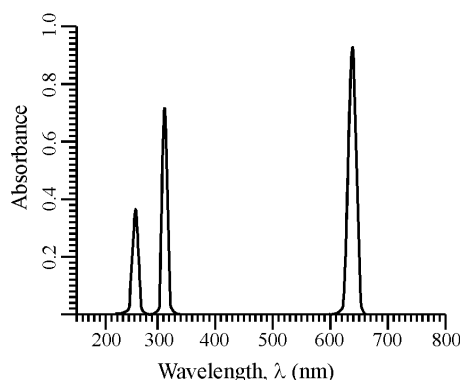


Fig. 14.2: Representation of a typical atomic spectrum.

The signals in an atomic spectrum are characterised in terms of three parameters viz.,

- position of the signal
- intensity of the signal
- line width

Let us learn about these parameters.

Position of the Signal

The position of the signal is determined by the difference in the energies of the energy levels involved in the transition. If E_2 and E_1 represent the energy of the higher and lower energy levels involved in the transition, the energy change during the transition from E_1 to E_2 level will be

$$\Delta E = (E_2 - E_1) = h\nu = hc/\lambda \quad \dots (14.1)$$

or
$$\lambda = hc/(E_2 - E_1) = \frac{hc}{\Delta E} \quad \dots (14.2)$$

where, h is the Planck's constant, c is the velocity of light, ν the frequency and λ the wavelength of the radiation.

Intensity of the Signal

The intensity of a signal depends on the population of the energy level from which the transition is originating. 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. The population of any excited state relative to that of the ground state is given by the following formula.

$$\frac{N^*}{N_0} = e^{-\frac{\Delta E}{kT}} \text{ or } N^* = N_0 e^{-\frac{\Delta E}{kT}} \quad \dots (14.3)$$

where,

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

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

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

T = Absolute temperature.

According to Eq. 14.3, after the ground state, the lowest energy excited state will be most populated, and the population of the higher excited states would decrease progressively. In addition to the population of energy levels, the intensity of a signal also depends on the concentration of the sample. 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.

Line Width

The atomic spectral lines are generally symmetric around $\lambda_{\max}$, i.e., the wavelength at which the intensity of radiation is maximum. The line width is

defined as the width of the signal measured at one half the height of the signal at $\lambda_{\max}$. It is expressed as $\Delta\lambda_{1/2}$ and is measured in the units of wavelength. The line width for a transition between two discrete energy levels is expected to be zero. The observed line width of the atomic spectral lines is due to the factors that depend on the nature of species and the instrument used. The detail of these factors is beyond the scope of this course.

Having learnt about the origin and characteristics of the atomic spectrum, let us now talk about the flame and its structure. However, before that answer the following simple question to assess your understanding.

SAQ 1

List different characteristics of an atomic spectral line.

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.

14.3 FLAME AND ITS STRUCTURE

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 by a flame, furnace, plasma, or electric arc. In this course we are going to discuss atomic spectroscopic methods using flame as a source of energy for atomisation of the element being analysed. Let us learn about flames and their characteristics.

A flame can be described as a gas phase reaction which takes place with the emission of light. It is produced by burning a mixture of fuel and air (or an oxidant) in a burner. In flame based spectroscopic methods 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 14.1 lists some common fuels and oxidants along with range of temperature attainable by using them.

Table 14.1: Fuel-oxidant mixtures and the attainable temperature

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

There are two types of flames commonly used in atomic spectroscopy. In one of these, the fuel and oxidant as air (or oxygen) are well mixed before combustion, these are called **premix** or **laminar flames** as they exhibit laminar flow. On the other hand, in second type of flame the fuel gas and the

oxidant are mixed in the flame itself. They are called **unpremix** or **turbulent flames** since they exhibit turbulence. We would take up the premix or laminar flame here.

14.4.1 Structure of Premixed Flame

Flames are not uniform in composition, length, or cross section. A schematic structure of a premixed or laminar flame is given in Fig. 14.3.

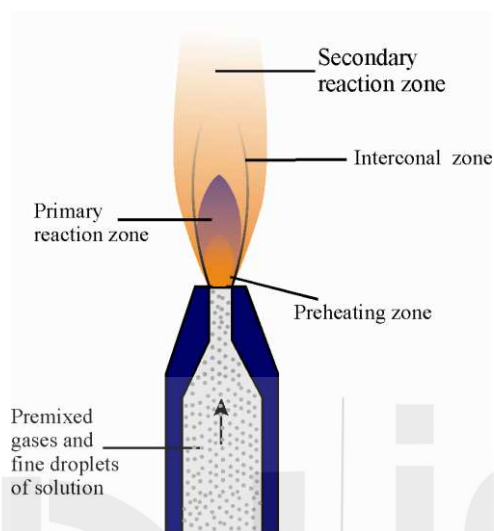


Fig. 14.3: Schematic structure of a laminar flow flame showing various zones .

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

- i) Preheating zone
- ii) Primary reaction zone or inner zone
- iii) Interconal zone
- iv) Secondary reaction zone

The first or the innermost region of the flame is the preheating zone where the fuel-oxidant 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. This region is not used for flame photometry. The maximum temperature is achieved just above the tip of the inner zone. The higher temperature favours the production of free atoms, and it is this zone that is used for flame based atomic spectroscopic methods.

Immediately above the primary reaction zone lies the third or **interconal zone** which can extend up to considerable height. The outermost fourth zone is the secondary reaction zone. In this zone, the products of the combustion processes are burnt to stable molecular species by the surrounding air. A laminar flame makes a strong hissing noise which gets louder when a liquid is atomised into it.

The shape of an unmixed flame is generally different. The inner zone can still be recognised, but it is very vague and is thickened. We will not discuss the unmixed flame here. Let us now learn about the principle of flame atomic

absorption spectrophotometry. However, before that answer the following simple question. Having learnt about the origin and characteristics of the atomic spectrum, let us now talk about the flame and its structure. However, before that answer the following simple question to assess your understanding.

SAQ 2

List different zones of a laminar flow flame. Which of these zones is used in flame based atomic spectroscopic methods?

14.4 PRINCIPLE OF FLAME ATOMIC ABSORPTION SPECTROPHOTOMETRY

It may be noted that as only ground state atoms are involved in this process. Therefore, the ionisation occurring due to high temperature of the flame needs to be kept to a minimum.

The concept of atomic absorption spectrometry (AAS) was proposed by two groups in 1955, A. Walsh of Australia and C T J Alkemade and J M W Milatz from the Netherlands. You have learnt that in atomic spectroscopy, the analyte must be present in the atomic vapour state. In flame atomic absorption spectrophotometry, the atomisation is performed by aspirating the sample solution into a flame where the analyte element is converted into gaseous phase atoms.

As the temperature of atomisation is low; most of the atoms remain in the ground state which can absorb characteristic radiation from the radiation source made from the analyte element. One such source is halogen cathode lamp (HCL) in which the cathode is made of the element that needs to be determined and gives radiations characteristic of the element. You would learn about HCL in Section 14. The radiation is absorbed by the atomic vapours and its intensity decreases. The degree of absorption is a quantitative measure of the concentration of ground state atoms in the vapours. The analysis is done by comparing the observed absorption with the one obtained by suitable standard samples of the analyte under similar experimental conditions, i.e., a calibration curve method is generally employed. For this we need to understand the concentration dependence of the absorption.

In AAS the absorption of resonant radiation by ground state atoms of the analyte is used as the analytical signal.

14.4.1 Concentration Dependence of Absorption

The absorption follows Lambert-Beer's law according to which the extent of radiation absorbed by the absorbing species is a function of the path length and the concentration of the absorbing species. You have learnt about this law in Unit 12.

$$\text{Mathematically, } \log \frac{P_0}{P} = \epsilon bc \quad \dots (14.4)$$

where,

P_0 = radiant power of incident light,

P = radiant power of transmitted light,

b = thickness of the absorbing medium,

ϵ = absorption coefficient, and

c = concentration of absorbing analyte atoms.

Typical absorbance must be in the range 0.1 to 0.3 or else precision is poorer at the extremes due to instrumental noise.

The term, $\log P_0/P$ is called **absorbance** and is represented as 'A'. Therefore, we can write it as follows.

$$\log \frac{P_0}{P} = A = \epsilon bc \quad \dots (14.5)$$

Thus, absorbance of the sample is directly proportional to the concentration of the analyte. The routine analytical methodology for quantitative determinations using AAS is based on calibration method. Let us learn about the calibration plot method.

Calibration plot method

In this method, a series of solutions of different known concentrations prepared by diluting a standard solution are aspirated into the flame and absorbance for each solution is measured. Then a graph is plotted between absorbance and concentration, Fig.14.4. 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 absorbances of the standard and unknown solutions under conditions that are as nearly identical as possible. Even though Beer's law is followed, in practice the departures from linearity are encountered.

The nonlinearity is due to the transmission of unabsorbed light from the radiation source. In addition, several uncontrolled variables in atomisation and absorbance measurements may also affect the measurements. Therefore, we need to find the concentration range in which the Lambert-Beer's law holds i.e., we get a straight-line the concentration versus absorbance plot. If the analyte concentration happens to be outside the limits of the standards used for calibration, then the analyte sample should be suitably diluted or concentrated.

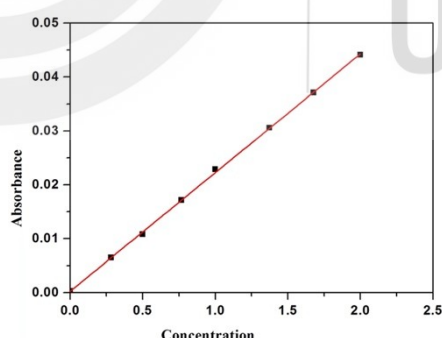


Fig. 14.4: Calibration plot: Absorption intensity versus Concentration of the sample solution.

As the test solution is often a complex whose all constituents are not known, it becomes almost impossible to prepare standard solutions having a similar composition to the analyte sample to obtain a calibration plot. In such cases we use internal standard method or the standard addition method. These methods are beyond the scope of this course.

Let us now learn about the instrumental aspects of flame atomic absorption spectrometry. However, before that answer the following simple question to assess your understanding.

SAQ 3

What is the importance of calibration plot in flame atomic absorption spectrophotometry?

14.5 INSTRUMENTATION FOR FLAME ATOMIC ABSORPTION SPECTROPHOTOMETRY

You have learnt above that in AAS the absorption of radiation by ground state atoms of the analyte is used as the analytical signal. Accordingly, a source delivering the characteristic radiation of the analyte is required along with an atom reservoir into which the analyte is introduced and atomised. The basic requirements of atomic absorption spectrophotometer instrument are like any regular spectrophotometer; the sample holder cell being replaced by a flame. Let us learn about the different components used in flame atomic absorption spectrophotometer.

14.6.1 Components of Flame Atomic Absorption Spectrophotometer

A typical flame atomic absorption spectrophotometer consists of the following components.

- A. Radiation source
- B. Atom reservoir (flame)
- C. Monochromator
- D. Detector
- E. Readout device

A block diagram showing the basic components of a flame atomic absorption spectrophotometer is given in Fig. 14.5. In a typical flame atomic absorption spectrophotometric determination, the radiation from a hollow cathode lamp is made to fall on the sample of the analyte aspirated into the flame, where a part of it is absorbed. The transmitted radiation is then dispersed by a monochromator and sent to the detector. The detector output is then suitably processed and is displayed by appropriate readout device.

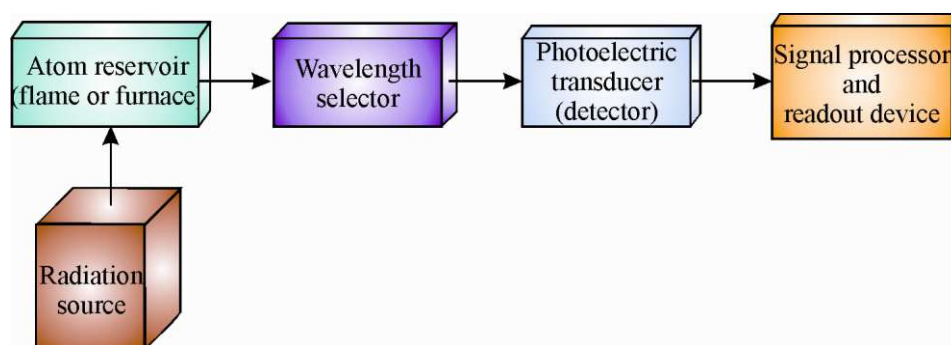


Fig. 14.5: Schematic diagram of an atomic absorption spectrophotometer showing its basic components

Such single channel instruments can perform measurements at a single wavelength. Nowadays, dual-channel instruments are also available that permit simultaneous measurements at two different wavelengths. These contain two independent monochromators for the purpose. Thus, these can be used for the simultaneous determination of two elements; one can be the analyte to be determined and the other may be a reference element. Let us learn about the components of a flame atomic absorption spectrophotometer.

A. Radiation Sources

All commercially available flame atomic absorption spectrophotometers use a radiation source that emits the characteristic spectrum of the element to be determined. The essential requirement of the radiation source is that it gives a constant and intense output. Generally, the hollow-cathode lamp (HCL), is widely used as the radiation source. The electrodeless discharge lamps (EDL) - another line source are also frequently employed for the purpose and in fact are superior for the elements such as As, Se and Te with low melting points. Let us learn about HCL and EDL.

Hollow cathode lamp (HCL): It consists of a sealed cylindrical glass tube with a quartz window at one end and a hollowed cylindrical cathode along with an anode wire made of tungsten. The cathode is fabricated from the analyte element and the lamp is filled with an inert gas such as argon or neon under vacuum (100-200 Pa). A schematic diagram of a hollow-cathode lamp is shown in Fig. 14.6. When a voltage of ~300 V corresponding to 5-50 mA current is applied between the two electrodes, a low-pressure glow discharge confined to the inside of the cathode material is produced.

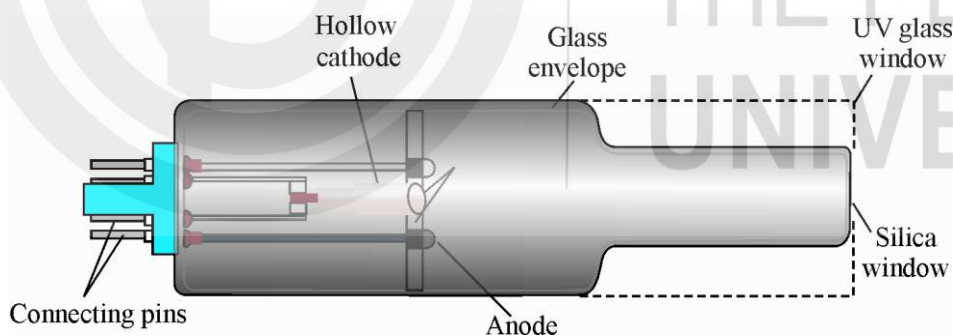


Fig. 14.6: Schematic diagram of hollow cathode lamp illustrating different components.

Basic function of the gas in the tube is to bombard the cathode and vapourise the atoms from the cathode surface. For this the gaseous cations are accelerated towards the cathode. The collision energy is sufficient to cause some atoms of the cathode to be transformed into gaseous atoms in a process called **sputtering**. These metal atoms are then excited by collisions with electrons and ions thus emitting characteristic emission lines.

The emission spectrum of the cathode material includes several intense, sharp lines due to transitions between excited states and the ground state, often called resonance lines. Intensity of resonance lines from an HCL increases with increasing current. As of now, HCL for over 60 elements are available.

Electrodeless discharge lamp (EDL): It contains a few milligrams of a volatile element or a volatile compound such as halide, along with neon or argon, under vacuum in a quartz tube. On the application of voltage, a discharge is produced, and the gaseous atoms are excited by application of microwave field or radio frequency of typical frequency. As the excited atoms decay to the ground state or to other low energy levels, characteristic radiation of the atom is emitted. The radiations emitted by EDLs are about 10-100 times more intense than for the corresponding HCL. The electrodeless discharge lamps are available for many elements. However, their performance is not as reliable as of the halogen cathode lamps.

B. Atomisers

The purpose of atomiser is to provide a small portion of the sample in the optical path and convert it into free neutral ground state atoms. In flame atomic absorption spectrophotometry, the flames are commonly used for atomisation. Let us learn about flame atomisers.

Flame atomiser

The flame atomiser assembly consists of two components viz., a nebuliser and a burner. In a typical flame atomisation process, the sample solutions are generally nebulised with the help of a nebuliser in which the sample in the form of a solution is drawn in and is converted into a fine mist or an aerosol. The aerosol so produced along with a mixture of a burning gas and an oxidant is directed into the second component i.e., a burner. You have learnt above that the flame temperature depends on fuel-oxidant ratio. The temperature required for analysis is obtained by varying the fuel-oxidant ratio. Let us first learn about the nebulisers.

Nebuliser is a device used for sample introduction into the flame. It consists of thermal vapourisation and dissociation of aerosol particles at high temperatures producing small particle size. Several nebulisation methods are available. A few are listed below.

- Pneumatic nebulisation
- Ultrasonic nebulisation
- Electrothermal vapourisation
- Hydride generation

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

However, we would discuss about the pneumatic nebuliser only. A common type of pneumatic nebuliser is called **concentric pneumatic nebuliser**. It consists of a fine capillary surrounded by concentric tube with a small opening near one end of the capillary. The capillary is dipped into the sample solution while the outer tube is connected to a high-pressure gas supply. The sample solution 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.

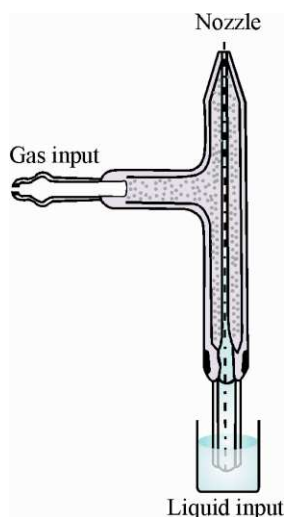


Fig. 14.7: Concentric type pneumatic nebulizer.

Burners

Two major types of nebuliser burners used in atomic absorption spectrophotometer are premix nebuliser-burner system and total consumption burner. However, in flame atomic absorption spectrophotometer the premix burner is generally used. Let us learn about it.

Premix burner

In a 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 mixture of aerosol, fuel gas and oxidant burn to yield stable noiseless flame. A schematic diagram of premix nebuliser burner system is given in Fig.14.8.

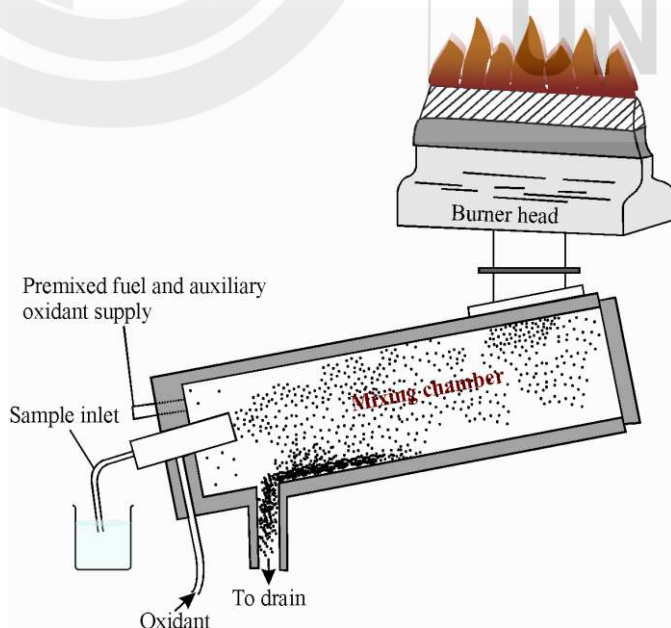


Fig. 14.8: Schematic diagram of premix nebuliser burner system used in AAS

Premix burners are called Bunsen, Méker, or slot burners depending on whether they have one large hole, several 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 advantage with the premix burner is that it is quiet to operate, and the analytical signal is significantly less noisy. However, it also has certain disadvantages like; low sensitivity in the determination of a given analyte.

Flame atomisation is a simple method; however, it has the following disadvantages.

- i) Only about 10% of the nebulised sample reaches the flame and it is then further diluted by the fuel and oxidant gases so that test material has very small concentration in the flame.
- ii) A minimum sample volume of 0.5-1.0 mL is needed to give a reliable measurement.
- iii) Viscous samples such as blood, serum, oils etc require dilution with a solvent.

To avoid such problems, nonflame methods involving electrical heating have been developed which are beyond the scope of this course.

C. Monochromators

You know that monochromators are the devices that can selectively provide radiation of a desired wavelength out of the range of wavelengths emitted by the source. In flame atomic absorption instruments, the monochromators select a given emission line and isolate it from other lines due to molecular band emissions and all non-absorbed lines. Some of these lines originate from the filler gas in the hollow cathode lamp while some others are the spectral emissions of various sample components during atomisation. Most commercial flame atomic absorption instruments use diffraction gratings as monochromators.

D. Detectors

As the wavelengths of resonance lines fall in UV region, the commonly used detector in flame atomic absorption spectrophotometry is a photomultiplier (PM) tube whose output is fed to a readout system. The radiation received by the detector may originate not only from the selected resonance lines but also from the emission within the flame. Therefore, in addition to absorption signal intensity I_A , the detector may receive signal intensity of $(I_A + S)$ where S is the intensity of emitted radiation from flame. Since, we need the signal intensity due to absorption only, therefore, the effects due to flame emission need to be eliminated. This is achieved by using a mechanical chopper device.

E. Readout Devices

The readout systems include meters, chart recorders and digital display meters. These days, however, microprocessor-controlled systems are commercially available where everything can be done by the touch of a button. Modern instruments provide a fast display of the experimental conditions, absorbance data, statistical values, and calibration curves, etc.

14.6.2 Types of Flame Atomic Absorption Spectrophotometers

Having learnt about the essential components of an atomic absorption spectrophotometer let us now learn about the different types of atomic

absorption spectrophotometers. You would recall the spectrophotometers used in UV-VIS spectrophotometry. It is important to mention here that the atomic and molecular absorption spectrophotometers are quite similar; the radiation source and the sample holder being different. Let us learn about the two types of atomic absorption spectrophotometers given below.

- Single beam atomic absorption spectrophotometer
- Double beam atomic absorption spectrophotometer

Single Beam Atomic Absorption Spectrophotometer

A simplified sketch of a single beam flame atomic absorption spectrophotometer is shown in Fig.14.9. It consists of hollow cathode lamp (HCL), a radiation source, flame as an atomisation device, a monochromator, a photomultiplier detector, and a recording system. The HCL radiation is chopped to eliminate the background signal arising from the radiation emitted by the sample itself, focused on the atomic vapour produced by the atomiser and then directed to the monochromator where the atomic line of interest is isolated.

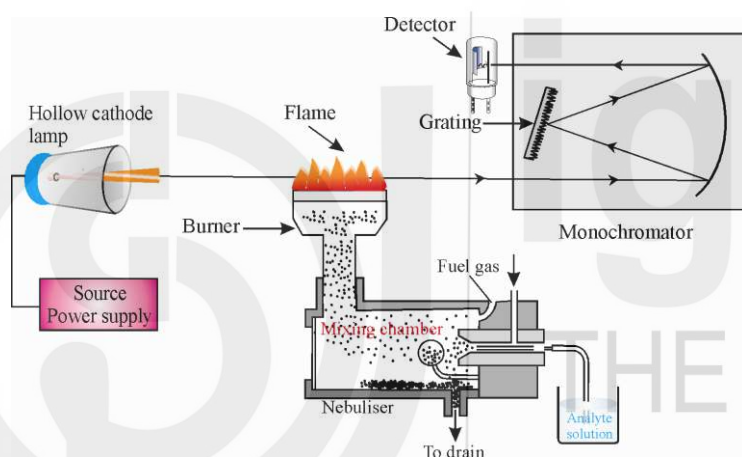


Fig.14.9: Schematic diagram of a single beam flame atomic absorption spectrophotometer.

Double Beam Flame Atomic Absorption Spectrophotometer

In this type of instrument, the beam from the HCL is split into two parts by a mirrored chopper, one half passing through the atomiser and the other half around it, as schematically shown in Fig.14.10.

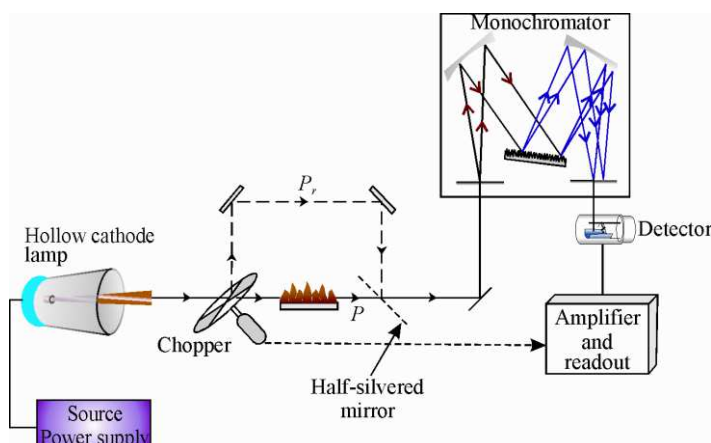


Fig.14.10: Schematic diagram of a double beam atomic absorption spectrophotometer.

The two beams are then recombined by a half-silvered mirror and passed through the monochromator. The ratio between the reference and sample signal is then amplified and fed to the readout display and recorder. It must be noted that reference beam in double beam instruments does not pass through the flame and thus corrects for the loss of radiant power due to absorption or scattering by the flame itself.

14.6.3 Sample Handling in Flame Atomic Absorption Spectrophotometry

Sample preparation is a crucial step in the AAS determination.

In principle, the sample in solid, liquid or in the gas phase can be analysed by flame AAS. However, in most cases, sample analysed is in the solution form. Therefore, the solid sample is first dissolved and converted into a solution. The gaseous samples, on the other hand, generally are pretreated by scrubbing to get the solution. Effectively, there are two steps i.e.,

- A. Preparation of the sample
- B. Sample Introduction

Let us learn how the dissolution of the solid sample, and its introduction into the flame is carried out.

A. Preparation of the Sample

The choice of proper reagents and techniques of decomposition and dissolution of the sample is a critical step for the success of the determination. This is often done by acid digestion, which produces a clear solution without loss of any of the elements to be determined. It is, therefore, essential that all the reagents and solvents used in wet decomposition should be of highest purity as any impurity may raise the blank value. Common acids used for dissolution are HCl, HNO₃, aqua regia (HCl: HNO₃: 3:1) or perchloric acid (HClO₄) which dissolve most of the inorganic materials.

In a typical dissolution step, a suspension of the sample in acid is heated by flame or a hot plate until complete dissolution i.e., when the entire solid has disappeared and a transparent solution is obtained. The decomposition temperature is the boiling point of acid. However, such a wet decomposition in open vessels may give rise to systematic errors due to volatilisation losses and contamination caused by the reagents and container material, and loss of elements caused by adsorption on the vessel surface. More so, sometimes the dissolution may not be complete, and it may also cause errors. To avoid such errors, wet decomposition methods in closed systems have been developed. These have the following advantages.

- There are no volatilisation losses.
- These have a shorter reaction time and improved decomposition due to high temperatures.
- The blank values are low.
- These do not have contamination from external sources.

If the concentration of the elements to be determined is too high, then the solution must be diluted quantitatively before commencing the absorbance

measurements. Conversely, if the concentration of the metal in the test solution is too low, a concentration procedure such as solvent extraction or ion-exchange must be followed.

B. Sample Introduction Methods

The sample introduction into the flame is an important step in flame AAS measurements as its accuracy, precision and detection limits depend on how the analyte sample is introduced. The aim of a sample introduction system is to transfer a reproducible and representative portion of a sample into an atomiser. It depends on the physical and chemical state (i.e., solid, liquid or gas) of the analyte and the sample matrix such as soil, water, blood, plant leaves, etc. For solution and gaseous samples, the introduction step is quite simple but for solid, it poses a major problem.

Having learnt about the instrumental aspects and sample handling in flame atomic absorption spectrophotometry, let us now take up the interferences in this analytical method. However, before that answer the following simple questions to assess your understanding.

SAQ 4

Name the line sources employed in flame atomic absorption spectrophotometry.

SAQ 5

In what way is a double beam atomic absorption spectrophotometer better than a single beam spectrophotometer?

14.6 INTERFERENCES IN FLAME ATOMIC ABSORPTION SPECTROPHOTOMETRY

All spectrometric methods have associated interferences that need to be addressed to put the technique to analytical use. We may define an interference to be a chemical, physical, or spectral effect that may cause the analyte signal to be altered in intensity. Accordingly, there are three types of interferences; these are spectral, chemical, and physical interferences. Let us learn about these.

14.6.1 Spectral Interferences

These refer to the presence of another atomic absorption line or a molecular absorption band close to the spectral line of the analyte element being monitored. Most probable spectral interferences are the ones of the molecular emissions from oxides of other elements in the sample. Another source of spectral interference is the light scattering or absorption by solid particles,

unvaporised solvent droplets or molecular species in the flame. This problem is significant at wavelengths less than 300 nm when solutions of high salt content are aspirated. This can be corrected by measuring the absorbance of a line close to the absorption line of the analyte element but not absorbed by the element itself. A yet another source of spectral interference is the background emission from the flame. This may be corrected by modulation of the output of the radiation source and the ac detection system.

14.6.2 Chemical Interferences

These include interferences due to ionisation, formation of low volatility compounds, dissociation, etc. During atomization in the flame, several reactions occur resulting in the formation of analyte compounds which decrease atomic population in the cell. Most important chemical interference is due to anions and formation of compounds of low volatility from the analyte element. For example, the absorbance due to Ca is decreased in presence of phosphate because of the formation of calcium phosphate having low volatility.

Such interferences can be avoided by increasing the flame temperature in which these interfering compounds are decomposed. In some cases, chemical interferences may be eliminated by using a releasing agent that reacts with interfering species and avoids its reaction with the analyte element. For example, in the determination of Ca; Sr and La can be used as releasing agents to minimise phosphate interference as these would react preferentially with the phosphate.

14.6.3 Physical Interferences

These are independent of the analyte type and may be due to variations in the gas flow rates, changes in the solution viscosity affecting its rate of aspiration into the flame which may finally change the atomic concentration in the flame. Errors due to changes in viscosity may be avoided by performing frequent calibrations.

SAQ 6

- How does phosphate interfere in the quantitative determination of calcium by atomic absorption spectrophotometry?
 - How is this interference removed?
-

14.7 APPLICATIONS OF FLAME ATOMIC ABSORPTION SPECTROPHOTOMETRY

FAAS is a promising analytical method that is extensively employed for quantitative determinations of different elements in wide range of samples.

Atomic absorption spectrophotometry (AAS) is now a routinely and widely employed technique for trace and ultra-trace analysis of complex matrices of geological, biological, environmental, industrial, glass, cement, marine

sediment, pharmaceutical or any other kind of samples. It has been employed for the determination of more than 60 elements at trace and ultra-trace levels. It is frequently used for the cases where the sample size is small e.g., in case of metalloproteins.

The data in Table 14.3 gives only representative detection limits which may vary with the analyte matrix, nebulisation conditions, flame temperature, sample path length, positioning of burner and other factors including interferences. You would learn in detail about the applications of atomic absorption spectrometry in Unit 11 along with that of atomic emission spectrometry.

As FAAS is a sensitive technique, all possible sources of contamination such as due to storage containers, impurities in reagents, and solvents and incomplete removal of earlier sample from the nebuliser system should be avoided.

Table 14.3: The resonance lines and approximate detection limits of some selected elements by Air-acetylene flame AAS.

Element	Resonance line (nm)	Detection limit
Ag	328.1	0.9
Ba	553.6	8
Ca	422.7	2
Cd	228.8	5
Cr	357.9	5
Cu	324.5	4
Fe	248.3	4
Hg	253.7	200
K	766.5	4
Mg	285.2	3
Mn	279.5	1
Na	589.0	0.2

Merits and Limitations of Flame Atomic Absorption Spectrophotometry

Some of the merits of atomic absorption spectrometry are as given below.

- The equipment is easy to use
- It is a robust technique
- The technique has a small turnaround time; of the order of few seconds
- Moderate cost of analysis per sample
- Low detection limits

Some limitations of AA spectrophotometry are given below.

- Requirement of furnace for the analysis of refractory elements
- Use of flammable gases
- Non-automated analytical procedure

Let us summarise what we have learnt in this unit.

14.8 SUMMARY

Flame atomic absorption spectrophotometry (FAAS) concerns the absorption of radiation by the atomised analyte element in the ground state. The atomisation is achieved by the thermal energy of the flame. The wavelength(s) of the radiation absorbed, and the extent of the absorption form the basis of the qualitative and quantitative determinations respectively. As it is not an absolute method of analysis, the routine analytical methodology for quantitative determinations using AAS is based on calibration method. Besides this the internal standard method and standard addition methods are also employed.

A typical flame atomic absorption spectrophotometer consists of a source delivering the characteristic resonant radiation of the analyte, an atom reservoir into which the analyte is introduced and atomised, a monochromator, a detector and a readout device. In a typical flame atomic absorption spectrophotometric determination, the radiation from a hollow cathode lamp is made to fall on the sample of the analyte aspirated into the flame, where a part of it is absorbed. The transmitted radiation is then dispersed by a monochromator and sent to the detector. The detector output is suitably processed and is displayed by appropriate readout device. Like, UV-VIS spectrophotometers the atomic absorption spectrophotometers are also of two types viz., single beam atomic absorption spectrophotometers and double beam atomic absorption spectrophotometers.

Three types of interferences viz., spectral, chemical and physical interferences are encountered in FAAS. These need to be suitably addressed to put the technique to analytical use. Sample preparation is a crucial step in the AAS determination. Though in principle, the sample in solid, liquid or in the gas phase can be analysed by flame AAS but in practice the sample is taken in the solution form. The solution of the solids is generally prepared by wet dissolution method using a suitable acid.

The accuracy, precision and detection limits of flame AAS depend on how the analyte sample is introduced into the atomiser. We need to transfer a reproducible and representative portion of a sample into an atomiser which depends on the physical and chemical state of the analyte and the sample matrix. The sample introduction is achieved with the help of a nebuliser. The commonly used nebulisation methods are pneumatic nebulisation.

Flame atomic absorption spectrophotometry (FAAS) is now a routinely and widely employed technique for trace and ultra-trace analysis of complex matrices of geological, biological, environmental, pharmaceutical, and other kind of samples. The atomic absorption methods using flame are rapid and precise and are applicable to about 67 elements.

14.9 TERMINAL QUESTIONS

1. Explain the origin of flame atomic absorption spectrum. What information can be obtained from the spectrum?
2. Give a description about the commonly used flame in flame spectrometry.

3. List the main parts of FAAS instrument and give the function of each one of them.
4. Describe hollow cathode lamp and explain the principle of its working.
5. Describe the calibration method used in FAAS.

14.10 ANSWERS

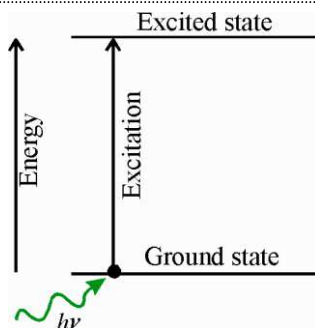
Self Assessment Questions

1. The characteristics of an atomic spectral line are as under
 - position of the signal
 - intensity of the signal
 - line width
2. The laminar flow flame has the following four zones:
 - a) Preheating zone
 - b) Primary reaction zone or inner zone
 - c) Interconal zone
 - d) Secondary reaction zone

Of these, the tip of the inner zone is used in flame based atomic spectroscopic methods
3. The calibration plot method provides a simple method to determine the concentration of the analyte in flame atomic absorption spectrophotometry.
4. The atomic absorption spectrophotometers generally use line sources. Two commonly used line sources are hollow-cathode lamp (HCL) and electrodeless discharge lamps (EDL).
5. Double beam atomic absorption spectrophotometers are better than a single beam spectrophotometer because these correct the fluctuations in the intensity of radiation coming from the radiation source and for changes in the sensitivity of the detector.
6.
 - a) Phosphate interferes in the quantitative determination of calcium as it forms calcium phosphate having low volatility which decreases atomic population in the cell.
 - b) The interference of phosphate in the determination of Ca can be removed by using a releasing agent like Sr or La. These act by reacting preferentially with the phosphate.

Terminal Questions

1. The flame atomic absorption spectrum is obtained by the absorption of UV-VIS radiation by the atomic vapours containing free atoms of an element in the ground state. The absorbed radiation causes excitation of electrons from the ground state to an excited state.



The wavelength of the absorbed radiation provides the information about the element and the intensity of the signal gives the quantitative measure of the concentration of the element.

2. In flame spectrometry premix or laminar flame is commonly used. Such a flame may be divided into four zones. The first or the innermost region of the flame is the preheating zone where the fuel-oxidant mixture is heated to its ignition temperature by thermal conduction from the primary reaction zone. The second zone or inner zone is about 0.1 mm thick and is visible due to its blue green light. This region is not used for flame photometry. The maximum temperature is achieved just above the tip of this zone and is used for flame based atomic spectroscopic methods.

Immediately above the inner zone lies the third or **interconal zone** which can extend up to considerable height. The outermost fourth zone is the secondary reaction zone in which the products of the fuel combustion are burnt to stable molecular species by the surrounding air.

3. The components of a typical flame atomic absorption spectrophotometer and their functions are as under.
 - A. Radiation source: it provides the characteristic spectrum of the element to be determined.
 - B. Atom reservoir (flame): it converts a small portion of the sample into free neutral ground state atoms.
 - C. Monochromator: it selects a given emission line from the emissions of the radiation source.
 - D. Detector: it detects and amplifies the unabsorbed radiation and converts into an electrical signal.
 - E. Readout device: it provides the spectral output on the basis of inputs from the detector.
4. It consists of a sealed cylindrical glass tube with a quartz window at one end and a hollowed cylindrical cathode along with an anode wire made of tungsten. The cathode is made of the element to be analysed and the lamp is filled with an inert gas under vacuum.

When a voltage of ~300 V is applied between the two electrodes, a low-pressure glow discharge is produced that is confined to the inside of the cathode material. The gaseous cations accelerate towards the cathode and bombard it to vapourise the atoms its surface. These metal atoms

are excited by collisions with electrons and ions and emit characteristic emission lines.

5. In this method, a series of solutions of different known concentrations of the analyte are aspirated into the flame and absorbance for each solution is measured. Then a calibration plot is prepared between the absorbance and concentration. The concentration of the element in the unknown sample can then be found out from this calibration plot.



FLAME ATOMIC EMISSION SPECTROMETRY (FLAME PHOTOMETRY)

Structure

15.1	Introduction	Qualitative Applications
	Objectives	Quantitative Applications
15.2	Principle of Flame Atomic Emission Spectrometry (FAES)	Methodology of Quantitative Analysis
	Fate of the Sample in the Flame	15.5 Interferences in Quantitative Determinations
15.3	Instrumentation for Flame Atomic Emission Spectrometry	Spectral Interferences
	Flame Atomiser	Ionisation Interferences
	Atomiser Burners	Chemical Interferences
	Monochromator	15.6 Merits and Limitations of Flame Photometry
	Detector	15.7 Summary
	Amplifier and Readout Device	15.8 Terminal Questions
15.4	Applications of Flame Atomic Emission Spectrometry	15.9 Answers

15.1 INTRODUCTION

In Unit 14, you have learnt in detail about the principles, instrumentation, and applications of flame atomic absorption spectrophotometry (FAAS). You would recall that in FAAS the atomic vapours in the ground state absorb the characteristic radiation of the element and the absorbed radiation and its intensity form the basis for the qualitative and quantitative applications. In contrast to this, in the current unit we take up atomic emission spectrometry (AES) that concerns the emission of radiation by the suitably excited atomic vapours of the analyte. Here, the emitted radiation and its intensity form the basis for the qualitative and quantitative applications of the technique.

As in AAS, atomic emission spectroscopy also requires some means for converting the analyte in solid, liquid, or solution form into a free gaseous atom. Generally, flames or plasmas, are used for this purpose in liquid or solution samples. These energy sources also act the excitation source. However, the solid samples are analyzed by dissolving them in a solvent and using a flame or plasma atomizer. When flame is used as atomisation-excitation source, the technique is called Flame Atomic Emission Spectroscopy (FAES) whereas when we use an inductively couple plasma (ICP) as an atomisation- excitation source; the technique is called ICP-AES.

In this unit we will take up FAES which is also called Flame Photometry. We would begin with by explaining the principle of FAES. In this context we would explain the fate of the sample aspirated into the flame. This will be followed by the instrumental aspects of flame photometry. Thereafter, we would take up the analytical methodology for qualitative and quantitative applications of AES. Having discussed these methodologies, we would discuss about the possible interferences in these determinations and their removal in atomic emission spectrometry. In the end we will take up the merits and limitations of flame atomic emission spectrometry.

Expected Learning Outcomes

After studying this unit, you will be able to:

- ❖ explain the principle of atomic emission spectrometry;
- ❖ enlist various excitation sources for atomic emission spectrometry;
- ❖ explain the principle of flame photometry;
- ❖ explain the fate of the analyte sample introduced into the flame;
- ❖ draw a schematic diagram illustrating different components of a flame photometer;
- ❖ enlist the applications of flame photometry;
- ❖ discuss the factors affecting flame photometric determinations;
- ❖ outline the interferences observed in flame atomic emission spectrometry; and
- ❖ state the merits and limitations of the flame photometric technique.

15.2 PRINCIPLE OF FLAME PHOTOMETRY

Flame Atomic Emission Spectrometry (Flame photometry) is a method used for the determination of elements which can be easily excited, for example, alkali and alkaline earth metals. As stated above, this method is based upon the measurement of intensity of radiation emitted, in the UV-VIS region, by the vapourised atoms after they are electronically excited by the thermal energy of the flame on being introduced into a flame. The wavelength of the radiation (or the colour) emitted tell us about the element present, and the intensity of the radiation tells us about its amount. The International Union of Pure and

Applied Chemistry (IUPAC) Committee on Spectroscopic Nomenclature has recommended abbreviation **FAES** (flame atomic emission spectrometry) for this technique.

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.

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

15.2.1 Fate of the Sample in the Flame

In a typical flame photometric experiment, a solution containing the 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.

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

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

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

- i) **Desolvation:** The sample containing metallic salt 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. The molecules are decomposed to atoms by the heat of the flame and the ions of the sample species are reduced by the action of the reducing gas (fuel), to give atoms. For example, $\text{Mg}^{2+}(\text{aq}) + 2\text{e} \rightarrow \text{Mg}(\text{g})$.
- iv) **Excitation:** The metal atoms at this stage absorb energy from the heat of the flame and get excited. As electrons absorb energy, they move to higher energy levels and are in the excited state.
- v) **Emission of radiation:** the atoms with electrons in the excited state are unstable and these electrons quickly move back to the ground state or to a lower energy state. 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 emitted 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 excited energy levels emit light of different wavelengths 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. 15.1 gives a block diagram representing the processes occurring in the flame.

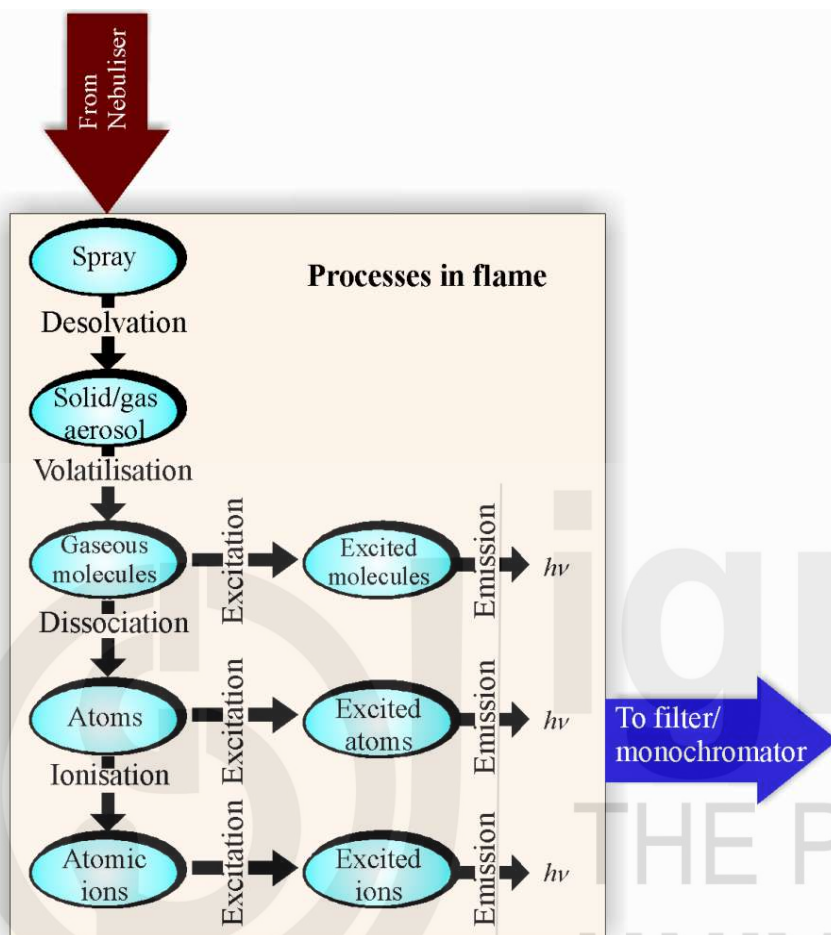


Fig. 15.1: Diagrammatic representation of the processes occurring in flame obtained from oxyhydrogen flame.

Let us take the case of determination of sodium. The flame emission spectrum of the element sodium can be obtained by placing a solution of its salt say sodium chloride in a suitable flame. At the temperature of the flame (2000°C to 3000 °C) the valence electron of the sodium atom is promoted from the ground state (3s orbital) to excited *p* orbitals (3*p*, 4*p*, 5*p*). 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 589 nm. This signal in fact consists of a pair of lines at 589 and 589.6 nm. This pair of lines originates from the relaxation of the excited electron in 3*p* level to the 3*s* 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. 15.2. In case of atomic emission, the intensity of emission signal depends upon the number of atoms in the excited state. In case of sodium, this will be from the first excited state, i.e., $^2P_{3/2}$ and $^2P_{1/2}$ states.

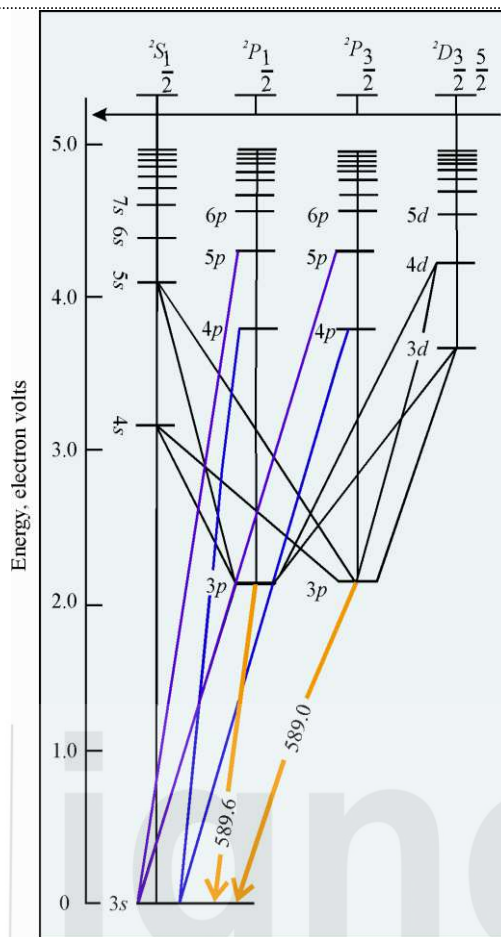


Fig. 15.2: The energy level diagram for sodium atom.

The fraction of atoms in the excited states (corresponding to the prominent spectral line) of different elements at various temperatures is given in Table 15.1. As these numbers are very small, we can say that nearly all the atoms are present in the ground state. Further, the fraction of atoms in the excited state increases with increase in temperature.

Table 15.1: Fraction of atoms in the excited states of different elements at various temperatures

Element	Emission Line (λ nm)	Temperature / Kelvin		
		2000	3000	4000
Lithium	670	4.4×10^{-5}	1.5×10^{-5}	9.4×10^{-3}
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}
Calcium	422	1×10^{-7}	4×10^{-7}	6×10^{-4}
Magnesium	285	3.4×10^{-11}	1.5×10^{-7}	1×10^{-5}

Therefore, in the flames with higher temperatures the fraction of excited atoms would increase, and the method would be more sensitive. Higher temperatures are also required for decomposition of the compounds having high lattice energies into atoms. However, higher temperatures may also cause ionisation of the atoms that may cause interference in the

determination. Therefore, we need to optimise the temperature of the flame to be used.

SAQ 1

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

15.3 INSTRUMENTATION FOR FLAME ATOMIC EMISSION SPECTROMETRY

You know by now that in flame emission spectrometry the sample is introduced into a flame wherein it undergoes several 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 consists of the following basic components.

- Flame atomiser
- Nebuliser and mixing chamber
- Atomiser burner
- Monochromator (or filter)
- Detector
- Amplifier and Readout Device

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

15.3.1 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 first 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 several processes occur that convert the analyte into excited species. Let us learn about the nebulisers used in flame photometers.

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. Several 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 employed nebulisation method in flame photometers.

Pneumatic nebuliser is the most 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.15.3.

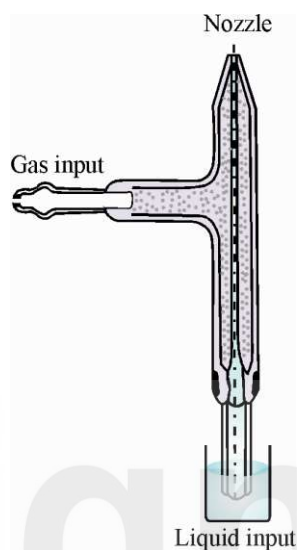


Fig.15.3: Concentric type pneumatic nebulizer.

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.

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 many processes as explained earlier. Two types of atomisation burners have been used in flame photometry as described below.

a) Premix or Lundegarh burner

In the premix burner, the 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.

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 schematic diagram of a premix burner is given in Fig.15.4. 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.

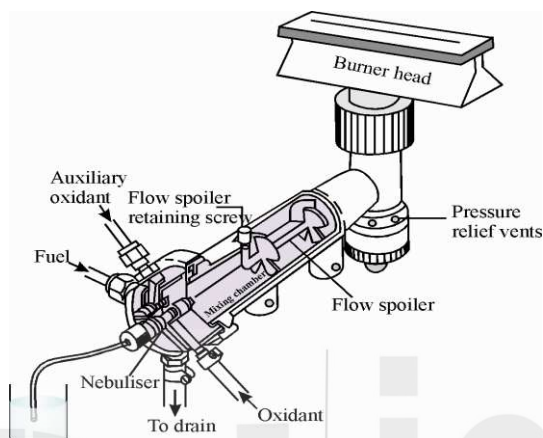


Fig. 15.4: Schematic diagram of a premix burner.

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.

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**".

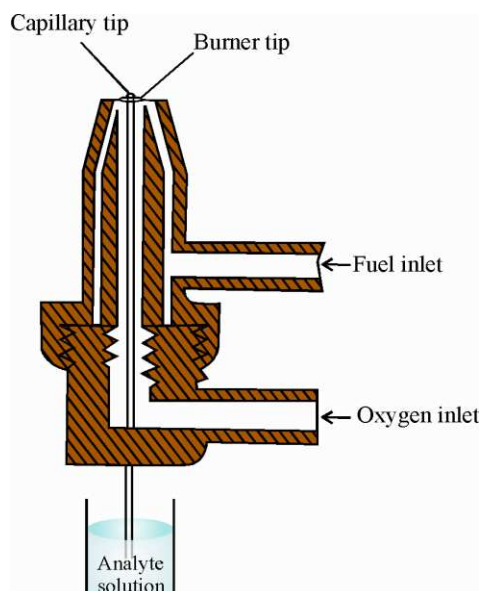


Fig. 15.5: Schematic diagram of a total consumption burner

Here the oxidant and fuel emerge from separate ports and are mixed above the burner holes 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 15.5.

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 generally not much used.

15.3.2 Monochromators

You have learnt in Unit 12 that role of a monochromator is to disperse the radiation falling on it. Generally, a grating or a prism monochromator is employed that disperses 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.

15.3.3 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 12. You are advised to have a relook at subsection 12.4.3 to recall the functioning of different types of detectors.

15.3.4 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.

The different components discussed above are put together to form a flame photometer. A schematic diagram showing the layout of various components of a flame photometer is given in Fig. 15.6.

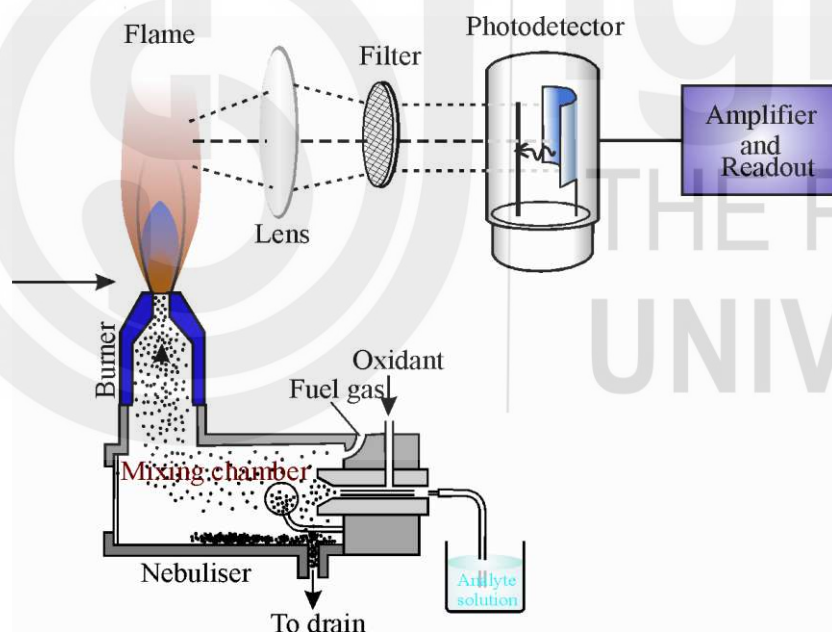


Fig. 15.6: Schematic diagram showing the layout of various components of a flame photometer.

Having learnt about the different components and their arrangement in a flame photometer let us now take up the applications of flame photometry. However, before that answer the following simple question to assess your understanding.

SAQ 2

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

15.4 APPLICATIONS OF FLAME PHOTOMETRY

You have learnt earlier 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.

15.4.1 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 having a filter or monochromator to separate radiation with the wavelengths that are 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 particular 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. Non radiating element such as carbon, hydrogen and halides cannot be detected. These can only be determined under special circumstances.

15.4.2 Quantitative Applications

Flame photometry was initially developed by Lundegarh 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. An analysis of a proper mixture of surface soil and subsoil is important to determine the fertilizer requirement of the soil. In these analyses, the soil 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.

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 wastewater.

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

15.4.3 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.

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 following factors

- flame temperature,
- the rate of flow of liquid into the flame,
- the pressure and rate of flow of fuel gases,
- other factors (affecting the nature of the flame or atomisation of the sample)

It is therefore, essential that a **calibration curve must be prepared that** relates the intensity of the emitted radiation and the concentration of the associated element. Such a 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. A sample calibration curve is given in Fig. 15.7.

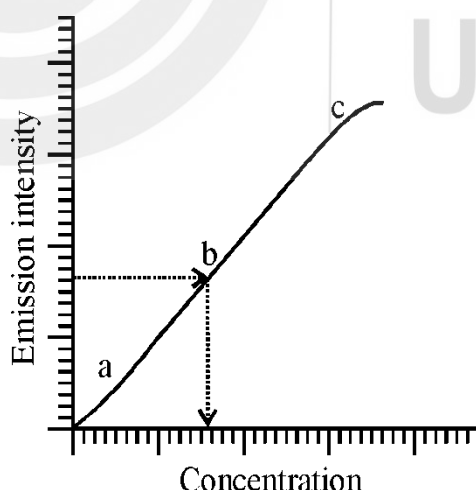


Fig. 15.7: Calibration plot: emission intensity versus concentration of the analyte.

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. The standard calibration plot is usually linear over wide range, but a deviation is generally observed at both low and high concentration ends.

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

In this method, 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 to understand the standard addition method.

Example 15.1: In the determination of sodium in an unknown solution, the following series of solutions were prepared. Each solution contained 10 cm^3 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 cm^3 . 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.15.8.

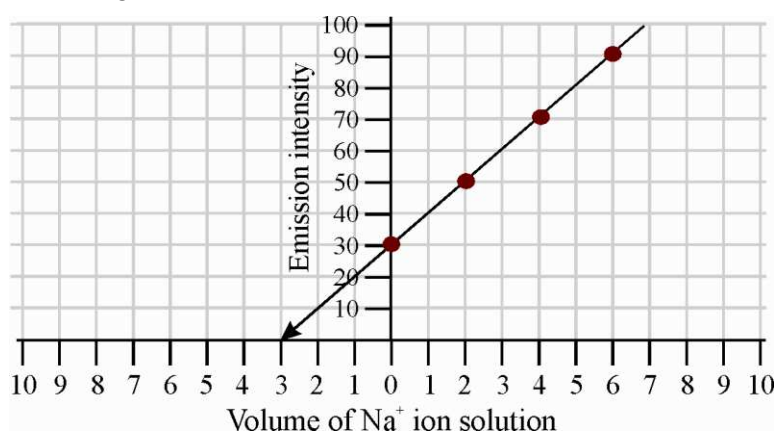


Fig. 15.8: Schematic calibration plot of emission vs. concentration in the determination of sodium by standard addition method.

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 being analysed 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 analysed 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 15.2: 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 15.4.

Table 15.4: 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.15.9.

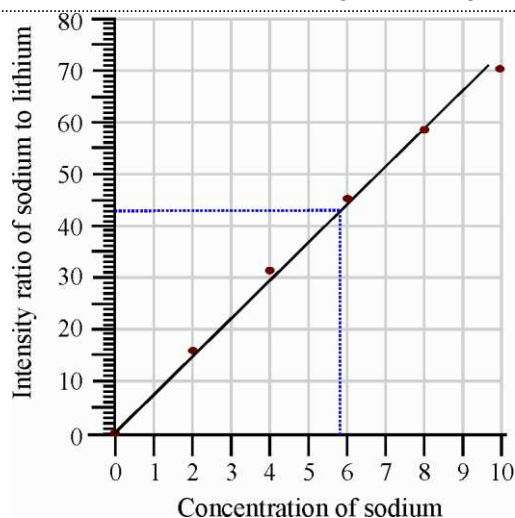


Fig. 15.9: Schematic calibration plot of Intensity ratios versus the Concentration during flame photometric determination of sodium by internal standard method.

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.

Having learnt about qualitative and quantitative applications and the methodologies of quantitative determination let us learn about the interferences observed in quantitative determinations. However, before that answer the following simple question to assess your understanding.

SAQ 3

What are the different methods for quantitative analysis?

15.5 INTERFERENCES IN QUANTITATIVE DETERMINATIONS BY FAES

The success of the quantitative determination by FAES 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. These 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 in flame photometry 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.

15.5.1 Spectral Interferences

These refer to the interferences that affect the spectral intensity or resolution of the signal. 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 specific 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 occurs when 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 by using a monochromator.
- 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.

15.5.2 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.

15.2.2 Chemical Interferences

The chemical interferences arise out of the reaction between different interferences and the analyte. These are of different types. One of these

interferences is called **Cation-anion interference**. In this case 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. 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.

SAQ 4

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 deal with the problem of this type of interference?

15.6 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 measurement of these elements is very useful in medicine, agriculture, and plant science. Let us learn about the merits and limitations of the flame photometry method.

Merits

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

15.7 SUMMARY

In this unit we started by introducing flame atomic emission spectroscopy also called flame photometry as another important atomic spectroscopic technique that concerns the emission of radiation by the suitably excited atomic vapours of the analyte. Thereafter we explained the principle of FAES in terms of the fate of the sample aspirated into the flame and the processes involved therein. Then we took up the instrumental aspects of flame photometry wherein we discussed about different components of flame photometer and their role and arrangement. Thereafter, we explained the analytical methodology for qualitative and quantitative applications of AES. Having discussed these methodologies, we discussed about the possible interferences in these determinations and way to minimise them. In the end of the unit, we outlined the merits and limitations of flame atomic emission spectrometry.

15.8 TERMINAL QUESTIONS

1. List major components of a flame photometer and draw a block diagram of the equipment.
2. What are the different kinds of interferences possible in quantitative analysis by flame photometry?
3. List different types of spectral interferences that may affect the accuracy of flame photometric determinations.
4. State the merits and limitations of flame photometry.
5. What are the applications of flame photometry?

15.9 ANSWERS

Self-Assessment Questions

1. 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

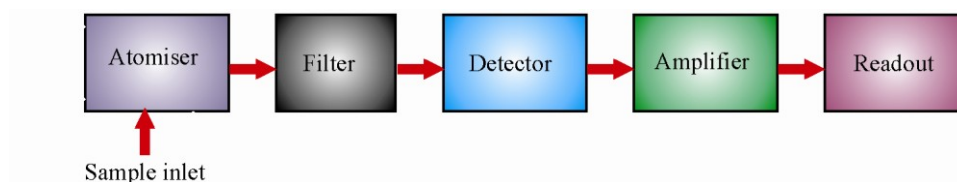
state, radiations of characteristic wavelength are emitted. The wavelength of the radiation emitted is characteristic of the element present and hence tells us what the element is. This forms the basis of the qualitative analysis by flame photometry. The intensity of the radiation emitted tells us how much of the element is present. This, therefore, is the basis of quantitative analysis using flame photometry.

2. 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.
3. 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
4. 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. The major basic components of instrumentation for flame photometry are:
 - Flame atomiser (consisting of nebuliser and burner)
 - Monochromator or filter
 - 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

2. The different kinds of interferences encountered in analysis by flame photometry are:
 - Spectral interferences
 - Ionisation interferences
 - Chemical interferences

3. 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 specific 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.
4. 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.
5. 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.
 - 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.