

## ANALYTICAL ( SP-2) LONG QUESTIONS

**Q: Explain various components of Czerny Turner monochromators?**

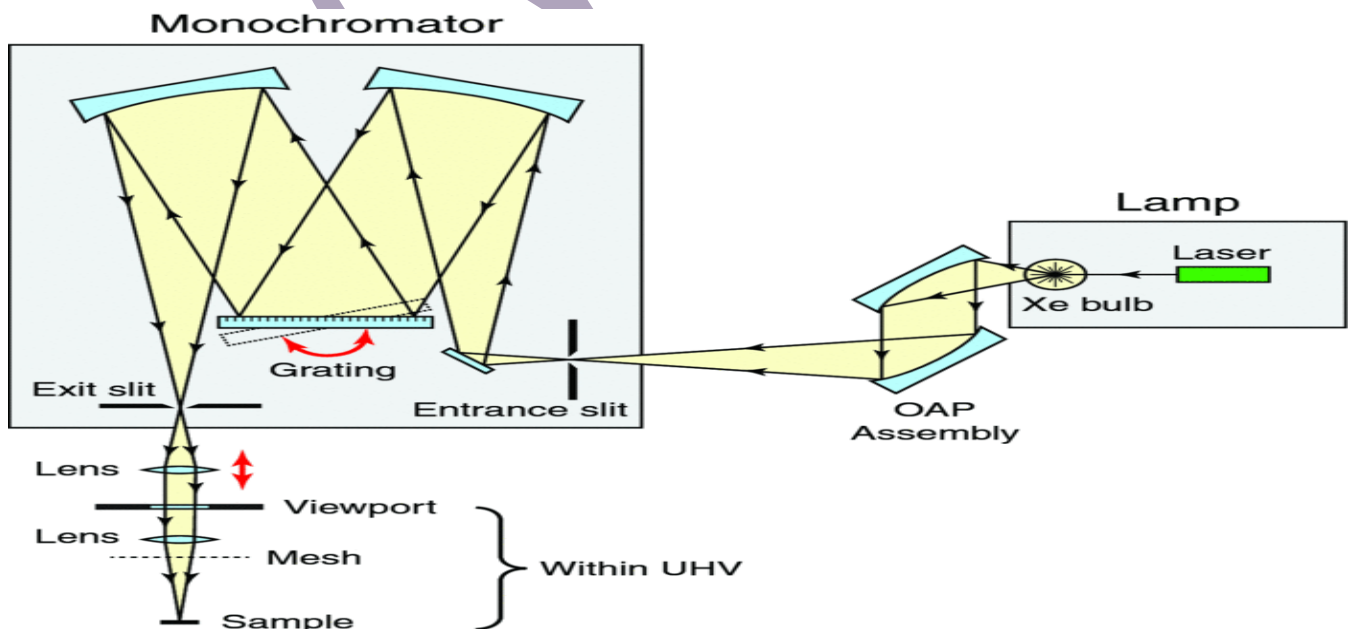
A Czerny-Turner monochromator is a common type of optical instrument used for separating light into its constituent wavelengths, typically employed in spectroscopy. It consists of several key components:

**Entrance Slit:** This is where the light enters the monochromator. It allows only a narrow beam of light to pass through, helping to control the amount of light entering the system and determine the spectral resolution.

**Collimating Mirror or Lens:** The collimating element helps to make the light rays parallel before they enter the dispersing element. This ensures that the light beam strikes the dispersing element at a consistent angle, which is important for accurate wavelength dispersion.

**Dispersing Element:** This component disperses the incoming light into its constituent wavelengths. The most common dispersing elements are diffraction gratings or prisms. Diffraction gratings are often used due to their ability to provide high spectral resolution and efficiency.

**Focusing Mirror or Lens:** After dispersion, the light needs to be focused onto the output slit. The focusing element helps to achieve this by directing the dispersed light onto the exit slit while maintaining spatial and spectral resolution.



**Exit Slit:** Similar to the entrance slit, the exit slit allows only a narrow band of wavelengths to pass through, further refining the spectral resolution of the monochromator. It also serves to control the amount of light exiting the system.

**Detector:** The detector measures the intensity of the light passing through the exit slit at different wavelengths. Common detectors include photomultiplier tubes (PMTs), photodiodes, and charge-coupled devices (CCDs).

**Drive Mechanism:** This component allows for precise control of the position of the dispersing element, typically a grating, which enables selection of specific wavelengths. This mechanism is often motorized and controlled by a computer for automated operation.

**Housing and Optics Mounts:** These provide mechanical support for the various components and ensure proper alignment and stability of the optical elements within the monochromator.

By carefully controlling the parameters of each component and their alignment, a Czerny-Turner monochromator can provide high spectral resolution and accuracy in wavelength selection, making it valuable for a wide range of spectroscopic applications.

**Q: Discuss working and advantages of charge injection devices?**

Charge Injection Devices (CIDs) are semiconductor-based image sensors that operate by injecting charge directly into the semiconductor substrate. They are primarily used in imaging applications, especially in situations where low-light sensitivity, high dynamic range, and high-speed operation are required. Here's how they work and their advantages:

**Working Principle:**

**Charge Injection:** CIDs utilize the principle of charge injection to capture and read out the image. When light strikes the semiconductor surface, it generates electron-hole pairs. These charge carriers are then injected directly into the semiconductor material, typically silicon, where they are collected and stored.

**Potential Wells:** Within the semiconductor substrate, potential wells are created to trap and hold the injected charge. These potential wells are created by applying voltage biases to various regions of the semiconductor material, such as gates and electrodes.

**Integration and Readout:** As the charge carriers accumulate in the potential wells, they create a signal that corresponds to the intensity of light at each pixel. The accumulated charge is then read out by sequentially addressing each pixel, transferring the charge to a readout circuit for further processing and conversion into a digital image.

**Advantages of Charge Injection Devices:**

**Low-Light Sensitivity:** CIDs are known for their excellent low-light sensitivity. Because they directly inject charge into the semiconductor substrate, they can capture and amplify weak signals, making them suitable for imaging in low-light conditions.

**High Dynamic Range:** CIDs offer high dynamic range, which refers to their ability to capture both bright and dark areas within the same image without saturation or loss of detail. This is achieved by adjusting the voltage biases applied to the potential wells, allowing for precise control over the signal amplification and integration time.

**High-Speed Operation:** CIDs can operate at high speeds, making them suitable for applications requiring rapid image acquisition, such as in scientific imaging, surveillance, and machine vision systems.

**Q: Describe multichannel spectrometer used in ICP, AES?**

In Inductively Coupled Plasma (ICP) and Atomic Emission Spectroscopy (AES), multichannel spectrometers are commonly used for elemental analysis. These spectrometers are designed to simultaneously measure the intensity of multiple emission lines across a broad wavelength range. Here's how they work and their key components:

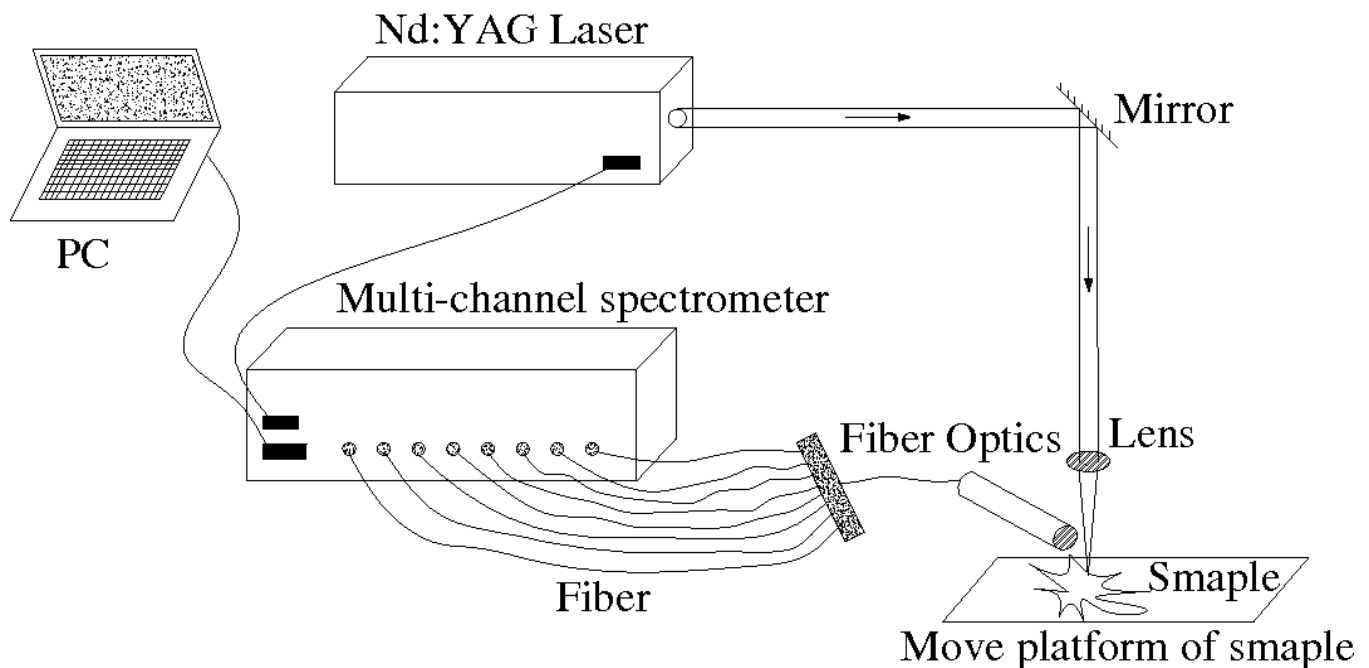
**Working Principle:**

**Emission Spectroscopy:** In both ICP and AES, atoms in a sample are excited by a high-temperature plasma (in ICP) or a flame (in AES). When excited, these atoms emit characteristic electromagnetic radiation in the form of spectral lines corresponding to the energy transitions of electrons within the atoms.

**Optical Emission:** The emitted radiation is collected and collimated by an optical system, typically consisting of lenses and mirrors, and then dispersed by a diffraction grating or prism. This dispersion separates the different wavelengths of light, allowing for the isolation and analysis of individual spectral lines.

**Multichannel Detection:** In a multichannel spectrometer, the dispersed light is detected simultaneously by an array of photo-detectors or charge-coupled devices (CCDs). Each detector corresponds to a specific wavelength range or spectral line, allowing for the simultaneous measurement of multiple emission lines.

**Signal Processing:** The output signals from the detectors are digitized and processed by a computer or data acquisition system. The intensity of each spectral line is determined by integrating the signal over a specified wavelength range, and the resulting spectrum is typically displayed as a graph showing intensity versus wavelength.



### **Components of a Multichannel Spectrometer:**

**Optical System:** This includes components such as lenses, mirrors, and a diffraction grating or prism for collecting, collimating, and dispersing the emitted radiation.

**Detector Array:** Multichannel spectrometers typically use an array of photo-detectors or CCDs arranged to cover a broad wavelength range. Each detector element corresponds to a specific wavelength or spectral line, allowing for simultaneous measurement of multiple lines.

**Signal Processing Electronics:** These electronics digitize and process the output signals from the detector array. They may include amplifiers, analog-to-digital converters (ADCs), and digital signal processing algorithms for extracting spectral information.

**Computer Interface:** A computer interface allows for control of the spectrometer and data acquisition, as well as visualization and analysis of the resulting spectra.

**Q: Describe the working of pyro-electric detector and compare it with bolometer?**

Pyroelectric detectors and bolometers are both types of thermal detectors used in infrared spectroscopy and thermal imaging. While they share the common function of detecting thermal radiation, they operate based on different principles. Here's a description of their working principles and a comparison between the two:

### **Pyroelectric Detector:**

**Working Principle:** Pyroelectric detectors exploit the pyroelectric effect, which is the ability of certain materials to generate an electric charge in response to a change in temperature. These materials possess a spontaneous polarization that changes when the temperature changes, leading to the generation of a temporary voltage across the material.

**Operation:** When infrared radiation is incident on the pyroelectric material, it causes a change in temperature, which, in turn, generates an electric charge. This charge is measured as a voltage across the detector's electrodes. The output voltage is proportional to the rate of change of temperature and, consequently, to the intensity of the incident radiation.

**Response Time:** Pyroelectric detectors have a relatively fast response time, typically on the order of milliseconds, making them suitable for applications requiring rapid detection of thermal changes, such as motion detection in security systems.

**Sensitivity:** Pyroelectric detectors can be highly sensitive to changes in temperature, allowing them to detect small variations in infrared radiation.

#### **Bolometer:**

**Working Principle:** Bolometers operate based on the principle of resistance change in response to absorbed radiation-induced temperature changes. These detectors consist of a thermally sensitive material, typically a thin film or semiconductor, whose resistance changes with temperature variations.

**Operation:** When infrared radiation is absorbed by the bolometer's sensing element, it heats up, causing a change in resistance. This change in resistance is measured using a Wheatstone bridge or similar circuit, and the output signal is proportional to the absorbed radiation intensity.

**Response Time:** Bolometers generally have a slower response time compared to pyroelectric detectors, typically on the order of milliseconds to seconds. However, advancements in technology have led to the development of faster bolometers with response times comparable to pyroelectric detectors.

**Sensitivity:** Bolometers can be highly sensitive to infrared radiation, particularly when operated at cryogenic temperatures. They are capable of detecting very weak signals, making them suitable for high-resolution spectroscopy and astronomy applications.

#### **Comparison:**

**Response Time:** Pyroelectric detectors generally have faster response times compared to bolometers, making them suitable for applications requiring rapid detection of thermal changes.

**Sensitivity:** Both pyroelectric detectors and bolometers can be highly sensitive to infrared radiation, but bolometers, especially when operated at low temperatures, can achieve higher sensitivity levels.

**Temperature Dependence:** Pyroelectric detectors rely on changes in temperature for operation, whereas bolometers measure changes in resistance directly. This difference in operation can affect their performance under varying temperature conditions.

**Q: Draw Jablonski energy diagram and discuss its various phenomena?**

A Jablonski diagram is an energy diagram that illustrates the electronic states and often the vibrational levels of a molecule, along with the transitions between them. Let's delve into its key features:

**Energy Levels:**

- The vertical axis represents energy levels.
- These levels can be quantitatively denoted, but Jablonski diagrams often use energy levels schematically.
- Columns represent specific spin multiplicities for a given species.

**Electronic States:**

Each column corresponds to a specific spin multiplicity.

Within each column, horizontal lines represent eigenstates for the molecule.

Bold horizontal lines denote the limits of electronic energy states.

**Vibronic Energy States:**

- Within each electronic energy state, there are multiple vibronic energy states.
- These vibronic states may couple with the electronic state.
- Only a portion of these vibrational eigenstates is typically represented due to the vast number of possible vibrations in a molecule.

**Transitions:**

- Straight lines show the conversion between a photon of light and the energy of an electron (absorption or emission).
- Curved lines represent transitions of electrons without direct interaction with light.

**Phenomena:**

**Absorption:** When a molecule absorbs a photon, it transitions from a lower energy state to a higher one.



**Fluorescence:** After absorption, the molecule relaxes back to a lower energy state by emitting a photon.

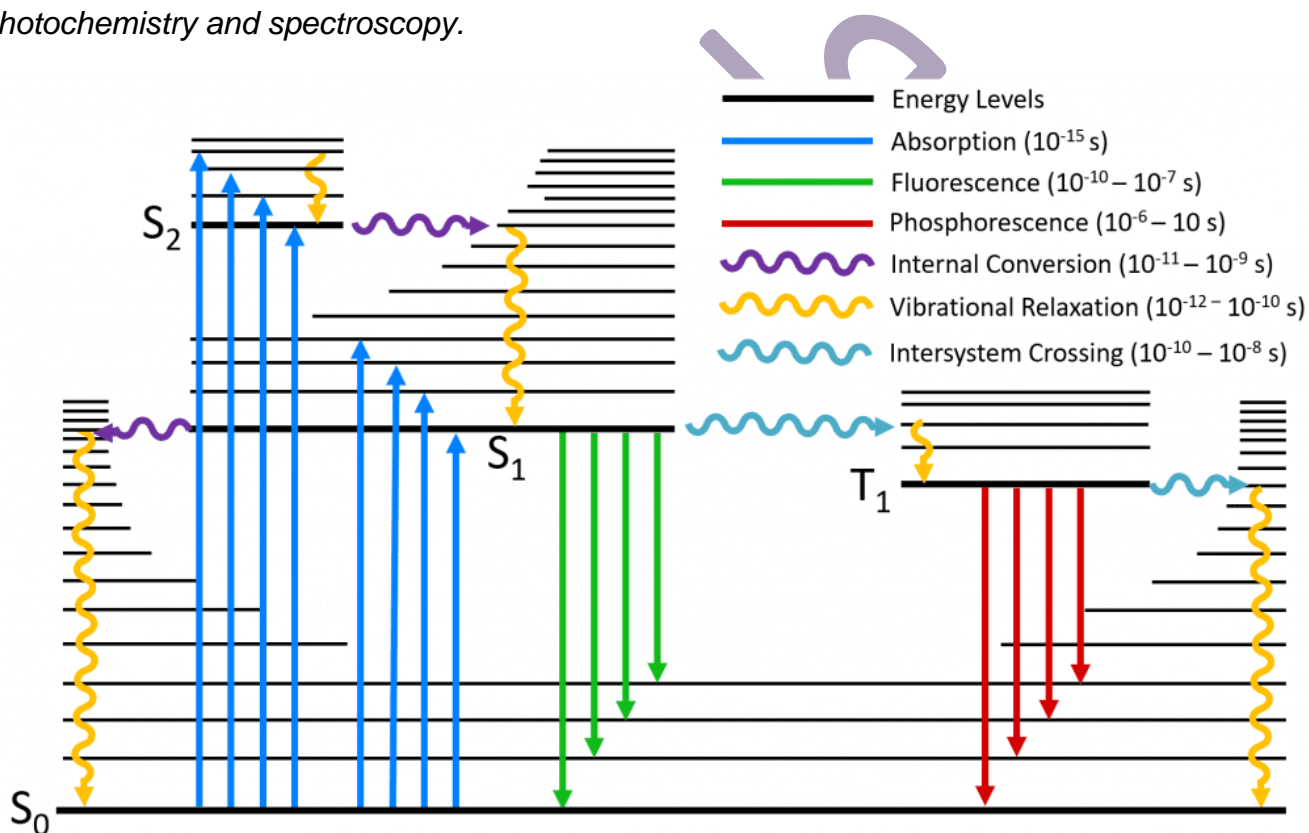
**Phosphorescence:** Similar to fluorescence, but with a longer lifetime due to spin-forbidden transitions.

**Intersystem Crossing:** A transition between electronic states of different spin multiplicities.

**Internal Conversion:** Non-radiative transitions within the same electronic state.

**Quantum Yield:** The efficiency of fluorescence or phosphorescence.

Jablonski diagrams provide insights into molecular processes, including fluorescence, phosphorescence, and energy transfer. They are essential tools in understanding photochemistry and spectroscopy.



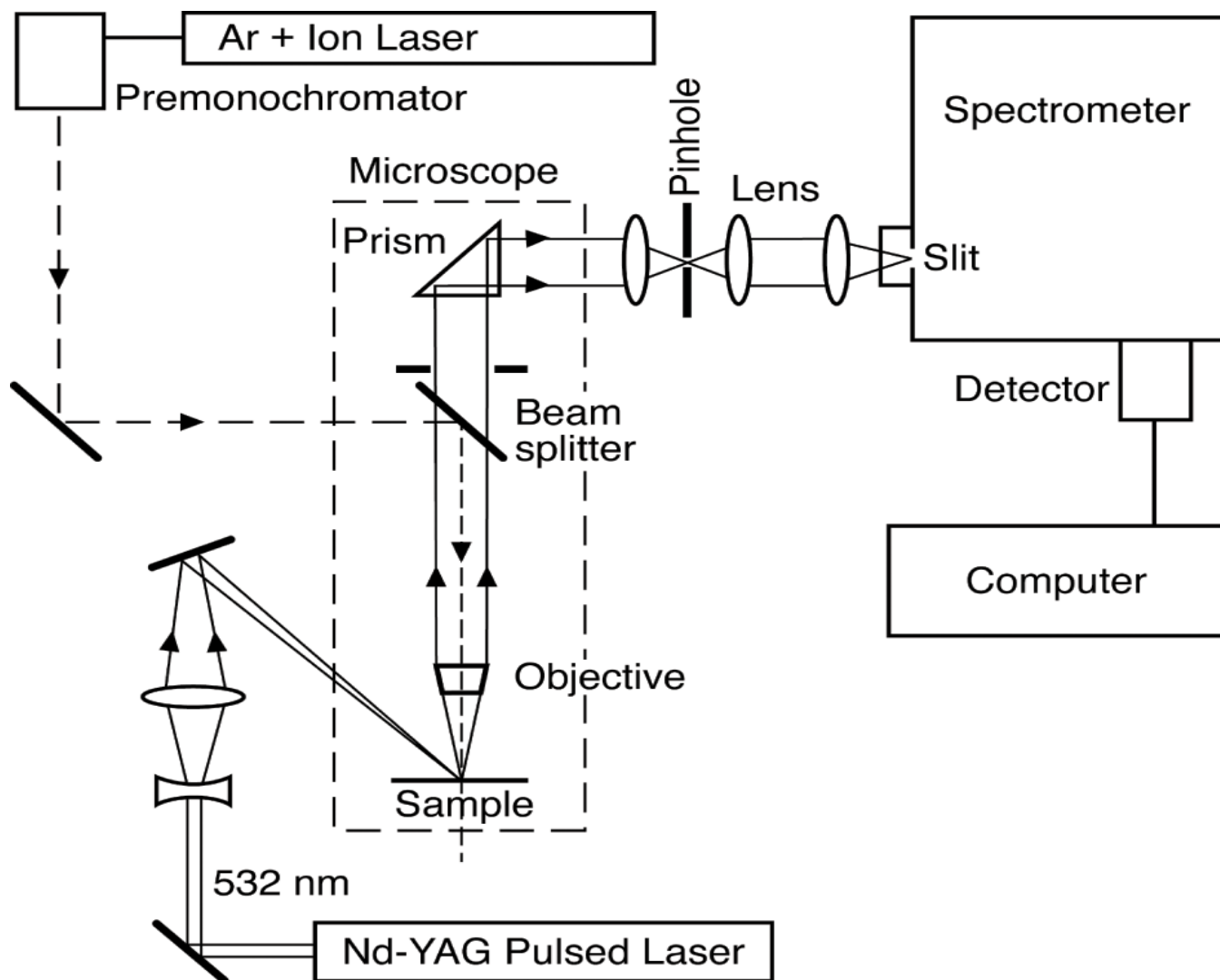
**Q: Explain various components of Raman Spectroscopy?**

Raman spectroscopy is a powerful analytical technique used to provide information about molecular vibrations, rotational, and other low-frequency modes in a sample. It relies on the inelastic scattering of monochromatic light by molecules, resulting in shifts in energy (frequency) due to molecular vibrational transitions. The components of a typical Raman spectroscopy setup include:

### **Laser Source:**

The laser source provides monochromatic light with a specific wavelength, typically in the visible or near-infrared range. Common laser sources used in Raman spectroscopy include diode lasers, solid-state lasers (e.g., Nd:YAG), and gas lasers (e.g., helium-neon).

### **Diagram**



### **Sample Excitation:**

The laser light is directed onto the sample, where it interacts with the molecules. A small fraction of the incident photons undergoes inelastic scattering, known as Raman scattering, while the majority undergoes elastic scattering (Rayleigh scattering).



### **Raman Scattering:**

Raman scattering occurs when incident photons interact with the sample molecules and undergo energy exchange, resulting in scattered light with shifted frequencies.

- **Two types of Raman scattering are observed:** Stokes Raman scattering, where scattered photons have lower energy (longer wavelength) than the incident photons, and anti-Stokes Raman scattering, where scattered photons have higher energy (shorter wavelength) than the incident photons.

### **Optical Path:**

The scattered light from the sample is collected and directed through an optical path, typically consisting of lenses, mirrors, and filters, to filter out the Rayleigh scattering and focus the Raman scattering onto the detector.

### **Raman Spectrometer:**

The Raman spectrometer disperses the collected Raman scattered light into its spectral components using a diffraction grating or prism. It consists of a monochromator or spectrometer to select specific wavelengths and a detector to measure the intensity of the Raman scattered light at each wavelength.

### **Detector:**

The detector measures the intensity of the Raman scattered light at different wavelengths.

Common detectors used in Raman spectroscopy include charge-coupled devices (CCDs), photomultiplier tubes (PMTs), and avalanche photodiodes (APDs).

### **Data Analysis Software:**

Data analysis software is used to process and analyze the Raman spectra obtained from the detector. It performs tasks such as background subtraction, baseline correction, peak identification, spectral deconvolution, and quantitative analysis.

### **Calibration Standard:**

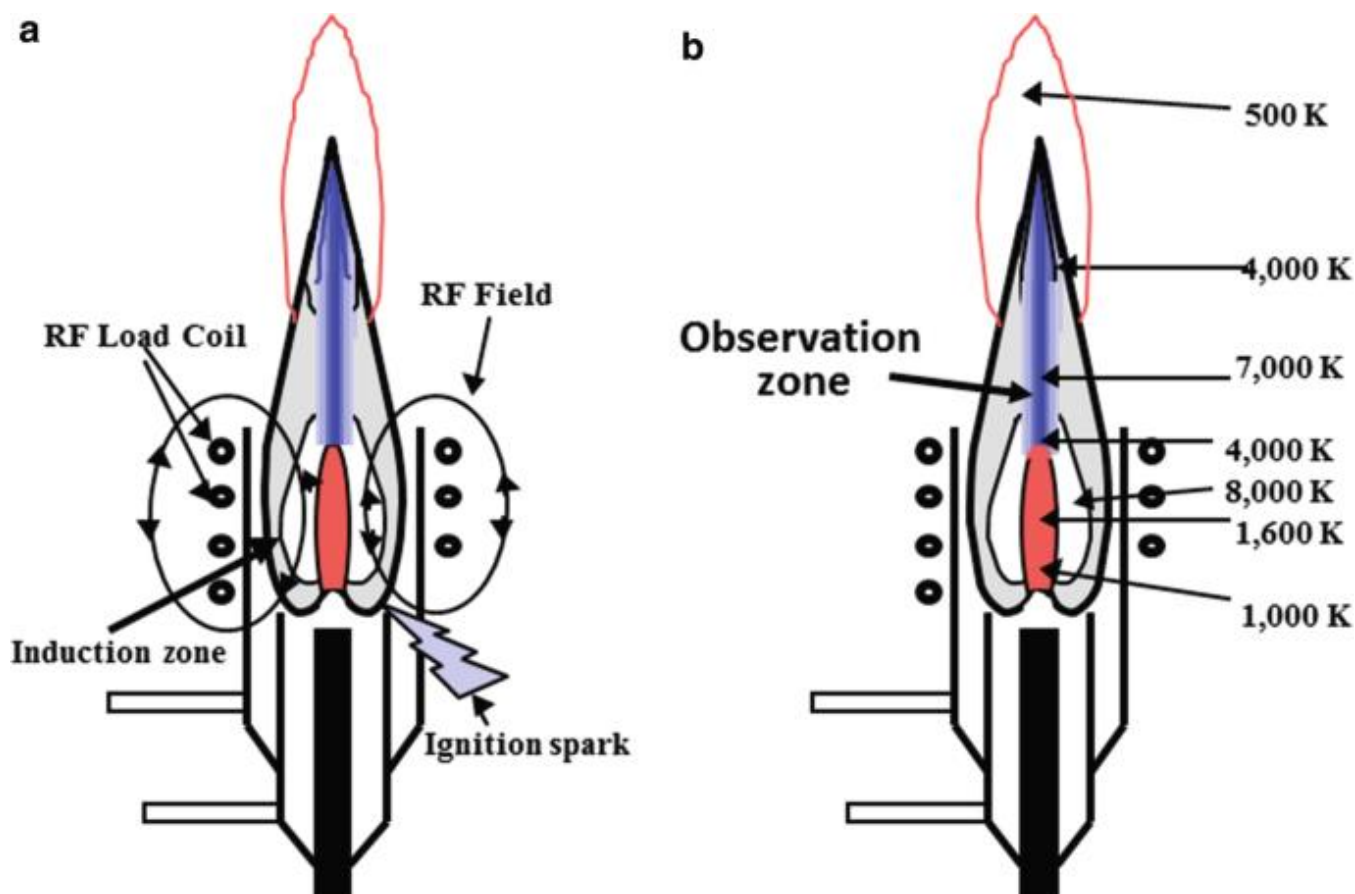
Calibration standards containing known Raman peaks are used to calibrate the instrument, validate its performance, and ensure the accuracy of spectral measurements.

### **Sample Handling Accessories:**

Sample handling accessories such as sample holders, cuvettes, or microscopes may be used to accommodate different types of samples (e.g., solids, liquids, gases) and enable *in situ* or microscopic Raman spectroscopy measurements.

**Q: Explain different zones in ICP Plasma?**

Inductively Coupled Plasma (ICP) is a high-temperature ionization source used in analytical chemistry for elemental analysis. It consists of several distinct zones, each playing a crucial role in the generation and stabilization of the plasma. Here are the main zones in an ICP plasma:



**Radiofrequency (RF) Coil:**

The RF coil is the primary component responsible for generating the high-temperature plasma in an ICP system. It consists of a coil made of a conductive material (usually copper) wrapped around a quartz tube or torch. The RF coil induces a high-frequency alternating current (typically around 27 MHz) that creates a strong electromagnetic field inside the torch.

**Plasma Torch:**

*The plasma torch is a quartz tube through which the sample aerosol is introduced into the plasma. It serves as the primary interface between the RF coil and the sample solution or aerosol. The plasma torch is designed to withstand the high temperatures (up to 10,000 Kelvin) generated by the plasma.*

**Sample Introduction Zone:**

*The sample introduction zone is where the sample solution or aerosol is introduced into the plasma. Depending on the ICP system configuration, sample introduction may occur through nebulization, vaporization, or direct injection methods.*

**Plasma Zone:**

*The plasma zone is the region where the sample is ionized and atomized by the high-temperature plasma. In this zone, the sample aerosol is rapidly heated to temperatures exceeding 6,000 Kelvin, causing it to vaporize and form a plasma of ionized atoms and electrons. The plasma zone is characterized by its high temperature, typically between 6,000 and 10,000 Kelvin, and its highly ionized state.*

**Ionization Zone:**

*The ionization zone is where the sample atoms are ionized by collisions with free electrons in the plasma. In this zone, high-energy electrons collide with neutral atoms, resulting in the ejection of one or more electrons from the atom, forming positively charged ions. The ionization zone is crucial for producing analyte ions that can be subsequently detected by the mass spectrometer or optical emission spectrometer.*

**Axial and Radial Regions:**

*Within the plasma zone, there are axial and radial regions that differ in temperature and ionization characteristics. The axial region, located along the central axis of the plasma, is typically hotter and more ionized than the radial region, which extends outward from the central axis. Analytical techniques such as axial viewing and radial viewing exploit these differences to optimize sensitivity and minimize spectral interferences.*

*By controlling the parameters of each zone, such as RF power, gas flow rates, and sample introduction rates, analysts can optimize the performance of the ICP system for accurate and precise elemental analysis in various sample matrices.*

**Q: Discuss working and advantages of PMT?**

A Photomultiplier Tube (PMT) is a highly sensitive device used for detecting and amplifying low-intensity light signals. It consists of several key components that work together to convert incoming photons into electrical signals. Here's how a PMT works and its advantages:

### **Working Principle:**

#### **Photocathode:**

The PMT begins by absorbing incoming photons through a photocathode, typically made of materials such as cesium antimonide (CsSb) or bi-alkali compounds. When a photon strikes the photocathode, it releases an electron through the photoelectric effect.

#### **Electron Multiplication:**

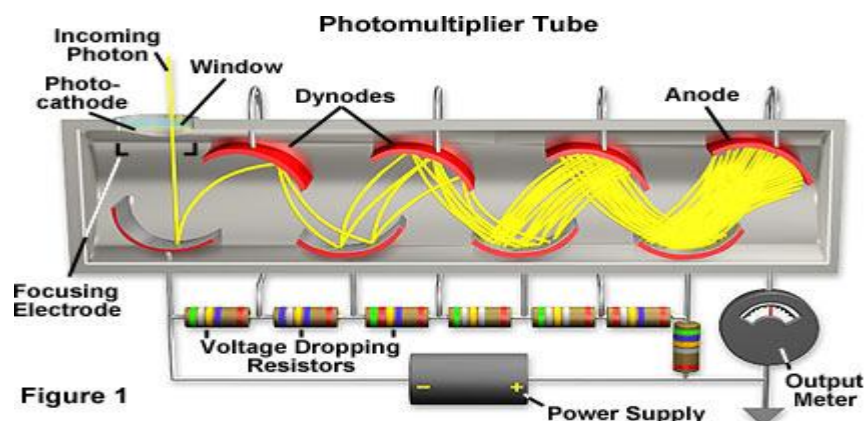
The released electron is accelerated toward a series of dynodes, which are a sequence of metal electrodes maintained at increasingly positive voltages. As the electron strikes each dynode, it releases multiple secondary electrons through a process called electron multiplication or secondary emission. The cascade of secondary electrons results in an exponential amplification of the initial electron signal.

#### **Anode:**

The amplified electron signal is collected at the anode, a positively charged electrode located at the end of the PMT. The anode generates an electrical current proportional to the number of incoming photons, providing a measurable output signal.

#### **Signal Processing:**

The output signal from the PMT is typically amplified, filtered, and processed by external electronic circuits to improve signal-to-noise ratio and extract useful information.



## **Advantages of PMT:**

### **High Sensitivity:**

PMTs offer exceptional sensitivity to low-intensity light signals, making them ideal for applications where detection of weak signals is critical, such as fluorescence spectroscopy, scintillation counting, and particle detection.

### **Wide Dynamic Range:**

PMTs have a wide dynamic range, capable of detecting signals spanning several orders of magnitude in intensity. This versatility allows PMTs to accommodate a broad range of sample concentrations and signal levels without saturation or loss of sensitivity.

### **Fast Response Time:**

PMTs exhibit fast response times on the order of nanoseconds, allowing for rapid detection and acquisition of transient light signals. This makes PMTs suitable for time-resolved measurements, such as fluorescence lifetime analysis and time-correlated single photon counting (TCSPC).

### **Q: Discuss working of FTIR spectrometer?**

Fourier Transform Infrared (FTIR) spectroscopy is a powerful analytical technique used to identify and quantify chemical compounds based on their infrared absorption spectra. It works on the principle of measuring the interaction of infrared radiation with a sample, providing information about the molecular structure, functional groups, and chemical composition of the material. Here's how an FTIR spectrometer works:

#### **Infrared Source:**

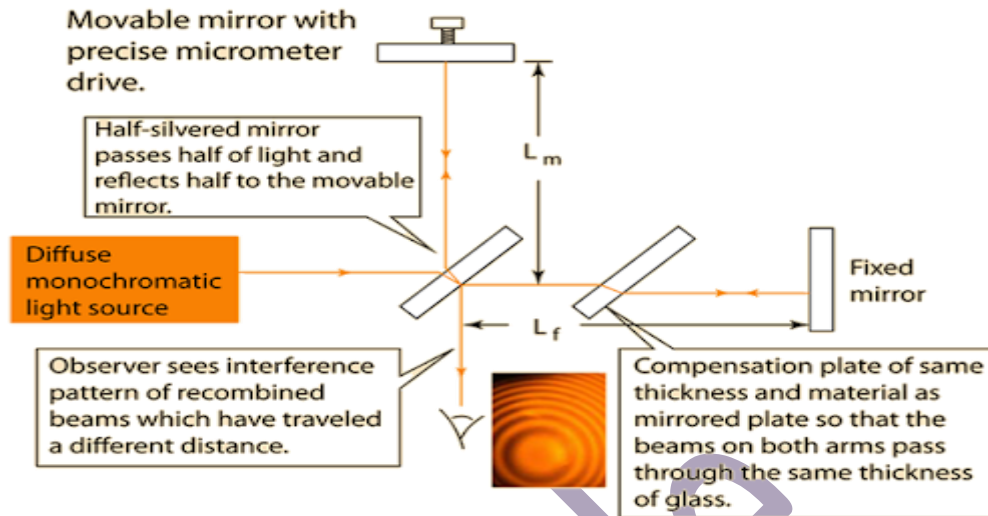
The FTIR spectrometer begins with an infrared source, which typically emits broadband infrared radiation covering a range of wavelengths (frequencies).

Common infrared sources include globar (silicon carbide rod), nichrome wire, or an array of quartz-halogen lamps.

#### **Interferometer:**

The key component of an FTIR spectrometer is the interferometer, which modulates the infrared radiation and converts it into an interferogram.

- The most common type of interferometer used in FTIR spectroscopy is the **Michelson interferometer**, consisting of a beam splitter, moving mirror (or retroreflector), and fixed mirror.



(Michelson interferometer diagram)

### Working Principle:

#### Interference:

The two beams of light (transmitted and reflected) travel along different paths before recombining at the beam splitter.

When the paths of the two beams are nearly equal in length, they interfere constructively or destructively depending on the phase difference between them.

#### Path Difference:

The interference pattern depends on the path difference between the two beams, which is determined by the displacement of one of the mirrors.

When the path difference corresponds to an integral number of wavelengths of the light, constructive interference occurs, resulting in a bright fringe.

Conversely, when the path difference corresponds to a half-wavelength or odd multiple thereof, destructive interference occurs, resulting in a dark fringe.

#### Displacement Measurement:

By measuring the position of the fringes (bright or dark bands) using the detector, one can determine the displacement of one of the mirrors with high precision.



*This displacement can be related to physical quantities such as length, wavelength, or refractive index.*

### **Beam Splitter:**

*The beam splitter divides the incident infrared beam into two components: a reference beam and a sample beam. Typically made of materials such as germanium or potassium bromide (KBr), the beam splitter transmits one portion of the incident light towards the sample and reflects the other portion towards the fixed mirror.*

### **Moving Mirror:**

*The moving mirror oscillates back and forth at a constant velocity, introducing a path difference between the reference and sample beams. As the moving mirror moves, the path length of the sample beam changes, leading to interference between the reference and sample beams.*

### **Fixed Mirror:**

*The fixed mirror remains stationary and reflects the reference beam back towards the beam splitter. The reference beam and sample beam recombine at the beam splitter, resulting in interference patterns that depend on the optical path difference between the two beams.*

### **Detector:**

*The interferogram produced by the interferometer is detected by a sensitive infrared detector, such as a mercury cadmium telluride (MCT) or deuterated triglycine sulfate (DTGS) detector. The detector converts the interferogram into an electrical signal proportional to the intensity of the infrared radiation at each wavelength.*

### **Fourier Transform:**

*The electrical signal generated by the detector is digitized and processed using a mathematical technique called Fourier transform. Fourier transform converts the time-domain interferogram into a frequency-domain spectrum, known as the Fourier transform infrared spectrum.*

### **Data Acquisition and Analysis:**

*The resulting Fourier transform infrared spectrum is displayed as a plot of infrared absorbance (or transmittance) versus wavenumber (or wavelength).*

**Q: Comparison between IR and Raman Spectroscopy?**

Raman spectroscopy	IR spectroscopy
<ul style="list-style-type: none"><li>• Analysis of scattered light of the vibrating molecules.</li><li>• Vibration is Raman active if it causes a change in polarizability.</li><li>• Molecules may not have a dipole moment.</li><li>• Water can be used as a solvent</li></ul>	<ul style="list-style-type: none"><li>• Analysis of absorption of the vibrating molecules.</li><li>• Vibration is IR active if a change in the dipole moment during the vibration occurs</li><li>• Chemical bond must have the characteristics of an electric dipole.</li><li>• Water cannot be used as a solvent due to intense absorption</li></ul>

**Q: State Beer's Lambert Law? How is transmittance defined and how does it relate to absorbance?**

#### ILMI Applied Chemistry (Paper D)

18

(انگریزی کو جذب کر کے حاصل ہونے والا سپیکٹر الہری کی لمبائی اور جذب کی ہوئی روشنی کی مقدار کا ایک گراف ہوتا ہے۔ اس گراف میں جہر نہیں بنتی ہیں وہ جذب کرنے والے میٹریل کہلاتے ہیں۔)

#### 1.4.2 Vacuum U.V region:

The range of U.V region is 10–400 nm or more simply as 100 – 400 nm. The far ultra-violet region i.e., below 200 nm is not much studied (یعنی 200 nm سے نیچے لہری لمبائی کا u.v. حصہ زیادہ کاملاً مد نہیں ہوتا)۔ The reason is that in this portion the absorption by oxygen (O<sub>2</sub>) and nitrogen (N<sub>2</sub>) present in air takes place. Moreover, studies in these regions require vacuum instruments (ایسے آلات جن میں خلا پیدا کیا گیا ہو)۔ Such instruments are very costly (مہنگے)۔

#### 1.4.3 The Absorption Laws

The two laws which govern the absorption of light by the molecules are:

- (i) Lambert's law
- (ii) Beer's law

##### (i) Lambert's Law:

According to this law,

When a beam of monochromatic radiation passes through a homogeneous absorbing medium, the rate of decrease of intensity of radiation with thickness of absorbing medium is proportional to the intensity of the incident radiation.

(ایک ہی لہری لمبائی والی شعاعیں جب ایک جیسے جذب کرنے والے میٹریل سے گزاری جائیں تو شعاعوں کی شدت جذب کرنے والے واسطے کی موٹائی کے ساتھ جو تبدیلی کی رفتار رکھتی ہیں وہ سبیل پر پڑنے والی روشنی کی شدت کا سیدھا تناسب ہوتی ہیں۔)

Mathematically, the law is expressed as

$$-\frac{dl}{dx} = kl \quad (i)$$

Here  $l$  = Intensity of radiation after passing through a thickness  $x$ , of the medium.

$dl$  = Infinitesimally small decrease (بہت ہی چھوٹی کمی) in the intensity of radiation on passing through infinitesimally small thickness,  $dx$  of the medium.

$-\frac{dl}{dx}$  = Rate of decrease of intensity of radiation with thickness of the absorbing medium.

(جذب کرنے والے واسطے کی موٹائی کے لحاظ سے شعاعوں کی شدت میں کمی کی رفتار)

$k$  = proportionally constant (تناسب کا مستقل) or absorption coefficient. Its value depends upon the nature of the absorbing medium.

Equation (i) is a differential equation. It tells the rate of change of intensity of radiation. Now, we want to integrate equation (i) between certain limits. For this purpose there should be separation of variables. The limits are that when  $x = 0$   $l = I_0$

and when  $x = x$   $l = I$

Here  $I_0$  is intensity of light falling on the sample and is greater than  $I$ . (The transmitted intensity)

The separation of variables in equation (i) gives the relationship

$$\frac{dl}{l} = -k dx$$

Let  $I_0$  be the intensity of radiation before entering the absorbing medium ( $x = 0$ ).

( $\frac{dl}{I}$  سادہ کی H.S. ہے۔ یہ دونوں چیزیں  $dx$  اور روشنی کی شدت کے بارے میں ہیں اور ہمیں سائنس  $dx$  یعنی فاصلے میں تبدیلی کو ظاہر کرتا ہے۔)

With the help of integration, we will be able to get the intensity  $I$  of radiation after passing through any thickness, say  $x$  of the medium.

$$\int_{I_0}^I \frac{dl}{I} = - \int_{x=0}^{x=x} k dx$$

$$\boxed{\int \frac{dl}{I} = \ln I} \quad \boxed{\int \frac{dx}{x} = \ln x}$$

$$[\ln I]_{I_0}^I = -k [x]_{x=0}^{x=x}$$

Putting limits

First upper limits minus lower limit

$$\ln I - \ln I_0 = -k [x - 0]$$

$$\ln \frac{I}{I_0} = -kx$$

Taking antilog

$$\frac{I}{I_0} = e^{-kx}$$

or

$$\boxed{I = I_0 e^{-kx}}$$

(iii)

So, the intensity of light transmitted depends upon thickness ( $x$ ) of medium and the constant ( $k$ ).

The intensity of the radiation absorbed,  $I_{abs}$  is the difference of  $I_0$  and  $I$ .

$$\boxed{I_{abs} = I_0 - I = I_0 - I_0 e^{-kx} = I_0 (1 - e^{-kx})}$$

(iv)

The above Lambert's law equation can also be written by changing the natural logarithm to the base 10. When natural log denoted by  $(\ln)$  is changed to common log, then we multiply by 2.303. Equation (ii) becomes

$$2.303 \log \frac{I}{I_0} = -kx$$

$$\log \frac{I}{I_0} = \frac{-k}{2.303} x$$

Taking antilog

کامن لاگ ( $\log$ ) کا انٹی لاگ لینے سے R.H.S کی پاور بن جائے گی۔ کیونکہ  $\log$  کا بیس (10) ہے۔

$$\frac{I}{I_0} = 10^{-\frac{kx}{2.303}}$$



$$I = I_0 10^{-\frac{kx}{2.303}}$$

$$I = I_0 \cdot 10^{-ax}$$

(v)

Comparing equations (iii) and (iv), we reach the conclusion that  $(a = \frac{k}{2.303})$  where  $a$  = extinction coefficient of the absorbing medium.

Equation (iii) and (v) are mathematical shapes of Lambert's law.

(ii) Beer's Law:

This law states that: *When a beam of monochromatic radiation (ایک ہی لہری لمبائی پر مشتمل شعاعیں) is passed through a solution of an absorbing substance, the rate of decrease of intensity of radiation with thickness of the absorbing solution is proportional to the intensity of incident radiation as well as the concentration of the solution.*

(اس لاء میں سائل میٹرل کی جگہ پر سولیوشن کا ذکر ہے جس میں سے روشنی گزرتا ہے۔)

#### Do You Know That!

Monochromatic light means light of single wavelength.

Mathematically, this law is stated as

$$-\frac{dl}{dx} = k'lc$$

(vi)

$l$  = Intensity of incident radiation

where  $c$  = conc. of the solution in  $\text{mol dm}^{-3}$ .

$k'$  = molar absorption coefficient and its value depends upon the nature of the absorbing solution.  $k'$  is different from  $k$  in equation (i)

Suppose  $I_0$  be the intensity of the radiation before entering the absorbing solution when  $x = 0$ , then the intensity of radiation,  $I$  after passing through the thickness  $x$ , of the solution can be calculated.

Separate the variables of equation (vi)

$$-\frac{dl}{l} = k'cdx$$

Now perform the integration within limits

$$\int_{I_0}^I \frac{dl}{l} = - \int_{x=0}^{x=x} k'cdx$$

$$\int \frac{dl}{l} = \ln l$$

$$[\ln l]_{I_0}^I = -k'c[x]_{x=0}^{x=x}$$

$$\ln I - \ln I_0 = -k'cx (-0) = -k'cx$$

$$\ln \frac{I}{I_0} = -k'cx$$

(vii)

Taking antiln

or

$$I = I_0 e^{-k'cx}$$

(viii)

The intensity of radiation emitted ( $I$ ) depends upon the thickness of the solution or path length of solution, concentration of solution ( $c$ ) and the constant ( $k'$ ).

The above equation (viii) can also be written by changing the nature of logarithm to the base 10.

$$I = I_0 \cdot 10^{-\frac{k'cx}{2.303}}$$

(ix)

Here  $\frac{k'}{2.303} = a'$  where  $a'$  = molar extinction coefficient of the absorbing solution.

Alternative expression:

On combining the two laws, the Beer-Lambert Law can be formulated as below:

$$\log \frac{I_0}{I} = \epsilon \cdot c \cdot l = A$$

(x)

where

$I_0$  = Intensity of incident light

$I$  = Intensity of transmitted light

$c$  = Concentration of solution in  $\text{mol dm}^{-3}$

$l$  = Path length of the sample (usually 1 cm)

$\epsilon$  = Molar extinction coefficient (or molar absorptivity)

$A$  = Absorbance =  $\log \frac{I_0}{I}$

(مساوات (vii) کو مساوات (x) میں تبدیل کیے کریں گے)

$$\ln \frac{I}{I_0} = -k'cx$$

$$\ln \frac{I_0}{I} = k'cx$$

$$\log \frac{I_0}{I} = \frac{k'}{2.303} cx$$

(ایک مول چیز کی جذب کرنے کی صلاحیت)

$$\log \frac{I_0}{I} = \epsilon \times c \times l = A$$

$x$  کی جگہ '1' اور  $\frac{k'}{2.303}$  کی جگہ  $\epsilon$  لگایا ہے۔  $\log \frac{I_0}{I}$  کی جگہ  $A$  لکھا ہے۔

#### Limitations of Beer-Lambert Law:

This law is not obeyed

- (i) When different forms of the absorbing molecules are in equilibrium as in keto-enol tautomers.
- (ii) When fluorescent (چمک دینے والے) compounds are present.
- (iii) When solute and solvent form complexes through some sort of association.



**Q: Write a detail note on Mass Spectrometer? Along its principal, instrumentation and applications.**

A mass spectrometer is a powerful analytical instrument used to measure the mass-to-charge ratio ( $m/z$ ) of ions. It works on the principle of ionization, separation, and detection of ions based on their mass-to-charge ratio. Mass spectrometry (MS) has become an indispensable tool in various fields, including chemistry, biochemistry, pharmacology, environmental science, and forensic analysis. Here's a detailed note on mass spectrometry, covering its principles, instrumentation, and applications:

### **Principle:**

#### **Ionization:**

The sample is ionized, typically by one of several ionization techniques such as electron ionization (EI), electrospray ionization (ESI), matrix-assisted laser desorption/ionization (MALDI), or chemical ionization (CI).

Ionization methods vary depending on the nature of the sample and the desired analyte.

#### **Ion Separation:**

The ions produced in the ionization source are then separated based on their mass-to-charge ratio ( $m/z$ ) using a mass analyzer.

The most common mass analyzers include quadrupole, time-of-flight (TOF), magnetic sector, ion trap, and Fourier transform ion cyclotron resonance (FT-ICR) analyzers.

#### **Ion Detection:**

The separated ions are detected by a detector, typically a electron multiplier or Faraday cup, which generates an electrical signal proportional to the number of ions hitting the detector.

The detector signal is then processed to generate a mass spectrum, which represents the relative abundance of ions at different  $m/z$  values.

### **Instrumentation:**

#### **Ionization Source:**

The ionization source generates ions from the sample molecules. It can be a source of different techniques like EI, ESI, MALDI, etc.

#### **Mass Analyzer:**

The mass analyzer separates ions based on their mass-to-charge ratio ( $m/z$ ).

*Different types of mass analyzers offer advantages in terms of resolution, mass accuracy, and scan speed.*

#### **Detector:**

*The detector records the ions that have been separated and quantifies their abundance.*

*It converts the ion signal into an electrical signal that can be processed and analyzed by a computer.*

#### **Data System:**

*The data system includes software for instrument control, data acquisition, and data analysis.*

*It allows users to set experimental parameters, acquire mass spectra, and analyze the resulting data.*

#### **Applications:**

##### **Identification of Compounds:**

*Mass spectrometry is widely used for the identification of unknown compounds based on their mass spectra.*

*It is particularly valuable in fields such as organic chemistry, drug discovery, and environmental analysis.*

##### **Quantitative Analysis:**

*Mass spectrometry enables precise and accurate quantification of analytes in complex mixtures.*

*It is used for quantitative analysis in fields such as clinical chemistry, pharmaceuticals, and food safety testing.*

##### **Proteomics and Metabolomics:**

*Mass spectrometry plays a key role in proteomics and metabolomics research by identifying and quantifying proteins and metabolites in biological samples.*

*It is used for biomarker discovery, disease diagnosis, and understanding cellular pathways.*

##### **Forensic Analysis:**

*Mass spectrometry is employed in forensic analysis for the identification of trace evidence, drugs of abuse, and explosive residues. It is used in criminal investigations, crime scene analysis, and forensic toxicology.*

*In summary, mass spectrometry is a versatile and powerful analytical technique with broad applications in various scientific disciplines. Its ability to provide accurate mass measurements, structural information, and quantitative data makes it an indispensable tool for research, industry, and forensic investigations. Continued advancements in mass spectrometry instrumentation and methodologies are driving innovation and expanding the capabilities of this indispensable analytical technique.*

**Q: Discuss the advantages and limitations of atomic emission spectroscopy compared to atomic absorption spectroscopy?**

<b>Advantages of Atomic Emission Spectroscopy (AES):</b>	<b>Advantages of Atomic Absorption Spectroscopy (AAS):</b>
<b>Detection Limit:</b> AES typically has lower detection limits compared to AAS. This is because AES measures the intensity of emitted light from excited atoms, which can be more sensitive than measuring absorption of light.	<b>Selective Detection:</b> AAS provides selective detection of specific elements based on their absorption of light at characteristic wavelengths. This allows for accurate quantification of individual analytes in complex samples.
<b>Multi-element Analysis:</b> AES is capable of simultaneous multi-element analysis, where multiple elements can be detected and quantified in a single analysis. This makes AES more efficient for analyzing complex samples containing multiple elements.	<b>Minimal Interference:</b> AAS is less prone to matrix effects and spectral interferences compared to AES. This makes AAS more suitable for quantitative analysis of samples with complex matrices.
<b>Higher Sensitivity for Certain Elements:</b> AES can be more sensitive for certain elements compared to AAS. This is particularly true for elements with strong emission lines and low ionization energies.	<b>High Sensitivity for Certain Elements:</b> AAS can be more sensitive for certain elements compared to AES. Elements with strong absorption lines and low ionization energies are often detected more effectively by AAS.

<b>Limitations of Atomic Emission Spectroscopy (AES):</b>	<b>Limitations of Atomic Absorption Spectroscopy (AAS):</b>
<b>Matrix Effects:</b> AES can be susceptible to matrix effects, where the presence of other elements or compounds in the sample matrix interferes with the emission signals of the analytes. This can lead to inaccuracies in quantitative analysis.	<b>Single-element Analysis:</b> AAS is typically limited to single-element analysis, where only one element can be analyzed at a time. This makes AAS less efficient for analyzing samples containing multiple elements.
<b>Limited Sensitivity for Certain Elements:</b> AES may have lower sensitivity for certain elements compared to AAS. Elements with weak emission lines or high ionization	<b>Sample Preparation:</b> AAS often requires extensive sample preparation, including digestion, dilution, and filtration steps, especially for solid samples.

<i>energies may not be detected as effectively by AES.</i>	<i>This can be time-consuming.</i>
--	------------------------------------

***THE END***

Cyanide