

# SPECTROSCOPIC METHODS

## Multiple Choice Type Questions

**1. IR Spectrometry**

[WBUT 2010, 2015]

- a) has a useful range of radiation from 2.5-15 micron
- b) is unsuitable for analysis of mixture of metals
- c) is unsuitable for analysis of organic gases
- d) uses bolometer as one of the detector

Answer: (d)

**2. Water vapour absorbs electromagnetic radiation primarily in the range of**

[WBUT 2010, 2014, 2018]

- a) X-ray
- b) IR-ray
- c) UV-ray
- d)  $\gamma$ -ray

Answer: (b)

**3. Vacuum ultraviolet wavelength range is**

[WBUT 2010]

- a)  $< 200$  nm
- b) 200 – 400 nm
- c) 400 – 800 nm
- d)  $> 800$  nm

Answer: (a)

**4. Detector used in Flame Atomic Absorption Spectrometer may be**

[WBUT 2010, 2014, 2017]

- a) silicon diode
- b) photomultiplier tube
- c) thermocouple
- d) thermistor

Answer: (b)

**5. Frequency of RF transmitter in high resolution NMR Spectrometer should be constant to about**

[WBUT 2010]

- a) 1 part in  $10^2$
- b) 1 part in  $10^4$
- c) 1 part in  $10^6$
- d) 1 part in  $10^8$

Answer: (d)

**6. Sample tube of ESR spectrometer is made of**

[WBUT 2010]

- a) high purity quartz
- b) borosilicate glass
- c) ZnSe
- d) corex glass

Answer: (a)

**7. IR spectrometry is based on**

[WBUT 2011, 2014]

- a) atomic absorption
- b) molecular absorption
- c) nuclear absorption
- d) none of these

Answer: (b)

**8. X-ray diffraction grating type monochromator obeys the equation of**

[WBUT 2011, 2012, 2013, 2015, 2016]

- a) Beer
- b) Bragg
- c) Michelson
- d) none of these

Answer: (b)

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9. In a spectrometer, the monochromator should be capable of resolving two wavelengths 599.9 nm and 600.1 nm. The required resolution is [WBUT 2011]

a) 100                    b) 1000                    c) 3000                    d) 5000

Answer: (d)

10. Non-dispersive type instrument uses

a) wide frequency band                    b) no restriction of frequency  
c) narrow frequency band                    d) single frequency

Answer: (c)

11. Typical detector of an ultraviolet gas analyzer is [WBUT 2012, 2013, 2015, 2016]

a) photomultiplier                    b) thermocouple  
c) thermistor                            d) none of these

Answer: (d) chemiluminescence detector (CLD)

12. In MMR spectroscopy source used for interaction with sample is [WBUT 2012]

a) hollow cathode lamp                    b) spark generator  
c) radio frequency                            d) none of these

Answer: (a)

13. Globar is source of

a) microwave                    b) UV                            c) IR

[WBUT 2013]

Answer: (c)

14. IR spectrometer is based on

a) molecular absorption                    b) atomic absorption  
c) nuclear absorption                            d) none of these

Answer: (a)

[WBUT 2013]

15. Xenon arc lamp wavelength is continuous over the range (nm)

a) 20 – 200                    b) 200 – 1000                    c) 400 – 800

[WBUT 2015]

d) 400 – 1000

Answer: (c)

16. Absorbity is a property of a substance for a given wavelength will vary with

a) concentration                            b) concentration and viscosity  
c) length of the light path                    d) concentration and length of the light path

[WBUT 2015]

Answer: (d)

17. IR spectra of water containing samples may be obtained by placing a drop of the liquid between two plates of

a) NaCl                            b) CaF<sub>2</sub>                            c) MgFe<sub>2</sub>

[WBUT 2015]

d) pure Co

Answer: (a)

18. ESR signal is detected by

- a) PIN diode
- b) Photodiode
- c) tunnel diode

Answer: (d)

[WBUT 2017, 2018]

- b) Photodiode
- d) silicon tungsten crystal diode

**Short Answer Type Questions**

1. Why is IR spectroscopy called vibrational spectroscopy? Show that molecular electronic excitation, vibrational excitation & rotational excitation take place in UV – Visible, NIR, FIR regions of electromagnetic wave spectrum respectively.

[WBUT 2009]

Answer:

1<sup>st</sup> Part:

IR absorption spectroscopy is basically a quantitative analysis technique. For absorption of IR radiation which is in association with an electric field, it is necessary that there occurs a net in its dipole moment as a consequence of its rotational and vibrational motion. With a matching between the electric field of the incident radiation and that of the molecules, an interaction between them is possible and a change in amplitude of one of its motion or in rate of rotation occurs.

2<sup>nd</sup> Part:

The spectral range for IR spectra is approximately  $4000 - 400 \text{ cm}^{-1}$ . This range, called the mid-IR, contains the fundamental vibrational modes and is most useful for qualitative and quantitative analysis of the polar and non polar substances.

2. What are the advantages of a Fourier transform NMR measurement over the continuous wave measurement? Calculate the resonance frequency of the  $^1\text{H}$  nucleus in a 5.0-T magnetic field.  $\gamma_H = 2.68 \times 10^8 \text{ T}^{-1}\text{S}^{-1}$ .

[WBUT 2010]

Answer:

1<sup>st</sup> Part:

Fourier transform (FT) NMR spectrum is mathematically equivalent to a data set that would be collected by scanning through all the individual resonance frequencies and measuring their absorption intensities, a so-called 'continuous wave' (CW) spectrum. There are many advantages of FT over CW measurement NMR spectroscopy. Data on all the nuclei of a particular isotope are collected simultaneously without the need for scanning, this therefore speeds data collection. Also consecutive pulse NMR scan data which is digital can be averaged in the computer memory, thus improving signal to noise ratios, as in FT NMR the signal strength increases in direct proportion to the number of scans whereas the noise, being random increases in proportion to the square root of the number of scans. Other advantages of FT NMR include the ability to use the computer to mathematically manipulate time domain spectra prior to Fourier transformation and so cosmetically improve resolution or signal to noise ratios. In modern FT NMR instruments, nearly all spectrometer functions are controlled by computer, allowing very complex multipulse experiments to be planned, executed and analyzed. The recent

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hardware and software developments in this area have been considerable and progress is expected to continue, allowing increasingly complex problems to be investigated by NMR spectroscopy.

**2<sup>nd</sup> Part:**

$$\nu^* = -\gamma B^0 / 2\pi$$

$\nu^*$  → nucleus precession frequency (Larmor frequency)

Given data:

$$B^0 = 5.0T \quad \gamma_R = 2.68 \times 10^8$$

$$\therefore \nu_R = -2.68 \times 10^8 \times 5 / 2\pi$$

$$= -\frac{2.68 \times 500}{2\pi} \times 10^8 = -\frac{2.68 \times 250}{\pi} \times 10^8 = -213.3757$$

**3. What is the function of the monochromator in the dispersive IR spectrometers. [WBUT 2010]**

**Answer:**

### Function of Monochromatic

The monochromator is mainly used to disperse a broad spectrum of radiation and provides a continuous calibrated series of electromagnetic energy bands of known wavelength or frequency range. Prisms or gratings are used to separate the radiation emanating from the source into a spectrum of wavelengths. A variable-slit mechanism, mirrors, and filters are used to introduce bands of radiation to the sample.

In case of a typical dispersive IR spectrometer, radiation from a broadband source passes through the sample and is dispersed by a monochromator into component frequencies the beams then fall off the detector, which generates an electrical signal that is recorded and displayed.

Most dispersive spectrometers have a double-beam design. Two equivalent beams from the same source pass through the sample and reference chambers, respectively. Using a sector mirror, the reference and sample beams are alternately focused on the detector. The change of IR radiation intensity caused by sample absorption is detected as an off-null signal that is translated into a recorder response through the actions of synchronous motors.

**4. State the Beer-Lamber's law for absorption of radiation.**

[WBUT 2010]

**Answer:**

Beer-Lambert's law states that when a monochromatic light passes through a transparent medium the rate of decrease in intensity which the thickness of the absorbing medium is proportional to the intensity of the penetrating radiation. Let us consider a thin layer of the medium of thickness  $dl$  and let  $I$  be the intensity of the radiation entering it, then Lambert's Law can be expressed by the differential equation as

$$-\frac{dI}{dl} = kI \quad \dots (1)$$

$$\text{or} \quad \int_I^0 \frac{dI}{I} = k \int_{l_0}^l dl \quad \dots (2)$$

$$\text{or, } \ln \frac{I}{I_o} = -kl \quad \dots(3) \quad \text{or, } I = I_o e^{-kl} \quad \dots(4)$$

where,  $I_o$  is the intensity at  $l=0$ , and  $I$ , the intensity at distance  $l$ , the proportionality constant 'k' is called the absorption coefficient of the substance.

By changing from natural to common logarithms the equation 4, can also be written as

$$I = I_o 10^{-al} \quad \dots(5)$$

where,  $a = \frac{k}{2.3026} = 0.4343k$  and is termed as 'extinction coefficient'

the extinction coefficient is generally defined as the reciprocal of the thickness (in cm) required to reduce the light by  $\frac{1}{10}$  of its intensity. It is obvious that the proportion of the

amount of light, absorbed  $\frac{(I_o - I)}{I_o}$  with equal thickness ( $l$ ) of the absorbing material will

be the same and this proportion is independent of the intensity of incident light.

5. Draw and describe the operation of a non-dispersive dual channel absorption type IR spectrometer. [WBUT 2011, 2014, 2016]

Answer:

Non-dispersive absorption type IR technique used to measure the quantities of many gases like  $CO$ ,  $CO_2$ ,  $SO_2$ , Nitrous Oxide,  $CH_4$ , water vapour, many hydrocarbons and vapours of benzene, ethyl alcohol acetone etc.

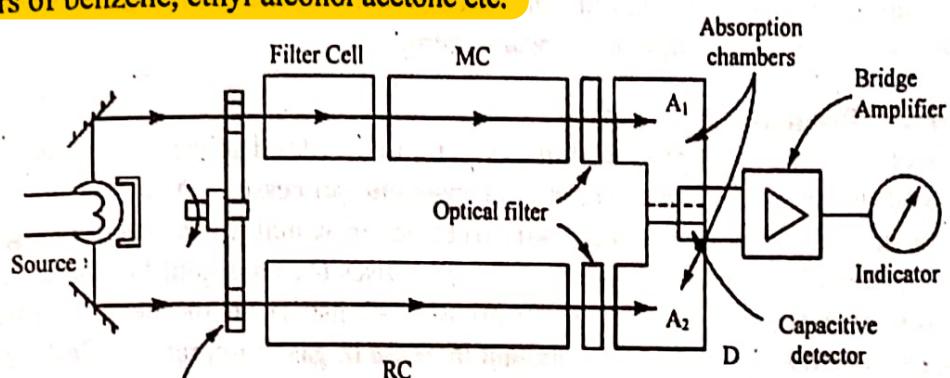


Fig.: Scheme of a non-dispersive dual channel absorption type IR spectrometer

The above diagram shows the arrangement of non dispersive dual channel absorption type IR spectrometer. Here MC stands for measuring cell and RC stands for reference cell. The chopped infrared beams with equal intensity are passed through a measuring cell and reference cell. The reference cell is filled with a standard non-absorbing gas while the measuring cell contains the process gas, i.e., the gas to be analyzed. Other gases that might absorb wavelengths in the given range are first filtered out, or, such gases are included in filter cells in the measuring line or both lines so that the radiation beams do not contain wavelengths the interfering gases are likely to absorb in the measuring cell. A Lufit pattern detector D is present there that consists of two sealed absorption chambers

$A_1$  and  $A_2$  filled with the measuring gas. These chambers are separated by a thin metal diaphragm which forms a parallel plate capacitor with an adjacent perforated fixed metal plate. These gas chambers will, therefore, selectively absorb radiation. Chamber  $A_1$  receives radiation which has already been absorbed in parts in the MC and the gas in  $A_1$  will not further absorb the same energy as would the gas in  $A_2$  so that the chamber gases would be unequally heated to cause a movement of the metal diaphragm to produce a change in the capacitance which is measured by a bridge and amplifier detector. The length of the measuring tube is known then the amount of the absorbing gas in the sample can be determined. If  $\lambda$  is the concentration,  $\alpha$  is the absorption constant and  $l$  is the cell length, then for an incident radiation energy  $\varepsilon$ , the energy absorbed by the gas in the measuring cell is given by

$$E_1 = \alpha \varepsilon \lambda l \quad \dots (1a)$$

$$E_h = \varepsilon (1 - \exp(-\alpha \lambda l)) \quad \dots (1b)$$

for low and high concentrations respectively. Usually if  $(\varepsilon - E) > 0.75$  the first relation is followed, otherwise the latter. In the latter case the length of the cell is generally kept small.

#### 6. What is plasma?

[WBUT 2011, 2012]

Draw the schematic-diagram of DCP source and briefly discuss it. [WBUT 2011]

Answer:

Plasma basically is a conducting gaseous mixture that contains large proportion of cations and electrons with their net charge being nearly, zero.

#### Direct-Current Plasmas

A high-temperature plasma is produced in a direct-current (dc) discharge by constructing the arc through mechanical, hydrodynamic, or magnetic processes. A dc plasma source consists of a dc arc discharge between two electrodes in which a gas, such as argon, is introduced. Tangential flow of the gas into the arc causes the emergent hot gases to cool in such a way that the resultant jet is constricted. Constriction of the arc causes an increase in electron density with a concomitant increase in gas temperature. Self-induced magnetic fields are created as a result of the increased current density. The magnetic fields further tend to constrict the arc.

Direct-current plasmas operate at a current of 5 to 30 amperes and gas flow rates up to 70 liters per minute. Temperatures in the plasma range from 4700 K to over 11,000 K. With higher currents, temperatures of 16,000 K have been achieved.

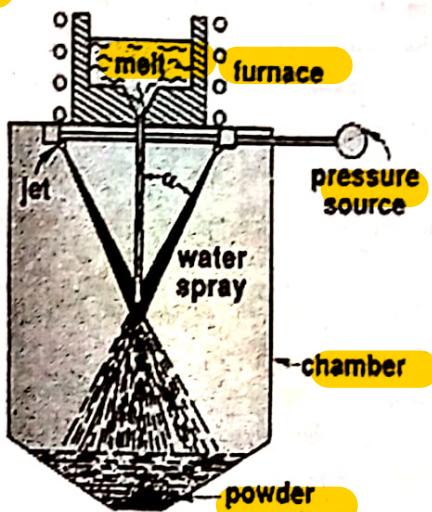
Direct current plasma sources are used for analyzing a wide variety of materials. It is possible to analyze solutions containing 40 to 45% total dissolved solids. Under these conditions calibration standards must be prepared in similar matrices to match the samples. The major advantages of dc plasmas over others are that the plasma is generated using a simple dc power supply. However, continuous operation over long periods of time is not recommended because the electrodes erode. Consequently,

electrode less plasma sources, such as inductively coupled plasmas, are more common in AES.

7. Describe the atomization process with a block diagram. [WBUT 2011, 2014]

Answer:

The process of converting an analyte in solid, liquid or solution form to a free gaseous atom is called 'atomization'.



The above figure shows a typical atomization process. In case of the water and gas atomization the raw material is first melted, then the liquid metal is broken into individual particles.

For this, the melted stock in the form of elemental, multi element metallic alloys are melted in an induction or some other type of furnace. After the melting process, it is transferred to a special type of chamber (tundish) that is used to supply a constant controlled flow of metal into the atomizing chamber.

As the metal stream exits the tundish, it is struck by a high velocity stream is disintegrated into fine droplets which can be solidified during their fall through the atomizing tank. Particles are collected at the bottom of the tank.

8. Draw and describe the operation of Flame Ionization Detector-(FID). [WBUT 2011]

OR,

Discuss with diagram the principle of operation of FID used in chromatography.

[WBUT 2013]

OR

Describe the working principle of flame ionization detector with suitable diagram.

[WBUT 2016]

Answer:

Flame ionization detectors are nowadays mostly used for determining the content of the hydrocarbons in car exhaust gases.

The operation of a flame ionization detector is based on the fact that increased ion current results from the combustion of air containing hydrocarbons in a pure oxygen flame, in comparison to combustion of air not containing any hydrocarbons. For the operation of

the flame constant portions of fuel gas ( $H_2$ ), measuring gas and purifying air are led to the burner. The ion current, proportional to the percentages of organically bound carbon per time unit, is indicated by means of a sensitive amplifier. The purifying air pressure of the pneumatic system of the flame ionization detector FIDAS is adjusted by means of a precision hand valve, dosing automatically the necessary flow of fuel gas and measuring gas by means of pneumatically coupled membrane valves.

The analyzer consists of the analytical part and a separate additional case. The analytical part mainly consists of the pneumatic part and the electronical part with a common thermostat, and the burner equipped with its own thermostat. The additional case contains the pumps for measuring gas and purifying air, the fuel gas controller and two membrane filters for gas preparation. Since the analyzer works with pure hydrogen as fuel gas, the interior of the analytical part is purged by  $2 \text{ m}^3 \text{h}^{-1}$  air in order to prevent eventual explosions.

The flame ionization detector was first designed for the special problems of exhaust gas resulting from combustion engines, since the best possible measuring quality is required. For example the 90% rise time of the instrument must be less than one second. The temperature of the total gas-containing system has to be higher than  $100^\circ\text{C}$  for measurement of Otto engines, and higher than  $180^\circ\text{C}$  for measurement of Diesel engines. For other applications such as immision measurement or ambient air control the same instrument arrangement can easily be used, even in a simplified design. The analyzer has always 6 measuring ranges which can be switched over with a total ratio of 1:300. The smallest measuring range is 0-10 ppm, referred to Methane ( $\text{CH}_4$ ). For other hydrocarbon components the other measuring ranges change proportionally to the C portions, as the total of the C atoms is determined in the measuring gas due to the measuring principle. In comparison with the infrared measuring method – representative determination of the hydrocarbons by selective measuring of the hexane content – the measuring method of the flame ionization detector determines the total of the organically bound carbon. Besides the emission measurement at motor vehicles, the same measurement can be applied to emission measurements in the atmosphere, due to its high measuring sensitivity.

**9. Describe an IR absorption method of measuring moisture in a suitably formed sample. [WBUT 2012]**

**Answer:**

Moisture content of materials is very important in Instrumentation processes. There are mainly two methods, used to measure the moisture content, these are with the use of microwaves or by measuring the reflectance of the material to infrared rays.

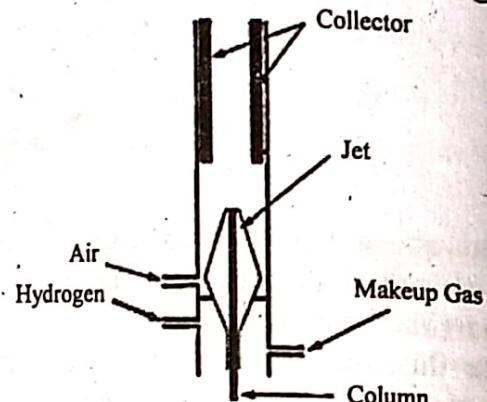


Fig: A schematic diagram of FID

Microwave absorption by water vapor is a method used to measure the humidity in a material. Microwaves (1 to 100 GHz) are absorbed by the water vapor in the material. The relative amplitudes of the transmitted and microwaves passing through a material are measured. The ratio of these amplitudes is a measure of the humidity content of the material.

An absorption calibrated technique is required for each chemical compound.

Since the water molecule absorbs infrared radiation at well defined wave lengths, this property can be used in both transmission and reflectance analyzers to measure moisture in gases, liquids and solids.

Infrared absorption uses infrared rays instead of microwaves. The two methods are similar. In the case of infrared, the measurements are based on the ability of materials to absorb and scatter infrared radiation (reflectance). Reflectance depends on chemical composition and moisture content. An infrared beam is directed onto the material and the energy of the reflected rays is measured. The measured wavelength and amplitude of the reflected rays are compared to the incident wavelength and amplitude, the difference between the two is related to the moisture content.

**10. Give a comparative study between prism monochromator and grating monochromometer.**

[WBUT 2015]

**Answer:**

No.	Grating	Prism
1.	Wavelength-independent dispersion provides simple design formula.	Not so in prism type.
2.	Constant bandwidth with setting of slit fixed.	For constant bandwidth slit width requires to be adjusted, for shorter wavelength narrower slit is required.
3.	Reflection gratings can be used in UV-visible-IR range.	Not possible because of absorption.
4.	Stray radiation and higher order spectra affect performance. Effect minimized with holographic gratings.	Stray radiations etc., affect less.
5.	More costly compared to prism types although other advantageous features have prompted for their use extensively	Less costly as such.

**11. Draw schematically a hollow cathode lamp and explain how it works as a radiation source. Why it is not suitable for volatile elements?**

[WBUT 2015]

**Answer:**

#### Radiation Sources:

**Hollow-Cathode Lamps** – The most widely used radiation sources in atomic absorption work are hollow-cathode spectral lamps. The purpose of a single-element lamp is the production of resonance radiation of narrow linewidth, usually  $< 0.001$  nm. of the element used as the cathode. Most elements have spectra consisting of several resonance lines as well as other lines. The most intense resonance line is used. Resonance radiation

results from the process of excitation of atoms in the ground state and the subsequent transition from the excited to the ground state.

A lamp, as shown in Fig. 1, is filled with an inert gas such as argon. A small current ionizes some of the gas. Interactions with the gas ions remove some atoms from the cathode. With excitation, these atoms provide the resonance radiation.

The lifetime of a lamp will depend on the element used as the cathode, hours of use, strength of the current, and filler gas leakage. However, good-quality lamps will last for several years. Each lamp should be operated for a brief time (about 30 min) each month even if it has not been required for analytical work. A weak lamp can sometimes be regenerated by reversing the leads to the electrodes and operating the lamp at a few milliamperes for about 10 min. Some multielement lamps are marketed on the basis of saving the cost of several single-element lamps. Dual-element lamps of closely related elements such as magnesium/calcium and sodium/potassium have performed well in the authors' laboratory. However, most multielement lamps are not recommended because of their overall poor performance.

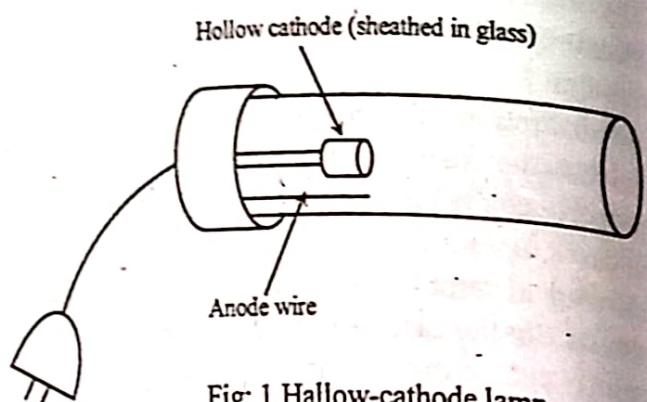


Fig. 1 Hallow-cathode lamp

**12. Define non-dispersive instrument.**

[WBUT 2016]

**Answer:**

NDIR technique uses fixed narrow-band filters with separate IR detectors to detect a few gas absorption lines across a restricted wavelength range. As a result, low-cost sensor parts can be used, and compact but robust sensor packages can be equipped into the instruments. This way, the concentration of gas can be obtained in real time from easy algorithms employed in the microprocessor of the instrument.

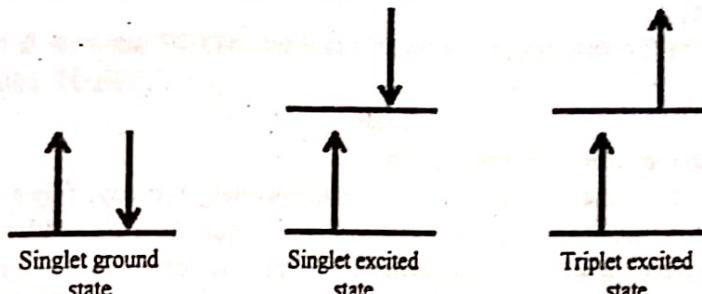
**13. Explain intersystem crossing in context of atomic spectroscopy. [WBUT 2017]**

**Answer:**

Intersystem crossing (ISC) is a radiationless process involving a transition between the two electronic states with different states spin multiplicity. When a singlet state nonradiatively passes to a triplet state, or conversely a triplet transitions to a singlet, that process is known as intersystem crossing. Molecules containing heavy atoms such as Iodine and Bromine generally show intersystem crossing. The reason of this phenomenon is due to the large spin/orbital interactions in presence of heavy metals.

When an electron with a single ground state in a molecule is excited (via absorption of radiation) to a higher energy level either an excited singlet state or an excited triplet state will form. A singlet-excited state is a molecular electronic state where all electron spins are paired. That is, the spin of the excited electron is still paired with the ground state electron (a pair of electrons in the same energy level must have opposite spins, according

to the Pauli's exclusion principle). In a triplet state, the excited electron is no longer paired with the ground state electron; that is, they are parallel (same spin). Since excitation to a triplet state involves an additional "forbidden" spin transition, it is less probable that a triplet state will form when the molecule absorbs radiation.



14. Briefly discuss different types of column used in gas chromatography.

[WBUT 2017]

**Answer:**

There are two main types of columns for the gas chromatography. These are

- Packed columns, which are characterized by their robustness and higher capacity. Liquidized stationary phases are used in packed columns. Packed columns are very tiny, erect, tube like structures. The internal diameter of a packed column is around 2-4 mm. The stationary phase is packed inside this tiny tube, thus calling this structure as packed column. The stationary phase can be a single solid adsorbent or liquid coated solid adsorbent. Packed columns are not long as capillary columns. Thus, the path length for the separation is slightly lower than the capillary column. Hence the packed columns separate the test sample much quicker than the capillary column. On the other hand use of packed columns takes more space than the capillary columns.
- Capillary columns are used in most applications nowadays because of their high separation efficiency. Capillary Columns (also Open Tubular Columns) usually consist of a fused silica (quartz,  $\text{SiO}_2$ ) capillary that is coated with a polyimide layer. The polyimide layer provides the capillary with flexibility and stability, as well as its characteristic brownish color. A capillary CG column has a more efficient separation of the sample than a packed column, but it is more easily overloaded by introducing too much of the sample.

15. Draw and describe the operation of the dual beam UV spectrometer.

[WBUT 2018]

**Answer:** Refer to Question No. 2(a) of Long Answer Type Questions.

**Long Answer Type Questions**

1. a) What is meant by Atomization? Briefly discuss flame atomizer in context of atomic spectroscopy. [WBUT 2009]

b) What is 'Plasma'? Draw the schematic diagram of ICP source & briefly discuss it. [WBUT 2009, 2012, 2015]

OR,

Explain Inductively-coupled plasma source.

[WBUT 2013]

c) Draw a typical scheme of atomic absorption spectroscopy. Give an example of commonly used source in atomic absorption spectroscopy. What is the basic difference between atomic absorption spectroscopy & atomic emission spectroscopy? [WBUT 2009, 2014]

Answer:

a) Atomization is the process, which converts molecular constituents of a sample into atomic particles and during this process UV and visible spectra of the atomized species are obtained by emission absorption which forms the basis of this analysis technique.

The flame technique is the oldest of the AAS techniques. Nowadays it is difficult to imagine a routine analytical laboratory without this technique. A nebulizer and burner are used to make up this atomizer. The nebulizer converts the liquid sample into a fine spray called aerosol which is fed into the flame of the burner. The flame must possess enough energy not only to vaporize but also to atomize the sample rapidly and quantitatively. The chemical composition of the flame can have a major influence on these processes. Nowadays two flame types are used usually, the air-acetylene flame and nitrous-oxide acetylene flame. The two flame types complement each other in ideal manner. Burners used for the purpose are of two types. (i) turbulent flow or total consumption burner and (ii) laminar flow or premixed burner. In the former the nebulizer and the burner constitute a single unit with the sample being drawn through a capillary, which is nebulized by the oxygen and fuel gases around the capillary tube where it is burnt, it being the burner tip as well. It has a short flame path length and the tip is likely to clog in use; besides, the burner is noisy. It is being gradually discarded in practice. In contrast, in the laminar flow type, sample is first nebulized by the oxidant at the capillary tip, the resulting aerosol is then mixed with fuel and allowed to flow past a series of baffles. In the process only the finest droplets are retained which are then burnt in a slotted burner to provide a flame path length of 5 to 10 cm. Because of baffle traps, the technique can introduce sample at a lower rate. The mixing chamber opportunities for selective evaporation of mixed solvents causing uncertainties in analysis. The longer path, however, gives better sensitivity and reproducibility. In laminar flow type burners a large part of the sample is drained out while in turbulent flow type, the sample is not often completely atomized making both to be poor in sampling efficiency.

b) Plasmas: Plasma basically is a conducting gaseous mixture that contains large proportion of cations and electrons with their net charge being nearly, zero.

ICP (Inductively coupled plasma) can be considered as a potentially effective ion source. The hardware of ICP is designed to generate plasma, which is a gas in which atoms are present in an ionized state.

The inductively coupled plasma is a high-temperature source in which energy to form the plasma is generated by a high-frequency magnetic field. The operation of the ICP source is analogous to that of a transformer in which the primary winding is an induction coil with an oscillatory current from a radio-frequency generator. The secondary winding, or load, consists of ionized argon gas, which is coupled inductively to the radio-frequency source. Interaction of the ions with the field produces an eddy current that flows in an annular path near the periphery. The plasma torch, which is shown in figure below, consists of two concentric silica tubes with argon gas flowing tangentially between the inner and outer tubes and a water-cooled induction coil near the periphery of the outer tube. Argon gas flowing through the smaller tube interacts with the magnetic field when sufficient energy is applied to ionize the gas. Initial ionization is provided by a Tesla discharge, and the plasma is sustained by ionized argon formed in the high-temperature plasma. The sample is directed into the plasma through a coaxial capillary tube mounted in the center of the torch assembly.

A radio-frequency generator with an output power of 1 to 5 kW at a frequency of 3 to 100 MHz will sustain an argon plasma. The temperature of the plasma varies from 5000 to 10,000 K, depending on the power, gas flow rate, composition and coupling efficiency. A matching network is used in the rf circuit to minimize reflected power.

The temperatures in an inductively coupled plasma vary over the length of plasma plume, with the hottest part within the annular region. The core of the plasma varies in temperature from 8000 K near the base to about 6000 K at a distance of 25 mm above the load coil. At these temperatures, many elements are >99% ionized. Because of the spatial variation in emission intensity in ICP sources, some instrument manufacturers have modified the optics in their spectrometers to allow emission measurements through the axial region of the discharge.

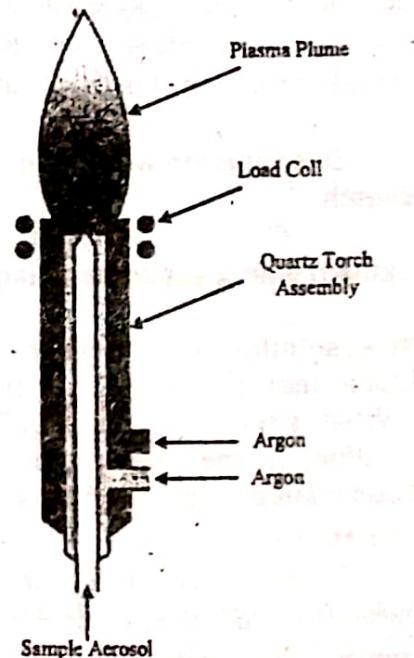
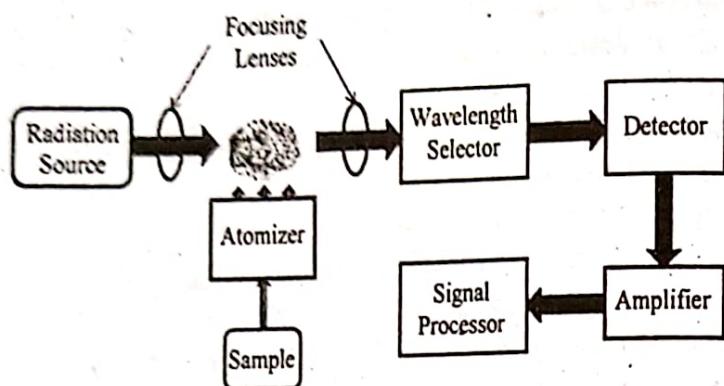


Fig: Diagram of inductively coupled plasma torch

c)



A hollow-cathode lamp of the element that is being measured may be used as a source. Atomic absorption spectroscopy (AAS) is a spectroanalytical procedure for the quantitative determination of chemical elements employing the absorption of optical radiation (light) by free atoms in the gaseous state.

Atomic emission spectroscopy (AES) is a method of chemical analysis that uses the intensity of light emitted from a flame, plasma, arc, or spark at a particular wavelength to determine the quantity of an element in a sample. The wavelength of the atomic spectral line gives the identity of the element while the intensity of the emitted light is proportional to the number of atoms of the element.

2. a) Describe the working of the dual beam type UV spectrophotometer with a neat sketch. [WBUT 2010, 2011]

OR,

Explain with a schematic diagram the operation of double beam UV Spectrometer. [WBUT 2013]

b) A solution containing the complex formed between Bi (III) and thiourea has a molar absorptivity of  $9.32 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$  at 470 nm.

i) What is the absorbance of  $3.79 \times 10^{-5} \text{ M}$  solution of the complex in 1.00 cm cell?

ii) What is the moiar concentration of the complex in a solution that has the absorbance 0.353 when measured in a 2.50 cm cell? [WBUT 2011]

Answer:

a) For typical analytic instrumentation application several spectrometers are used now these days, like dual or double beam spectrometer which consists of a UV-visible light source, two cells through which the light passes, and a detector (usually a photomultiplier) to measure the amount of light passing through the cells.

There are basic spectrometers that measure the absorbance at a specific wavelength, set by the user, and others that can scan the entire UV-V is range. But now these days spectrometers are usually computer controlled and allow the user greater flexibility. For example, in overlaying spectra of a reaction mixture over time, or constructing a calibration graph to determine the concentration of an unknown.

In case of a Single-beam UV-V is spectrometer, it works on the same general principles, but measure the absorption of the reference first, followed by the sample. They can scan across the entire UV-V is range or can be used at a single wavelength. Detector technology has improved recently, the diode array detector enables simultaneous

detection over the entire range to be achieved, allowing rapid quantification of absorbing species.

The double-beam UV-V is spectrophotometer contains two cells, one cell contains the sample dissolved in solvent and the other cell contains the solvent alone. Ethanol is transparent to UV above 200 nm and is, therefore, commonly used as the solvent in UV-V is spectroscopy.

Here the light is split into two parallel beams, each of which passes through a cell. The detector measures the intensity of the light transmitted through the solvent alone ( $I_0$ ) and compares it to the intensity of light transmitted through the sample cell ( $I$ ). The absorbance, A, is then calculated from the relationship shown in equation below

$$A = \log_{10} \frac{I_0}{I}$$

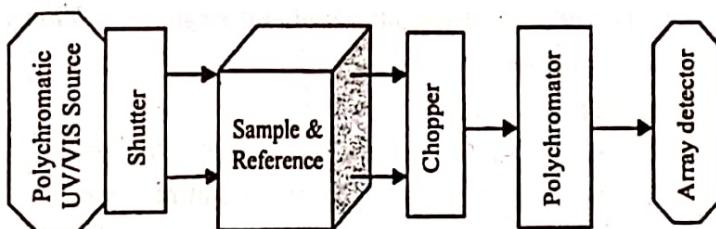


Fig: dual beam UV Multichannel Spectrometer

The term UV-V is normally applied to radiation with a wavelength in the range 200-800 nm. There are many groups that absorb below 200 nm, but this part of the spectrum is difficult to examine (as oxygen absorbs UV radiation below 200 nm) unless the spectra are recorded in a vacuum (vacuum UV-V is).

b) (i) Let us assume

Absorbance  $A=?$

$$a=9.32 \times 10^3 \text{ } l \text{ mol}^{-1} \text{ cm}^{-1}$$

$$b=1.00 \text{ cm}$$

$$c=3.79 \times 10^{-5} \text{ M}$$

$$\therefore A=abc = 9.32 \times 10^3 \times 1 \times 3.79 \times 10^{-5} = 9.32 \times 3.79 \times 10^{-2} = .3532$$

(ii)  $A_{\text{known}}=.3532$

$$A_{\text{unknown}}=.353; \quad c_{\text{known}}=3.79 \times 10^{-5}; \quad c_{\text{unknown}}=?$$

$$c_{\text{unknown}} = \frac{A_{\text{unknown}}}{A_{\text{known}}} \times c_{\text{known}} = \frac{.353}{.3532} \times 3.79 \times 10^{-5} = 3.7878 \times 10^{-5} \text{ M}$$

3. a) Why is RF source necessary for NMR spectroscopy? Describe NMR spectroscopy with schematic diagram.

b) What is the principle used in Electronic Spin Resource? Mention two applications of ESR spectroscopy. [WBUT 2011]

Answer:

a) NMR spectroscopy is one of the principal techniques used to obtain physical, chemical, electronic and structural information about molecules due to either the chemical shift, Zeeman effect, or the Knight shift effect, or a combination of both, on the resonant frequencies of the nuclei present in the sample. It is a powerful technique that can provide detailed information on the topology, dynamics and three-dimensional structure of molecules in solution and the solid state.

Figure below shows the block diagram of a nuclear magnetic resonance spectrometer. It is a complex system integrating several technologies into an analytically powerful, information rich system.

The key parts of the system are:

- A magnet, which produces a magnetic field in the range 10,000 to 25,000 gauss,
- Radio-frequency transmitting system,
- The signal amplifier and detector,
- A display device, which may be a recorder or an oscilloscope
- A non-magnetic sample holder, which holds the sample, and
- Computer work station which stores and process the NMR data using complex software to generate spectrum for the same.

The various sub-systems in an NMR spectrometer are shown in Figure below.

In case of the NMR spectrometer, it must be tuned to a specific nucleus. The actual procedure for obtaining the spectrum varies, but the simplest is referred to as the continuous wave (CW) method. A typical CW-spectrometer is shown in the following diagram. A solution of the sample in a uniform 5 mm glass tube is oriented between the poles of a powerful magnet, and is spun to average any magnetic field variations, as well as tube imperfections. Radio frequency radiation of appropriate energy is broadcast into the sample from an antenna coil (colored red). A receiver coil surrounds the sample tube, and emission of absorbed rf energy is monitored by dedicated electronic devices and a computer. An nmr spectrum is acquired by varying or sweeping the magnetic field over a small range while observing the rf signal from the sample. An

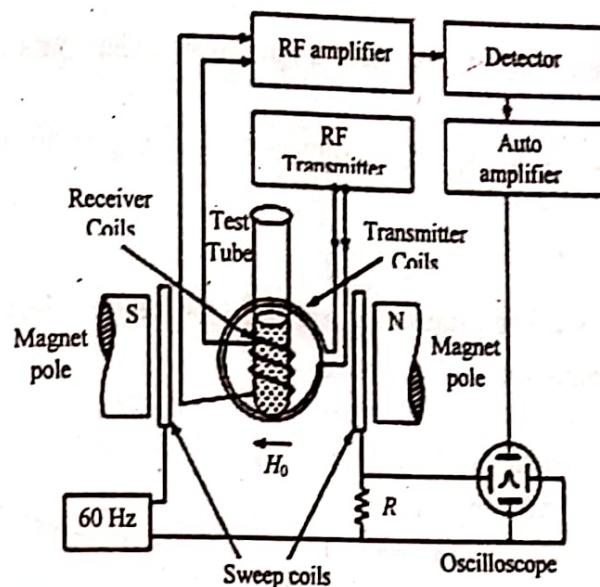


Fig: Block diagram of a nuclear magnetic resonance spectrometer

equally effective technique is to vary the frequency of the rf radiation while holding the external field constant.

b) When the molecules of a solid exhibit paramagnetism as a result of unpaired electron spins, transition can be induced between spin states by applying a magnetic field and then supplying electromagnetic energy, usually in the microwave range of frequencies. The resulting absorption spectra are described as electron spin resonance (ESR) or electron paramagnetic resonance (EPR). Electron spin resonance has been used as an investigative tool for the study of radicals formed in solid materials, since the radicals typically produce an unpaired spin on the molecule from which an electron is removed. Particularly fruitful has been the study of ESR spectra of radicals produced as radiation damage from ionizing radiation. Study of the radicals produced by such radiation gives information about the locations and mechanisms of radiation damage. The interaction of an external magnetic field with an electron spin depends upon the magnetic moment associated with the spin, and the nature of an isolated electron spin is such that two and only two orientations are possible. The application of the magnetic field then provides a magnetic potential energy which splits the spin states by an amount proportional to the magnetic field (Zeeman effect) and then radio frequency radiation of the appropriate frequency can cause a transition from one spin state to the other. The energy associated with the transition is expressed in terms of the applied magnetic field, the electron spin g factor and the constant which called the Bohr magneton.

Every electron has a magnetic moment and spin quantum number  $s = \frac{1}{2}$ , with magnetic

components  $m_s = +\frac{1}{2}$  and  $m_s = -\frac{1}{2}$ . In the presence of an external magnetic field with

strength  $B_0$ , the electron's magnetic moment aligns itself either parallel ( $m_s = -\frac{1}{2}$ ) or

antiparallel ( $m_s = +\frac{1}{2}$ ) to the field, each alignment having a specific energy due to the Zeeman effect:

$$E = m_s g_e \mu_B B_0 \text{ where}$$

- $g_e$  is the electron's called g-factor).  $g_e = 2.0023$  for the free electron
- $\mu_B$  is the Bohr magneton.

Therefore, the separation between the lower and the upper state is  $\Delta E = g_e \mu_B B_0$  for unpaired free electrons. This equation implies that the splitting of the energy levels is directly proportional to the magnetic field's strength, as shown in the diagram.

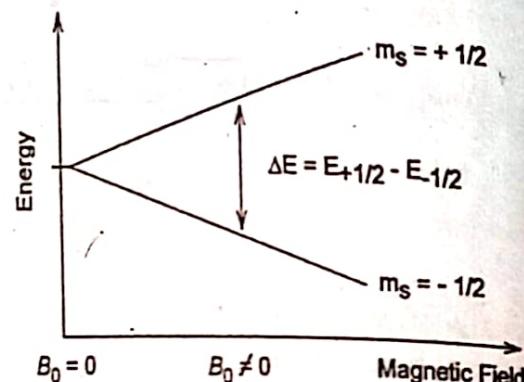
An unpaired electron can move between the two energy levels by either absorbing or emitting a photon of energy  $h\nu$  such that the resonance condition,  $h\nu = \Delta E$ , is obeyed.

This leads to the fundamental equation of EPR spectroscopy:  $h\nu = g_e \mu_B B_0$ .

Experimentally, this equation permits a large combination of frequency and magnetic field values, but the great majority of EPR measurements are made with microwaves in the 9000–10000 MHz (9–10 GHz) region, with fields corresponding to about 3500 G (0.35 T). Furthermore, EPR spectra can be generated by either varying the photon frequency incident on a sample while holding the magnetic field constant or doing the reverse. In practice, it is usually the frequency that is kept fixed. A collection of paramagnetic centers, such as free radicals, is exposed to microwaves at a fixed frequency. By increasing an external magnetic field, the gap between the  $m_s = +\frac{1}{2}$  and

$m_s = -\frac{1}{2}$  energy states is widened until it matches the energy of the microwaves, as

represented by the double-arrow in the diagram above. At this point the unpaired electrons can move between their two spin states. Since there typically are more electrons in the lower state, due to the Maxwell-Boltzmann distribution, there is a net absorption of energy, and it is this absorption that is monitored and converted into a spectrum. The upper spectrum is the simulated absorption for a system of free electrons in a varying magnetic field. The lower spectrum is the first derivative of the absorption spectrum. The latter is the most common way to record and publish EPR spectra.



*Applications*

1. ESR spectroscopy has its in various branches of science, such as biology, chemistry and physics. It mainly provide the information about the free radicals. The detection and identification of free radicals and paramagnetic centers such as F centers is possible by this. EPR is a sensitive, specific method for studying both radicals formed in chemical reactions and the reactions themselves. For example, when ice (solid H<sub>2</sub>O) is decomposed by exposure to high-energy radiation, radicals such as H, OH, and HO<sub>2</sub> are produced. Such radicals can be identified and studied by EPR. Organic and inorganic radicals can be detected in electrochemical systems and in materials exposed to UV light. In many cases, the reactions to make the radicals and the subsequent reactions of the radicals are of interest
2. EPR is also used to know about the radical's geometry and the orbital of the unpaired electron.

4. What is the basic principle used in a FT-IR Spectrometer. Explain FT-IR Spectrometer with its block diagram. [WBUT 2013]

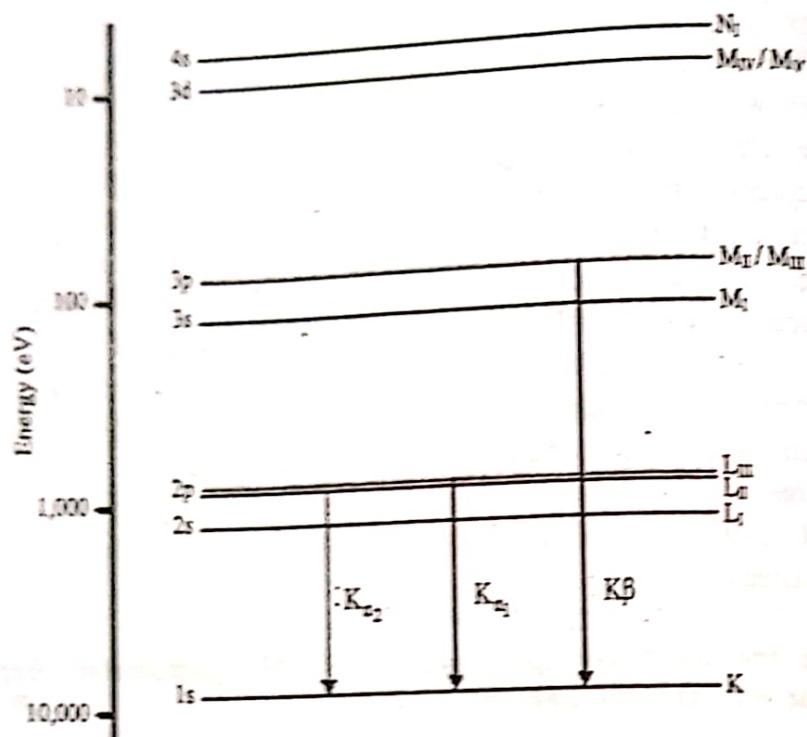
Answer:

Refer to Question No. 7(d) of Long Answer Type Questions.

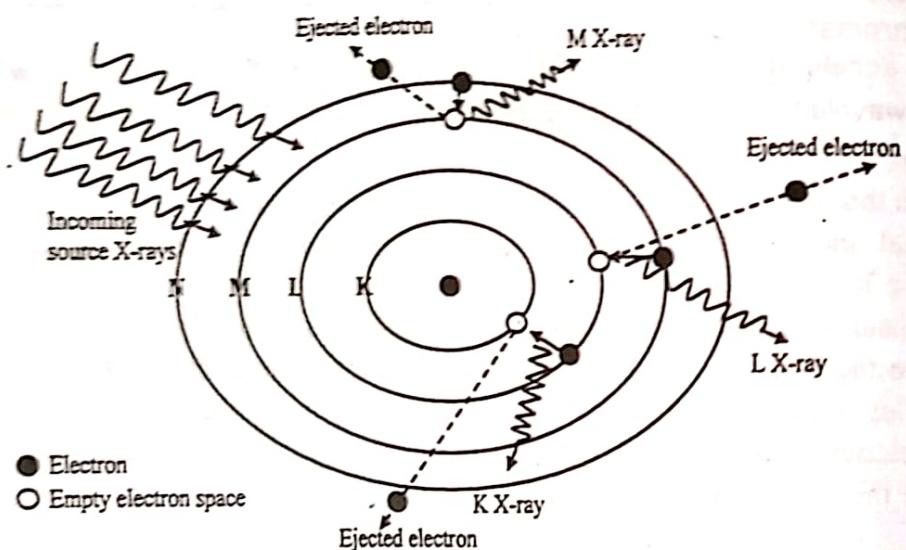
5. a) Explain the atomic processes involved in the generation of an X-ray spectrum.
- b) Draw a schematic diagram of an X-ray tube and explain its principle of operation.
- c) Derive the Bragg condition that is utilised to produce more or less monochromatic X-radiation.
- d) If an accelerating potential of 30 kV is applied in an X-ray tube, what will be the cut-off wavelength  $\lambda_0$  of the generated X-ray spectrum? [WBUT 2013, 2017]

Answer:

- a) When the energy of the accelerated electrons is higher than a certain threshold value of the metal anode, a type of spectrum is obtained superimposed on top of the white radiation. It is called the characteristic radiation and is composed of discrete peaks. The energy (and wavelength) of the peaks depends solely on the metal used for the target and is due to the ejection of an electron from one of the inner electron shells of the metal atom. This results in an electron from a higher atomic level dropping to the vacant level, which causes emission of an X-ray photon characterized by the difference in energy between the two levels.

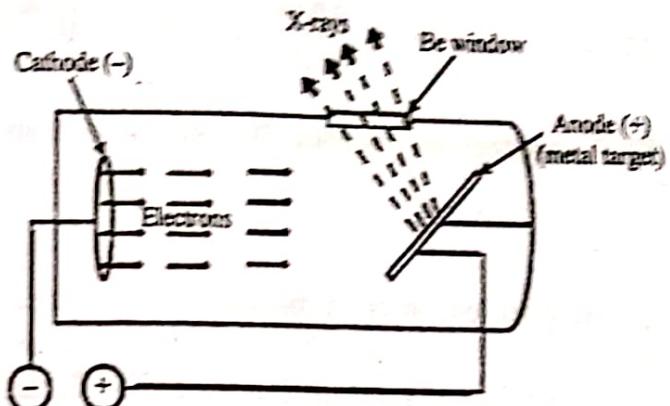


The characteristic lines in this type of spectrum are called K, L, M,... and they correspond to transitions to orbitals with principal quantum numbers 1, 2, 3,... When the two orbitals involved in the transition are adjacent (e.g.  $2 \rightarrow 1$ ), the line is called  $\alpha$ . When the orbitals are separated by another shell (e.g.  $3 \rightarrow 1$ ), the line is called  $\beta$ . Since transition for  $\beta$  is bigger than for  $\alpha$ , i.e.  $\Delta E_\beta > \Delta E_\alpha$  then  $\lambda_\beta < \lambda_\alpha$ .



The incoming x-rays knocking out inner-shell electrons and having outer-shell electrons fill their space. The outer-shell electrons are bound to the atom with less energy than inner-shell electrons. When the outer-shell electron fills the inner-shell vacancies (empty spaces) the energy difference is accounted for by the energy of the emitted x-ray therefore energy is conserved.

b) 1<sup>st</sup> Part:



2<sup>nd</sup> part: Refer to Question No. 1 (a) of Long Answer Type Questions.

c) Any wavelength of electromagnetic radiation can undergo diffraction, which occurs as a result of interference between electromagnetic waves. This interference can be either constructive or destructive.

For example, two monochromatic waves with equal intensity and wavelength can form a wave with the same wavelength and twice the intensity, or they can cancel either completely. Maximum intensity occurs when both component waveforms are out-of-phase by some integer multiple of their wavelength, and zero intensity occurs when they are out-of-phase by some integer multiple of  $\frac{1}{2}$  their wavelength. In general, shifting the phase of either component wave with respect to the other will either amplify or attenuate the overall signal. Bragg's Law describes the condition that must be met for constructive reinforcement of scattered x-rays (Figure 1). Specifically, Bragg's Law describes the relationship between the path length of an x-ray beam within a crystal lattice and the resulting phase shift of the beam (Equation 1).

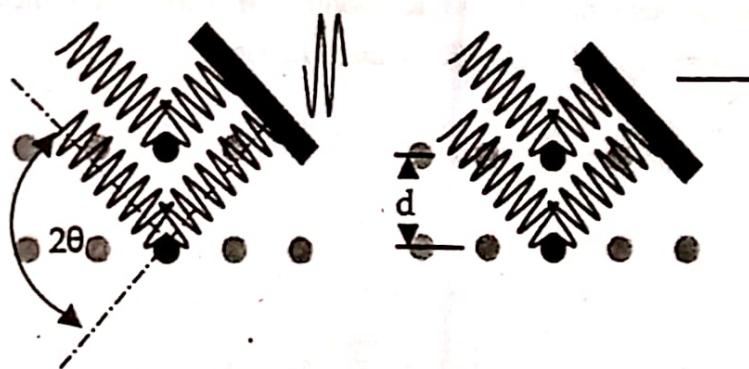


Fig: Illustration of Bragg's Law, depending on the difference in overall distance

$$n\lambda = 2d \cdot \sin\theta \quad \dots(1)$$

Equation 1 : Bragg's law in which

n: any integer,  $\lambda$ : wavelength, d: distance between Bragg planes,  $\theta$ : angle between incident beam and Bragg plane

d) Cut-off wavelength  $\lambda_0 = \frac{ch}{eV} = \frac{3 \times 10^8 \times 6.6 \times 10^{-34}}{1.6 \times 10^{-19} \times 30 \times 10^3} = .4125 \times 10^{-10} \text{ m}$

6. Describe how FTIR spectrometry works. Do you need monochromatic ray for FTIR analysis? [WBUT 2014]

Answer:

1<sup>st</sup> Part:

Michelson interferometer principle where a moving mirror is used and that based on a moving wedge. The system schematic is shown in figure below. Radiation from IR source  $S_1$ , is split by the beam splitter  $BS_1$ , half of which is reflected to the mirror  $M_1$  to be reflected back to  $BS_1$ , the rest half passes through  $BS_1$  and falls on the moving mirror  $MM_1$ .  $MM_1$  is moved forward and backward by a linear motor LM over a certain distance, about 20 to 200 mm, and it also reflects back to  $BS_1$ . A portion of radiation reflected from  $M_1$  combines with another portion reflected from  $MM_1$  at  $BS_1$  and passes through the sample on to a detector. Because of the movement of  $MM_1$ , if the distance travelled by the two split beams differ by one wavelength, they are in phase. For  $MM_1$  moving by a distance  $\pi/4$  from such a situation, the differences if  $\pi/2$  and a phase opposition in the beam occurs so that destructive interference would be pattern will be produced which will change at the rate of change of the mirror position on as also on the change of frequency or wavelength of radiation. Hence by controlling the rate of change of mirror position, a series of simultaneous signals oscillating at frequencies proportional to the frequencies of the incoming radiation will arrive at the detector after passing through the sample. The detector measures all the frequencies simultaneously and passes the measured value to the computer for decoding using FT. This converts the time domain spectrum into frequency domain one which is then appropriately displayed. The purpose of the second laser interferometric system  $S_2M_2MM_2T_2$  and the third white light interferometric system  $S_3M_3MM_3T_3$  will be taken up later.

## ANALYTICAL INSTRUMENTATION

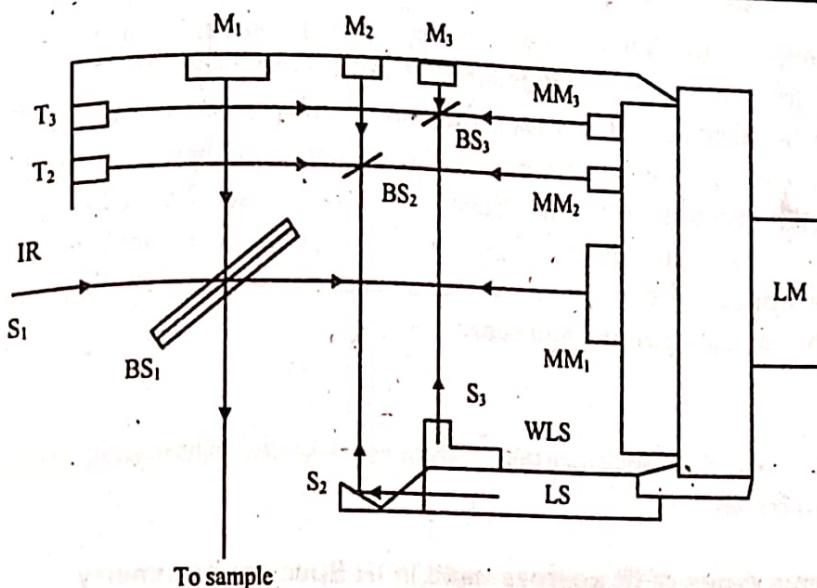


Fig: The FT IR spectrometer based on Michelson interferometer principle

Now assuming  $MM_1$  moving at a constant linear velocity  $V \text{ cm/sec}$ , the interferogram frequency  $f = V/(\lambda/2)$ . The interferogram is the plot of the output intensity versus the difference in the two path lengths  $\delta$ , usually called retardation. Hence,

$$f = 2Vf_r/c = 2V\sigma$$

where  $f_r$  is the radiation frequency.

### 2<sup>nd</sup> Part:

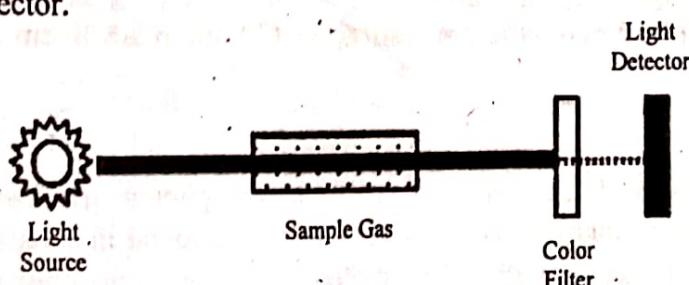
No monochromatic ray is used in FTIR.

**7. a) Discuss the principle of operation of an NDIR analyzer. Name the gases which can be analyzed by NDIR analyzer.** [WBUT 2015]

**Answer:**

### 1<sup>st</sup> Part:

The term non-dispersive refers to the fact that all the light passes through the gas sample and is *only filtered* immediately before the detector. Dispersive IR detectors use a *grating or prism* to pre-select the desired wavelength of light and pass only this through the gas-sample to the detector.



Non-Dispersive IR-All light through sample

The key components of an NDIR system are an infrared source, a sample chamber or light tube, a light filter and an infrared detector. The IR light passes through the sample chamber towards the detector. In parallel, there is another chamber with an enclosed reference gas, typically nitrogen. The gas in the sample chamber absorbs IR rays of specific wavelengths according to the Beer -Lambert's law. The detector receives attenuated rays of these wavelengths. The detected output is a function of the gas concentration. An optical filter in front of the detector eliminates all light except the wavelength that the selected gas molecules can absorb.

2<sup>nd</sup> part:

Molecules like  $\text{CO}_2$ ,  $\text{SO}_2$ , C-H hydrocarbons, Alkenes, Alkynes, Aldehydes, Ketones etc. are measured using NDIR.

b) Name the various types of IR sources used in IR Spectrophotometry.

[WBUT 2015, 2017]

Answer:

*The Nernst glower* is a cylinder (1-2 mm diameter, approximately 20 mm long) of rare earth oxides. Platinum wires are sealed to the ends, and a current passed through the cylinder. The Nernst glower can reach temperatures of 2200 K.

*The Globar source* is a silicon carbide rod (5mm diameter, 50mm long) which is electrically heated to about 1500 K. Water cooling of the electrical contacts is needed to prevent arcing. The spectral output is comparable with the Nernst glower, except at short wavelengths (less than 5 mm) where it's output becomes larger.

*The incandescent wire source* is a tightly wound coil of nichrome 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.

8. a) State how UV absorption spectroscopy can be used for quantitative analysis of the different samples? Describe the working of the dual beam type UV spectrophotometer with a neat sketch.

b) A solution containing the complex formed between (Bi(III)) and thiourea has a molar absorptivity of  $9.32 \times 10^3 \text{ L mol}^{-1}$  at 470 nm.

i) What is the absorbance of a  $6.24 \times 10^{-5} \text{ M}$  solution of the complex in 1.00 cm cell?

ii) What is the molar concentration of the complex in a solution that has the absorbance described in (i) when measured at 470 nm in a 5.00 cm cell?

[WBUT 2016]

Answer:

a) 1<sup>st</sup> Part:

**Quantitative analysis:** Ultraviolet and visible spectrophotometric methods have been used to determine the unknown concentration of a compound in solution. The essential condition to develop such a method is that Beer's law.  $A = \epsilon cb$ , must be obeyed in the range of concentration to be used. The absorbance  $A$  is measured directly from spectrophotometer at various concentrations 'C' of the solution. A graph is then plotted between  $A$  and  $C$  as shown in Fig. 1. Absorbance  $A'$  of the solution of unknown

concentration is then determined by spectrophotometer and its concentration  $C'$  is then determined from the graph. The extinction coefficient ( $\varepsilon$ ) can also be determined from the slope of the graph.

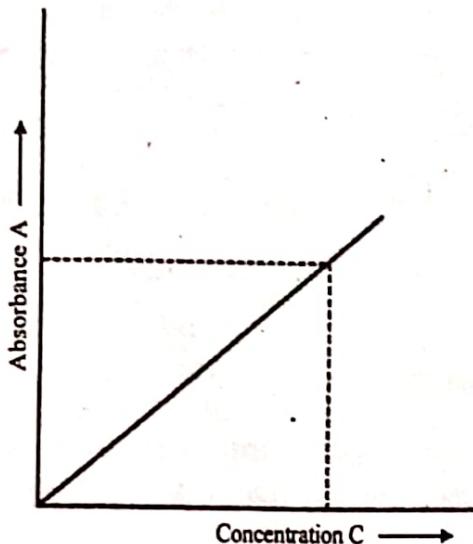


Fig: 1 Graph between concentration and absorbance

2<sup>nd</sup> part: Refer to Question No. 2(a) of Long Answer Type Questions.

b) Refer to Question No. 2(b) of Long Answer Type Questions.

9. a) Write down the Beer's Law for absorption of radiation by a gas medium. Find the expression relating concentration and power of incident and emergent radiation from the shell. [WBUT 2017]

Answer:

Beer's Law is expressed as differential equation

$$\left(\frac{1}{I}\right) \frac{dI}{dx} = -\alpha \rho$$

where, I is the intensity of radiation, L is the distance traveled in a medium,  $\rho$  is the molecular volume density of absorbers in the medium, and  $\alpha$  is a parameter, called the *absorption coefficient*, characteristic of the medium. The law can be expressed in different terms such as the density being the linear density of absorbers. Then the absorption coefficient is correspondingly changed. For the purposes here it is most convenient to have the density being the number of absorbing molecules per unit volume. The solution to the differential equation is

$$I(L) = I(0) r^{-\alpha \rho x}$$

*Derivation*

Consider a beam of light of cross section area A passing through a medium of depth L. Suppose that for a quantum of light to pass through the medium unabsorbed there has to be cylindrical tunnel of cross section area a where there are no absorbing molecules.

The probability p that the center of one molecule is not located in that area a is

$$p = \frac{(A-a)}{A} = \left( \frac{1-a}{A} \right)$$

The probability P that all of N molecules are located outside of the area a is then

$$P = p^N. \text{ Since } p = \frac{1-a}{A}, \text{ therefore, } \ln(p) = \ln\left(\frac{1-a}{A}\right) \text{ and for small values of } \frac{a}{A}$$

$\ln(p)$  is approximately equal to  $-\frac{a}{A}$ .

The number of molecules in the beam is the volume times the molecular density; i.e.,  $N = (A \times L) \rho$  where  $\rho$  is the molecular volume density of the molecules.

$$\text{Thus } P = e^{-\left(\frac{a}{A}\right)(A \cdot L) \rho}, \text{ which reduces to } P = e^{-a \rho L}.$$

The light intensity at a distance L in the medium is then  $I(L) = I(0) e^{-a \rho L}$

$$\text{and thus } \frac{dI}{dL} = -a \rho I$$

The proportion not absorbed is the same as the probability of a quantum not being absorbed, P. Thus,

$$\frac{I(L)}{I(0)} = P = e^{-a \rho L} \text{ and hence } I(L) = I(0) e^{-a \rho L}.$$

b) Draw and explain a scheme of a non-dispersive dual channel absorption type IR spectrometer. [WBUT 2017]

Answer: Refer to Question No. 5 of Short Answer Type Questions.

c) Name two IR sources and two IR detectors.

[WBUT 2017]

Answer:

- IR Sources    i) The Nernst glower  
                  ii) The Globar source (A silicon carbide rod)

- IR detectors    i) Thermocouples  
                  ii) Mercury cadmium telluride

10. a) What is plasma? Draw the schematic diagram of ICP source and DCP source and briefly discuss it.

b) State why RF source is necessary for NMR spectroscopy. Describe NMR spectroscopy with schematic diagram.

c) What is the principle used in Electron Spin Resonance? Mention two applications of ESR spectroscopy. [WBUT 2018]

**Answer:**

a) 1<sup>st</sup> part & 2<sup>nd</sup> part: Refer to Question No. 1(b) of Long Answer Type Questions.

3<sup>rd</sup> part: Refer to Question No. 6(2<sup>nd</sup> part) of Short Answer Type Question.

b) Refer to Question No. 3(a) of Long Answer Type Questions.

c) Refer to Question No. 3(b) of Short Answer Type Questions.

11. Write short notes on the following:

a) IR Sources

[WBUT 2009, 2013, 2014, 2016]

b) X-ray Spectroscopy

[WBUT 2009]

c) Monochromator

[WBUT 2010]

d) FT-IR Spectrometer

[WBUT 2010, 2016]

OR,

FTIR

[WBUT 2018]

e) Atomizers.

[WBUT 2013]

f) Deuterium Source for UV-VIS Spectrometer

[WBUT 2015]

g) Non-dispersive instrument

[WBUT 2017]

h) ESR

[WBUT 2017]

**Answer:**

a) IR Sources:

Several consideration must be made in the selection of an infrared source. In all cases, the sources which used in IR instrument must produce adequate radiant power at the frequency so that it is possible to detect the radiation above a given noise level. The operation of the crystal oscillator method of moisture measurement output of the source must also have sufficient stability over the measurement time frame of the instrument. Other important consideration includes the cost and lifetime of the source.

Generally IR instruments used continuum sources. For example electrically heated resistive materials. It can be used as IR source because everything which has temperature above absolute zero can radiation IR radiation.

Some time Infrared sources can be described in terms at black body. But the radiant intensity of real sources will differ from the ideal black body. Real sources are not perfect emitters and are sometimes enclosed in an external housing. The window in the enclosure will alternate some frequencies of radiation by absorption or by reflection.

Some of these IR sources are:

**LED (Light Emitting Diode):** Infrared light emitting diodes emit a continuum of IR radiation over a limited spectral range. By using different semiconductor materials, LED can be fabricated that emit at various wavelength over most of the near IR and mid IR regions.

**Lasers:** Laser emits over very narrow frequency ranges. Lasers can either have fixed wavelengths or can be tunable over a wavelength range. Carbon dioxide and diode lasers are frequently used for IR spectroscopy in research applications.

b) X-ray Spectroscopy:

Electron Spectroscopy for Chemical Analysis (ESCA) is an effective technique for detecting the elements and their bonding states on the surface of solids, also known as X-ray Photoelectron Spectroscopy (XPS). The methods use soft X-rays to eject electrons from inner-shell orbitals. The kinetic energy of these photoelectron energies are dependent upon the chemical environment of the atom, it makes XPS useful to identify the oxide state and ligands of an atom. On the other hand, however, the binding energy may shift (up to several eV) reflecting the chemical state of the atom, it is also possible to get information on the valence number and oxidation number, and the type of functional group present. Moreover, the ion etching technique provides the depth profiling from the surface.

Electron spectroscopy is based on the ionization phenomenon brought about by either a photon (X-ray) or an electron. An X-ray photon ionizes an atom, thereby producing an ejected free electron. The kinetic energy of the ejected photoelectron is dependent upon the energy of the impinging photon expressed as  $E_K = h\nu - E_b - \Phi$ ,

where  $E_K$  is the kinetic energy of the photon ejected,  $h\nu$  is the X-ray energy,  $E_b$  is the binding energy of the parent atom relative to the ejected electron and  $\Phi$  is the work function, typically < 2 eV and often ignored.

c) Monochromator:

The monochromator is included as an important device of the optical system of an atomic absorption spectrophotometer. The function of this device is to separate the spectral line of interest from other spectral lines of different wavelengths emitted by the hollow cathode lamp. The desired spectral line is chosen with the preferred wavelength and bandwidth with the help of a grating (Fig. (i)).

A grating is a collection of closely spaced parallel slits on a surface. It can be of transmission or reflective-type and can be designed for different wavelength regions. Generally, most of the instruments are equipped with two reflective-type gratings with a view to covering a wavelength range of 189 nm to 851 nm which is used in atomic absorption.

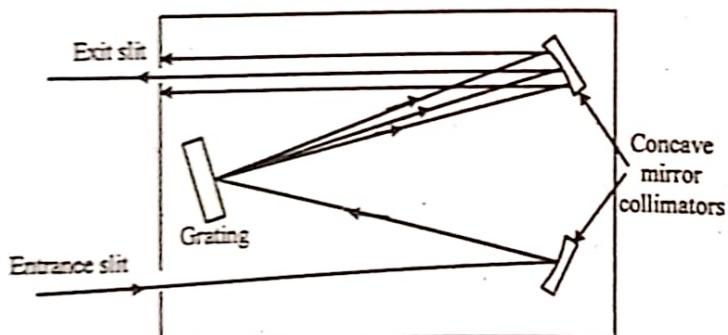


Fig: (i) Grating monochromator

d) **FT-IR Spectrometer:**

Fourier Transform Infrared (FTIR) spectroscopy is a novel infrared technique. As a conventional infrared spectroscopy, FTIR is used to detect vibrational transitions of a molecule.

The advantage of FTIR compared to conventional infrared spectroscopy is that all wavenumbers are measured at once with help of Michelson interferometer.

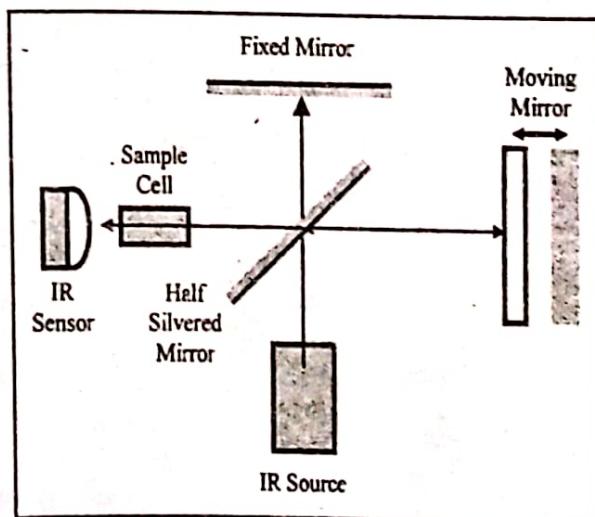
**Fourier Transform Spectrometers:**

Is the most modern infrared spectrometers (spectrophotometers) operate on a different principle. The design of the optical pathway produces a pattern called an **interferogram**. The interferogram is a complex signal, but its wave-like pattern contains all the frequencies that make up the infrared spectrum. An interferogram is essentially a plot of intensity versus time (a **time-domain spectrum**). A mathematical operation known as a **Fourier transform (FT)** can separate the individual absorption frequencies from the interferogram, producing a spectrum virtually identical to that obtained with dispersive spectrometer. This type of an instrument is known as a **Fourier transform infrared spectrometer**, or FT-IR.

The advantage of an FT-IR instrument is that it acquires the interferogram in less than a second. It is thus possible to collect dozens of interferograms of the same sample and accumulate them in the memory of a computer. When a Fourier transform is performed on the sum of the accumulate interferograms, a spectrum with a better signal-to-noise ratio can be plotted. An FT-IR instrument is therefore capable of greater speed and greater sensitivity than a dispersion instrument.

**Working of FTIR spectrometer:**

A typical arrangement of a FTIR spectrometer is shown bellow.



Collimated light from a broadband infrared source passes into the optical system and impinges on a Beam Splitter that comprises a very thin film of germanium. Approximately 50% of the light passes through the film and is reflected back along its path by a fixed mirror, where half of the light intensity (25% of the original light

intensity) is reflected by the same Beam Splitter, through the sample cell, to the infrared sensor. The other 50% fraction of the incident light is reflected at right angles to its incident path onto a moving mirror. Light from the moving mirror returns along its original path and half of the light intensity is transmitted through the Beam Splitter, through the sample cell, to the infrared sensor. As a result, 25% of the incident collimated light from the source reaches the sensor from the fixed mirror and 25% from the movable mirror. Now the path length of the two light beams striking the sensor will be different so there will be destructive and constructive interference. Actually, the system constitutes a form of the Michelson interferometer.

As the movable mirror traverses its programmed path and constructive and destructive interference takes place, a series of maxima and minima signals will be monitored by the sensor. It is also seen that the frequency of this waveform will be determined by the velocity of the moving mirror, which is experimentally controllable. This results in the interferometer actually taking a Fourier transform of the incoming signal. An example of an Interferogram obtained from the FTIR is shown in figure.



e) Atomiser:

The principle of atomic absorption requires light absorption by "free atoms". A "free atom" means an atom, which is not combined with other atoms. However, elements in the sample are invariably combined with other elements to form molecules. The combination must be broken by some means to free the atoms. This is called atomization. Of all the methods described at the beginning of this section, the most popular method of atomization used in AAS is the flame excitation source. Samples are heated to a high temperature by oxy-acetylene (or acetylene-nitrous oxide) flame so that molecules are converted into free atoms. The appearance of an actual nebuliser-cum-burner is shown in Fig. 1.

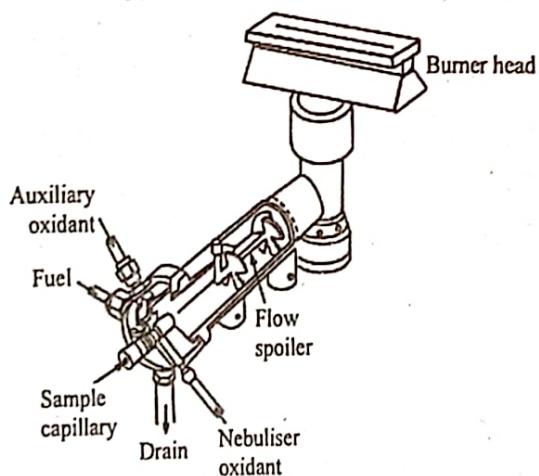


Fig: 1 Appearance of an actual nebuliser-cum-burner

The alternative to the flame method is the electrothermal method, described earlier. The comparison of the flame atomization method and electrothermal atomisation method is shown in Table 1.

Table 1 Comparison between flame and electrothermal methods of atomization

Characteristic	Flame atomisation	Electrothermal atomisation
Sensitivity	ppm level in the solution	ppb level in the solution
Sample volume	~1 ml for one analysis	5 to $\mu$ l for one analysis
Atomizing efficiency	About 10%	Nire tgas 90%
Sgaoe if sugbak	Plateau shape	Peak shape
Repeatability	0.5 to 1.0% of the reading	2.0 to 5.0% of the reading
Time for analysis	10 to 30 s for one sample	2 to 5 min for one sample

#### f) Deuterium Source for UV-VIS Spectrometer:

Deuterium arc lamps emit rays in the UV region 190 - 370 nm. As Deuterium lamps operate at high temperatures, normal glass housings cannot be used for the casing. Instead, a fused quartz, UV glass, or magnesium fluoride envelope is used. When run continuously typical lamp life for a Deuterium lamp is approximately 1000 hours, however this can be extended by up to a factor of three using PTR technology. Deuterium lamps are always used with a Tungsten halogen lamp to allow measurements to be performed in both the UV and visible regions.

#### *Principle of operation:*

A deuterium lamp uses a tungsten filament and anode placed on opposite sides of a nickel box structure designed to produce the best output spectrum. Unlike an incandescent bulb, the filament is not the source of light in deuterium lamps. Instead an arc is created from the filament to the anode, a similar process to arc lamps. Because the filament must be very hot before it can operate, it is heated for approximately twenty seconds before use. Because the discharge process produces its own heat, the heater is turned down after discharge begins. Although firing voltages are 300 to 500 volts, once the arc is created voltages drop to around 100 to 200 volts.<sup>11</sup>

The arc created excites the molecular deuterium contained within the bulb to a higher energy state. The deuterium then emits light as it transitions back to its initial state. This continuous cycle is the origin of the continuous ultraviolet radiation. This process is not the same as the process of decay of atomic excited states (atomic emission), where electrons are excited and then emit radiation. Instead, a molecular emission process, where radiative decay of excited states in molecular deuterium ( $D_2$ ), causes the effect.

The spectral line structure of deuterium does not differ noticeably from that of light hydrogen, but deuterium has a slightly stronger molecular bond (439.5 vs. 432 kJ/mol) and is less-well ionized at the temperature of the arc, and this causes a larger population of molecules and a greater emissivity (light output) of UV in the molecular part of the spectrum that is farthest into the ultraviolet.

Because the lamp operates at high temperatures, normal glass housings cannot be used for a casing. They would also block UV radiation. Instead, a fused quartz, UV glass, or magnesium fluoride envelope is used depending on the specific function of the lamp. The typical lifetime of a deuterium lamp is approximately 2000 hours (Most manufacturers guarantee 2000 hours, but newer lamps are consistently performing well out to 5000 hours and more).

g) Non-dispersive instrument:

*Refer to Question No. 12 of Short Answer Type Questions.*

h) ESR:

ESR (electron spin resonance) spectroscopy is an absorption spectroscopy, which involves the absorption of radiation in the microwave region ( $10^4$ – $10^6$  MHz) by substances containing one or more unpaired electrons. When the molecules of a solid exhibit paramagnetism as a result of unpaired electron spins, transitions can be induced between spin states by applying a magnetic field and then supplying electromagnetic energy, usually in the microwave range of frequencies. The resulting absorption spectra are described as electron spin resonance (ESR) or electron paramagnetic resonance (EPR). Electron spin resonance has been used as an investigative tool for the study of radicals formed in solid materials, since the radicals typically produce an unpaired spin on the molecule from which an electron is removed

*Components of ESR and their functions*

(a) **Klystrons:** Klystron tube acts as the source of radiation. It is stabilized against temperature fluctuation by immersion in an oil bath or by forced air cooling. The frequency of the monochromatic radiation is determined by the voltage applied to klystron. It is kept a fixed frequency by an automatic control circuit and provides a power output of about 300 milli watts.

(b) **Waveguide:** Waveguide is a hollow, rectangular brass tube. It is used to convey the wave radiation to the sample and crystal.

(c) **Attenuators:** The power propagated down the waveguide may be continuously decreased by inserting a piece of resistive material, called as the variable attenuator, into the waveguide and used in varying the power to the sample from the full power of klystron.

(d) **Sample cavities:** The heart of the ESR spectrometer is the resonant cavity containing the sample. Rectangular cavity and cylindrical cavity have widely been used. In most of the ESR spectrometers, dual sample cavities are generally used. This is done for simultaneous observation of a sample and a reference material. Since magnetic field interacts with the sample to cause spin resonance the sample is placed where the intensity of magnetic field is greatest. A measure of quality of the cavity is 'Q factor', which is defined as the sensitivity of the spectrometer is directly proportional to this value of Q.

(e) **Crystal detectors:** A Silicon crystal detectors, which converts the radiation in D.C., has widely been used as a detector of microwave radiation!

## ANALYTICAL INSTRUMENTATION

**(f) Magnet system:** The resonant cavity is placed between the poles pieces of an electromagnet. An electro magnet capable of producing magnetic field of at least 5000 gauss is required for ESR. The field should be stable and uniform over the sample volume. A highly regulated power supply energizes the magnet to achieve a stable magnetic field. The ESR spectrum is recorded by slowly varying the magnetic field through the resonance condense by sweeping the current supplied to the magnet by the power supply. A variable speed motor drive is used to accomplish such a sweep. Both the magnet as well as the power supply may require water-cooling. Figure below shows the block diagram of the ESR.

