UNIT 24

ANALYTICAL CHEMISTRY

Learning Outcomes:

After Studying this unit Students will be able to:

- compare the classical method of analysis with modern methods.
- discuss the procedure/purpose of combustion analysis.
- define spectroscopy and discuss its applications in analytical chemistry.
- explain the origin of electromagnetic spectrum used in IR and uv-vis spectroscopy.
- explain the origin of IR absorption by the simple molecules.
- determine structures of phenol, toluene, acetone and ethanol by their IR spectrum.
- predict whether a given molecule will absorb in the uv-visible/IR region or not.
- predict the color of a transition metal complexe from its uv-vis spectra.
- outline in simple terms the principles of proton NMR spectroscopy.
- explain how chemical environment of proton affects the magnetic field it experiences and hence the absorption of energy at resonance frequency.
- describe standard scales used in proton NMR.

- explain instrumentation and working of MS.
- outline the use of MS in determination of relative isotopic masses and isotopic abundance.
- define and explain atomic emission and atomic absorption spectrum.
- calculate the average atomic mass of an element from isotopic data.
- calculate percentage of C,H and O from given data and determine empirical and molecular formula.

Analytical Chemistry:

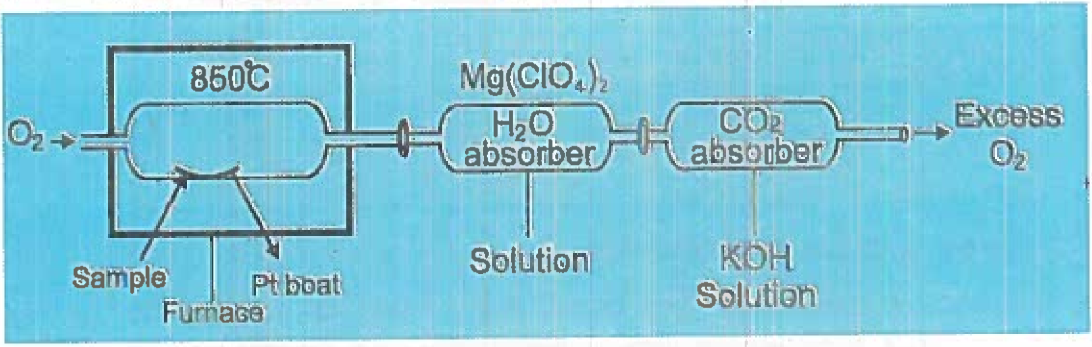
Analytical chemistry is a branch of chemistry which deals with the identification of substances and finding their weights. A set of experiments used to know about the quality of a substance is called qualitative analysis. The methods used for finding the quantities of substances are called quantitative analysis. Analytical chemistry deals with both qualitative and quantitative analysis.

Identification of acidic and basic radicals in a salt involves qualitative chemical analysis. On the other hand, volumetric analysis (titrations) and gravimetric analysis are quantitative chemical analysis.

24.1

Classical methods of Analysis, Combustion analysis and determination of Molecular formula:

Burning of a substance in the presence of oxygen is called combustion. Combustion is an exothermic process in which heat energy is evolved. Combustion analysis is carried out for finding the percentage composition of an organic compounds cantaining C,H or C,H and O. If any other element such as N,S,Cl etc. is present in the compound, combustion analysis can not be used. In combustion analysis a known weight of an organic compound is mixed with CuO and taken in a platinium boat, which is placed in a furnace heated to about 850°C, and a stream of oxygen gas is passed over the sample.



Organic compound on burning produces CO_2 and H_2O vapours which are swept out of the furnace and traped in a pair of absorbers. The water is absorbed in a sample of Magnesium perchlorate [$Mg(ClO_4)_2$] of known mass. The carbon dioxide is absorbed in a known mass of KOH. Percentage of C and H are calculated by the following formulae.

$$\%C = \frac{\text{mass of } CO_2}{\text{mass of org.compound}} \times \frac{12}{44} \times 100$$

$$\%H = \frac{\text{mass of } H_2O}{\text{mass of org.compound}} \times \frac{2.02}{18.02} \times 100$$

Percentage of oxygen is calculated as %O = 100 – (%C + %H). If percentage of oxygen comes out to be zero, it means the organic compound does not contain oxygen.

Calculation of Empirical formula:

Empirical formula is the formula that gives the simplest whole number ratio of the atoms of elements present in the compound.

In order to find the empirical formula of a compound, number of moles of carbon, hydrogen and oxygen is calculated by the following formulae.

$$\text{Moles of C} = \frac{\text{\%age of C}}{\text{At. mass of C}}$$

$$\text{Moles of H} = \frac{\text{\%age of H}}{\text{At.mass of H}}$$

$$\text{Moles of O} = \frac{\text{\%age of O}}{\text{At.mass of O}}$$

In second step the simplest ratio between the number of moles is found out by dividing the number of moles of each element by the smallest number of moles. If the ratio is not in whole numbers then number of moles of each element is multiplied by a suitable small number to get the whole number ratio.

Finally the symbol of each element are written and their number of moles are written as subscripts. This gives the empirical formula of a compound.

Example 24.1: The combustion analysis of 0.003g of Aspirin produced 0.0066g of CO_2 and 0.0012g of H_2O. Calculate the empirical formula of aspirin.

Solution: Calculate the percentage of elements

$$\text{Percentage of C} = \frac{\text{mass of } CO_2}{\text{mass of org.compound}} x \frac{12}{44} x100$$

$$= \frac{0.0066}{0.003} x \frac{12}{44} x100$$

$$= 60.0\ \%$$

$$\text{Percentage of H} = \frac{\text{mass of } H_2O}{\text{mass of org.compound}} x \frac{2.02}{18.02} x100$$

$$= \frac{0.0012}{0.003} x \frac{2.02}{18.05} x100 = 4.48\%$$

$$\text{Percentage of O} = 100 - (60.0 + 4.48)$$

$$= 35.5\ \%$$

Let us find the number of moles of elements

$$\text{Moles of C} = \frac{\text{\%age of C}}{\text{At.mass of C}} = \frac{60.0}{12.01} = 4.99$$

$$\text{Moles of H} = \frac{\text{\%age of H}}{\text{At.mass of H}} = \frac{4.48}{1.01} = 4.43$$

$$\text{Moles of O} = \frac{\text{\%age of O}}{\text{At.mass of O}} = \frac{35.5}{16.0} = 2.21$$

$$\begin{array}{lccccc} \text{Molar ratio :} & C & : & H & : & O \\ & 4.99 & & 4.43 & & 2.21 \\ \text{Simplifying the molar ratio} & \frac{4.99}{2.21} & : & \frac{4.43}{2.21} & : & \frac{2.21}{2.21} \\ & 2.25 & & 2.00 & & 1.00 \end{array}$$

To convert the fractional number into whole number, each value is multiplied by 4.

$$\begin{array}{ccccc} C & : & H & : & O \\ (4 \times 2.25) & & (4 \times 2.00) & & (4 \times 1.00) \\ 9.00 & : & 8.00 & : & 4.00 \end{array}$$

Thus empirical formula of Aspirin is $C_9H_8O_4$. Empirical formula of a compound shows the simplest ratio between different kinds of atoms present in a compound. It does not show the exact number of atoms.

Calculation of Molecular formula:

Molecular formula shows the actual number of atoms of each kind of element in molecule of a compound. Molecular formula is either same to empirical formula or integral multiple of the empirical formula.

Molecular formula = n x (empirical formula)

$$n = \frac{\text{Molecular weight}}{\text{Empirical formula weight}}$$

Example: Empirical formula of a compound is CH_2O. Molecular weight of this compound as obtained from other experiments is 180.12 g/mol. Find the molecular formula of the compound.

Solution: Let find the value of n

$$n = \frac{\text{Molecular weight}}{\text{Empirical formula weight}} = \frac{180.12}{30.02} = 6$$

Thus molecular formula = n (empirical formula)

$$= 6\,(CH_2O)$$

$$= C_6\,H_{12}\,O_6$$

24.2 Modern methods of Analysis:

In inorganic chemistry, a molecular formula is informative enough to distinguish one substance from another. However, this is not the case in organic chemistry, where molecular formula may represent more than one substance e.g. C_2H_6O is a molecular formula, the atom may be arranged as:

CH_3-CH_2-OH Ethanol

CH_3-O-CH_3 Dimethyl ether

So in organic chemistry structural formula is often used to represent a particular organic substance. Previously, the structure of newly discovered organic compounds was based almost entirely on its molecular formula and chemical reactions. This way of finding the structure of organic compounds was time consuming and not always 100% accurate. Now a days spectroscopic methods are used for analysis and structure determinations.

Modern methods of analysis include infrared spectrophotometry, ultraviolet and visible spectrophotometry, Atomic abosption and emission spectrophotometry and mass spectrometry. Modern methods of analysis are superior to classical methods because of the following reasons.

(i) Small amounts of chemical are required.

(ii) Chemicals are not wasted in large amounts.

(iii) These methods are rapid and less time consuming.

(iv) They give more accurate results.

(v) These methods are simple and do not involve much chemistry as compared to the classical methods.

24.2.1 Spectroscopy:

After finding the molecular formula of an organic compound, we need to find its exact structural formula. For structural formula of a compound mainly three aspects are considered;

i. Physical properties of the compound.

Physical properties are dependent on the structure and provides enough information about the structure formula of the compound. For example C_2H_6O is the molecular formula of both ethanol and diethyl ether. Ethanol (C_2H_5–OH) at room temperature is liquid and its boiling point is 341K, while dimethyl ether ($CH_3 — O — CH_3$) is gas at room temperature having a boiling point of 248K.

ii. Chemical properties:

Functional group is defined as "an atom or a group of atoms that gives certain characteristic properties to the compound". Different compounds having the same molecular formula but different functional groups (structural formula) behave differently to the same reactants. For example ethanol reacts with sodium metal liberating hydrogen, while demethyl ether do not react with it.

iii. Instrumental methods of analysis.

Modern chemistry laboratories use instruments that help to identify atoms/group of atoms in the organic compound to elucidate its structure. Spectroscopy is one of these instrumental methods.

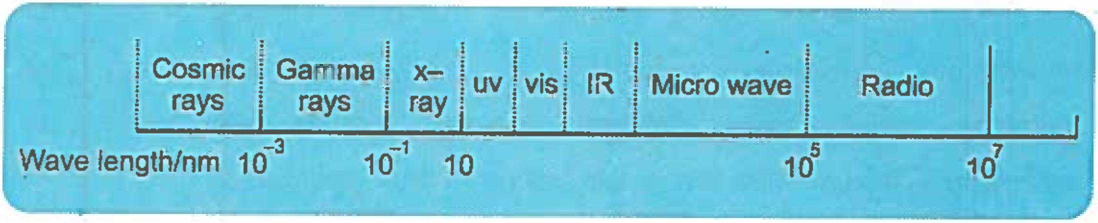
Organic compounds absorb energy on interaction with electromagnetic radiations. The electromagnetic radiation (emr) extend from high-energy cosmic rays to low-energy radio waves, according to the equation

$E=h\upsilon$ and

$\upsilon=c/\lambda$

So $E=hc/\lambda$

That is energy of the e.m.r depends on its frequency and wave length.



The regions of electromagnetic spectrum of e.m.r is given in above figure.

During the interaction of organic compounds with electromagnetic radiations certain wavelengths are absorbed, which excites the molecules/atoms to higher energy level. In atoms the transition results due to changes in distribution of electrons, while in molecules along with changes in electronic distribution, changes in the molecular rotations and bonds vibration (stretching, bending) also occurs.

The bond vibration and rotation of molecules need less energy, i.e. in IR region, than the electronic excitation i.e. in uv/vis region.

The instrument used to record the wavelengths absorbed and the concentration of the absorbing species is called spectrophotometer.

Spectrophotometry is a technique used to identify the different substances as a result of their interactions with the electromagnetic radiations, spectrophotometry is used both for qualitative as well as quantitative analysis. Before discussing the different spectrophotometric techniques let us study the electromagnetic spectrum.

Electromegnetic spectrum.

The electromagnetic spectrum covers a wide range of wavelengths of different radiations. Electromagnetic radiations are divided into different regions, each region being defined by the limits of any of the four parameters, i,e. frequency, wavelength, wave number or energy. The following table shows different spectral regions alongwith their wavelength, frequencies, wave numbers and their energies.

Table 24.1: Gamma Rays and the Electromagnetic Spectrum

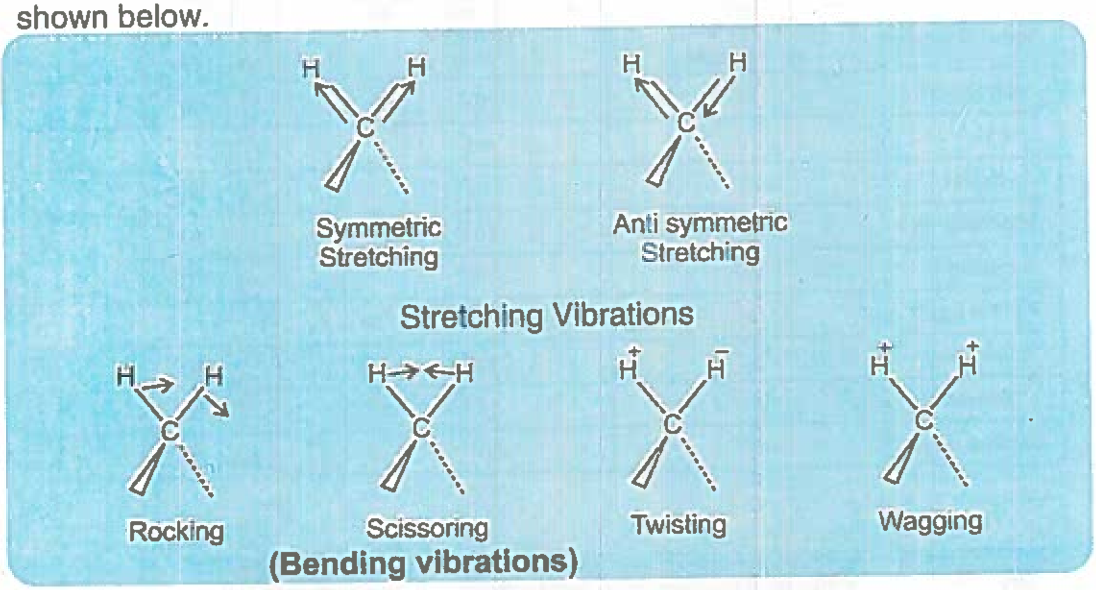
Name of Wave	Wavelength (m = meters)	Frequency (Hz)	Energy per Photon (eV)
AM Radio	10^2	10^6	10^{-9}
FM, TV	1	10^8	10^{-7}
Radar	10^{-1}	10^9	10^{-6}
Microwaves	10^{-2}	10^{10}	10^{-5}
Infrared	10^{-5}	10^{13}	10^{-2}
Visible Light	10^{-7}	10^{15}	1
Ultraviolet	10^{-8}	10^{16}	10^1
X-Rays	10^{-10}	10^{18}	10^3
Gamma Rays	10^{-13}	10^{21}	10^6

24.2.2 Spectroscopic method:

24.2.2.1 Infrared (IR):

In IR spectroscopy organic compounds are exposed to weak radiations in the range 5000–667cm^{-1} (wave number $\bar{\upsilon}$), which increases vibration of bonds in its molecules and also rotation of molecules.

Atoms in a molecule do not maintain fixed positions with respect to each other, the bonds undergo stretching and bending vibrations about the average value of interatomic distance. Such vibrations are particularly important with bonds involving H atoms, because of its low atomic mass. Vibrations may be stretching or bending. In stretching vibrations the bond angle does not change but only the distances between the atoms change. Stretching vibrations may be symmetric or anti symmetric. Bending vibrations do not change the interatomic distance but change the angles between the atoms. The various stretching and bending vibrational modes for Ax_2 system, e.g, the methylene group in a hydrocarbon molecule are shown below.



Stretching Vibrations

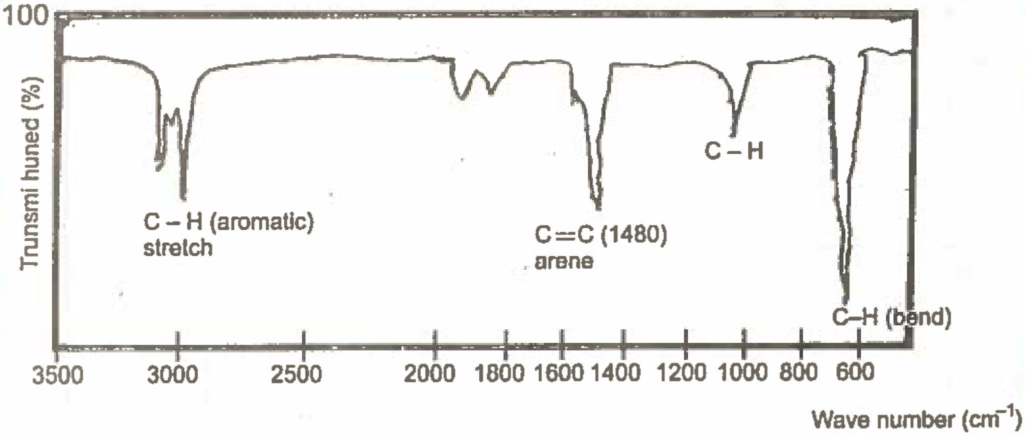
(Bending vibrations)

An infrared spectrum, commonly referred to as IR spectrum is usually expressed in microns (μ) or in the form of wave number (cm^{-1}). Wave number is plotted on *x-axis* and % transmittance on *y-axis*. Each dip in a spectrum is called a band or peak. A 100% transmittance means no absorption.

IR spectrum of an organic compound is characteristic of the structure of the compound, and is of great assistance in establishing its identity. No two different organic compounds would give rise to identical spectra.

IR region is divided into two. The region between 600 – 1500 cm^{-1} is called finger print region because the absorption in this region is characteristic of a compound. Two different compounds will give different absorptions peaks in this region. This region is used to identify a compound. The region between 1500 – 4000 cm^{-1} is called functional group region. Different functional groups show absorption at different frequencies. The following table shows the IR absorption frequencies of different functional groups.

Functional group	Wave number/cm^{-1}
O – H aliphatic and aromatic	3600 – 3000
N – H primary, secondary, tertiary amines	3600 – 3100
C – H aliphatic	3000 – 2850
C – H aromatic	2280 – 2200
C – C arene	1600
C – O	1300 – 1000
O – H free	3670 – 3580
C ≡ C alkynes	2250 – 2070
COOR ester	1750 – 1700
COOH carboxylic acid	1740 – 1670
C = O aldehydes, ketones and esters	1750 – 1680
CONH$_2$ amides	1720 – 1640



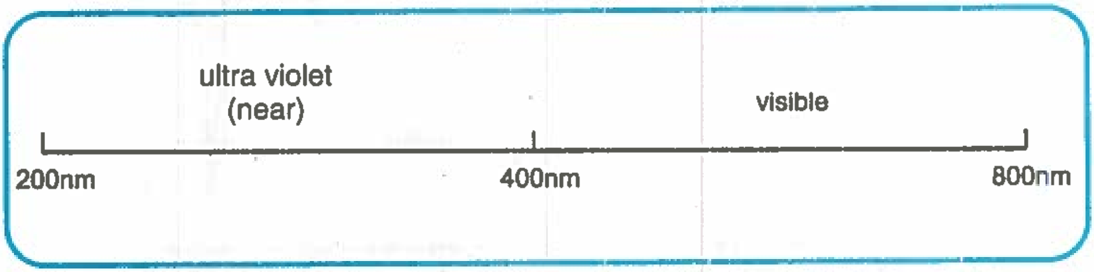
IR spetrum of benzene

Uses

1. IR spectroscopy is helpful in identification of unknown compounds.
2. It is used for detection of impurities. The presence of absorption peak at positions where the compound does not absorb indicates the presence of impurities e.g. the presence of cyclohexanone is readily detected in cyclohexanol by the intense carbonyl band.
3. The progress of most reactions can be followed by examining the infra-red spectra of aliquots withdrawn from the reaction mixture. For example, the oxidation of secondary alcohol to ketone is accompanied by the disappearance of the O–H band near 3600cm^{-1} and the appearance of C = O band near 1715cm^{-1}.

24.2.2.2 Ultraviolet and visible (uv/vis) spectrophotometry:

In uv/vis spectroscopy radiation having wavelength in the range 200–800nm are used. These are more energetic and therefore, can change the distribution of loosely bonded ($\pi-$bond) and non-bonded electrons in molecules/atoms.



As all matter contains electrons, almost all substances absorb certain wavelength in this range.

The absorption is according to Beer-Lambert's law

$$A = Ecl$$

where A is the absorbance, c is the concentration of solution in mole per litre and l is the path length of the sample solution in centimetres. E is called molar absorptivity or molar extinction coefficient, a constant characteristic of the solute at a given wavelength.

Uv-vis spectrophotometry is used both for qualitative and quantitative analysis. For quantitative analysis we use Beer Lambert law. The absorption of uv-vis light by a solution kept in a quartz cell of known path length is directly proportional to the concentration of solution. Solutions of different concentration are prepared and are introduced into the uv-vis spectrophotmeter in order to record their absorbances.

A graph is constructed by plotting the concentrations on x-asis and absorbances on y-axis. This graph is called working curve. During this experiment a selected wavelength λ(max) at which maximum absoption occurs is used throughout the study. When a solution of unknown concentration is placed in the spectrophotometer, its concentration is displayed on the screen. UV light ranges from 10-400nm and visible light from 400-800mn.

The electronic transition that are associated with the absorption of uv/vis radiation, are of four types. i,e $\sigma \to \sigma^*$ saturated $n \to \sigma^*$, $\pi \to \pi^*$ and $n \to \pi^*$

$\sigma \to \sigma^*$ transition occur in a saturated hydrocarbon such as $CH_3 - CH_3$ which contain only sigma bonds. $\sigma \to \sigma^*$ transition requires greater energy, thus C–C bond absorbs 135nm and C – H bond absorbs at about 125nm.

The $n \rightarrow \sigma^*$ transition occurs in a saturated molecules containing hetero atoms, such as oxygen, sulphur, nitrogen or halogens. This transition requires slightly less energy than required for $\sigma \rightarrow \sigma^*$ transition.

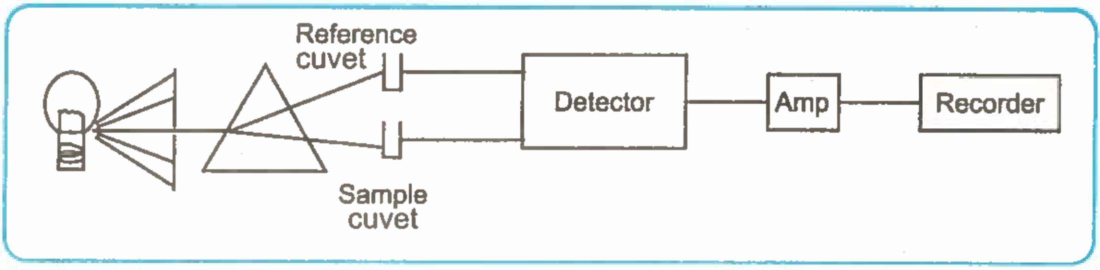
The $\pi \rightarrow \pi^*$ transitions occur in molecule, containing double or triple bonds or aromatic rings. Ethylene absorbs at 171nm. However, a conjugated system of unsaturated bonds absorbs at much longer wavelength, e.g. butadiene absorbs at 217mn. ($CH_2 = CH - CH = CH_2$)

The $n \rightarrow \pi^*$ transitions occur in molecules that contain double or triple bonds involving hetero atoms e.g. $>C=O$: ,$-C \equiv N$: etc.

Transition metal complexes are usually coloured due to d-d transition. Such compounds absorb radiations in the visible region. When a compound absorbs viclet light (400-435nm), it refects all the remaining (six) colours which electively appear as a single colour (complementary colour). Complementary colour of violet colour is yellow green. The following table shows relationship between the colour of transition metal complexes and the wavelength of light absorption.

Colour of light absorbed	Wave length (nm)	Colour of complex
Violet	400 – 435	Yellow green
Blue	435 – 480	Yellow
Blue green	490 – 500	Red
Green	500 – 560	Purple
Yellow	580 – 595	Blue
Orange	595 – 650	Green blue

From the above discussion it is concluded that from the uv-vis spectrum of transition metal complex, the colour of the compound can be predicted. A schematic diagram of double beam uv-vis spectrophotometer is given below.

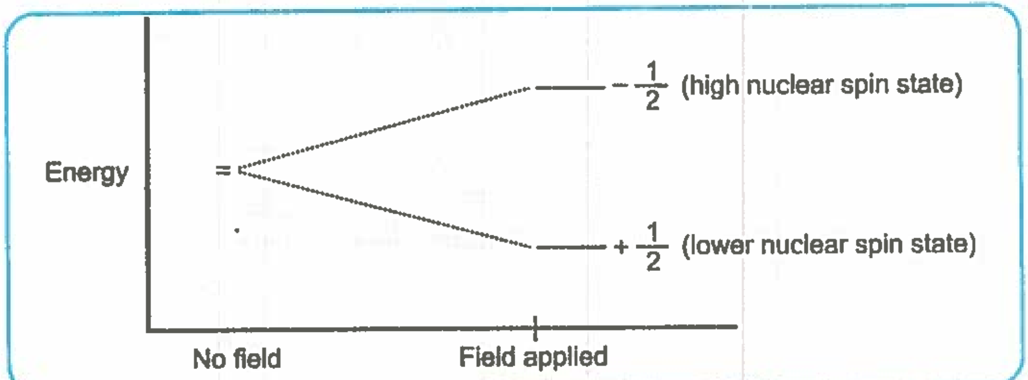


24.2.2.3 Nuclear Magnetic Resonance (NMR) :

Like electrons atomic nucleus also spin about an axis. Thus the atomic nuclei behave like tiny magnets, as the spinning charged bodies produce magnetic field. The nuclear spin is quantised, therefore, the magnetic moment of nucleus is also quantised. In a proton (H) the spin quantum number is = ½. Other nuclei which contain odd number of protons or neutrons or both also have a spin quantum number = ½ e.g. ^{13}C ^{15}N ^{19}F ^{31}P.

Nuclei which have even number of protons and neutrons have zero spin and zero magnetic moment e.g. ^{12}C and ^{16}O. Such nuclei are invisible in NMR spectrometry.

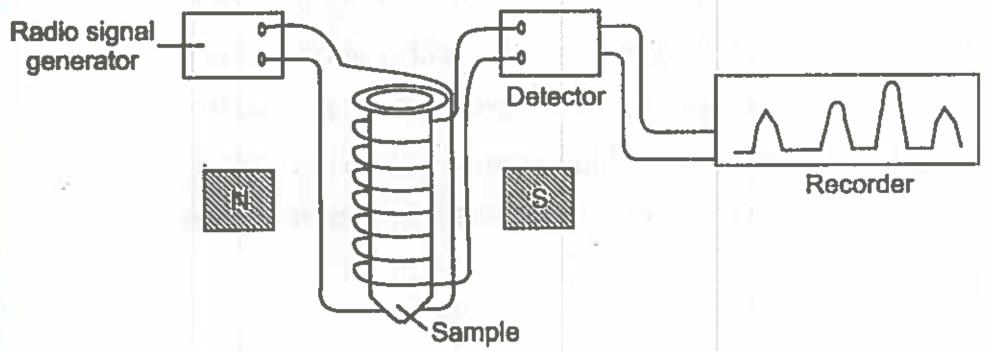
The spin states of a nucleus have equal energies, in the absence of applied magnetic field. If a magnetic field is applied, the spin states are no longer of equal energy. Thus two nuclear spin states, one of lower energy (+ ½) and other of high energy (– ½) are produced. Proton with magnetic field aligned with the applied field is at a lower energy than that which aligns against the field.



Nuclei with magnetic field aligned with the applied field can absorb energy and change their spin state (high energy state). The phenomenon is called flipping. The quantity of energy absorbed depends on the energy gap between the two states.

$E_{absorbed} = E_{(-\frac{1}{2})} - E_{(+\frac{1}{2})}$.

In this case energy absorbed belongs to radio frequency region of the electromagnetic spectrum. The absorption of energy is recorded an a chart paper. When a sample is placed in NMR spectrophotometer, the magnetic field is varied and energy of a specific frequency is absorbed. A schematic diagram of NMR spectrophotometer is shown in the following figure.



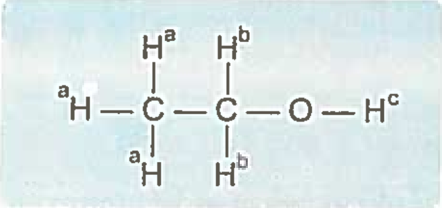
NMR spectrometer

Position of signals (chemical shift)

NMR spectrophotometer can differentiate between protons of different environments. Protons of the same environment are called equivalent protons (represented by the same letter) while protons of the other type are indicate by other letter.

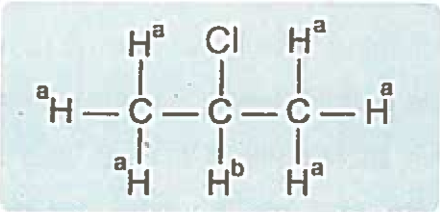
All the six protons of benzene are equivalent, therefore the NMR spectrum of benzene shows a single peak.

Ethanol has three different types of protons and its spectrum contains three peaks.



$$\begin{array}{ccccccccc} & & H^{a} & & H^{b} & & & & \\ & & | & & | & & & & \\ {}^{a}H & - & C & - & C & - & O & - & H^{c} \\ & & | & & | & & & & \\ & & {}^{a}H & & H^{b} & & & & \end{array}$$

Isopropyl chloride has six equivalent protons which give a single peak. The remaining proton, gives a peak at a different position.



$$\begin{array}{ccccccccc} & & H^{a} & & Cl & & H^{a} & & \\ & & | & & | & & | & & \\ {}^{a}H & - & C & - & C & - & C & - & H^{a} \\ & & | & & | & & | & & \\ & & {}^{a}H & & H^{b} & & H^{a} & & \end{array}$$

The area under the peak is directly proportional to the number of protons.

For taking the NMR spectrum of a substance a little amount of TMS (Tetramethyl silane $(CH_3)_4Si$) is added to it. It has been chosen as a standard. NMR spectrum is a plot of absorption (y-axis) and chemical shift on x-axis. For TMS the value of chemical shift (δ) has been chosen as zero arbitrarily. Chemical shifts of other compounds are compared with this reference value. All other compounds have chemical shift (δ) value higher than zero. TMS has been chosen as a standard because its all protons are equivalent and show absorption at lowest δ value. Moreover it is highly volatile and can be separated from the compound after its spectrum has been recorded. Chemical shift is expressed as delta (δ) or Tau (τ) scale. NMR spectrum is rectangular chart paper with a linear scale of δ (delta) usually arranging from 0 to 12 ppm, the TMS signal is taken as δ = 0.

$$\delta = \frac{\text{Observed shift from TMS in (Hz)}}{\text{Operating frequency of spectrophotometer (Hz)}} \times 10^{6}\ \text{ppm}$$

The relationship between δ and Tau scale is τ = 10 – δ. Usually ppm scale is used, where TMS signal is at 10 ppm.

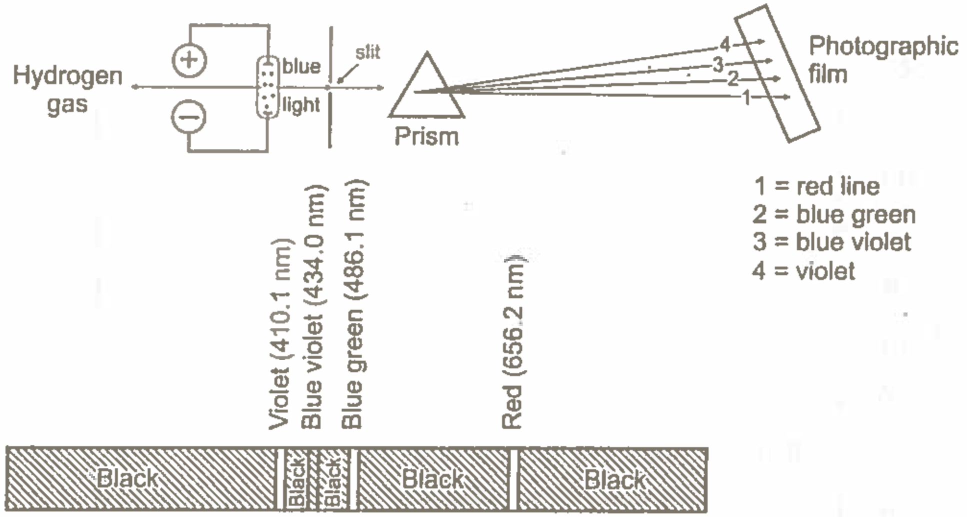
Different protons give peaks at different δ value. Protons with greater electron clouds are called (less deshielded protons) and they require higher frequency for flipping from lower energy to higher energy states. Such peaks appear as upfield (lower δ value). Protons in the vicinity of higher electronegative atoms (like Cl, F, O etc) have lower electron densities around them and require little energy for flipping. Such protons are called more deshielded protons. Such protons show peak at higher δ value (downfield). From the values of δ, the different protons of a compound can be differentiated from one another.

24.2.2.4 Atomic emission and absorption spectra:

When a metal is strongly heated, it starts glowing. The light emitted from the metal when passed through a prison forms a continuous spectrum (emission spectrum) ranging from violet to red.

The emission spectra of atoms in the gas phase on the other hand, do not show a continuous spread of wavelength from red to violet, rather the atoms produce bright lines in different parts of the visible spectrum. Such spectra are called line emission spectra. Each element has a characteristic line spectrum.

When hydrogen gas is taken in a discharge tube under low pressure it emits blue light. The light is emitted by atoms when they go from excited to ground state. When this blue light is passed through a prism, four bright lines against a dark background are produced. The colours and wave lengths of these are red (656.2nm), blue green (486.1 nm), blue-violet (434.0 nm) and violet (410.1 nm). This spectrum is called emission spectrum of hydrogen. These lines of hydrogen spectrum are collectively called Balmer series. In the invisible part of H-spectrum four more series are also obtained; Lyman (uv-region), Paschen (IR-region), Brackett (IR region) and P fund series (IR-region).



(Emission spectrum of hydrogen)

Wavelength of the different bright lines of Balmer series can be calculated by the formula

$$\boxed{\frac{1}{\lambda}=R_H\left[\frac{1}{(2)^2}-\frac{1}{n^2}\right]}$$

R_H is called Rydberg constant. Its value is 2.18×10^{-18} J.

Red, blue green, blue violet and violet lines of Balmer series actually correspond to the electronic transition from 6th, 5th, 4th and 3rd orbit to 2nd orbit respectively.

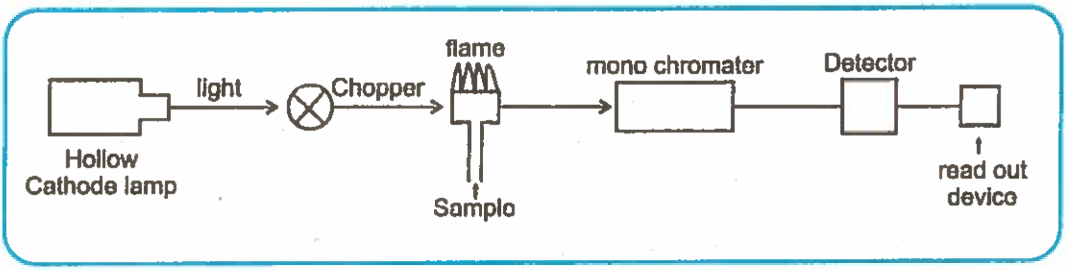
Emission spectrum of sodium can be obtained when sodium salt is added to the Bunsen flame, yellow flame is produced. When this yellow light is passed through a prism, two closely spaced yellow lines are produced. These lines are called D_1 (589 nm) and D_2 (589.6nm).

For every element there is a unique emission or absorption spectrum. Thus the emission or absorption atomic spectra are used as finger print to identify the elements.

One of the widely used emission spectroscopic technique is flame photometer. This technique is usually used to find the concentration of Ni, Na, K etc in, biological samples. An aqueous analyte is introduced into flame. Water evaporates and solid salt is left behind. The salt breaks into constituent atoms. The atoms go to vapour state. The gases atoms get excited in the flame. The excited atoms loose energy of characteristic wavelength, which is dispersed by a grating or prism and detected in the spectrophotometer. The intensity of light emited by the atoms is directly proportional to the concentration of analyte.

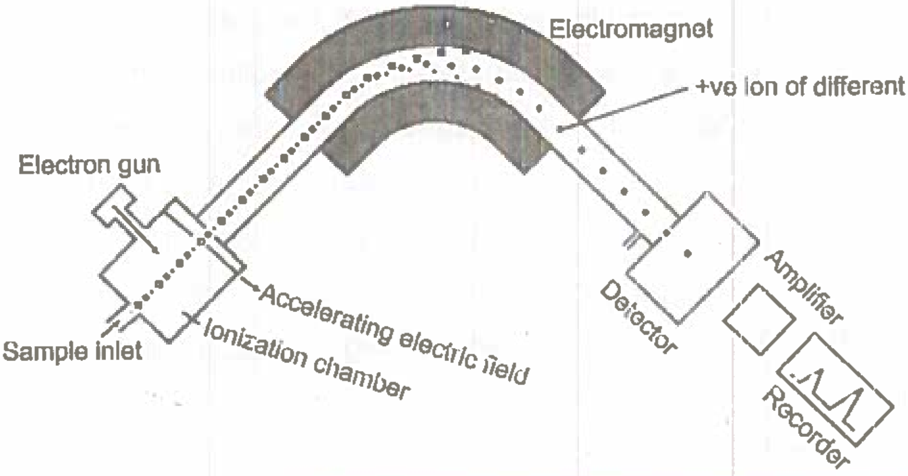
Atomic absorption spectrometry is used for the analysis of elements. The sample solution is evaporated in a flame as in flame emission spectrometry and the sample is converted to atomic vapour. Some of the atoms in the flame get excited but majority of them are in ground state. When a light of particular wave length from the Hollow cathode lamp is passed through these atoms, they absorb the light for excitation from ground state to high energy state. The absorbance of light by atoms is directly proportional to the concentration of atomic vapours in the flame. For the analysis of different elements different types of lamps are used which produce light of different wave lengths. Each element shows absorption of particular wave length.

Before introducing the sample of unknown concentration, solution of known concentrations of that element are aspirated into the flame one by one. Their absorbances are recorded and a working curve is constructed. Then sample of unknown concentration is aspirated into the flame and its concentration is read from instrument. The simple diagram of an atomic absorption spectrometer is shown below.



24.2.2.5 Mass spectrometry:

Atomic and molecular mass are determined by mass spectrometry. Mass spectrometer is a very highly sensitive instrumental technique. The following figure shows the design of a modern mass spectrometer.

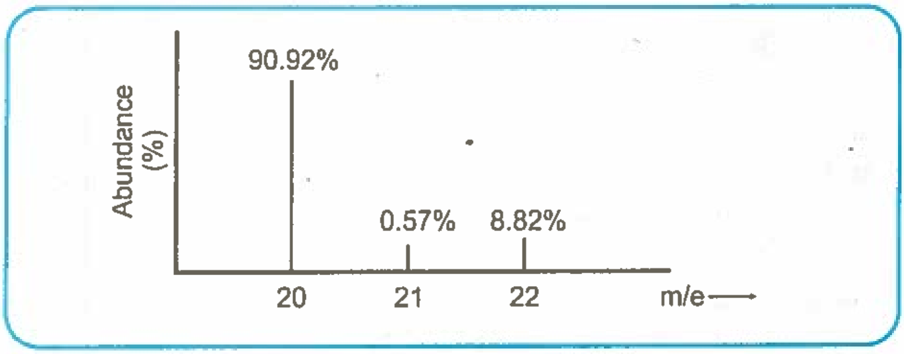


The sample is injected as a gas into the ionization chamber. Electrons, come from the electron gun collide with the sample atoms or molecules. As a result of these collisions electrons from the sample atoms or molecules are knocked out and they become positive ions. Usually oppositely charged ions are produced. The positive ions are accelerated by the electric field and finally reach a region where an electromagnet is applied. Different ions now separate on the basis of m/e ratio. In the magnetic field the ions deflect in circular path. Lighter ions (low m/e) deflect to large extent than heavier ions. At a time only one kind of ions strikes the detector. Here electric signal is produced which is later on amplified by an amplifier. In recorder the electric current operates a pen which traces peaks on a chart. The intensity of the electric signal is directly proportional to the number of ions striking the detector.

If the magnetic field is kept constant while the accelerating voltage is continuously changed, one kind of ions after other will reach detector and thus more peaks are produced on the chart.

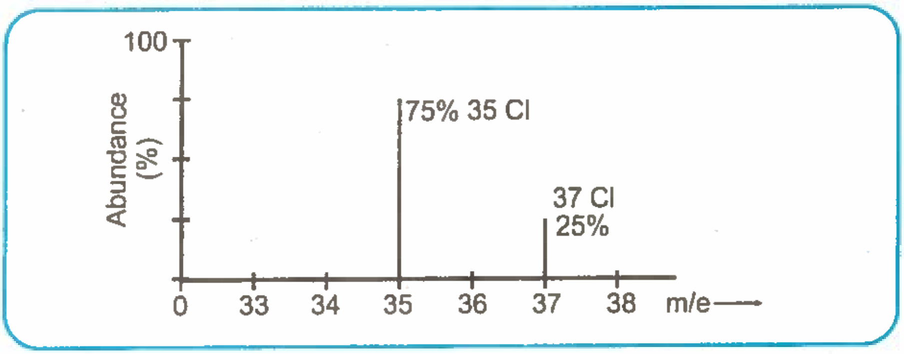
Mass spectrum is a chart in which m/e is taken on x-axis and relative abundance is taken on y-axis. Higher is the peak of a species higher is its abundance.

Mass spectrum helps in finding the number of isotopes of an element and also their relative abundances. Following the mass spectrum of Neon.



The above spectrum shows three peaks with m/e equal to 20,21, and 22 which correspond to ^{20}Ne, ^{21}Ne and ^{22}Ne. Neon –20 is the most abundant and Neon –21 is the least abundant isotope as clear from the heights of their peaks.

Mass spectrum of chlorine (Cl) is shown in the following figure.



When a molecule is introduced into mass spectrometer, the molecular ion (M^+) is produced due to loss of an electron. In addition to the molecular ion, more ions are produced due to fragmentation of the molecule. Fragmentation occurs due to rupture of chemical bonds.

The fragmentation pattern of a molecule gives an idea of the structure of the molecule. Thus mass spectrometry is very helpful in the identification of molecular structures as well.

Science, Technology and Society

In Analytical Chemistry classical method use separations such as precipitation, extraction and distillation and qualitative analysis by color, odor or melting point. Quantitative analysis is achieved by measurement of weight or volume.

Whereas instrumental method use an apparatus to measure physical quantities of the analyte such as light absorption, fluorescence, or conductivity. The separation of materials is accomplished using chromatography, electrophoresis or Field Flow Fractionation methods.

Analytical chemistry has applications in forensics, bioanalysis, clinical analysis, environmental analysis, and materials analysis.

A method frequently used in forensic chemistry is that employing luminol, a derivative of phthalic acid, which reacts with metal cations and hence to detect traces of blood. The process involves mixing luminol with a dilute solution of hydrogen peroxide, which is spread carefully in places where it is thought that there are remnants of blood.

Thus, the iron-shaped cation found in the heme group of hemoglóbin reacts with luminol observing a blue luminescence of the reaction itself is carried out.

In this process, the final product is the 3-aminophthalate anion which is in an excited state. Upon returning to the ground state (or basal) releases energy in the form of light, which is known as blue luminescence.

One particularly useful method for the simultaneous separation, identification, and quantitation of one or more individual components of an unknown substance or mixture is the use of a gas chromatograph-mass spectrometer (GC-MS). A GC-MS is actually two instruments that are attached together physically, and together comprising one of the so-called "tandem" or "hyphenated" techniques. A combined GC-MS instruments has a very high sensitivity and can analyse sample present at concentration of 1ppb. MS uses high voltage to produce charged ions. Gas ions or isotopes are separated in magnetic field according to their masses.

The gas chromatograph (GC) is essentially a hot (150-350°C), temperature-controlled oven holding a bent or coiled, specially packed or coated glass column between one and a few dozen meters long. A small volume of a drug sample is quickly injected into the hot column. Volatile components in the sample are vaporized by the heat of the oven and are forced toward the end of the column by the flow of an inert "carrier gas" (typically helium). The special chemical component(s) within the column bind to substances contained in the moving vaporized sample mixture with slightly different force. As a result, different substances eventually are "eluted" (i.e. emerge from the end of the column) in differing amounts of time, which is known as the "retention time". In general the GC portion of the technique is used as a separation and quantitation tool, not an identification tool.

Key Points:

- A set of experiments used to know about the quality of a substance is called qualitative analysis.
- Methods used to find the quantities of substances are quantitative analysis.
- Burning of substances in the presence of oxygen is called combustion.
- Most organic compounds on burning produce CO_2 and H_2O.
- Empirical formula shows the simplest ratio of atoms present in a molecule of compound.
- Molecular formula gives the exact number of atoms present in a molecule of a compound.
- Two or more compounds may have the same molecular formula.
- Structural formula gives the arrangement of atoms in molecule of a compound.
- Spectroscopy helps us to identify atoms/functional groups in a substance by the interaction of electromagnetic radiation with the substance.
- In IR spectroscopy organic compounds are exposed to weak radiations in the range of 5000–667cm^{-1} $(\bar{v})$.
- A 100% transmittance means no absorption.
- In uv/vis spectroscopy radiations having wavelengths in the range of 200—800nm are used.
- These radiations are more energetic and can change the distribution of losely bound electrons.
- Like electrons, atomic nuclei also spin about an axis.
- Spinning charged bodies produce magnetic field.

Exercise

Q.1 A compound containing C,H and oxygen is found to contain C=32% and Hydrogen = 4%. Its molecular weight is 150. Find its molecular formula.

Q.2 Calculate the empirical formula of the compound that contains C=27.3% and O=72.7%.

Q.3 What does EMR stand for?

Q.4 Write the range and unit of IR radiations.

Q.5 What is meant by stretching, bending vibrations.

Q.6 If a compound shows 100% transmittance, what do we infer from it?

Q.7 What does λ_{max} mean to you?

Q.8 Define and explain Bear-Lambert's Law.

Q.9 Why tetramethyl silance is used as a standard in nmr spectroscopy.

Q.10 Give units used in nmr spectroscopy.

Q.11 Explain the use of ionization chamber in mass spectrometer.

Q12 Multiple Choice Questions.

1. Which one of the following is quantitative chemical analysis?

(a) Salt analysis (b) Titration
(c) Flame test (d) Borax Bead Test

2. C_2H_6O is the molecular formula of ?

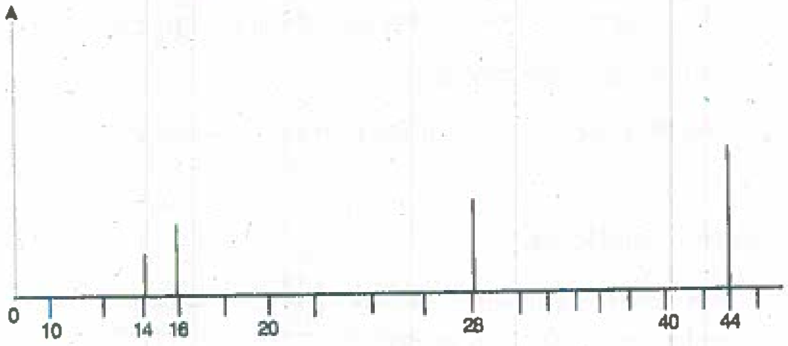
(i) Ethanol (ii) Methanol
(iii) Dimethyl ether (iv) diethyl ether
(a) (i) & (ii) (b) (ii) & (iii)
(c) (i) & (iii) (d) (ii) & (v)

3. Which one of the following technique is used for determination of functional group in a compound?
(a) IR Spectroscopy (b) NMR
(c) UV Spectroscopy (d) Mass spectroscopy

4. Two different compounds will give different absorption peaks in ____________ region of IR ?
(a) 600-1500cm^{-1} (b) 1500-4000cm^{-1}
(c) 3000-2500cm^{-1} (d) 2500-3500cm^{-1}

5. Which one of the following methods would be best for finding the identity of an organic compound.
(a) Mass spectroscopy (b) NMR
(c) IR (d) uV

6. A mass spectrunm is shown below.



Which one of the following gives complete mass spectrum illustrated?
(a) CO_2 (b) N_2O
(c) C_3H_8 (d) mixture of CH_4 and N_2

7. UV ranges from

(a) 400nm-800nm (b) 800-1200 nm

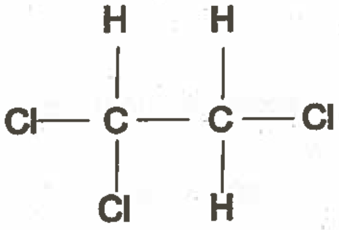
(c) 1200-1600nm (d) 10-400nm

8. Which one of the following hydrocarbon produces an NMR spectrum with more than one peak.

(a) Methane (b) Ethane

(c) Butane (d) Cyclobutane

9. For the compound below, how many single peaks would you expect in its NMR spectrum?



$Cl-CHCl-CH_2-Cl$

(a) 2 (b) 4

(c) 6 (d) 8

10. How many types of "NMR" protons are there in butanoic acid?

(a) 8 (b) 2

(c) 6 (d) 4

Q11 Short Questions

(i) Why magnesium perchlorate is used as H_2O absorber?

(ii) Acetic acid contains only C, H and O.A 5gm sample of acetic acid is completely burnt. It gives 3.00gm of water and 7.33gm of CO_2 is produced. What is the mass precentage of each elements in acetic acid. Also calculate the empirical formula of acetic acid.

(iii) Isoprene is a liquid compound that can be polymerized to form synthetic rubber. It is composed of 88.17% carbon and 11.83%

hydrogen. Its molar mass is 68.11g/mole. What are its empirical and molecular formulae?

(iv) Why modern method of analysis is superior over classical methods of analysis?

(v) Write down the main functions of IR, UV-visible and NMR spectroscopy?

(vii) Why it is necéssory to use quartz cuvets in the U.V region, but less expensive glass or plastic cuvets are acceptable in the visible region.

Q12 Long Question

(i) Define mass spectroscopy. Explain the construction and working of mass spectrometery.

(ii) Differentiate between Atomic emission and absorption spectra.

(iii) What is meant by NMR. Explain chemical shift in different cases.

(iv) Explain in detail spectroscopy. Write down its applications.

(v) Write notes on the following.

  (a) IR spectroscopy

  (b) uv visible spectroscopy