

# CHAPTER 24

# ANALYTICAL CHEMISTRY

**After completing this lesson, you will be able to:**

- Compare the classical method of analysis with modern methods.
- Discuss the procedure of combustion analysis.
- Define spectroscopy and discuss its application in analytical chemistry.
- State the regions of electromagnetic spectrum used in IR and UV/vis spectroscopy.
- Explain the origin of IR absorption of simple molecules.
- Determine structure of phenol toluene, acetone and ethanol from its IR spectrum.  
(Analyzing)
- Predict whether a given molecule will absorb in the UV/visible region. (Analyzing) Predict the color of a transition metal complex from its UV/visible spectrum. (Analyzing)
- Outline in simple terms the principles of proton NMR spectroscopy
- Explain how chemical environment of a 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.

**Q1. What is analytical chemistry? Give its classical method of analysis and Drawbacks.**

**Answer**

Analytical chemistry is the branch of chemistry that deals with separation and analysis of a sample to identify its components. The separation is carried out prior to qualitative and quantitative analysis. Qualitative analysis provides the identity of a substance (composition of chemical species). On the other hand, Quantitative analysis determines the amount of each components present in the

sample. Hence, in this branch different techniques and instruments used for analysis are studied. The scope of this branch covers food, water, environmental and clinical analysis.

### **Classical Method of Analysis**

#### **1) Combustion Analysis and determination of Molecular Formula**

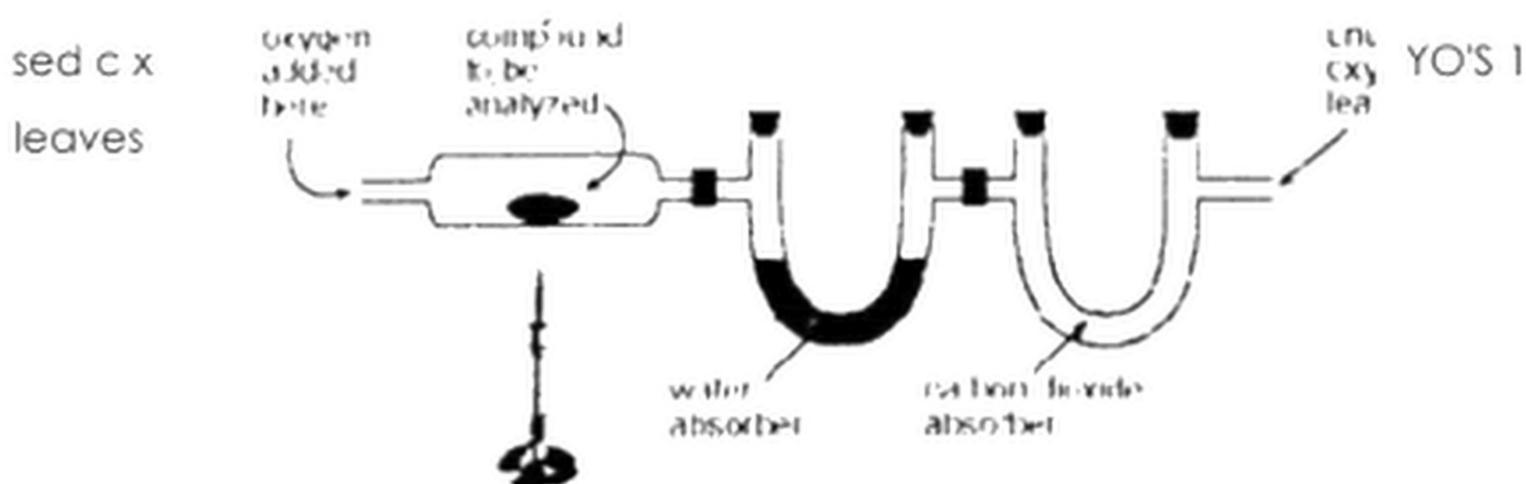
Empirical and molecular formulas for compounds that contain only carbon and hydrogen ( $C_xH_y$ ) or carbon, hydrogen, and oxygen ( $C_xH_yO_z$ ) can be determined with a process called combustion the sole products will be  $CO_2$  and  $H_2O$  and these two products of combustion are separately collected.

#### **Procedure**

The steps for this procedure are:

- 1)** Weigh a sample of the compound to be analyzed and place it in the apparatus shown in the image below.
- 2)** Burn the compound completely. The only products of the combustion of a compound that contains only carbon and hydrogen ( $C_xH_y$ ) or carbon, hydrogen and oxygen ( $C_xH_yO_z$ ) are carbon dioxide and water.
- 3)** The  $H_2O$  and  $CO_2$  are drawn through two tubes. One tube contains a substance that absorbs water, and the other contains a substance that absorbs carbon dioxide. Weigh each of these tubes before and after the combustion. The increase in mass in the first tube is the mass of  $H_2O$  that formed in the combustion, and the increase in mass for the second tube is the mass of  $CO_2$  formed.
- 4)** Assume that all the carbon in the compound has been converted to  $CO_2$  and trapped in the second tube. Calculate the mass of carbon in the compound from the mass of carbon in the measured mass of  $CO_2$  formed.

- 5) Assume that all of the in the compound has been converted to  $\text{H}_2\text{O}$  and trapped in the first tube. Calculate the mass of hydrogen in the compound from the mass of  $\text{H}_2\text{O}$  hydrogen in the measured mass of water.
- 6) If the compound contains oxygen as well as carbon and hydrogen, calculate the mass of the oxygen by subtracting the mass of carbon and hydrogen from the total mass of the original sample of compound.
- 7) Use this data to determine the empirical and molecular formulas in the usual way.



Apparatus for Combustion analysis A compound containing carbon and hydrogen ( $\text{C}_x\text{H}_y$ ) or carbon, hydrogen, and oxygen ( $\text{C}_x\text{H}_y\text{O}_z$ ) is burned completely to form  $\text{H}_2\text{O}$  and  $\text{CO}_2$ . The products are drawn through two tubes. The first tube absorbs water, and the second tube absorbs carbon dioxide.

To illustrate the empirical and molecular formulas can be determined from data derived from combustion analysis, let's consider a substance called trioxane. Formaldehyde  $\text{CH}_2\text{O}$  is unstable as a pure gas, readily forming a mixture of a substance called trioxane and a polymer called paraformaldehyde. That is why formaldehyde is dissolved in a solvent, like water, before it is sold and used. The molecular formula of trioxane, which contains carbon, hydrogen, and oxygen,

can be determined using the data from two different experiments. In the first experiment, 17.471 g of trioxane is burned in the apparatus shown above, and 10.477 g H<sub>2</sub>O and 25.612 g CO<sub>2</sub> are formed. In the second experiment, the molecular mass of trioxane is found to be 90.079.

We can get the molecular formula of a compound from its empirical formula and its molecular mass. To get the empirical formula, we need to determine the mass in grams of the carbon, hydrogen, and oxygen in 17.471 g of trioxane. Thus, we need to perform these general steps.

- 1) First, convert from the data given to grams of carbon, hydrogen, and oxygen.
- 2) Second, determine the empirical formula from the grams of carbon, hydrogen, and oxygen.
- 3) Third, determine the molecular formula from the empirical formula and the given molecular mass.

Because we assume that all the carbon in trioxane has reacted to form CO<sub>2</sub>, we can find the mass of carbon in 17.471 g trioxane by calculating the mass of carbon in 25.612 g CO<sub>2</sub>.

$$?gC = 25.612 \cancel{gCO_2} \left( \frac{1 \cancel{molCO_2}}{44.010 \cancel{gCO_2}} \right) \left( \frac{1 \cancel{molC}}{1 \cancel{molCO_2}} \right) \left( \frac{12.011 \cancel{gC}}{1 \cancel{molC}} \right) = 6.9899gC$$

Because we assume that all of the hydrogen in trioxane has reacted to form H<sub>2</sub>O, we can find the mass of hydrogen in 17.471 g trioxane by calculating the mass of hydrogen in 10.477 g H<sub>2</sub>O.

$$?gH = 10.477 \cancel{gH_2O} \left( \frac{1 \cancel{molH_2O}}{18.0153 \cancel{gH_2O}} \right) \left( \frac{2 \cancel{molH}}{1 \cancel{molH_2O}} \right) \left( \frac{1.00797 \cancel{gH}}{1 \cancel{molH}} \right) = 1.1727gH$$

Because trioxane contains only carbon, hydrogen, and oxygen, we can calculate the mass of oxygen by subtracting the masses of carbon and hydrogen from the total mass of trioxane.

$$? \text{ go} = 17.471 \text{ g trioxane} - 6.9899 \text{ g C} - 1.1724 \text{ g H} = 9.309 \text{ g O}$$

We now calculate the empirical formula.

$$? \text{ mol C} = 6.9899 \text{ g C} \left( \frac{1 \text{ mol C}}{12.011 \text{ g C}} \right) = 0.58196 \text{ mol C} \div 0.5818 \cong 1 \text{ mol C}$$

$$? \text{ mol H} = 1.1724 \text{ g H} \left( \frac{1 \text{ mol H}}{1.00797 \text{ g H}} \right) = 1.1631 \text{ mol H} \div 0.5818 \cong 2 \text{ mol H}$$

$$? \text{ mol O} = 9.309 \text{ g O} \left( \frac{1 \text{ mol O}}{15.9994 \text{ g O}} \right) = 0.5818 \text{ mol O} \div 0.5818 \cong 1 \text{ mol O}$$

The empirical formula is  $\text{CH}_2\text{O}$ , which can be used to calculate the molecular formula.

$$\begin{aligned} \text{Empirical formula mass} &= 1(12.011) + 2(1.00794) + 1(15.9994) \\ &= 30.026 \end{aligned}$$

$$n = \frac{\text{molecular mass}}{\text{empirical formula mass}} = \frac{90.079}{30.026} \cong 3$$

Molecular formula  $\text{C}_3\text{H}_6\text{O}_3$

### Drawback

The classical method i.e. combustion analysis is only limited to those organic compounds which contain carbon, hydrogen and oxygen. So, there is a need of such methods which explain/find all types of atoms/elements present in an organic compounds. So now modern methods are used which are being discussed in next topic.

### Q2. What are different Modern Methods of Analysis?

#### Answer

Modern chemistry laboratories use sophisticated instruments to find the structure of organic chemicals. These instruments are very sensitive and they usually need

only very small amounts of the chemical to work on. Laboratories in industry and universities are equipped with a range of instruments, but they tend to be very expensive, so you don't find many of them in schools.

Spectroscopy involved using instruments to examine the radiation emitted or absorbed by chemicals giving information about their molecular structure.

When electromagnetic radiation, such as light or infrared, shines on a chemical the chemical may interact with the radiation in some way. The commonest example is color. Color is produced when chemicals emit or absorb visible light of a particular frequency.

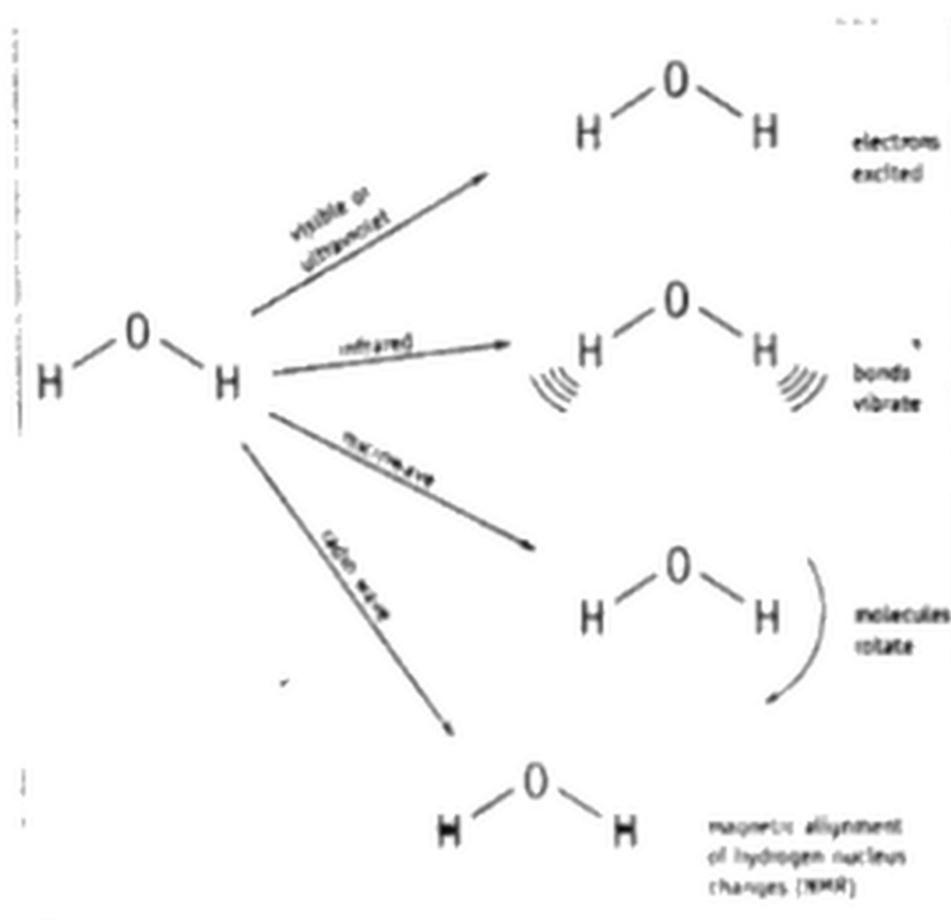
The way a particular chemical interacts with radiation can tell chemists about its molecules. A spectroscope is an instrument which allows radiation to interact with a sample of a chemical, then analyses the changes.

Different kinds of radiation interact with chemicals in different ways (fig. 24.2). The effects are summarized in table 24.1. In this section we will look at five types of spectroscopy that are particularly useful to chemists: infrared, ultraviolet/visible, nuclear magnetic resonance, atomic emission and absorption, spectroscopy and mass spectroscopy.

#### HOW DIFFERENT TYPES OF RADIATION INTERACT WITH CHEMICALS

Type of radiation	Frequency range /Hz	Effect on molecule	Type of spectroscopy
Ultraviolet	$10^{15} - 10^{17}$	Excites the electrons	Ultraviolet/visible spectroscopy (see below)
Visible light	$10^{14} - 10^{15}$	Excites the electrons	Ultraviolet/visible spectroscopy (see below)
Infrared	$10^{11} - 10^{12}$	Makes bonds vibrate	Infrared spectroscopy (page

Microwaves	$10^9 - 10^{11}$	Makes molecules rotate	385)
Radio waves	$10^6 - 10^8$	Changes the magnetic alignment of the nuclei of some atoms	Microwave spectroscopy Nuclear magnetic resonance page (387)



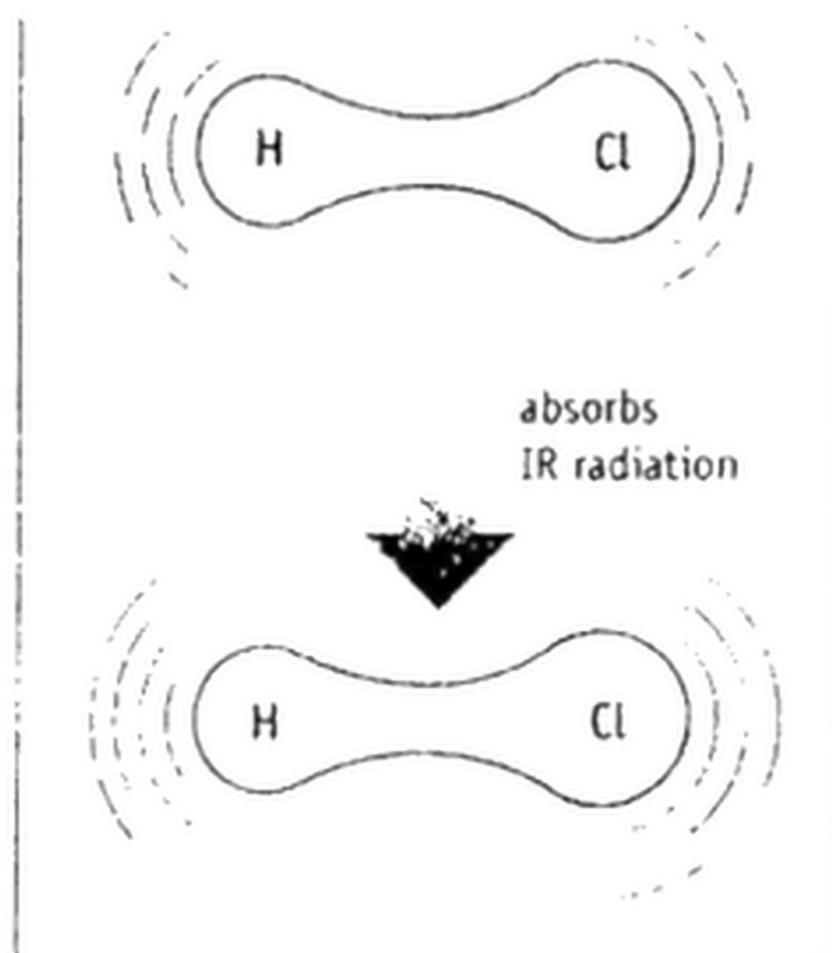
**Q3. How Infrared Spectroscopy (IR) Functions? Give its method of analysis.**

**Answer**

Infrared spectroscopy makes use of the fact that molecules absorb infrared (IR) radiation which has a wavelength longer than visible light, between about 2500 nm and 25000 nm. The energy of the radiation is absorbed in making the bonds

vibrate (fig 24.3). When the molecule absorbs the radiation, the bonds vibrate more energetically. Different bonds absorb radiation of different frequencies and the frequency is characteristic of the particular bond concerned. We can use IR absorption to identify the bonds, the therefore the functional groups in an organic molecule.

The spectrometer produces an infrared spectrum on a chart recorder, and an example is shown in figure 24.4 this is the IR spectrum of propanone,  $\text{CH}_3\text{COCH}_3$ .



When an HCl molecule absorbs infrared radiation, it vibrates more energetically. The frequency of radiation absorbed is  $7.21 \times 10^{13}$  Hz, and this frequency is characteristic of the H-Cl bond.

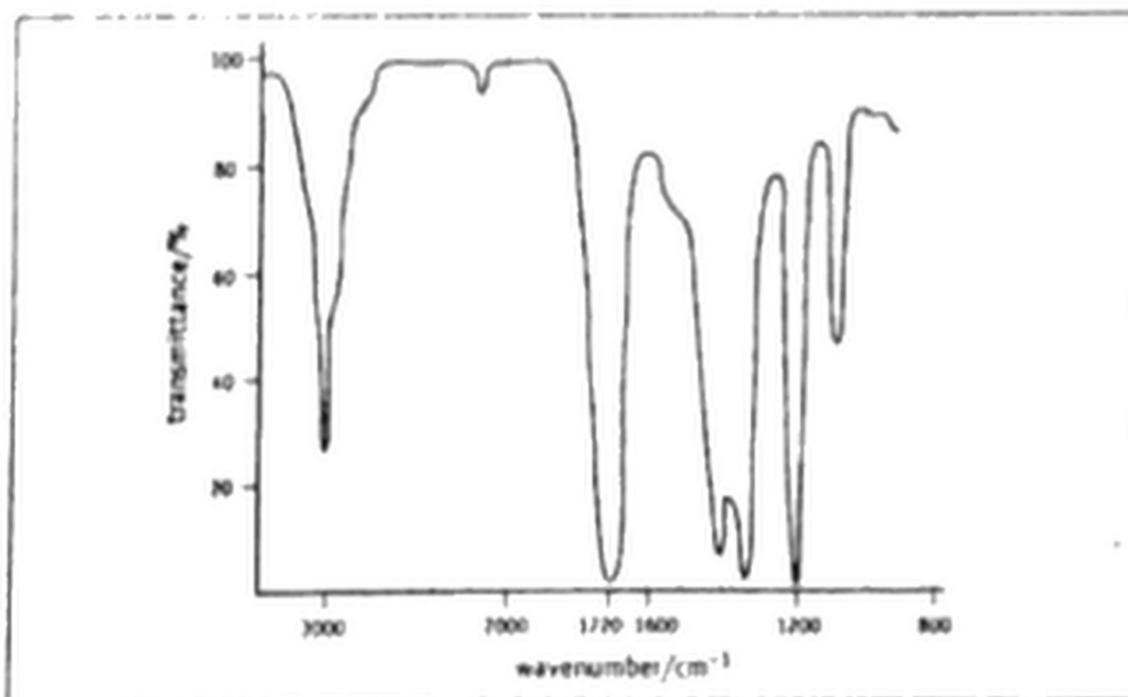


Figure 24.4 The infrared spectrum of propanone

You will see that the spectrum is quite complicated even though propanone is a simple molecule with only three types of bond. The complexity arises because each bond can vibrate in a number of different ways and the vibrations can interact with each other. Nevertheless it is possible to see some characteristic peaks of absorption which we can use to identify functional groups in the molecule.

Table 24.2 gives the characteristic absorption of some common bonds. In the spectrum of propanone in figure 24.4 the strong peak at about  $1720\text{cm}^{-1}$  corresponds to the C=O bond. The weaker absorption at  $3000\text{cm}^{-1}$  corresponds to the C-H bond. This peak is weaker even though there are more H atoms in the molecule: in IR spectroscopy the strength of the peak is a characteristic of the bond itself not of the number of bonds

present.

Most of the interesting parts of an IR spectrum are found in the region above about  $1500\text{cm}^{-1}$ . The peaks outside this region are less useful, but they are helpful in showing the fingerprint of the compound: the characteristic pattern of its IR

spectrum. The fingerprint can be used to compare the compound's spectrum with IR spectra of known compound given in standard reference books.

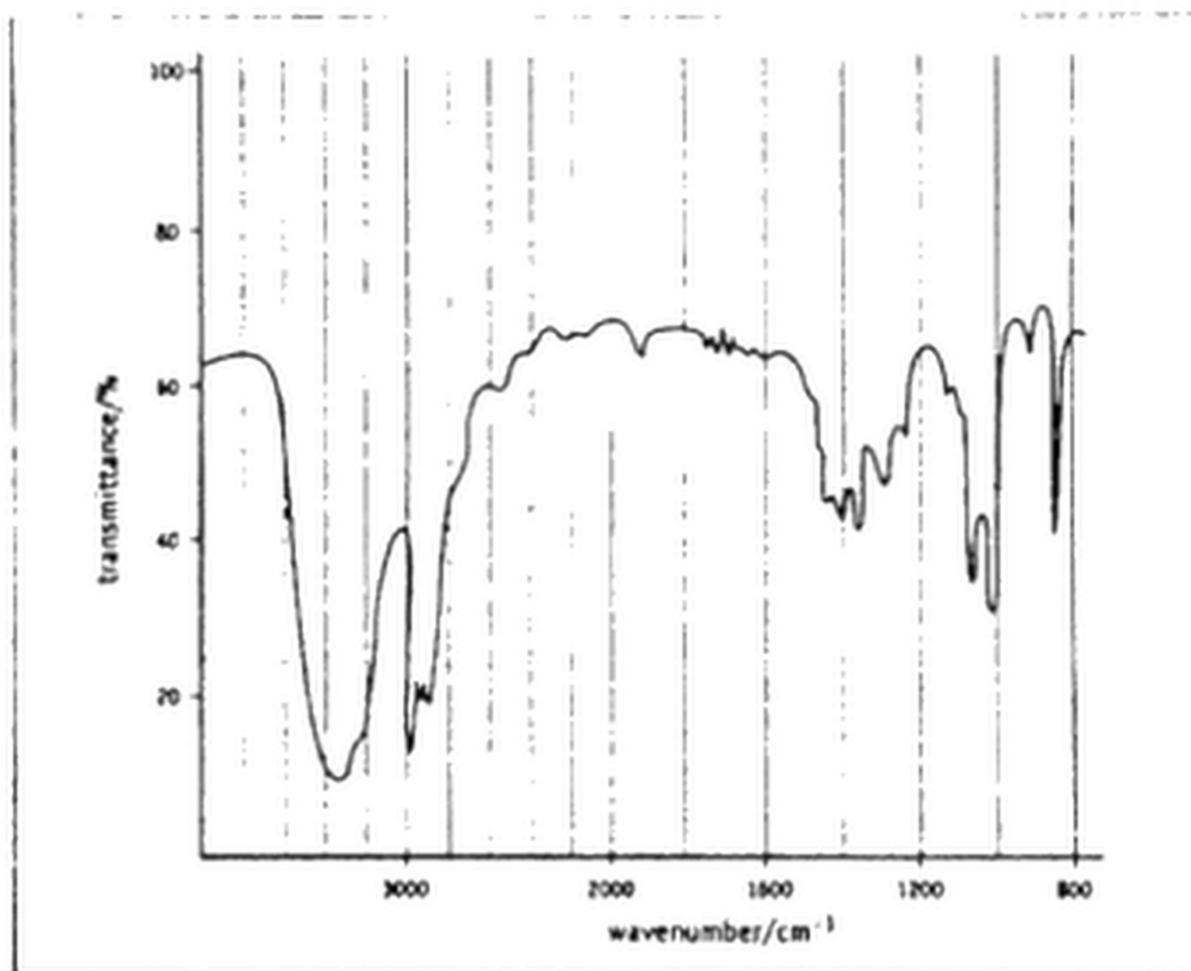


Fig. 24.5 (a) the infrared spectrum of ethanol  $\text{CH}_3\text{CH}_2\text{OH}$

Infrared spectra are very useful; they are particularly helpful for identifying the functional groups in an unknown compound. In the IR spectrum for ethanol in figure 24.5 (a) the peak just below  $3000\text{cm}^{-1}$  is from the C-H bonds, and the peak at about  $3400\text{cm}^{-1}$  is from the O-H bond.

#### Q4. How Visible and ultraviolet Spectroscopy (UV-Vis) Functions?

##### Answer

When you heat sodium chloride in a flame, it gives a yellow flame color. This is an example of a visible emission spectrum, where a substance emits certain visible frequencies when its electrons have been excited by heating or by an electrical

discharge. The radiation may be in the ultraviolet region of the ultraviolet region of the spectrum as well as the visible.

By examining the frequencies emitted, chemists can get information about the substance. The emission spectrum of hydrogen gave chemists the first clues about the energy levels of electrons in an atom.

When white light shines on methylene blue (an organic dye), some of the electrons in the dye's molecules become excited. The electrons absorb certain frequencies of light radiation and change their energy level. The radiation they absorb happens to be in the

red end of the spectrum. Removing red from white light makes it look blue — but you can only tell the color of methylene blue if light is shining on it. This is an example of a visible absorption spectrum, where a chemical absorbs certain frequencies of visible radiation. Ultraviolet radiation can be absorbed in a similar way it is not visible but can be detected by instruments. By finding which frequencies have been absorbed chemists can get information about the chemical. You can read about visible spectra and the way they give rise to color in transition metal compounds by considering an aqueous solute of titanium (III) chloride. This contains the octahedral complex ions,  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  and  $\text{Cl}(\text{aq})$  ions. A solution of titanium(III) chloride is violet. An absorption spectrum shows that the solution absorbs most effectively in the green-yellow region of the spectrum figure 24.5(b)

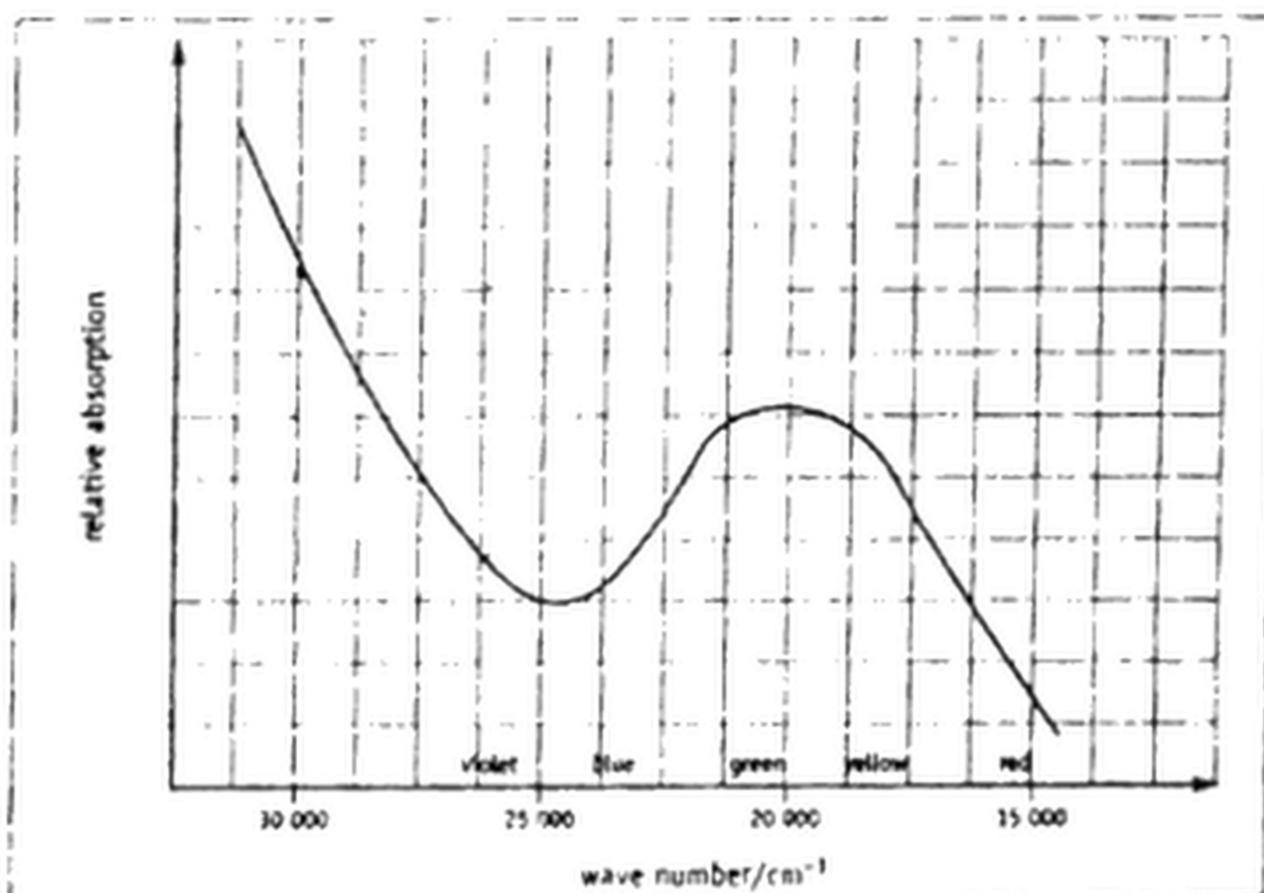


Figure 24.5(b) The absorption spectrum of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$

Red blue and violet radiations are absorbed less efficiently, so the solute looks violet. Both water and  $\text{Cl}^-$  (aq) are colorless, so the  $\text{Ti}^{3+}$ (aq) ion must be responsible for the color of the solution.

#### Interesting Information

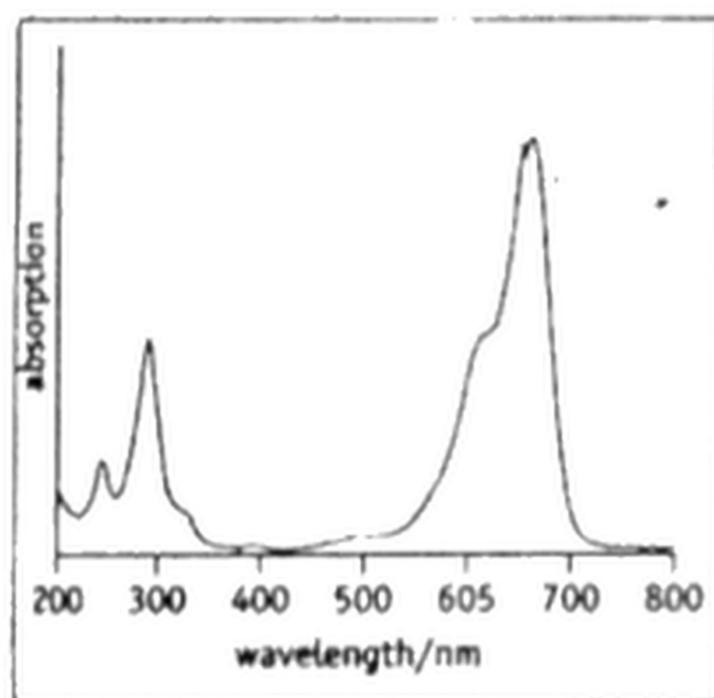
Most of the compounds of transition elements are colored. The color of these compounds can often be related to incompletely filled d-orbitals in the transition metal ion.

In general, when light hits a substance, part is absorbed, part is transmitted (if the substance is transparent) and part may be reflected.

If all the incident radiation is absorbed then the substance look black. If all the incident radiation is reflected then the substance look white. On the other hand if only a very small proportion of the incident white light is absorbed and if all the radiation in the visible region of the spectrum are transmitted equally then the substance will appear colorless.

In an ultraviolet/visible spectroscope, radiation consisting of a mixture of ultraviolet and visible frequencies is shone through a sample of a compound. A detector measures the frequencies of radiation that have been absorbed and the spectrometer prints out an absorption spectrum. Figure shows the ultraviolet/visible absorption spectrum of methylene blue. Notice the axes: the horizontal axis shows the wavelengths of radiation absorbed, in nanometers nm, and the vertical axis shows the relative absorbance: how strongly it is absorbed.

The ultraviolet/visible spectrum of an organic compounds is characteristic of that compound. The compound can be identified by comparing its spectrum -with the spectra of known compound. However other types of spectroscopy particularly infrared and nuclear magnetic resonance, are more useful for piecing together the structure of an organic compound.



The visible/UV spectrum of methylene blue

The approximate wavelengths of visible radiation of different colours

Colour	Approximate wavelength/nm
[infrared]	above 700
red	620-700

orange	600-620
yellow	580-600
green	520-580
blue-green	490—520
blue	440 490
indigo	420—440
violet	400 - 420
[ultraviolet)	below 400

Table 24.3 the approximate wavelength of visible radiation of different colors.

Look at the visible/UV spectrum of methylene blue in figure 24.6

- 1) What colors of visible light does methylene blue absorb?
- 2) Explain methylene blue has a blue color.
- 3) How can we get information about a compound using UV/visible spectroscopy
- 4) What is color of  $[\text{Ti}(\text{H}_2\text{O})\text{Cl}_3]$  complex solution
- 5) Give color of following wavelength (i) 600-620 (ii) 490-520

**Q5. How Nuclear Magnetic Resonance (NMR) Functions? Give in detail.**

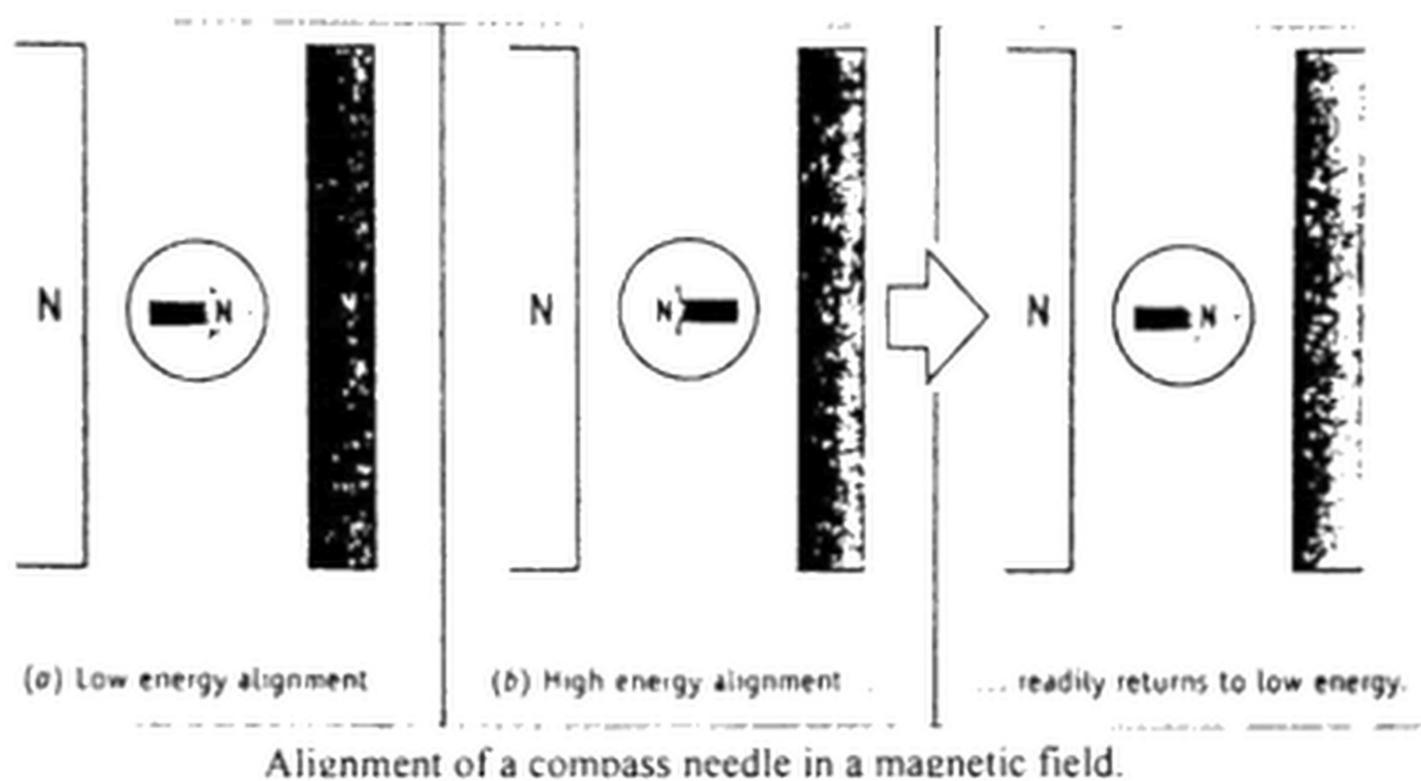
**Answer**

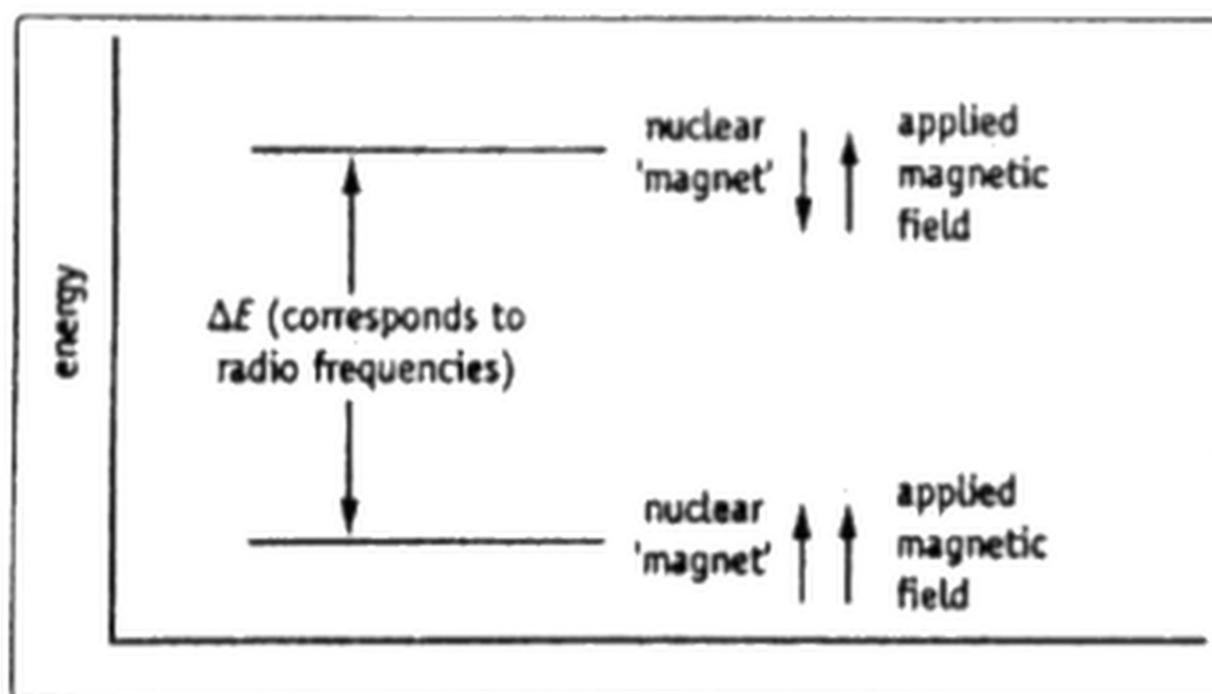
When certain atoms are placed in a strong magnetic field, their nuclei behave like tiny bar magnets and align themselves with the field. Electrons behave like this too, and for this reason both electrons and nuclei are said to possess Spin since any spinning electron charge has an associated magnetic field.

Just as electrons with opposite spin pair up together, a similar thing happens with the protons and neutrons in the nucleus. If a nucleus has an even number of protons and neutrons, their magnetic fields cancel out and it has no overall magnetic field. But if the number of protons and neutron is odd the nucleus has a magnetic field.

If the substance is not placed in external magnetic field, the nuclear magnets line up with the field, in the same way as a compass needle line up with a magnetic field (Fig. 24.7)

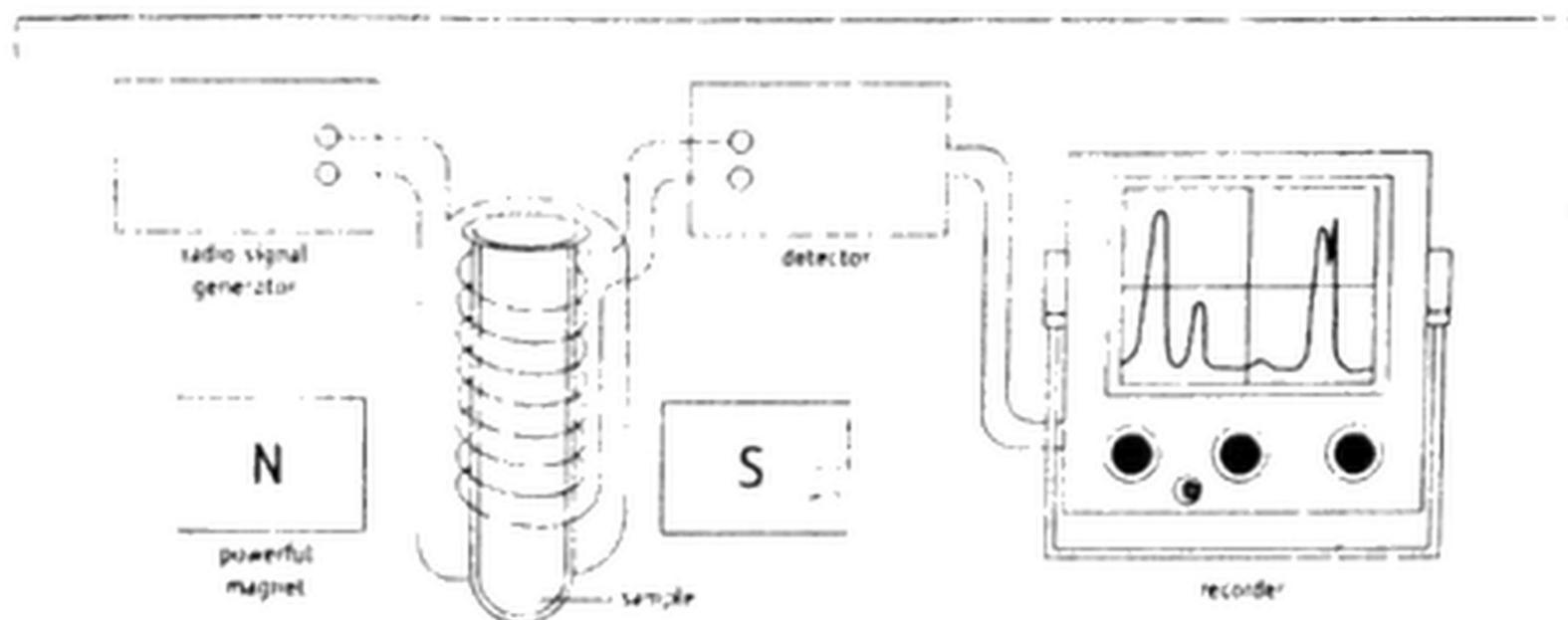
The nuclear magnet can have alignment of low and high energy (fig 24.8). To make the nucleus change to the high energy alignment energy must be supplied.





Two alignment of the nuclear magnet in an external magnet field. The energy difference between the two orientations is the basis of the technique of NMR

It happens that the energy absorbed corresponds to radio frequencies. The precise frequency of energy depends on the environment of the nucleus, in other words, on the other nuclei and electron in its neighborhood. So, by placing the sample being examined in a strong magnetic field and measuring the frequencies of radiation it absorbs information can be obtained about the environments of nuclei in the molecule. The technique is called nuclear magnetic resonance (NMR). Figure 24.9 shows a simplified diagram of NMR spectrometer.



A simplified NMR spectrometer. The sample is dissolved in a solvent such as  $^2\text{H}_2\text{O}$  or  $\text{CCl}_4$  which does not have nuclear magnetic properties.

The technique of NMR is particularly useful for identifying the number and type of hydrogen atoms ( $^1\text{H}$ ) in a molecule. It is also used to find the position of carbon atoms. The common isotope of carbon,  $^{12}\text{C}$  does not have a nuclear magnet but natural carbons contains 1% of the  $^{13}\text{C}$  isotope which does show magnetic behavior and can be

identified using NMR

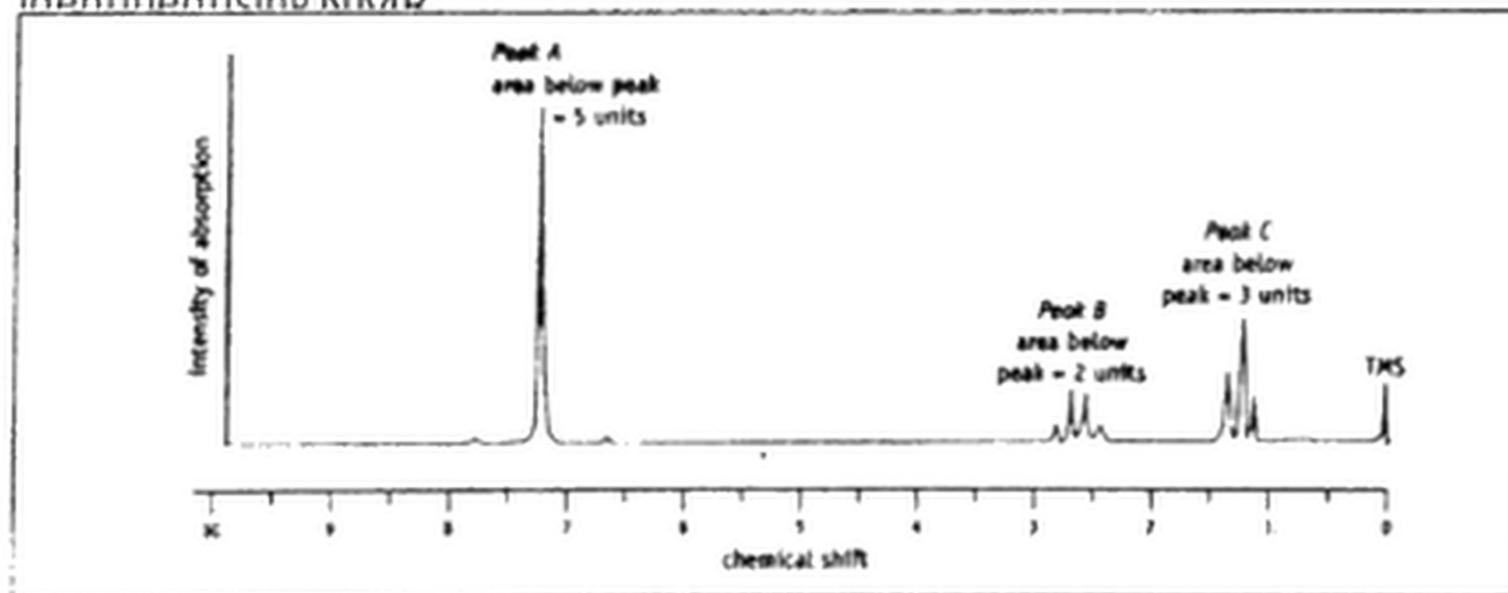


Figure 24.10 The proton NMR spectrum of ethylbenzene,  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$

Figure 24.10 shows the NMR spectrum of ethylbenzene  $C_6H_5CH_2CH_3$ . This is a proton NMR spectrum: the frequencies correspond to the absorption of energy by  $^1H$  nuclei, which are protons. Notice that there are three major peaks of differing heights. Each peak corresponds to H atoms in a different molecular environment. This area under each peak is proportional to the number of that type of H atom in the molecule. The largest peak (A) corresponds to the 5 H atoms in  $C_6H_5$ , the benzene ring. The second largest (C) corresponds to the 3 H atoms in the  $-CH_3$  group and the third peak (B) corresponds to the 2 H atoms in the  $CH_2$  group.

The H atoms in a particular type of environment have similar positions in the NMR spectrum normally this position is measured as a chemical shift, from a fixed reference point. The reference point normally used is the absorption of a substance known as TMS. The chemical shift of TMS is set at zero.

TMS stands for tetramethylsilane,  $Si(CH_3)_4$ . This non-toxic and unreactive substance is chosen as the NMR reference because its protons give a single peak that is well separated from the peaks found in the NMR spectra of most organic compounds.

Table 24.4 gives the chemical shifts for some common proton environments.

Type of proton	Chemical shift, $\delta$ , in region of
$R-CH_3$	0.9
$R-CH_2-R$	1.3
$\begin{array}{c} R \\   \\ R-CH-R \end{array}$	2.0
$\begin{array}{c} -C-CH_2- \\    \\ O \end{array}$	2.3
$-O-CH_3$	3.8
$-O-CH_2-R$	4.0
$-O-H$	5.0
	7.5
$\begin{array}{c} -C=O \\   \\ H \end{array}$	9.5
$\begin{array}{c} -C=O \\   \\ O-H \end{array}$	11.0

Shows a simplified proton NMR spectrum for ethanol,  $CH_3CH_2OH$ . It has been simplified by removing some of the detail, so the peaks appear single. Notice that it includes the peak for TMS. Notice too that an integrated trace is shown: this gives the relative areas under each of the peaks.

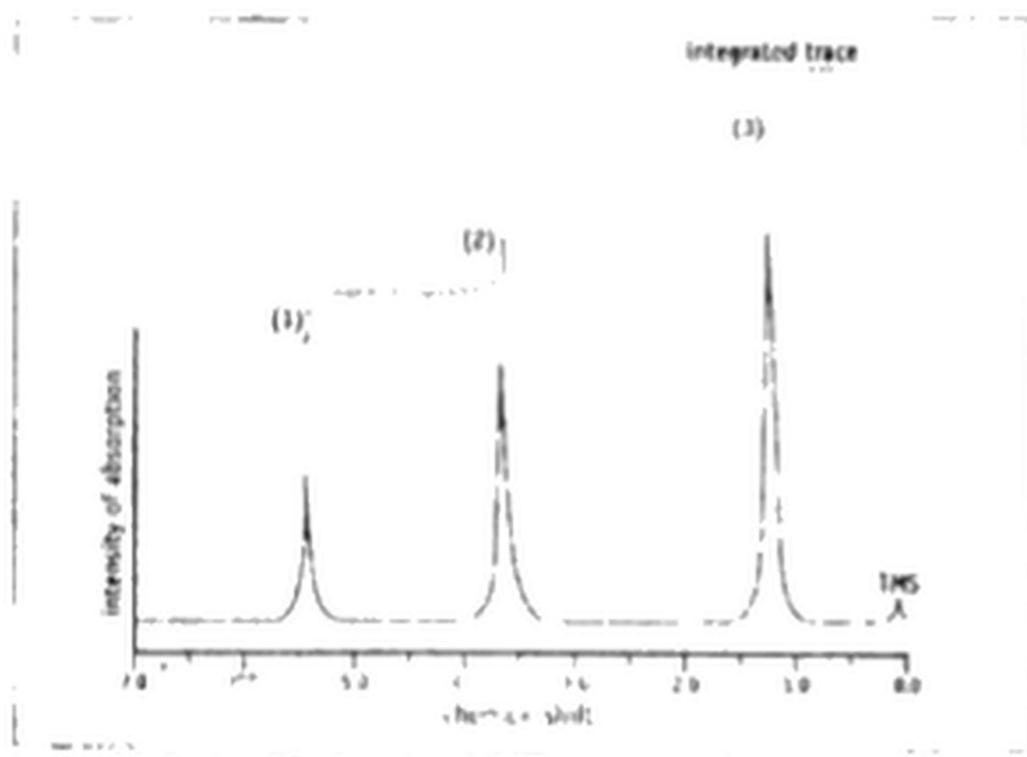


Figure 24.11 A simplified proton NMR spectrum for ethanol,  $CH_3CH_2OH$ .

The integrated trace shows that areas under the peaks are in the ratio 1:2:3

## Spin-spin coupling

The simplified NMR spectrum of ethanol, in figure 24.11, shows three single peaks. The smallest peak corresponds to the single OH proton; the middle peak corresponds to the two CH<sub>2</sub> protons and the largest peak corresponds to the three CH<sub>3</sub> protons. A detailed high-resolution spectrum of ethanol shows that the CH<sub>2</sub> and CH<sub>3</sub> peaks are in fact split into a number of subsidiary peaks (figure 24.12). This splitting is caused by spin-spin coupling protons on neighboring carbon atoms

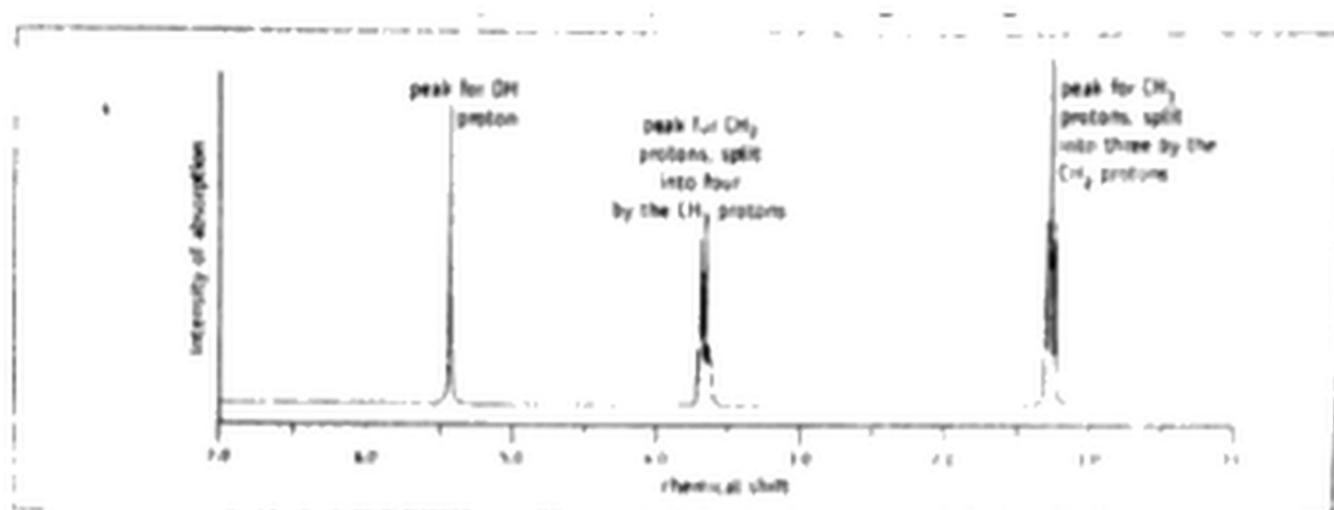


Figure 24.12 A detailed high-resolution NMR spectrum for ethanol

Here is what happens. One of the carbon atoms in ethanol has protons on it (CH<sub>2</sub>)<sub>2</sub> the other has three (CH<sub>3</sub>). Consider CH<sub>3</sub> protons which act like tiny magnets. When the external magnetic field is applied, these three tiny magnets can arrange in four different ways.

- 1) All three aligned with the magnetic field
- 2) All three aligned against the magnetic field
- 3) Two aligned with the field and one aligned against it
- 4) One aligned with the field and two aligned against it.

Each of these four arrangements a slightly different overall magnetic field. Each different field interacts with the neighboring CH<sub>2</sub> protons slightly, differently so these CH<sub>2</sub> protons four different peaks close to one another. These peaks are called a quartet.

Similarly, the two protons on the CH<sub>2</sub> group can arrange themselves differently, in the external magnetic field. This time there are three different arrangements see if you work out what they are. Each of these different fields interacts with the neighboring CH protons slightly differently so we see three different peaks close to one another. These three peaks are called triplet.

As a general rule: A group carrying protons will cause the protons on a neighboring group to split into  $n+1$  peaks

When you are interpreting a high-resolution spectrum like the one in figure 24.12 you can

- Use the position of each overall peak to identify the type of protons causing the peak
- Use the integrated trace to find the number of each type of proton
- Use the  $n+1$  rule above to get information about the number of protons on neighboring groups.

**Q6. Give Principle and functions of Atomic Emission Spectroscopy. Also give its advantages and disadvantages.**

**Answer**

Atomic emission spectroscopy pertains to electronic transitions in atoms which use and an excitation source like flames sparks. Emission spectroscopy is related to atoms. Emission spectroscopy is concerned with the characteristic radiation produced when atoms are excited. They emit radiations in the form of discrete

wavelengths of light, called spectral lines while returning to the lower energy states.

### **Principle**

The source vaporizes the sample and causes electronic excitation of elementary particles in the gas. Excited molecules in the gas phase emit band spectra. Thus, a molecule in an excited state of energy,  $E_2$  undergoes a transition to a state of lower energy  $E_1$  and a photon of energy  $h\nu$  is emitted where

$$E_2 - E_1 = h\nu$$

In each electronic state a molecule may exist in a number of vibrational and rotational states of different energies.

### **Advantages of Emission Spectroscopy**

Emission method is extremely important in analysis

- 1) This technique is highly specific
- 2) This method is extremely sensitive. With this technique all metallic elements can be detected even if they are present in very low concentration.
- 3) Even metalloids have been identified by this technique.
- 4) This analysis can be performed either in solid or liquid state with almost equal convenience.
- 5) This technique requires minimum sample preparation as a sample can be directly introduced in to the spark.
- 6) The technique provides results very rapidly. If automated, time required is just 30 sec to one minute.
- 7) This method has been used for a wide variety of samples like metals, alloys, paints, geological specimen, environmental and biological samples.

### **Disadvantages of Emission Spectroscopy**

- 1) The equipment is costly and wide experience is required for its successful handling and interpretation of spectra.
- 2) Recording is done on a photographic plate which takes some time to develop, print and interpret the results.
- 3) Radiation intensities are not always be reproducible.
- 4) Relative error exceeds 1 to 2 %
- 5) The accuracy and precision are not high.

### **Applications**

- 1) Emission spectroscopy has been employed in determining the impurities of Ni, Mn, Cr, Si, Al, Mg, As Sn, Co, V, Pb, Bi, P and MO in iron and steel in metallurgical processes.
- 2) Alloys of Zn, Cu, Pb, Al, Mg and Sn have been analyzed.
- 3) Lubricants oils have been analyzed for Ni, Fe, Cr, Mn, Si Al and so on. If the concentration of metal in lubricating oil has increased during use, it indicates excessive wear and tear need for engine overhaul.
- 4) In petroleum industry oil is analyzed for V, Ni, Fe the presence of which makes fuel poor.
- 5) Solid samples and animal tissues have been analyzed for several elements including K, Na, Ca, Zn, Ni, Fe and Mg etc.
- 6) Emission spectroscopy has been used to detect 40 elements in plants and soil. Thus metal deficiency in pants and oil can be diagnosed.
- 7) The following materials have been analyzed by emission spectroscopy:
  - i) Trace and major constituents in ceramics.
  - ii) Traces of Co, Ni, MO and V in Graphite.
  - iii) Trace metal impurities in analytical reagents.

- iv) Trace of Ca, Cu, Zn in blood.
- v) Zinc in pancreatic tissues.

**Q7. Give Principle and Applications of Atomic Absorption Spectroscopy (AAS).**

**Answer**

The technique has been particularly useful in the determination of trace metals in liquids. The versatility of AAS can be realized from the fact that 60-70 elements have been analyzed by this method in concentration as low as 1 ppm. The greatest advantage of AAS is the analysis of one metal in the presence of another metal, thus saving time and eliminating error.

**Principle of AAS**

Atomic absorption spectroscopy involves the study of the absorption of radiant energy, usually visible by neutral atoms in the gaseous states. If light of the resonance wavelength passes through a flame containing the atoms, then part of the light will be absorbed, and the extent of absorption will be proportional to the number of ground state atoms present in the flame. This is the underlying principle of AAS.

**Applications of Atomic Absorption Spectroscopy (AAS)**

- 1) The AAS technique has become the most powerful tool of analysis. The method is well-suited to the analysis of a substance at low concentration
- 2) It has several advantages over conventional absorption or emission spectroscopic methods.
- 3) AAS methods are highly specific, hence analysis of a metal from a complex mixture is possible and a high energy source needs not be employed.
- 4) The technique is firmly established in analytical chemistry ceramics mineralogy, biochemistry, metallurgy, water supplies and soil analysis.

**Q8. Give Method of analysis of Mass Spectrometry (MS).****Answer**

The mass spectrometer is an instrument which turns atoms and molecules into ions and measure their mass.

In 1919, Aston invented the mass spectrometer. This gave chemists a reliable and accurate method of comparing the relative masses of atoms. At one time, the relative masses of atoms were known as atomic weights, but nowadays refer to them as relative atoms masses.

The basic idea of a mass spectrometer can be demonstrated using the apparatus in figure 24.13. Wooden balls of different sizes but with identical iron cores, roll down a sloping plane. At the bottom of the slope a magnet attracts the iron cores and the moving balls are deflected.

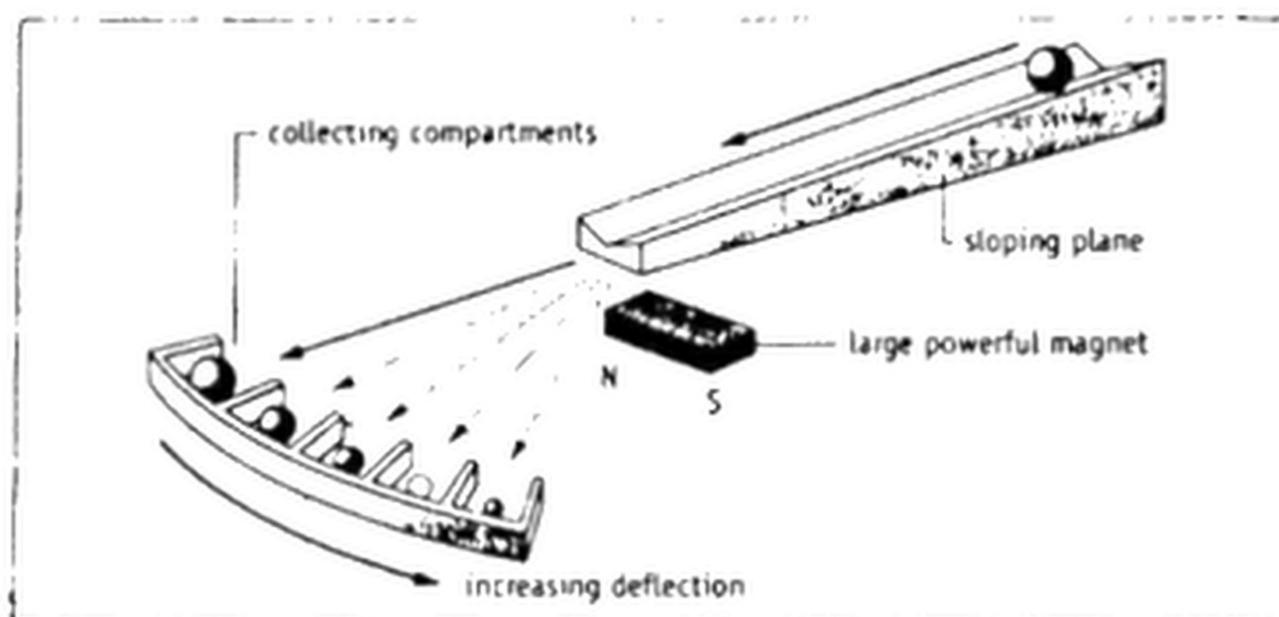


Figure 24. 13 A simple model to illustrate the working of a mass spectrometer.

As the balls have identical iron cores, they are all attracted equally by the magnet. But the smaller balls are lighter and therefore they are deflected the most. The balls collect in different compartments depending on their mass. All balls of the same mass collect in the same compartment. Using this simple

apparatus, it is possible to separate the different sized balls according to their mass and to find the relative numbers of each present.

A real mass spectrometer according works in a similar fashion to this simple model. It separates atoms according to their mass and shows the relative numbers of the different atoms present. Before the atoms can be deflected and separated. These must be converted positively charged ions.

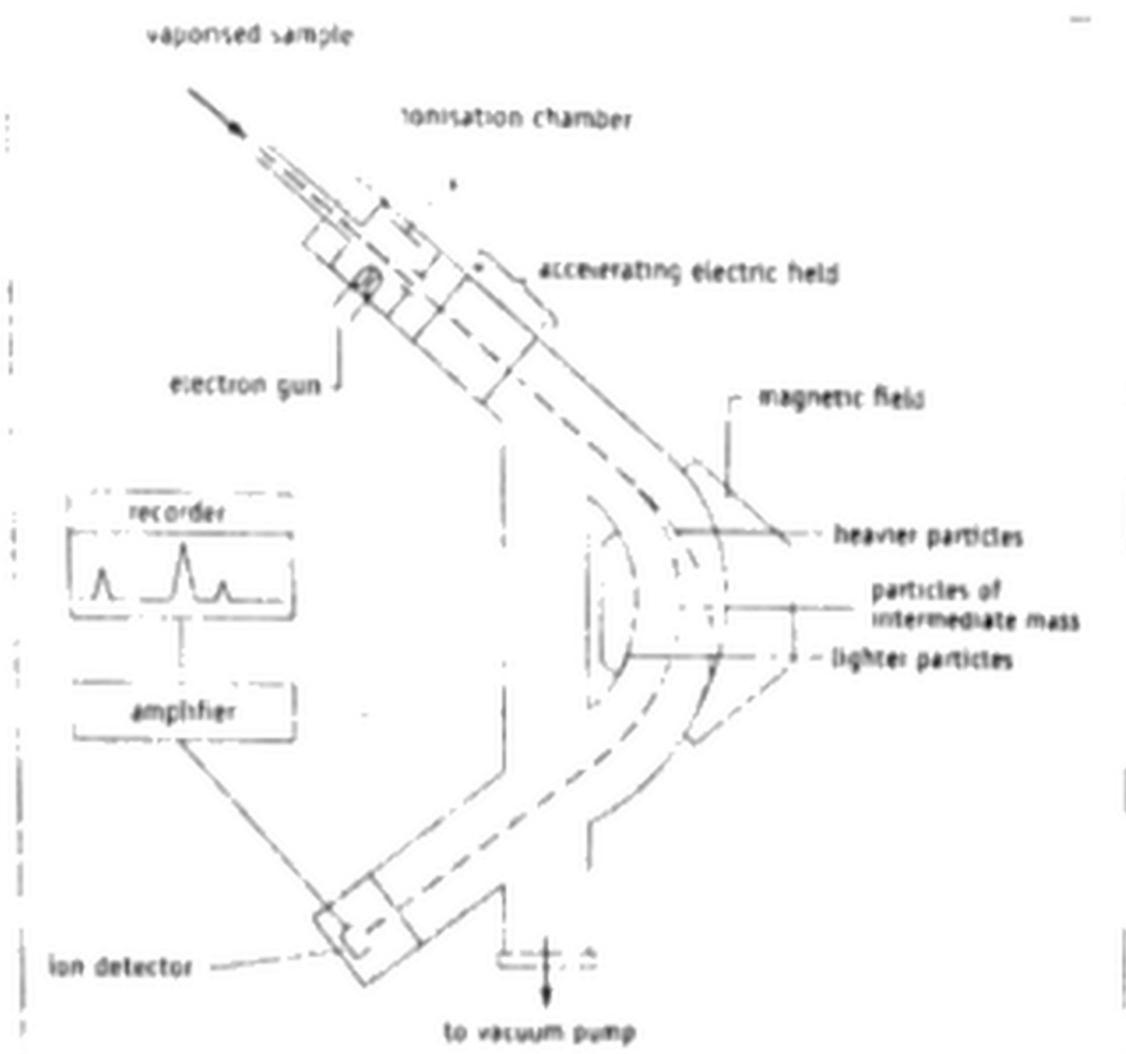


Figure 24.14 A diagram of a mass spectrometer.

Figure shows a simple mass spectrometer. There are five main stages.

- 1) Vaporization — the sample of elements is vaporized.
- 2) Ionization — positive ions are obtained from the vapor.
- 3) Acceleration — the positive ions are accelerated by an electric field.

4) Detection — the ions are detected and a record is made.

### Instrumentation and Working

It can be explained as follows

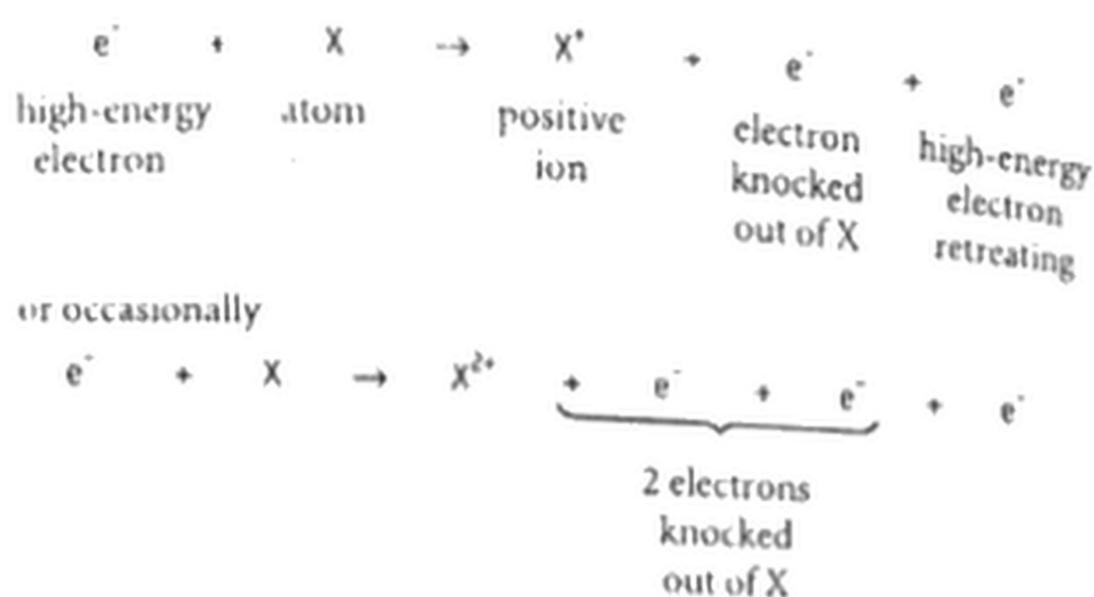
#### 1. Vaporization

Gases, liquids and volatile solids are injected into the instrument just before the ionization chamber. Less volatile solids must be preheated to vaporize them.

#### 2. Ionization

After vaporization the elements pass into the ionization chamber. Here atoms of the elements are bombarded with a stream of high energy electron. This causes ionization. One or occasionally two electrons are knocked out of the atoms leaving positive ions.

Thus for an atom X we have:



#### 3 — Acceleration

These positive ions such  $X^+$  and  $X^{2+}$  now pass through holes in parallel plates to which an electric field is applied. The electric field accelerates the ions into the instrument towards the magnetic field.

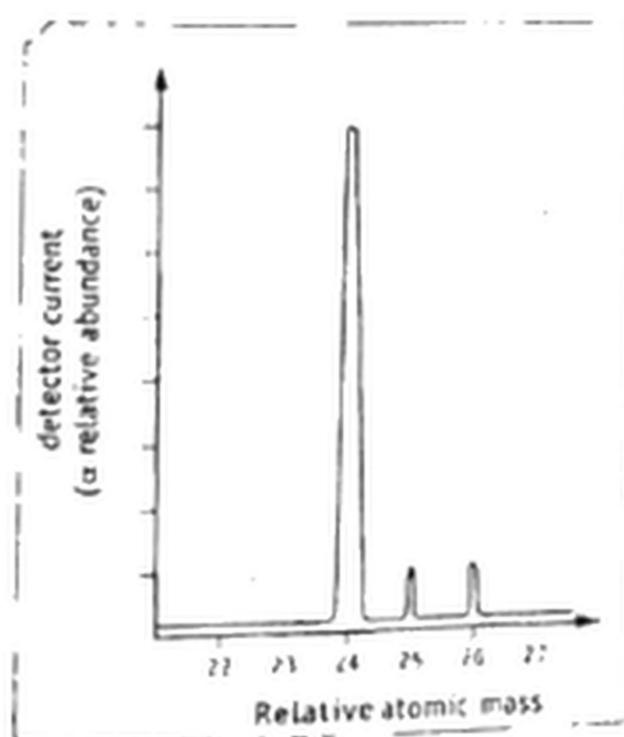
#### 4 — Deflection

As the ions pass through the magnetic field, they are deflected according to their mass and their charge. Notice that particles can only pass through the instrument if they are positively charged.

#### 5 — Detection

If the accelerating electric field and the deflecting magnetic field stay constant, ions of only one particular mass/charge ratio will hit the ion detector at the end of the apparatus. Ions of smaller mass/charge ratio will be deflected too much. Ions of greater mass/charge ratio will be deflected too little.

The ion detector is usually linked through an amplifier to a recorder. As the strength of the magnetic field is slowly increased ions of increasing mass will be detected and mass spectrum similar to that shown in figure 24.15 is traced out by the recorder.



A mass spectrometer trace for naturally occurring magnesium

The relative heights of the peaks in the mass spectrum give a measure of the relative amounts of the different ions present.

In practice a reference peak using a known substance is first obtained on the mass spectrum the relative masses of other particles can then be obtained by comparison with this.

**Q9. What are different zones of a flame? Discuss with reference to temp.**

**Answer**

Temperature Variations with a flame.

There are four different parts or zones of a flame i.e.

Blue zone(a zone of complete combustion)

Dark zone(a zone where no combustion occurs)

Luminous zone(a zone of partial or incomplete combustion)

Non-luminous zone(a zone of complete combustion)

Luminous zone where incomplete combustion takes place has the temperature between 600-850C (1,112-1,562 °F).

Non luminous zone where complete combustion takes place has the temperature of about 2000C (3,632 °F).

In fires (particularly house fires), the cooler flames are often red and produce the most smoke. Here the red color compared to typical yellow color of the flames suggests that the temperature is lower. This is because there is a lack of oxygen in the room and therefore there is incomplete combustion and the flame temperature is low, often just 600—850 °C (1,112—1,562 °F). This means that a lot of carbon monoxide is formed (which is a flammable gas if hot enough) which is when in Fire and Arson investigation there is greatest risk of backdraft. When this occurs flames get oxygen, carbon monoxide combusts and temporary temperatures of up to 2,000 °C (3,632 °F) occur.

Flame temperatures of common items include a candle at 1,400 °C (2,600 °F), a blow torch — at around 1,600 °C (2,900 °F) a propane torch at 1,995 °C (3,620 °F), or a much hotter oxyacetylene combustion at 3,000 °C (5,400 °F).

**Q10. Write a note on Forensic Chemistry and problem-solving skill.**

**Answer**

Forensic chemistry is the application of chemistry to criminal investigation. This major is recommended for individuals who wish to pursue a career in criminal investigation, in the laboratory analysis of forensic evidence, or pursue graduate study in forensic science. This course of study would also develop the analytical skills required for careers in other areas of civil law such as environmental pollution, accident investigation and product liability. Due to the nature of forensic investigations, the forensic chemist requires a strong background in chemical analysis and problem solving skill and must be able to effectively communicate the results of laboratory analysis in reports and in the courtroom. So a forensic chemist must have a strong theoretical and experimental background in analytical chemistry as well as in problem solving skills.

Forensic chemists must have good attention to detail and superior problem-solving skills. They need critical thinking abilities to solve crime puzzles based on fragmentary evidence. Forensic chemists must take accurate notes and make accurate records of their findings. They need strong writing skills to produce clear reports on highly technical subjects so that others can understand.

Analytical measurements are essential to everyday life, required to determine the composition and control the quality of many products, to protect the environment and to monitor health. Consequently Analytical Chemistry has a major impact, not only in chemistry, but also, in fields such as biochemistry, and

the forensic, food, environmental and pharmaceutical sciences. Forensic chemistry is the application of analytical chemistry to the law and involves the examination of physical traces, such as body fluids, bones, fibres and drugs. Success in analytical chemistry requires the ability to make rigorous measurements, an appreciation of the principles and practice of modern instrumentation, and a problem-solving approach.

**Q11. Write a note on Chemical Instrumentation and Technology.**

**Answer**

Chemical instruments are used extensively in research and development activities, laboratories being one of the major users. Use of chemical instruments for disease diagnosis is on a rise.

Chemical equipment market is growing at a rapid rate due to the continuous requirement of these instruments in pharmaceutical and biotechnology industries. Besides, the increase in number of biotechnology firms worldwide, advances in life science research and technology innovations with human genome mapping, and emergence of proteomics have enabled industry growth; as such high and research projects require quality instruments with high throughput capacity. All these factors are driving the life science and chemical instrumentation market.

The global life science and chemical instrumentation market was estimated to be \$302 billion in the year 2011 and is expected to grow at a CAGR of 8.4% from 2011 to 2016 to reach \$45.2 billion.

**Q12. What is Connection between Chromatography and MS?**

**Answer**

Chromatography is the collective term for a set of laboratory techniques for the separation of mixtures and for the detection of small amounts of materials present in those mixtures. The mixture is dissolved in a fluid called the mobile phase, carries it through a structure holding another material called the stationary phase. The various constituents of the mixture travel at different speeds, causing them to separate the separation is based on differential partitioning between the mobile and stationary phases. subtle differences in a compound's partition coefficient result in differential retention on the stationary phase and thus changing the separation.

Mass spectrometry (MS) is an analytical technique that measures the ratio of charged particles. It is used for determining masses of particle the determining the elemental composition of a sample or molecule, and for elucidatingunds. MS chemical structures of molecules, such as peptides and other chemical components works by ionizing chemical compounds to generate charged molecules or molecule fragments and measuring their mass-to-charge ratios.

Gas chromatography—mass spectrometry (GC-MS) is a method that combines the features of gas-liquid chromatography and mass spectrometry to identify different substances, even present in small amounts, within a test sample. Applications of GCMS include drug detection, fire investigation, environmental analysis, explosives investigation, and identification of unknown samples. GC-MS can also be used in airport security to detect substances in luggage or on human beings. Additionally, it can identify trace elements in materials that were previously thought to have disintegrated beyond identification. GC-MS has been widely heralded as a "gold standard" for forensic substance identification because it is used to perform a specific test. A specific test positively identifies the actual presence of a particular substance in a given sample.

Liquid chromatography—mass spectrometry (LC-MS, or alternatively HPLC-MS) is a chemistry technique that combines the physical separation capabilities of liquid chromatography (or HPLC) with the mass analysis capabilities of mass spectrometry. LC-MS is a powerful technique used for many applications which has very high sensitivity and selectivity. Generally, its application is oriented towards the general detection and potential identification of chemicals in the presence of other chemicals (in a complex mixture). Preparative LC-MS system can be used for fast and mass directed purification of natural-products extracts and new molecular entities important to food, pharmaceutical, agrochemical and other industries. The limitations of LC-MS in urine analysis drug screening is that it often fails to distinguish between specific metabolites, in particular with hydrocodone and its metabolites. LC-MS urine analysis testing is used to detect specific categories of drugs. However, gas chromatography (GC-MS) should be used when detection of a specific drug and its metabolites is required.

