

# MASS Spectrometry

Topics :- [Complete Hand Made Notes]

1. Basic Principle [Theory]
2. Instrumentation
3. Ionization Techniques.
4. Electron impact technique
5. Chemical ionisation technique.
6. Field Desorption
7. Fast atom bombardment [FAB]
8. Matrix Assisted Laser Desorption Ionization.
9. Thermospray Ionization.
10. Electrospray Ionization.
11. Mass Analyser
12. double focusing Mass analyser.
13. Quadrupole Mass analyser.
14. Molecular Ion or Parent Ion
15. Fragmentation Pattern
16. McLafferty Rearrangement
17. Factors Affecting Fragmentation.
18. The Nitrogen Rule
19. Ring Rule
20. GAS chromatography.



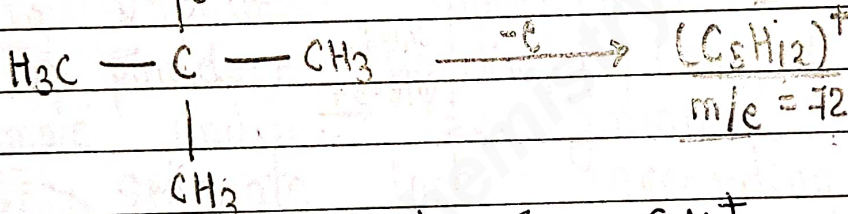
# Mass Spectrometry

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★ **Basic Principle** :- Mass Spectrometry is the most accurate method for determining the molecular mass of the compound and its elemental composition. In this technique, the compound under investigation is bombarded with a beam of energetic electrons. The molecules are ionised and dissociate into several fragments, some of which are positive ions. Each kind of ion has a particular ratio of mass to charge i.e.,  $m/e$  ratio.

For neopentane  $m/e$  ratio is 72



molecular ion,  $\text{C}_5\text{H}_{12}^+$

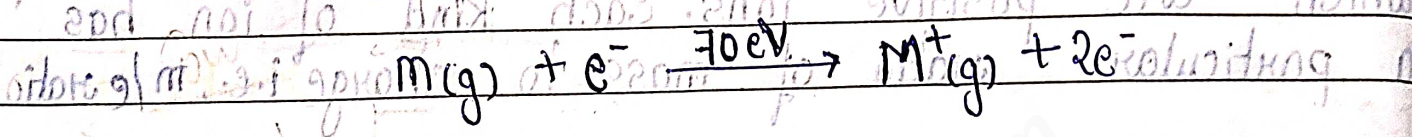
Fragmentation

	$\text{C}_4\text{H}_9^+$	$\text{C}_3\text{H}_5^+$	$\text{C}_2\text{H}_5^+$	$\text{C}_2\text{H}_3^+$
$m/e \Rightarrow$	57	41	29	27
Relative Intensity $\rightarrow$	100	41.5	38.5	15.7

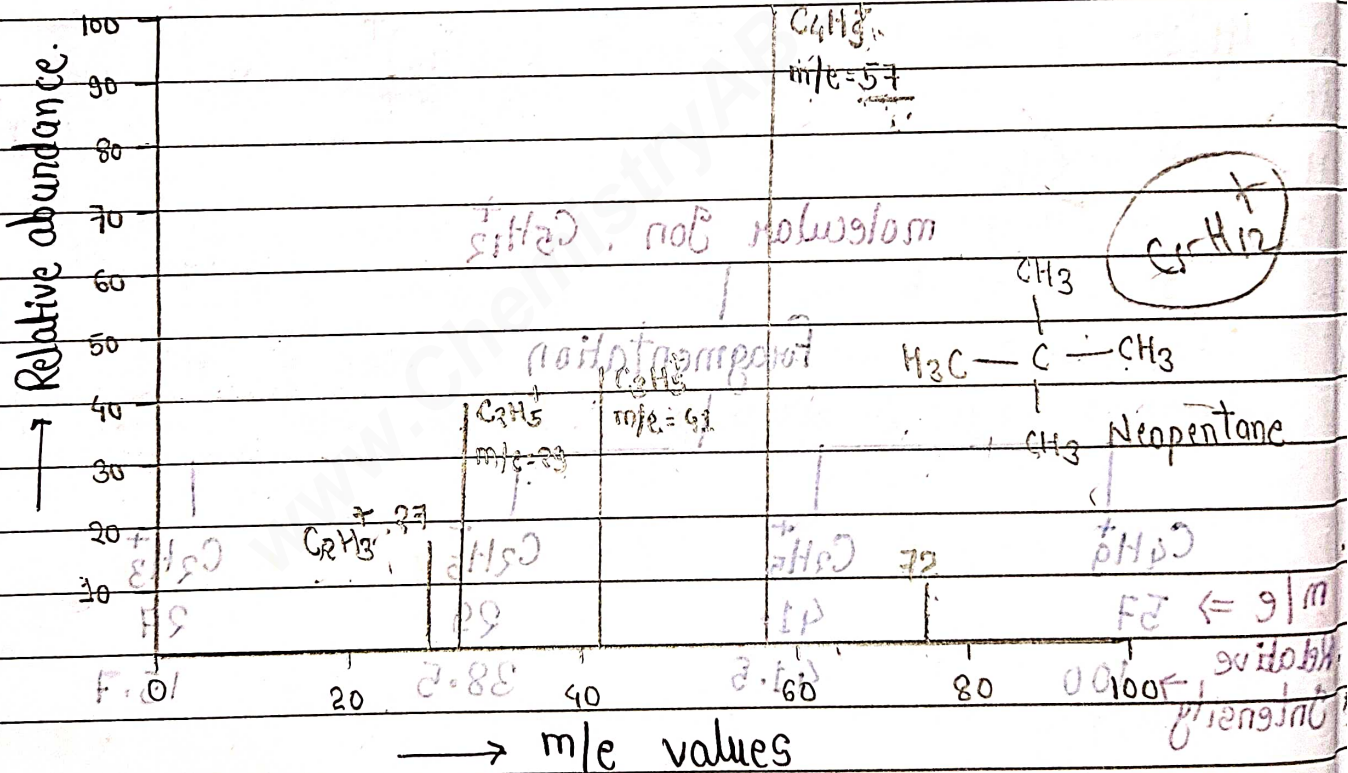
Mass Spectrometry is not a true spectroscopic technique because absorption of electromagnetic energy is not involved and any wavelength is assigned a value of 100.



Theory: A mass spectrum consists of an array of peaks of different heights. The nature of the spectrum is dependent on properties of the molecule, ionisation potential, sample pressure and the instrument design. The mass spectrometer bombards a molecule M with high energy electrons i.e.,



### Mass Spectrum of neopentane.



The largest most intense peak in the structure is called the base peak and its intensity is arbitrarily assigned a value of 100%.



★ The important advantages of mass spectrometry are its high sensitivity, reproducibility, accuracy and the small amount of sample required for mass spectral analysis.

### ★ Basic Functions of Mass Spectrometer:-

The mass spectrometer is designed to perform the following functions:-

1. To vapourise compounds of varying volatility.
2. To produce positively charged ions from the sample under investigation.
3. To separate ions according to their mass to charge ratio.
4. To detect the ions, recording their relative abundances and producing a corresponding signal.



# Mass Spectrometer

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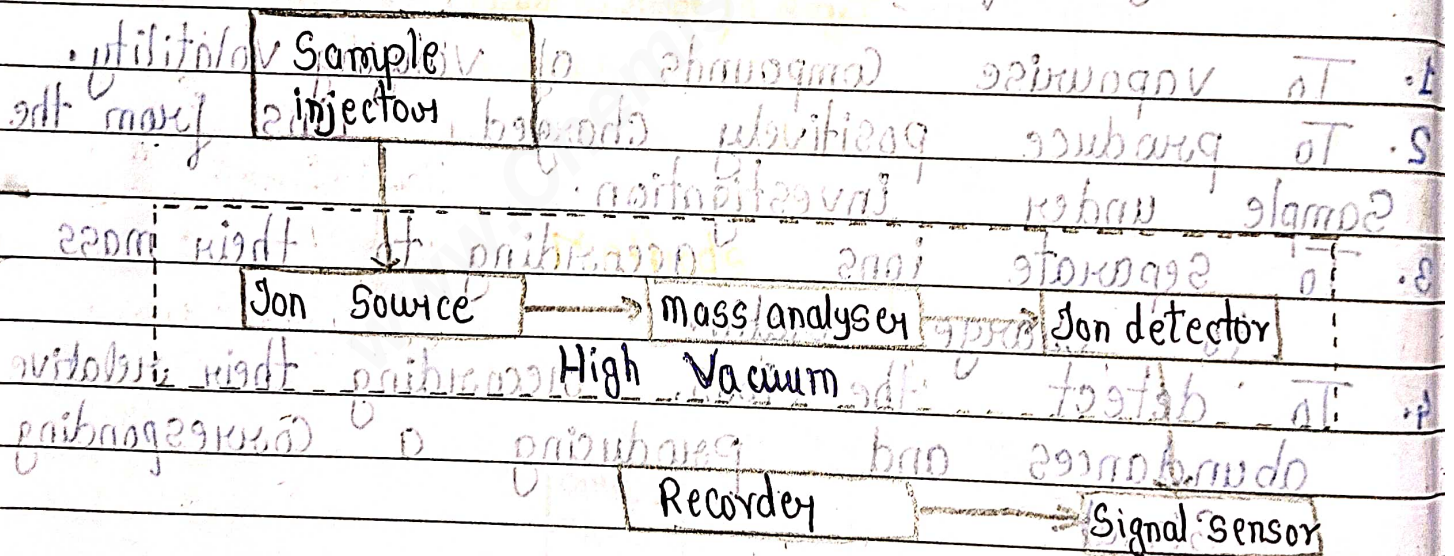
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Instrumentation :- Common mass spectrometer

Consists of

1. Sample introducing System
2. The ion source
3. Mass analyser
4. Ion detector and amplifier
5. Recorder

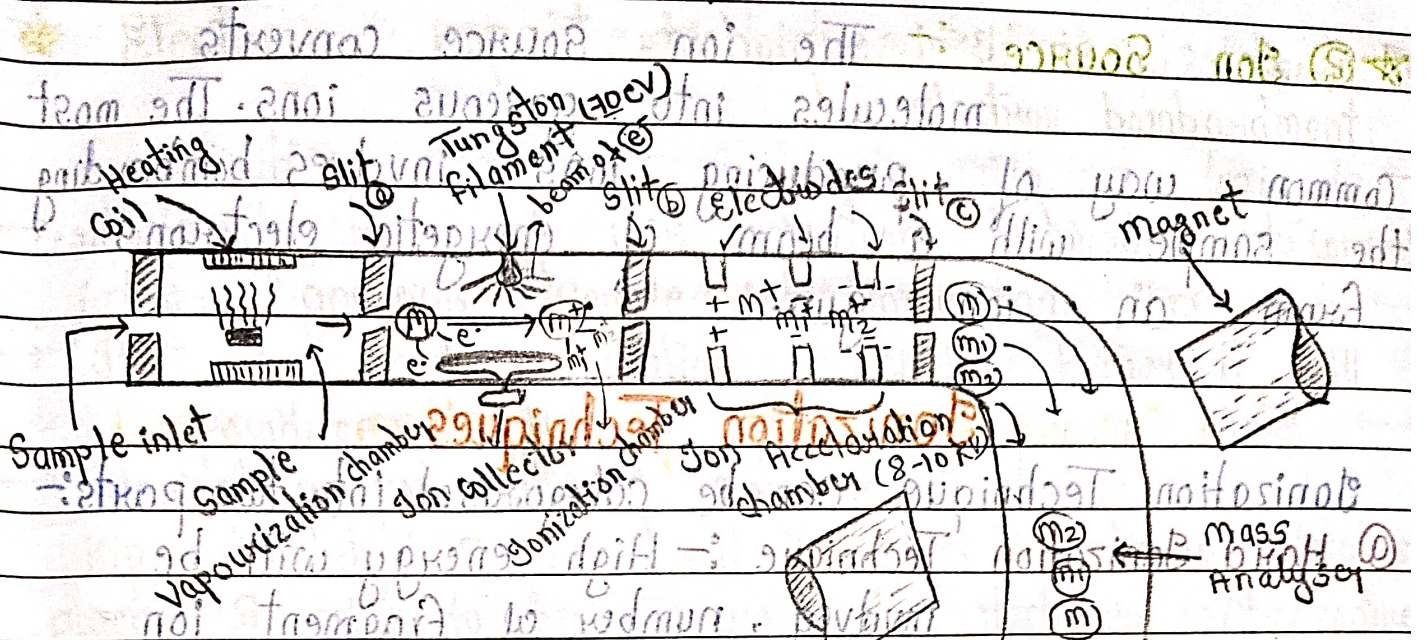
The whole system from ion source to the collector electrode is maintained at high vacuum.



Schematic diagram of mass spectrometry.



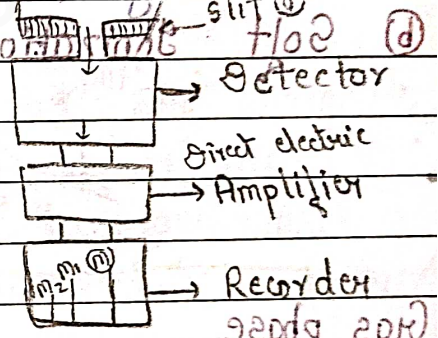
# Mass Spectrophotometer.



## Types of mass analyser

1. Magnetic field deflection
2. Double focusing
3. Quadrupole
4. Time of flight
5. FTICR

- Sample
- Liquid
- Solid
- Gas



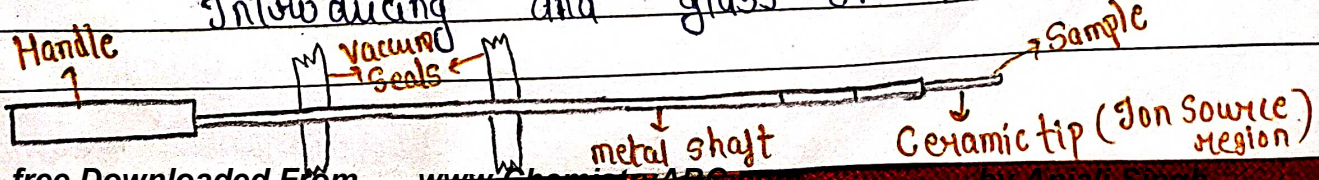
Ionization chamber :-  
 Ionization potential - Minimum potential required to convert  $m$  to  $m^+$ , approximate value is 19.8 to 15 eV

## ★ ① Sample Introducing System :- Sample introducing

Systems are divided into two parts :-

① Internal Sample Introducing System :- The sample is placed within the ionisation chamber either as part of the ion source or coated on a filament.

② External Sample introducing System like Direct Introducing and glass or metal inlet.





★ ② Ion Source :- The ion source converts molecules into gaseous ions. The most common way of producing ions involves bombarding the sample with a beam of energetic electrons from an ion gun.

## Ionization Techniques

Ionization Technique can be categorised into two parts:-

① Hard Ionization Technique :- High energy will be involved, number of fragment ion will be higher and number of molecular ion will be low.

② Soft Ionization Technique :- Low energy, low fragmentation, high molecular ion.

## Methods

Gas phase	Desorption	Evaporative
① Electron Impact	① Field desorption	① Thermospray
② Chemical Impact	② FAB	② ESI
	③ MALDI	③ APCI ④ APPI

Gas phase Ionization :- oldest and most popular method, in this method sample is vapourised before ionized.

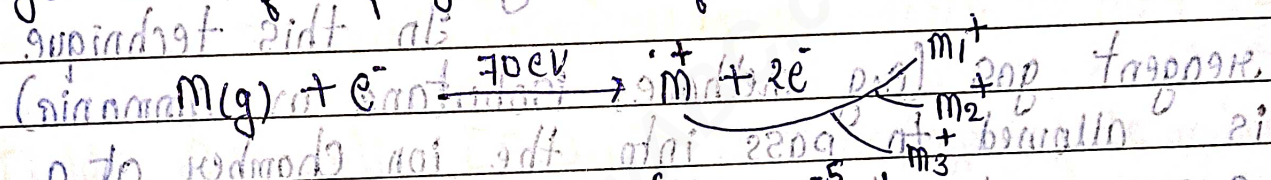
These are two types of ionization techniques

- ① Electron impact Technique
- ② Chemical impact Technique

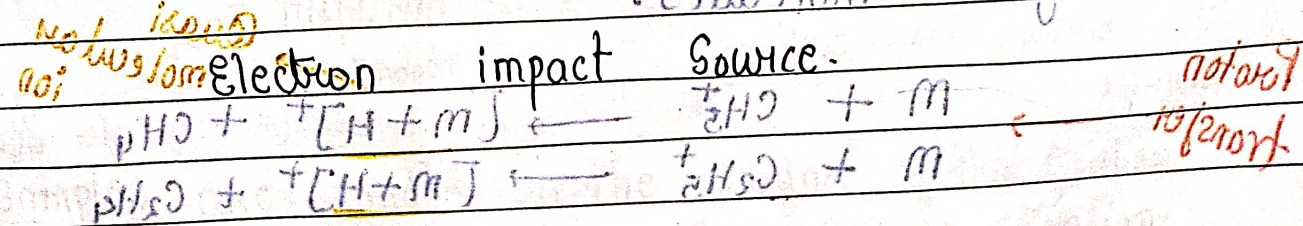
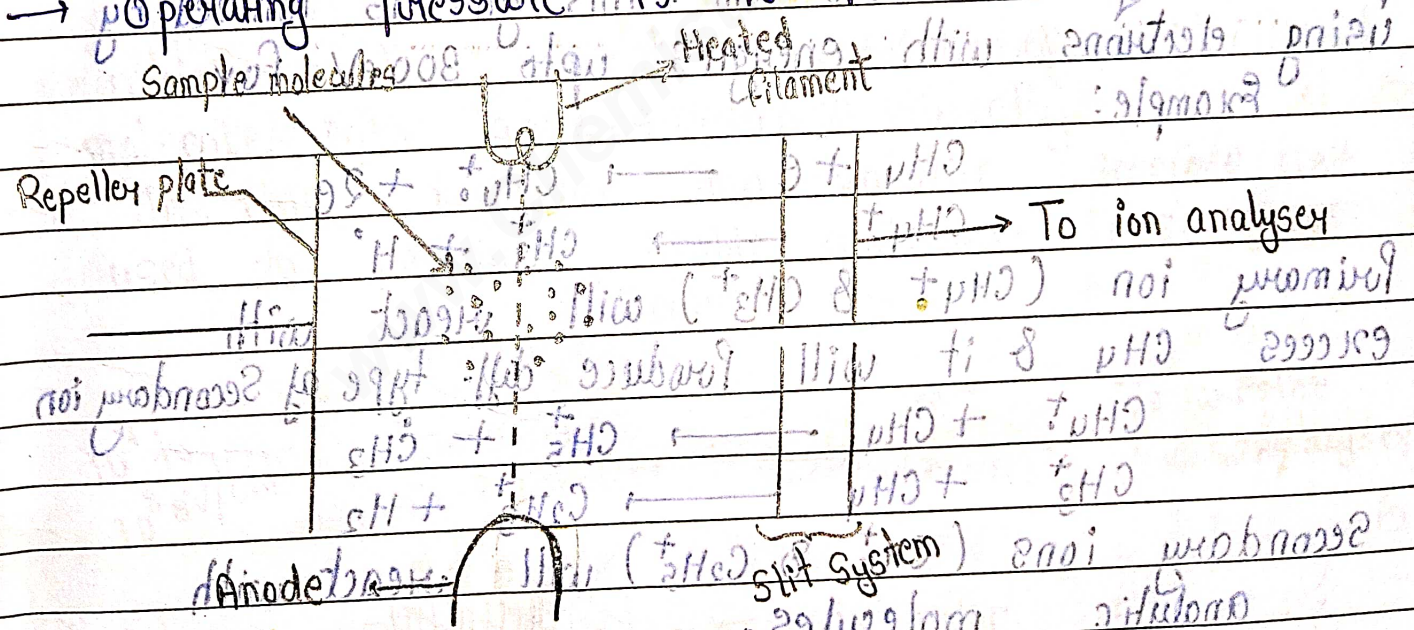


**★ Electron impact technique** :- It is also known as electron bombardment

- Main function of this ionization technique is to convert the gaseous sample into molecular ions.
- It is a hard ionization technique because it will produce  $7-10\text{ eV}$ .
- Ionization potential of organic compounds are approximately  $8-15\text{ eV}$  and direct bombardment takes place. So due to high energy, this technique will produce large amount of fragmentation from molecular ions.



Operating pressure is  $10^{-6}$  to  $10^{-5}$  Torr.





## ★ Chemical ionisation technique

→ chemical ionization is a gaseous phase ionization method, it is very important soft ionization technique.

→ Fragmentation is less, and give intense peak of molecular ion.

→ Some molecules like alcohols, ethers, amines, esters, amino acids are highly fragmented in electron ionization. So molecular ion peaks will not be detected. So to get proper molecular ion peak we are using chemical ionization.

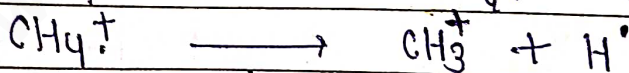
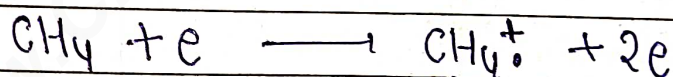
In this technique a

reagent gas (e.g. methane, isobutane or ammonia)

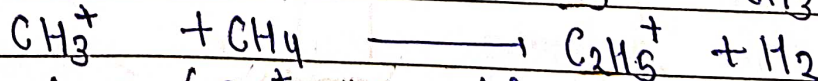
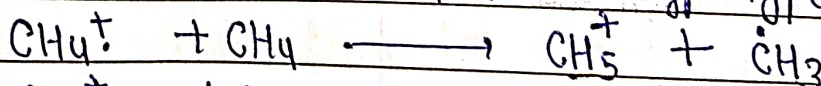
is allowed to pass into the ion chamber at a

pressure of about  $10^{-2}$   $\text{Nm}^{-2}$ . This gas is ionized by using electrons with energies upto 300 eV.

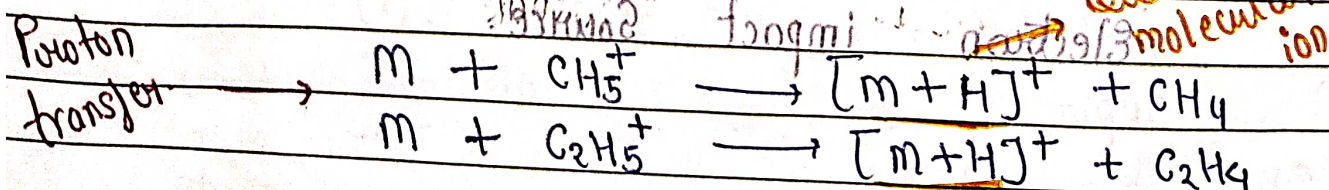
Example:



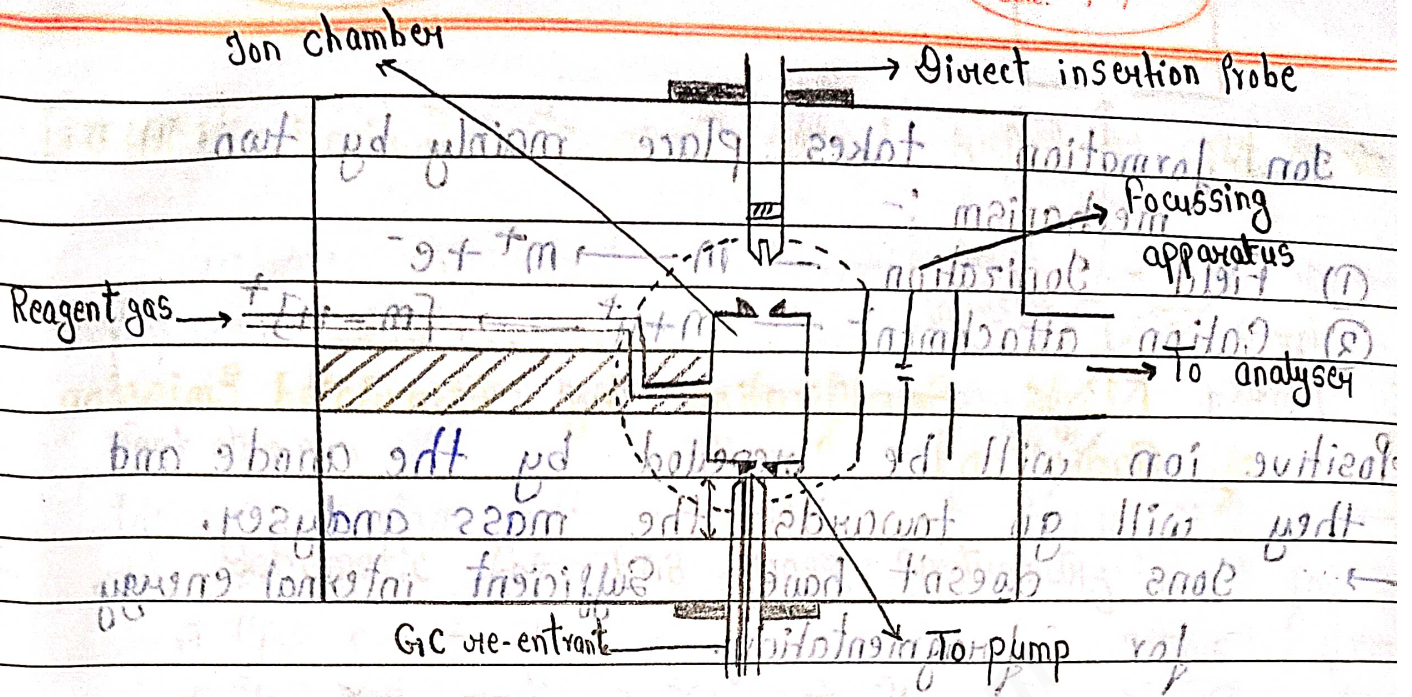
Primary ion ( $\text{CH}_4^+$  &  $\text{CH}_3^+$ ) will react with excess  $\text{CH}_4$  & it will produce diff. type of Secondary ion



Secondary ions ( $\text{CH}_5^+$  &  $\text{C}_2\text{H}_5^+$ ) will react with analytic molecules.



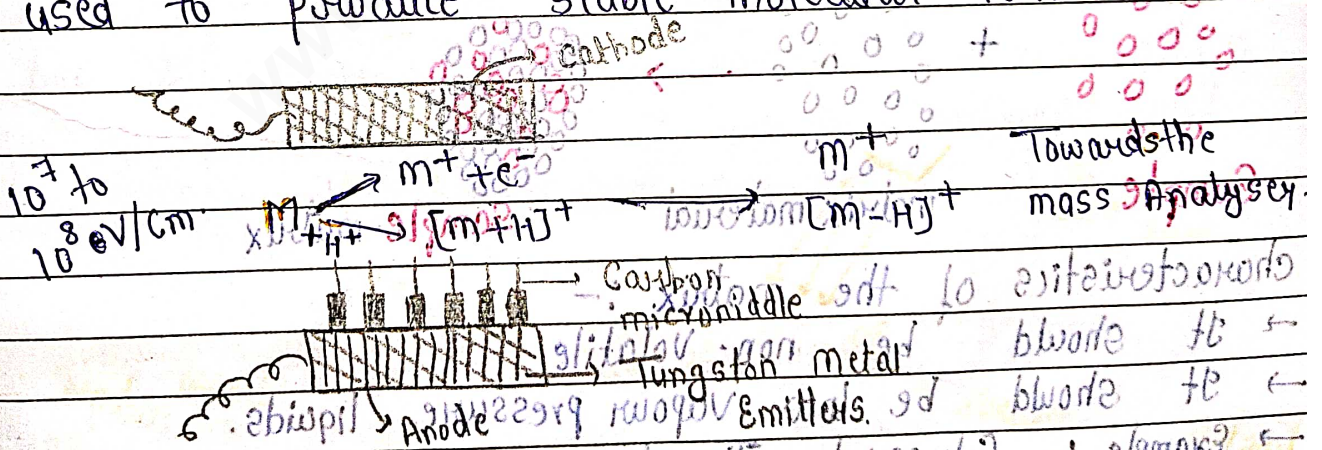




### Schematic diagram of C.I. Source

★ **Field Desorption [FD]** is a type of desorption ionization technique which involves direct conversion of solid/liquid molecule into gaseous ion directly.

→ In this technique low volatile samples are used to produce stable molecular ions.

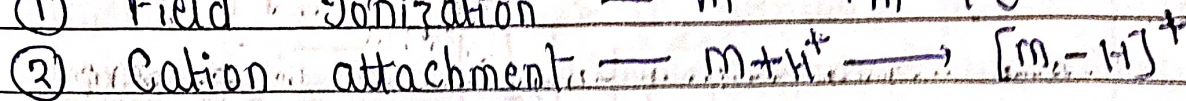
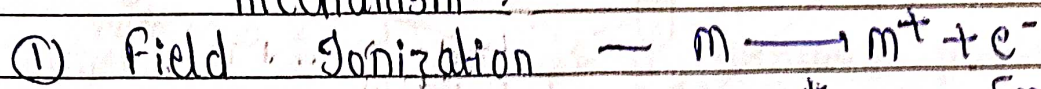


→ Samples are loaded on the surface of the Carbon microneedle by dipping in the sample solution.

→ Carbon microneedle will produce high gradient voltage on their tips. That is why sharp tips is



Ion formation takes place mainly by two mechanism :-

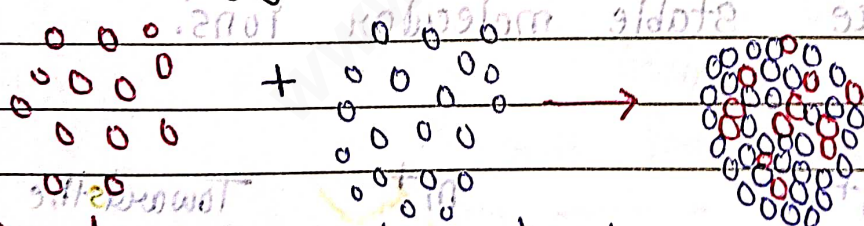


→ Positive ion will be repelled by the anode and they will go towards the mass analyser.  
→ Ions doesn't have sufficient internal energy for fragmentation.

★ Fast atom bombardment [FAB] :-

→ It is a soft ionization method classified under soft ionization method. [FAB] is used to determine the molecular weight of the compounds having the size from 300 to 6000 Daltons.  
→ Generally used to determine molecular weight of peptides.

Methodology :-



Sample

matrix material

Sample-matrix

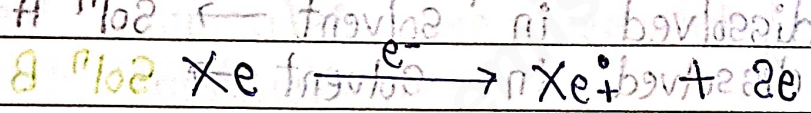
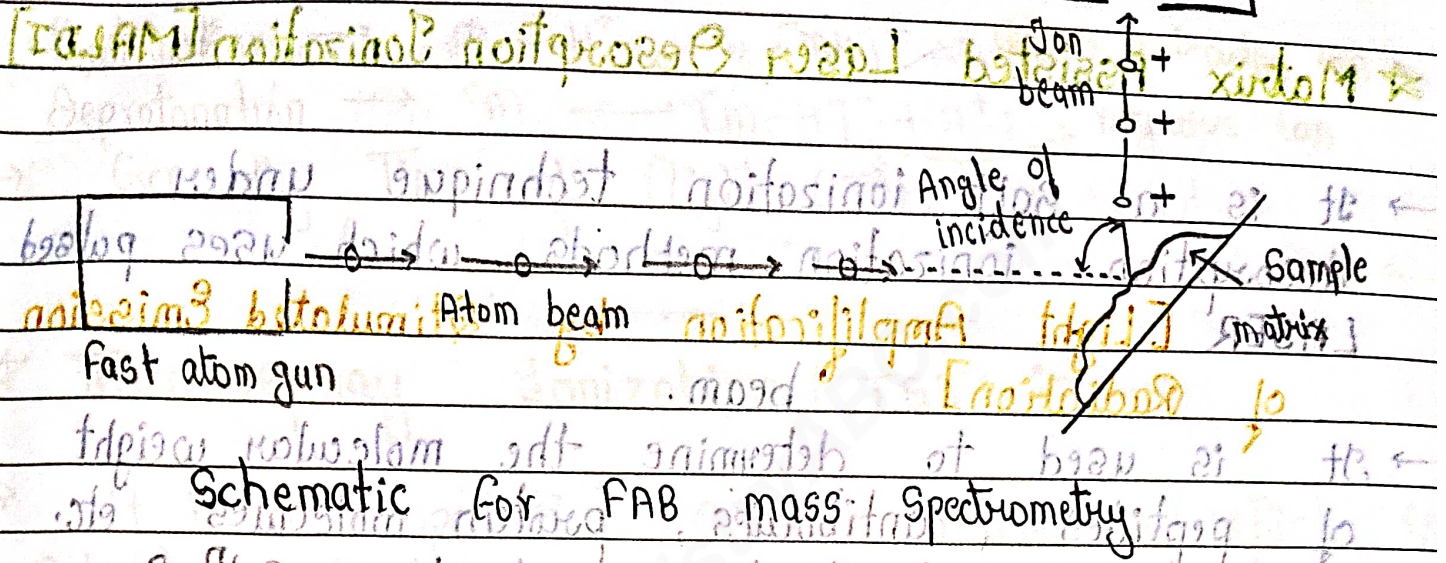
characteristics of the matrix :-

→ It should be non-volatile  
→ It should be low vapour pressure liquids.  
→ Example :- Glycerol, Thioglycerol, 3-Nitrobenzyl-alcohol, Methanol amine, Triethanol amine.

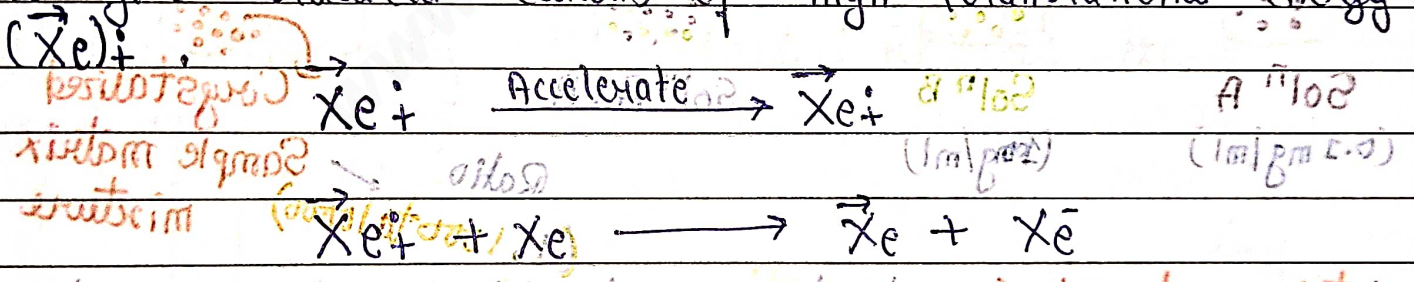


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Mass analyzer  
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The radical cations are accelerated to  $\sim 10kV$  to give radical cations of high translational energy



matrix material is dissolved in solvent in which sample is dissolved in solvent etc. Under dynamic and static conditions. matrix material spray low molecular weight. acidic nature and strong laser beam operation and

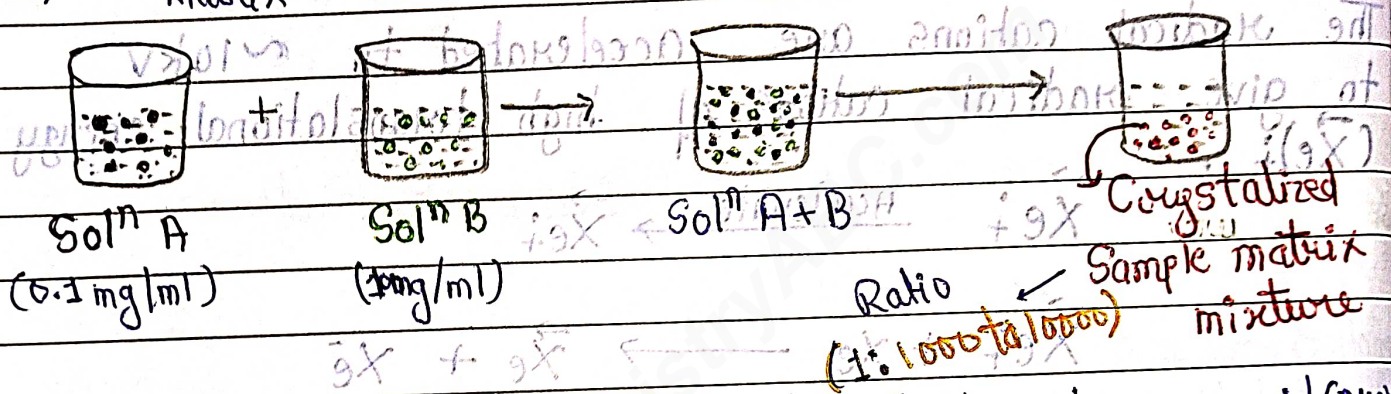


# ★ Matrix Assisted Laser Desorption Ionization [MALDI]

→ It is a soft ionization technique under desorption ionization methods, which uses pulsed LASER [Light Amplification by Stimulated Emission of Radiation] beam.

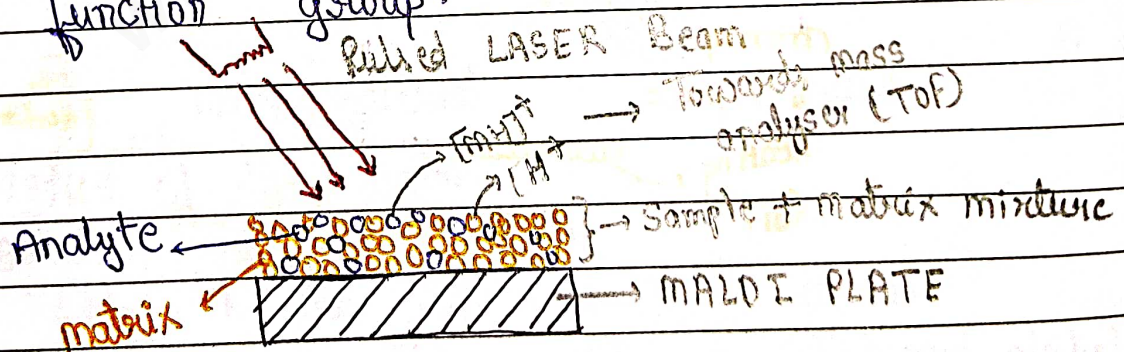
→ It is used to determine the molecular weight of peptides, antibodies, protein molecules etc.

→ Sample is dissolved in solvent → Sol<sup>n</sup> A  
 → matrix is dissolved in solvent → Sol<sup>n</sup> B



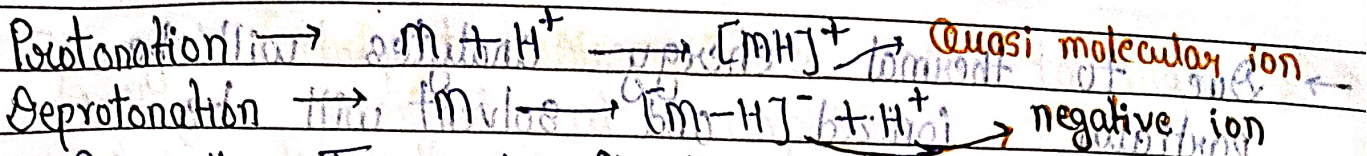
matrix material :- Nicotinic acid, Dihydroxy benzoic acid (DHB), Urea, Cinnamic acid etc.

→ matrix material should have low molecular weight, acidic nature, strong laser beam absorption and Polar function group.



→ LASER Beam will heat the Sample matrix mixture & analyte/sample will convert into the form of gas  
 → Analyte/sample & matrix will also convert into ions also due to translational energy.



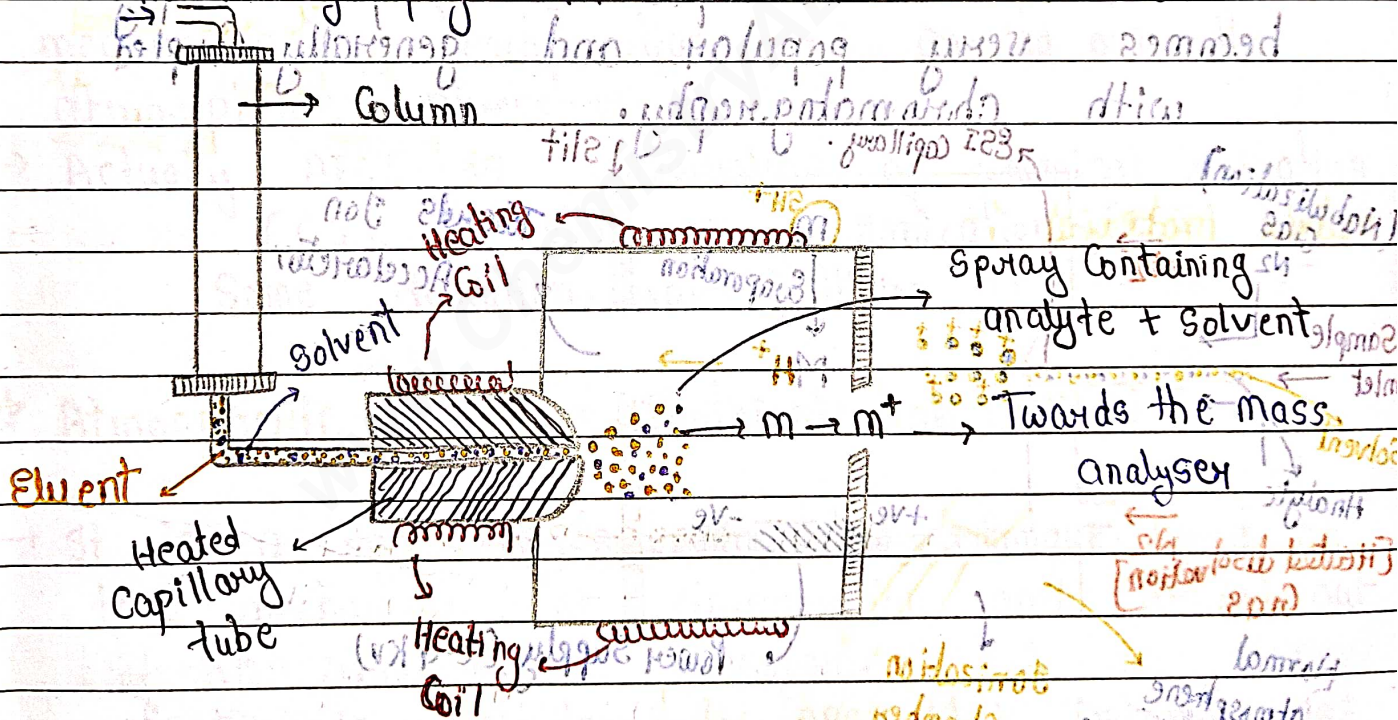


→ Generally Time of Flight (TOF) is used.

### ★ Thermospray Ionization [TSI] :-

→ It is a evaporative ionization method in which solvent molecules are removed from the analyte by evaporation.

→ This technique is very popular for coupling with chromatography instrument specially liquid chromatography like HPLC or RP-HPLC etc.



→ Heated Capillary tube will nebulize the eluent partially evaporate the solvent and form a stream of fine spray containing analyte.

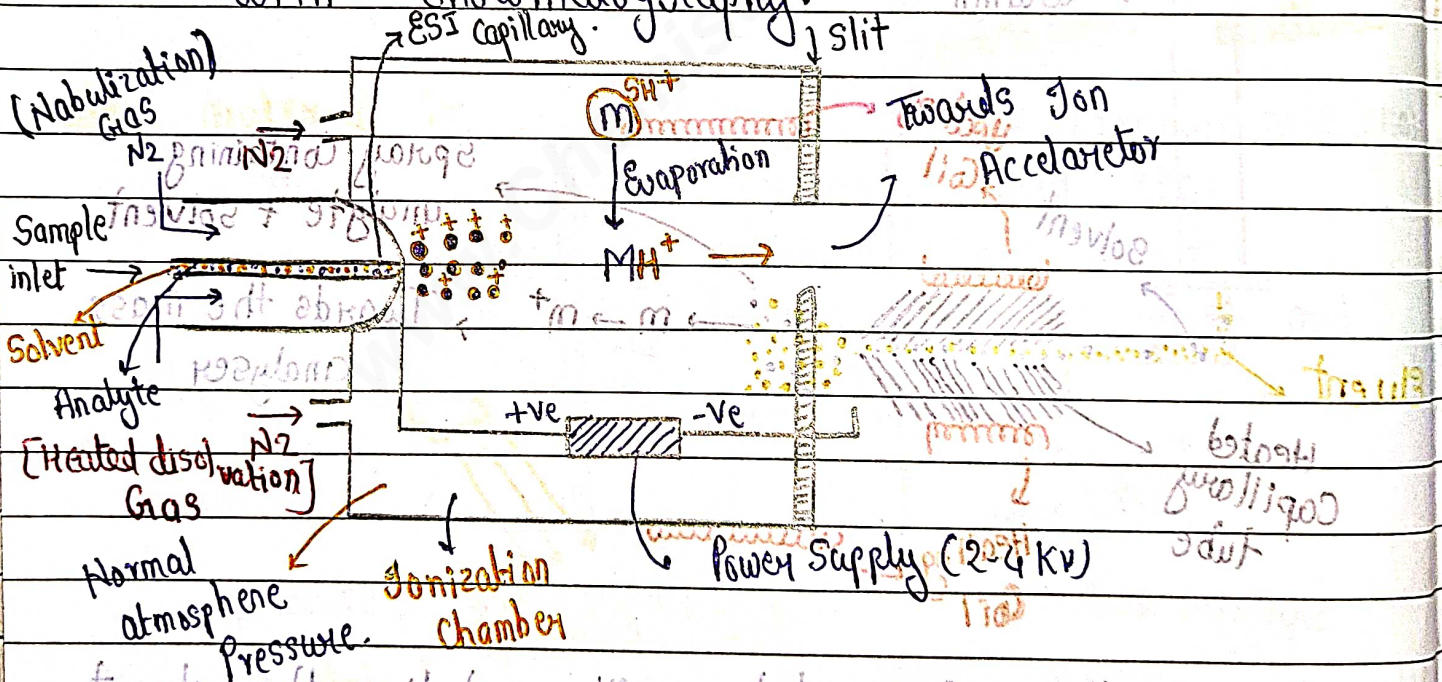
→ Fine spray droplets will be partially charged by thermal energy and solvents gets evaporated from spray.



- Due to thermal energy analytes will be partially ionized and solvent will evaporated.
- Ionised analytes will move towards the mass analyser for further analysis.

## ★ Electrospray Ionization [ESI]

- It is a type of evaporative ionization technique used to analyze the high molecular weight biomolecules, labile and non-volatile compounds.
- Due to ESI technique mass Spectroscopy becomes very popular and generally coupled with chromatography.



- A solution containing the sample molecule is sprayed through the high voltage potential of capillary by the help of nebulization gas.



→ Sprayed droplets are ionized due to high voltage potential at capillary.

→ Heated nebulization of gas will evaporate the solvent and will produce the molecular ion.

→ As it reacts, it also produces multiply charged ions.

→ This technique is used to ionize proteins, peptides, lipids, oligosaccharides etc.

★ Atmospheric Pressure Chemical Ionization (APCI)

→ It is a type of soft ionization technique based on the mechanism of evaporation and carried out the atmospheric pressure.

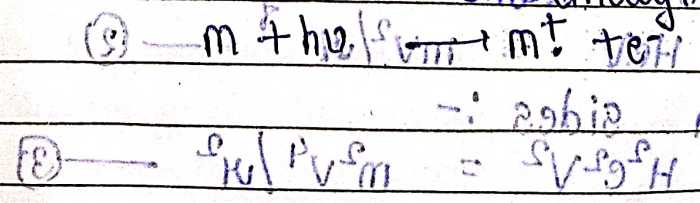
→ Actually APCI is combination of chemical ionization (CI) & electrospray ionization (ESI) with some deviation. Exa. →  $MH^+ + A + S^+ \rightarrow MH^+ + S^-$

★ Atmospheric Pressure Photoionization (APPI) :-

→ It is a type of soft ionization technique based on the mechanism of evaporation and carried out the atmospheric pressure.

→ APPI is similar to APCI but ionization is due to photons generated by uv light of Krypton lamp.

→ photon will ionize the analyte by direct APPI

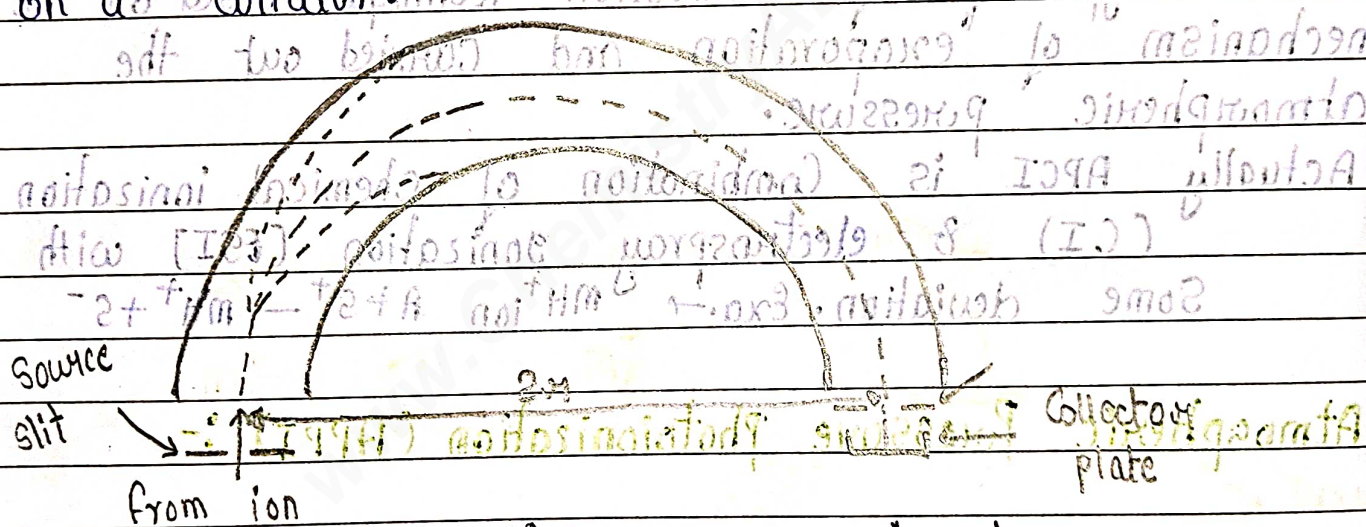




### ★ (3) Mass Analyser [Separation of Ions]

In the positively charged ions (Parent ions/fragment ions) produced in the ion chamber are accelerated by applying an acceleration potential. These ions then enter the mass analyser. Here, the fragment ions are differentiated on the basis of their  $m/e$  ratio.

Dempster's mass spectrometer is used for this purpose. The positive ions accelerated by electric field travel in a circular path through  $180^\circ$  under a magnetic field  $H$  and fall on a collector plate.



Chamber Dempster's mass spectrometer.

Suppose an ion having a charge  $e$  is accelerated through a voltage  $V$ , then the kinetic energy of the ions is expressed as :-

$$\frac{1}{2} mv^2 = eV \quad \text{--- (1)}$$

From Newton's second law of motion

$$HeV = mv^2/u \quad \text{--- (2)}$$

Squaring both sides :-

$$H^2 e^2 V^2 = m^2 v^4 / u^2 \quad \text{--- (3)}$$



$$H^2 e^2 = \frac{m^2 v^2}{r^2} \quad (4)$$

But  $\frac{1}{2} m v^2 = eV$  (from equa. 1)

$$\therefore m v^2 = 2eV$$

Putting the value of  $m v^2$  in equa. (4) we get

$$H^2 e^2 = \frac{m \cdot 2eV}{r^2}$$

$$H^2 e = \frac{2mV}{r^2}$$

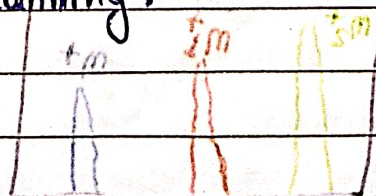
$$\frac{m}{e} = \frac{H^2 r^2}{2V} \quad (5)$$

Equa. (5) indicates that at a given magnetic field strength and accelerating voltage, the ion of  $m/e$  value will follow a circular path of radius  $r$ . The ions of various  $m/e$  values reach the collector, amplified and recorded. The mass spectrum can be obtained either by

(a) changing  $H$  at constant  $V$

(b) changing  $V$  at constant  $H$ .

When magnetic field is varied, the method is called magnetic scanning.





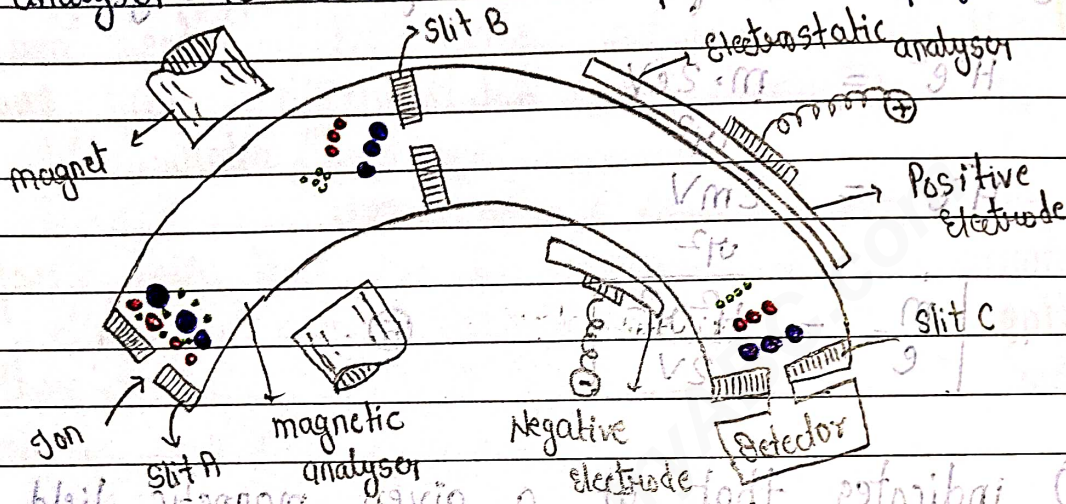
# Mass Spectrometers

## [Type of Mass analyzer]

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★ Double focussing mass spectrometer :-  $90^\circ H$

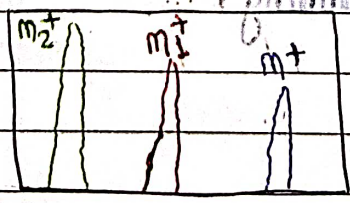
→ It gives high resolution compared to magnetic deflection mass analyser because electrostatic analyser is added to improve the performance.



→ Positively charged ions will enter into the magnetic analyser through slit A & B, deflected just like in magnetic mass analyser.

molecular weight (100)

→ Magnetic analyser will separate the ions according to the deflection in the magnetic field as per the mass difference between the ions.



→ When positive ions will be entered into the electrostatic analyser then all ions will be aligned.



→ Velocity of ions having same  $m/e$  value will be same under electrostatic analyser.

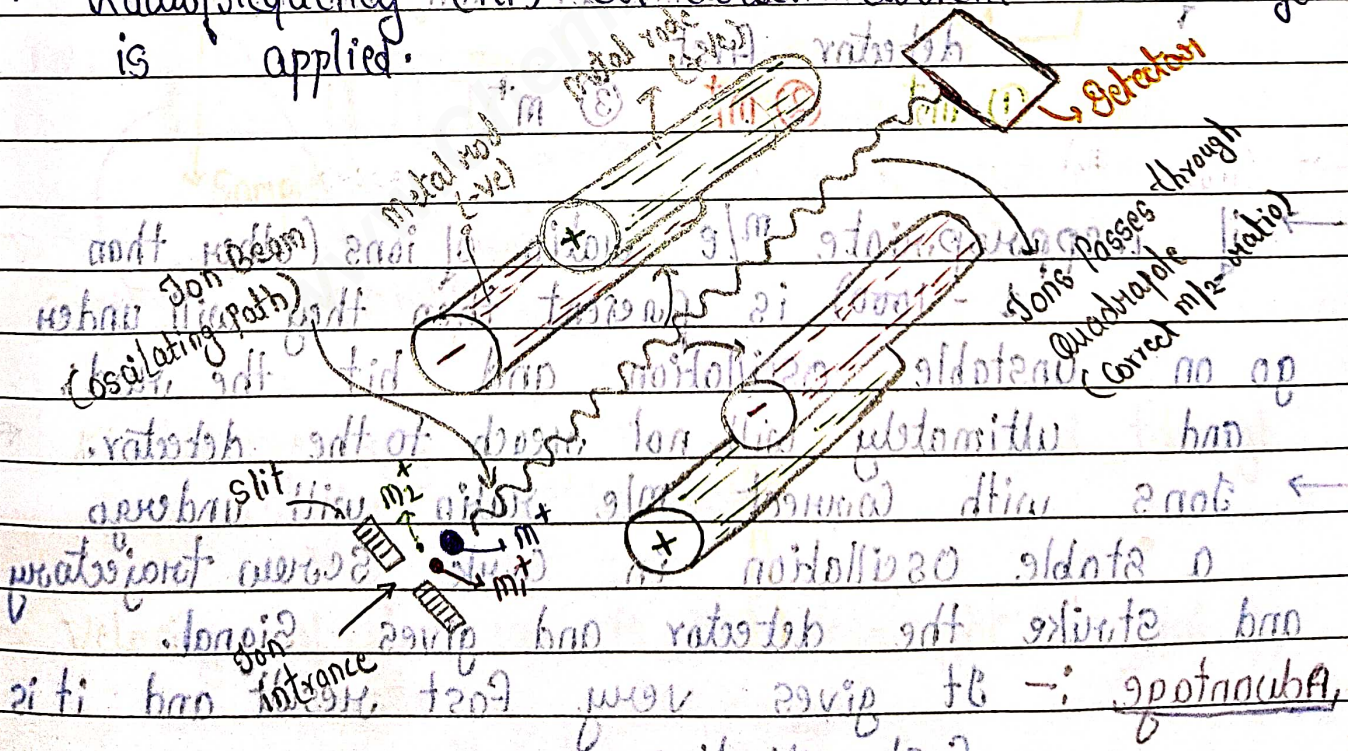
90 <sup>m+</sup>	111 <sup>m+</sup>	200 <sup>m+</sup>
100 <sup>m+</sup>	120 <sup>m+</sup>	210 <sup>m+</sup>

9V- Peaks are more than 10 times higher resolved as compared to normal magnetic deflection analyser.

→ Now a days double focussing mass analyser is used only in the double focussing mode.

### ★ Quadrupole Mass Analyser

- It consists of cylindrical metal rods arranged in a square parallel to the direction of ion beam
- hyperbolic rods can also be used.
- Radio frequency (RF) or direct current (DC) voltage is applied.



→ Combination of RF and DC will generate oscillating electrostatic field between the regions of rods.



	(+ve)	Two +ve rods will be diagonal to each other.
	(-ve)	
	(-ve)	Two -ve rods will be diagonal to each other.
	(+ve)	

→ Ions will enter into the mass analyzer.

→ Depending on the ratio of RF amplitude and DC voltage an oscillating electrostatic field will be generated for ions.

→ Ions will either acquire oscillation in 2 ways

① If  $RF > DC$  then larger ion will hit the detector first

①  $m_2^+$  ②  $m_1^+$  ③  $m^+$

② If  $RF < DC$  then smaller ion will hit the detector first

①  $m_2^+$  ②  $m_1^+$  ③  $m^+$

→ If inappropriate  $m/e$  ratio of ions (other than 1 - 1000) is present then they will undergo on unstable oscillation and hit the rods; and ultimately will not reach to the detector.

→ Ions with correct  $m/e$  ratio will undergo a stable oscillation in cork screw trajectory and strike the detector and gives signal.

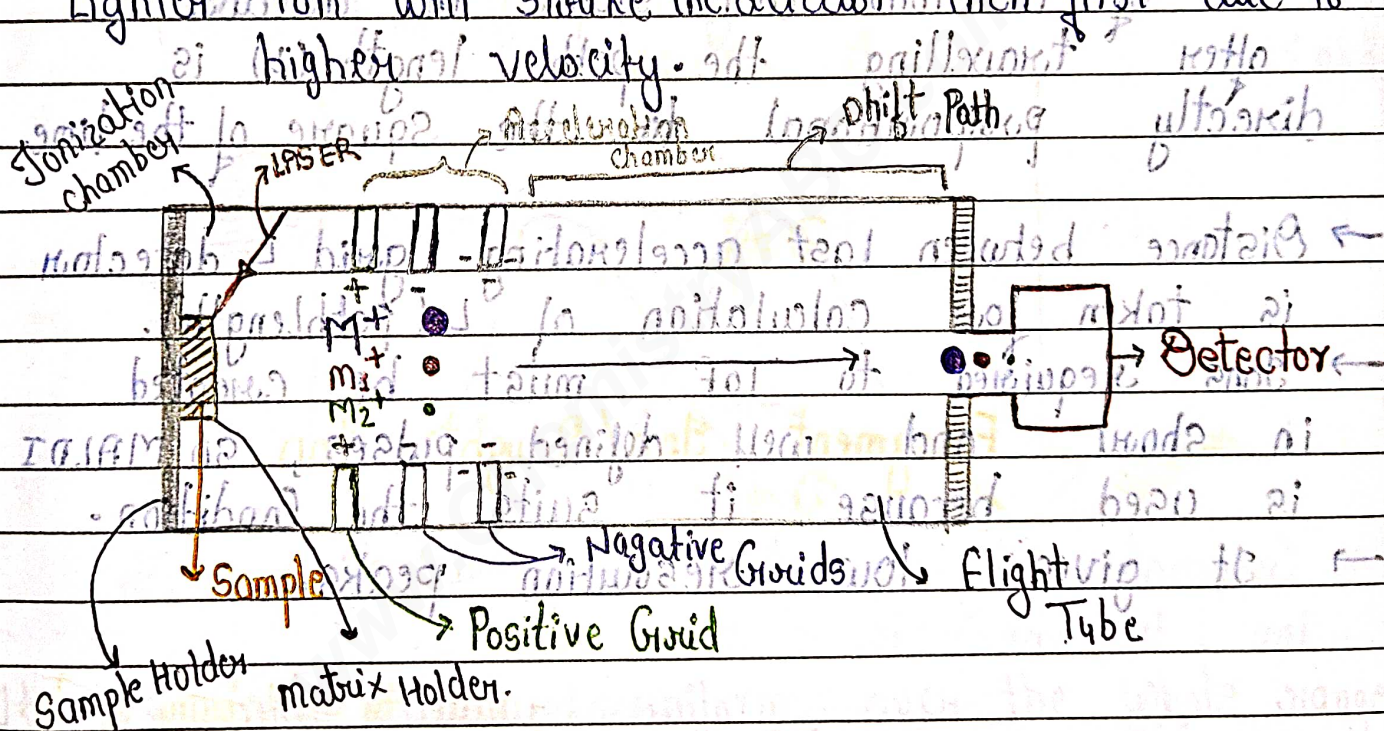
Advantage :- It gives very fast result and it is cost effective.

Disadvantage :- This method is that gives low resolution of peaks.



## ★ Time of Flight mass Analyser (TOF) :-

- TOF is based on the simple idea that the velocities of two ions varies depending on the mass of the ions.
- Ions should have created at same instant and should have same kinetic energy.
- Lighter ion have the higher velocity as compared to the heavier ion.
- If ion are travelling towards the detector then lighter ion will strike the detector first due to higher velocity.



- Kinetic energy of an ion accelerated through an electrical potential will be

$$zV = \frac{1}{2}mv^2 \quad \text{--- (1)}$$

Velocity of the ion is the pathlength divided by time (t)

$$v = L/t \quad \text{--- (2)}$$

Put the value of v from equa. (2) To equa. (1)

$$zV = \frac{1}{2}m \frac{L^2}{t^2} \quad \text{--- (3)}$$



→ Rearrangement of equa. (3) of mass

$$m/z \cdot t = \sqrt{2V} \times t^2 \quad (4)$$

$$k = 2V \quad (5)$$

$$m/z = k t^2 \quad (6)$$

$$m/z \propto t^2 \quad (7)$$

→  $m/z$  of the ions that strike the detector after travelling the path length ( $L$ ) is directly proportional to the square of the time.

→ Distance between last accelerating grid & detector is taken for calculation of  $L$  (path length).

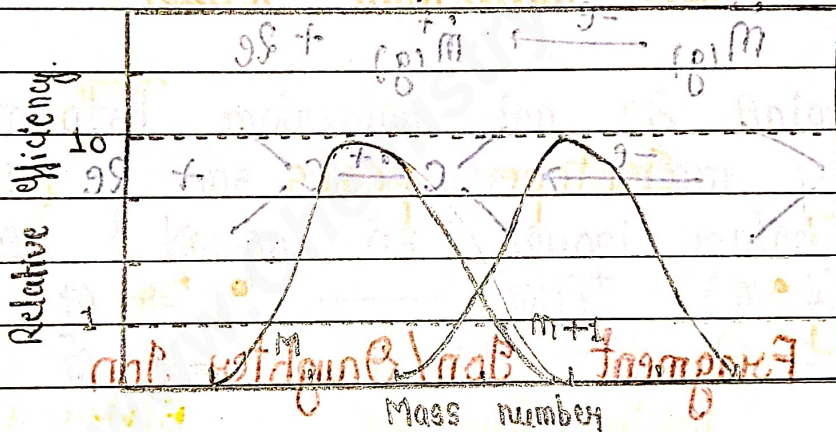
→ Ions required to TOF must be created in short and well defined pulses, so MALDI is used because it suits the condition.

→ It gives low resolution peaks.

← Kinetic energy of an ion accelerated through an electrical potential will be



\* ④ Resolution of Compounds :- The ability of an instrument to distinguish between two ions of equal mass is called the resolution of the instrument. A Spectrum consists of narrow peaks. Resolution is expressed as  $m/\Delta m$ . The resolution is a function of slit width, deflection radius and homogeneity of the ion source. Resolution of an instrument depends upon its applications and can be represented graphically.



Resolution of Spectra :- Resolution is not always uniform over the whole range of masses which can be detected.  $M$



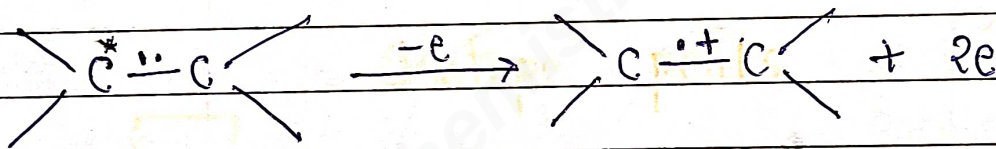
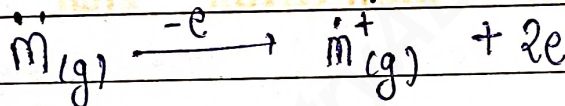
## \* Types of Ions and Peak in MS

### Molecular Ion or Parent Ion

Then electron bombardment with energy usually removes one electron from the molecule of the organic compound in the vapour phase. Its results in the formation of molecular ion.

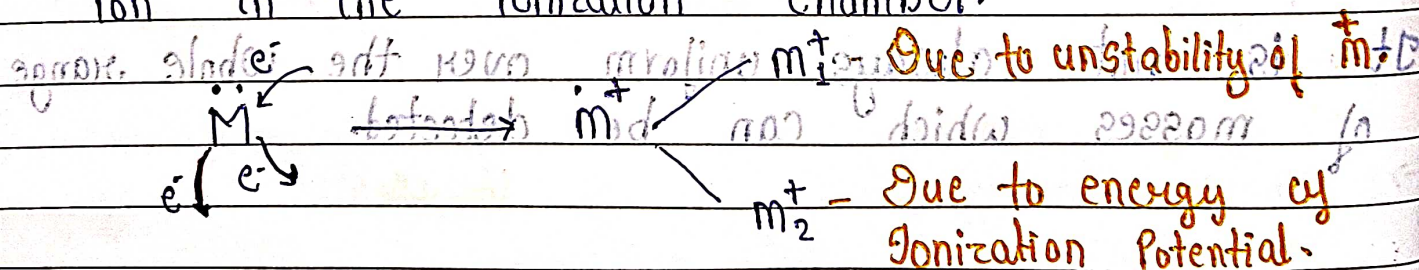
Single electron has lowest ionization potential from a molecule.

Exa:-



### Fragment Ion / Daughter Ion

→ Generated by the fragmentation of molecular ion in the ionization chamber.





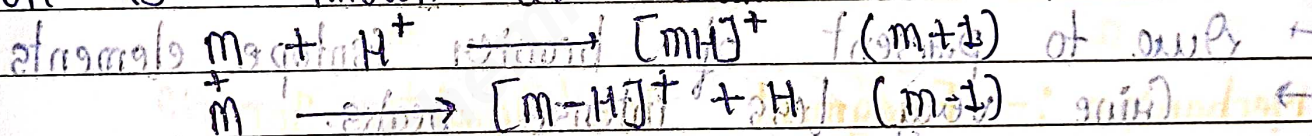
## Metastable Ions

Some fragmentation may occur during their flight down the ion tube field free region instead of ionization chamber and known as metastable ions.

They reach to the detector at masses lower than the actual mass and gives broader peaks.

## Quasi molecular Ion

A protonated molecular ion OR Anion formed by removal of one hydrogen atom from molecular ion is known as Quasi molecular ion.



## Multiple charged Ions

- Some double / triple charged ions are observed
- Mainly occurs in ESI Spectrum.
- Different m/e ratio.

$$M = 100 \text{ (mol. wt.)}$$

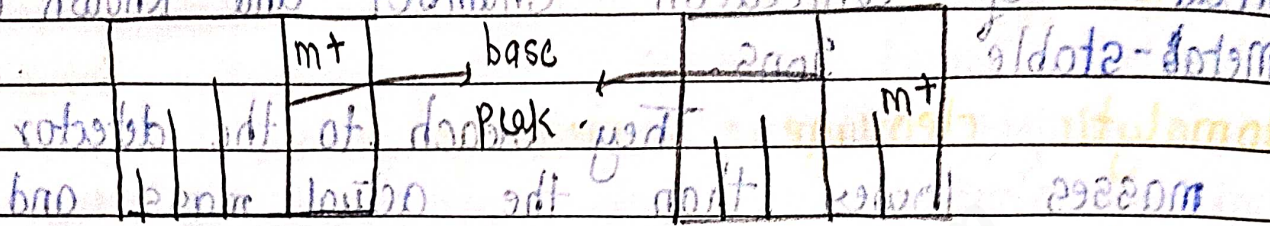
$$\frac{m}{e} = \frac{100}{1} = 100$$

$$\frac{m}{e} = \frac{100}{2} = 50$$



## Base Peak

The most intense/tallest peak in the mass spectrum is due to the greatest relative abundance.



→ always molecular ion will not be base peak and always base peak will not be molecular ion.

## Isotope peaks

→ Due to presence of heavier isotopes elements give very less intense peaks.

	Relative abundance.		Relative abundance.
$^1_1\text{H}$	→ 99.985%	$^{12}_6\text{C}$	→ 98.89%
$^2_1\text{H}$	→ 0.015%	$^{13}_6\text{C}$	→ 1.11%

$^{14}_7\text{N}$	→ 98.89%
$^{15}_7\text{N}$	→ 1.11%

$$\frac{100}{100} = 100\%$$

$$\frac{100}{100} = 100\%$$



## ★ Fragmentation Pattern

simple cleavage

① Homolytic cleavage

② Heterolytic cleavage

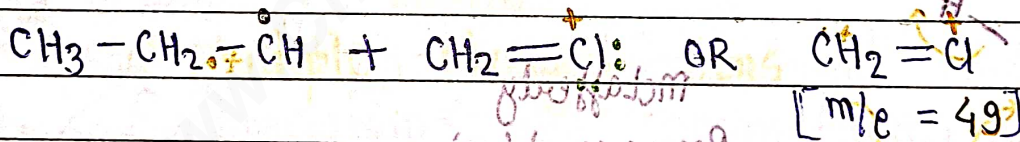
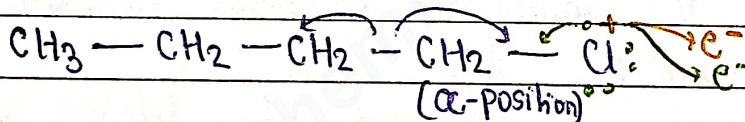
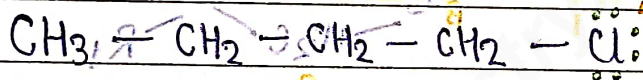
1) Homolytic cleavage ( $\alpha$ -cleavage) :-

→ It is initiated by the radical site.

→ odd electron ions have an unpaired electron which is having the tendency to create a new bond.

→ If any new bond is formed then energy will be released and that energy will be used for cleavage of other bond.

Exa:-

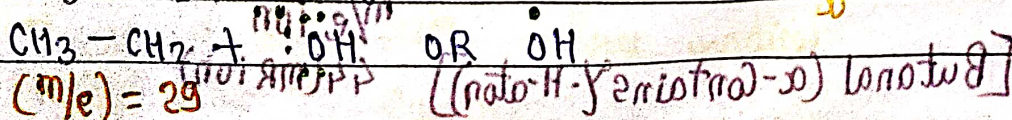
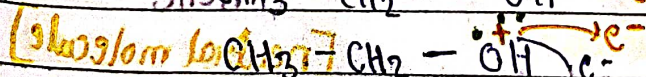
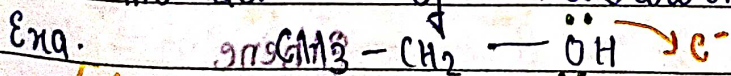


2) Heterolytic cleavage :-

→ cleavage of C-X bond takes place which is more difficult than C-C bond.

→ Here X = Heteroatoms like N, O, S, Cl, etc.

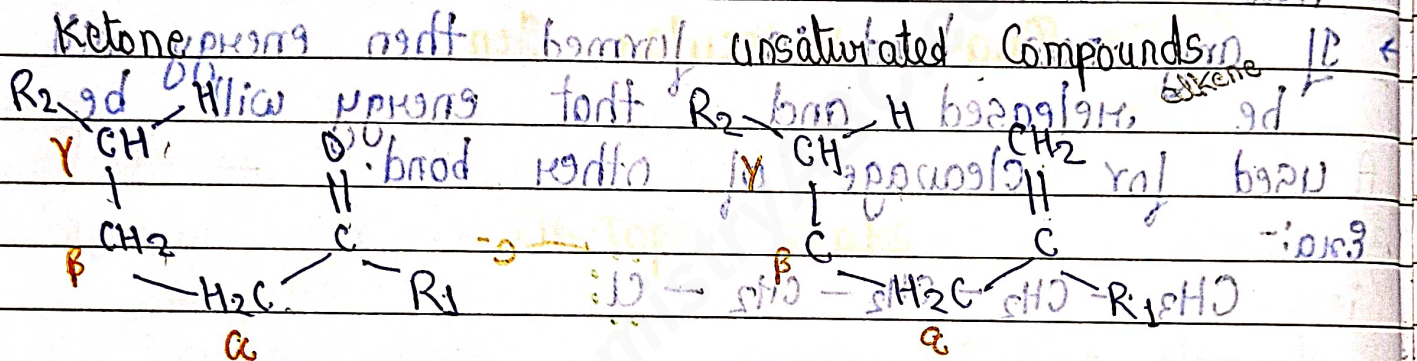
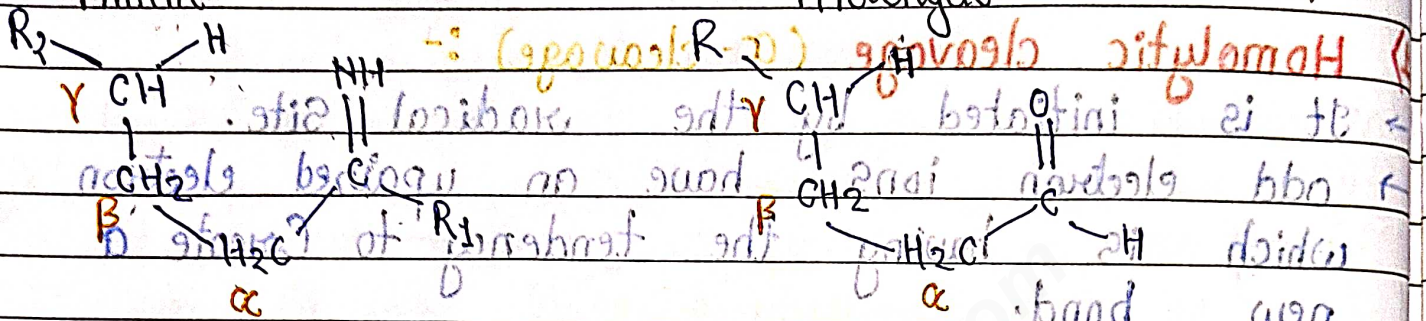
→ Positive charge is carried by Carbon atoms instead of Heteroatom.



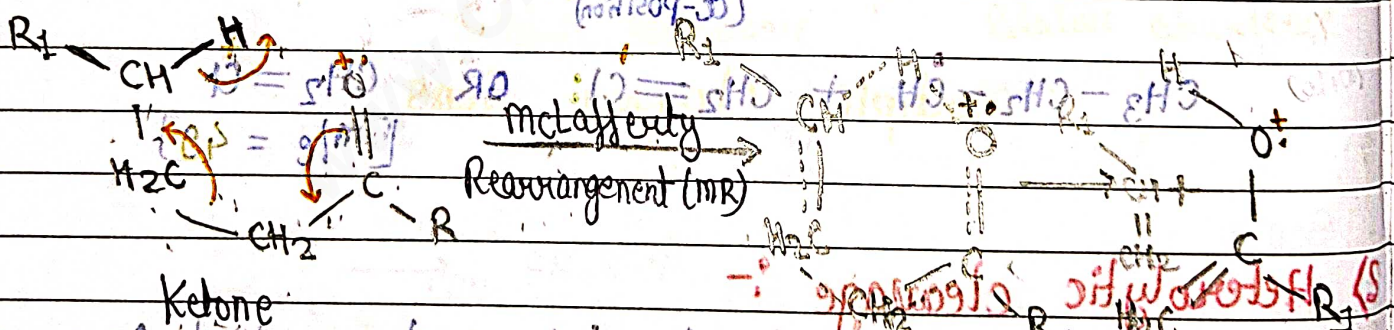


# ★ McLafferty Rearrangement

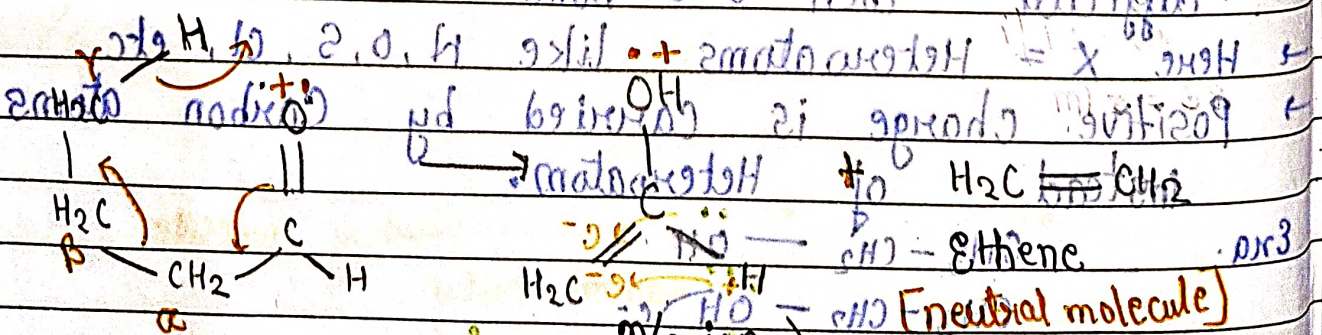
→ It involves cleavage of  $\alpha$ - $\beta$  bond followed by transfer of gamma ( $\gamma$ ) hydrogen atom.  
 → This McLafferty Rearrangement leads to the elimination of neutral atom like  
 Amine Aldehyde



Mechanism :-



Ketone

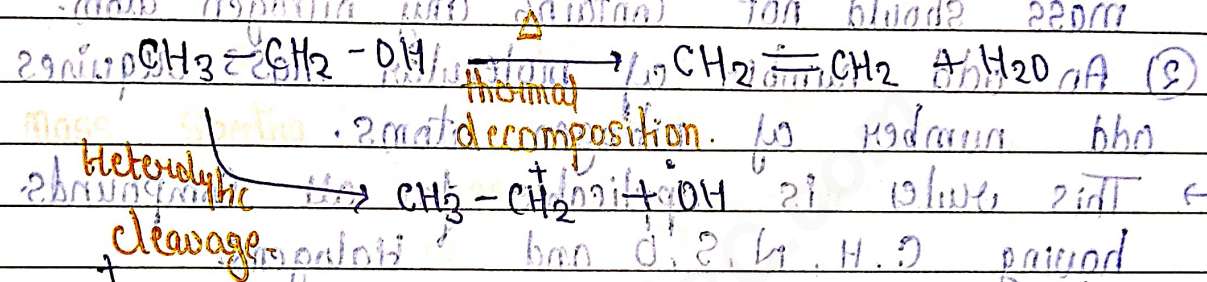


[Butanal ( $\alpha$ -Contains  $\gamma$ -H-atom)]



# \* Factors Affecting Fragmentation :-

① Thermal Decomposition :- Thermolabile Compounds may undergo thermal decomposition in the ion source before ionization. → Due to thermal decomposition fragmentation of the compound will be affected and problems will occur during interpretation of the mass spectra.

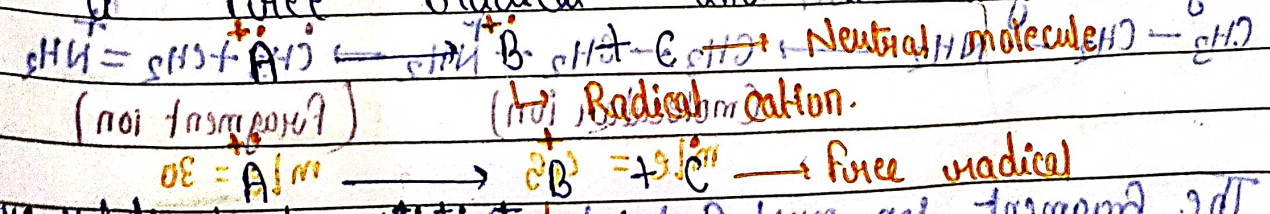


→ CH<sub>3</sub>-CH<sub>2</sub> will not appear as base peak due to thermal decomposition.

② Bombardment Energies :- More number of fragments will occur if bombardment energy will be high. → In case of the less bombardment energy less fragmentation will occur and gives more favoured fragment ions.

## ③ Relative Rates of Competing Fragmentation routes :-

→ As per even electron rule the radical cation will undergo fragmentation and will form a free radical and a cation.



Here relative abundance of A, B & C depends upon the relative rates of competing reactions.



"The nitrogen rule is not a rule, per se, as much as a general principle which may prove useful when attempting to solve organic mass spectrometry structures."

## ★ The Nitrogen Rule

→ Nitrogen rule is useful for identification of molecular ion because many signals/peaks can be ruled out on the basis of structural requirements.

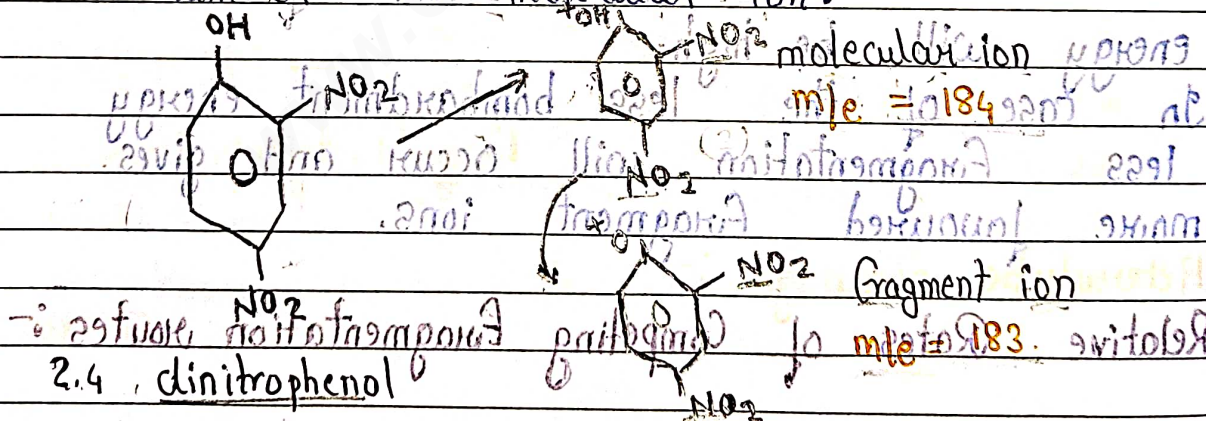
① Nitrogen Rule states that if a molecule of even number of molecular mass should not contain any nitrogen atom.

② An odd number of molecular mass requires odd number of nitrogen atoms.

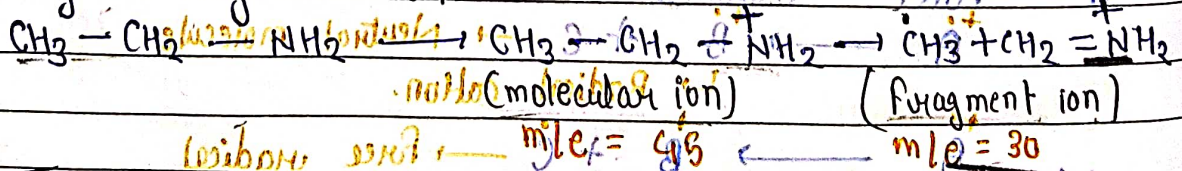
→ This rule is applicable for all compounds having C, H, N, S, O and Halogens.

Important Conclusion of these statements:-

① Fragmentation at a single bond gives an odd numbered fragment ion and an even numbered molecular ion.



② Odd number of molecular ion will give the even no. of fragment ion and vice versa.

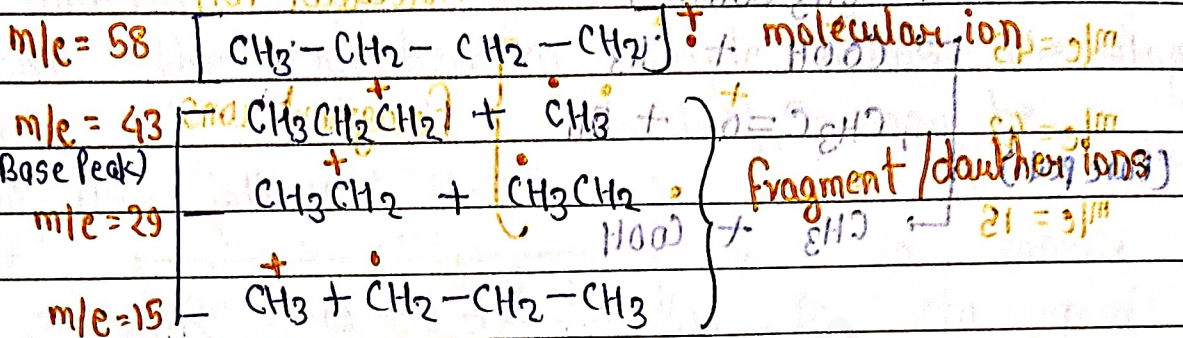
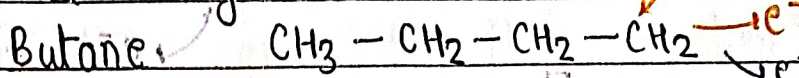


→ The fragment ion must contain all nitrogen atoms present in the molecular ion. This rule is applicable.

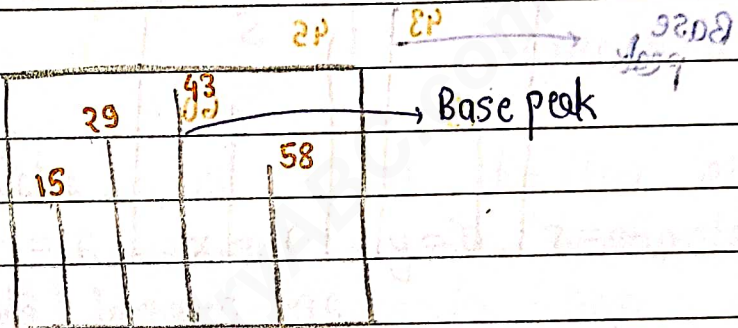


# \* Fragmentation and Interpretation

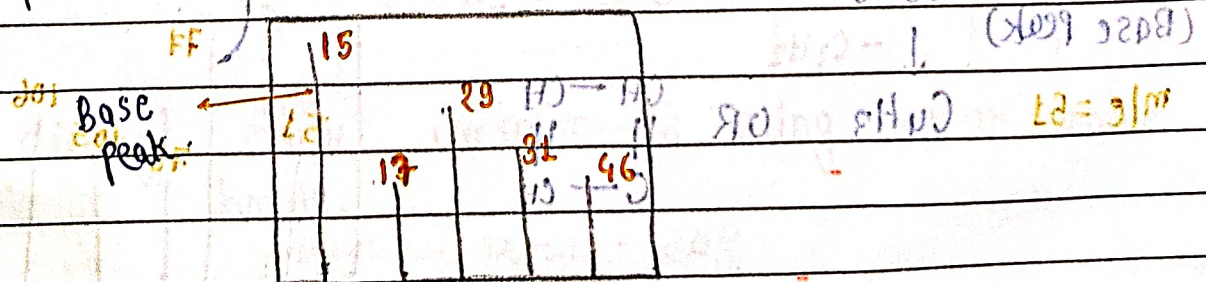
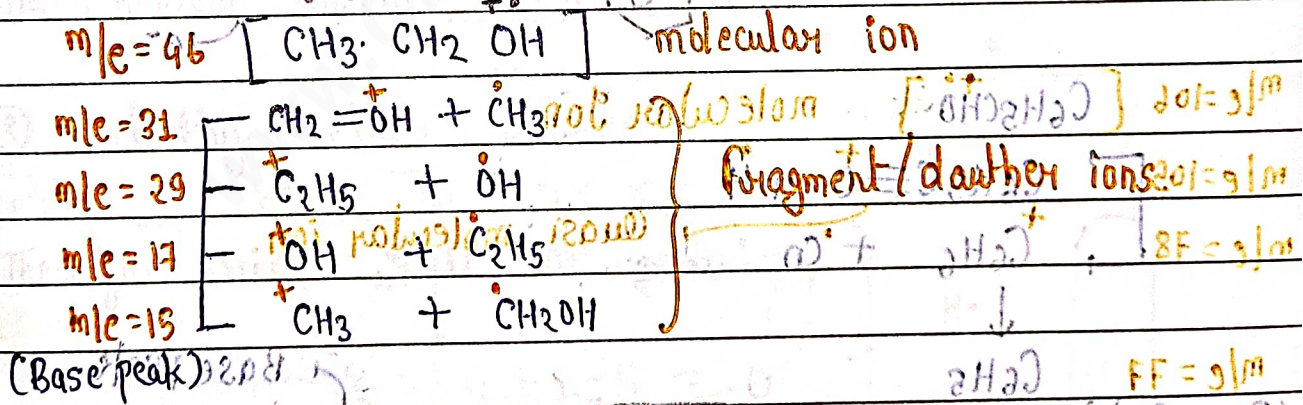
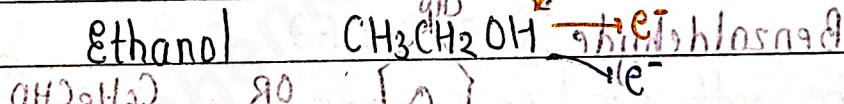
① Saturated Hydrocarbon :- Butane



Mass Spectra :-

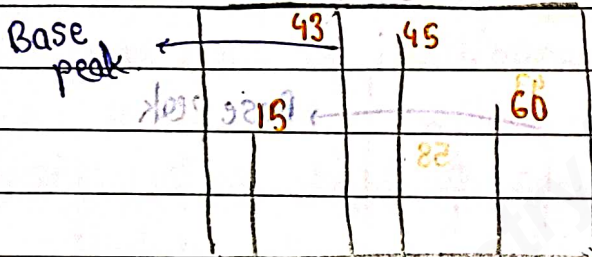
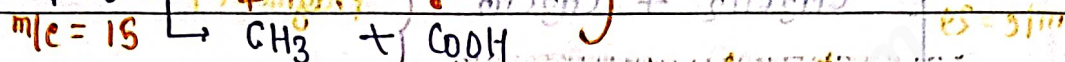
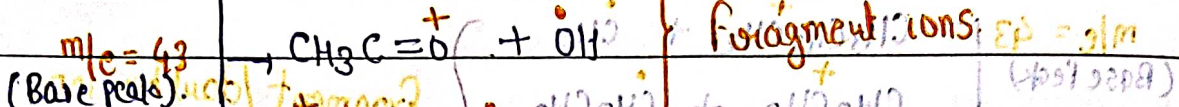
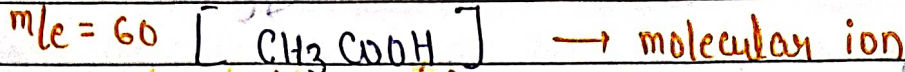
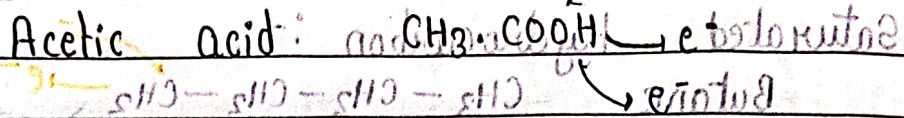


② Alcohol :- Ethanol

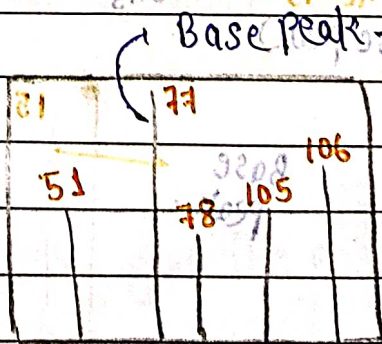
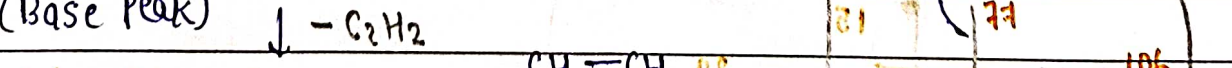
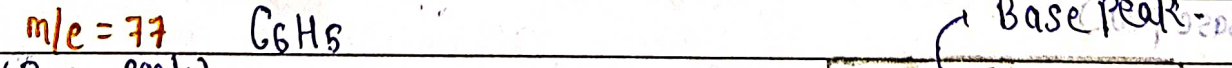
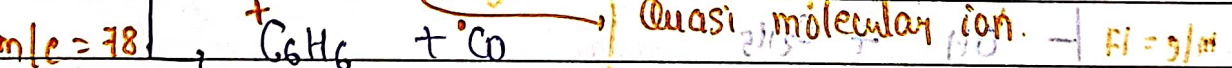
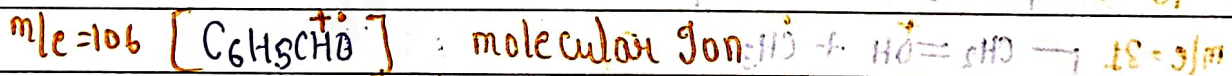
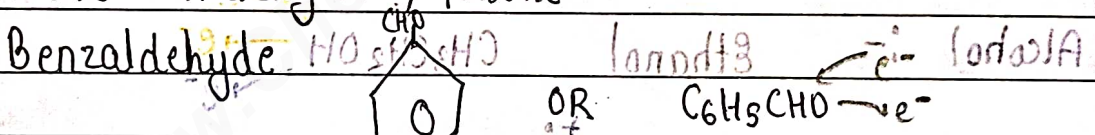




③ Carboxylic Acid :-



④ Aromatic Aldehyde / Ketone :-





## ★ RING RULE

According to Ring rule, the number of unsaturated sites,  $R$ , is equal to the number of rings in the molecule plus the number of double bonds plus twice the number of multiple bonds. The ring rule for the molecule  $C_wH_xNyO_z$  may be stated as follows:

$$R = w + 1 + \frac{y - x}{2}$$

Exa ① Benzene  $C_6H_6$

Here  $w = 6$ ,  $x = 6$ ,  $y = 0$ ,  $z = 0$

Therefore Ring rule becomes

$$R = 6 + 1 - 3 = 4$$

Thus benzene contains one ring and three double bonds.

Exa. ② diethyl ether  $C_2H_5OC_2H_5$

Here  $w = 4$ ,  $x = 10$ ,  $y = 0$

Therefore ring rule as follows:-

$$R = 4 + 1 - 5 = 0$$

Thus diethyl ether contains no ring and no double bonds.



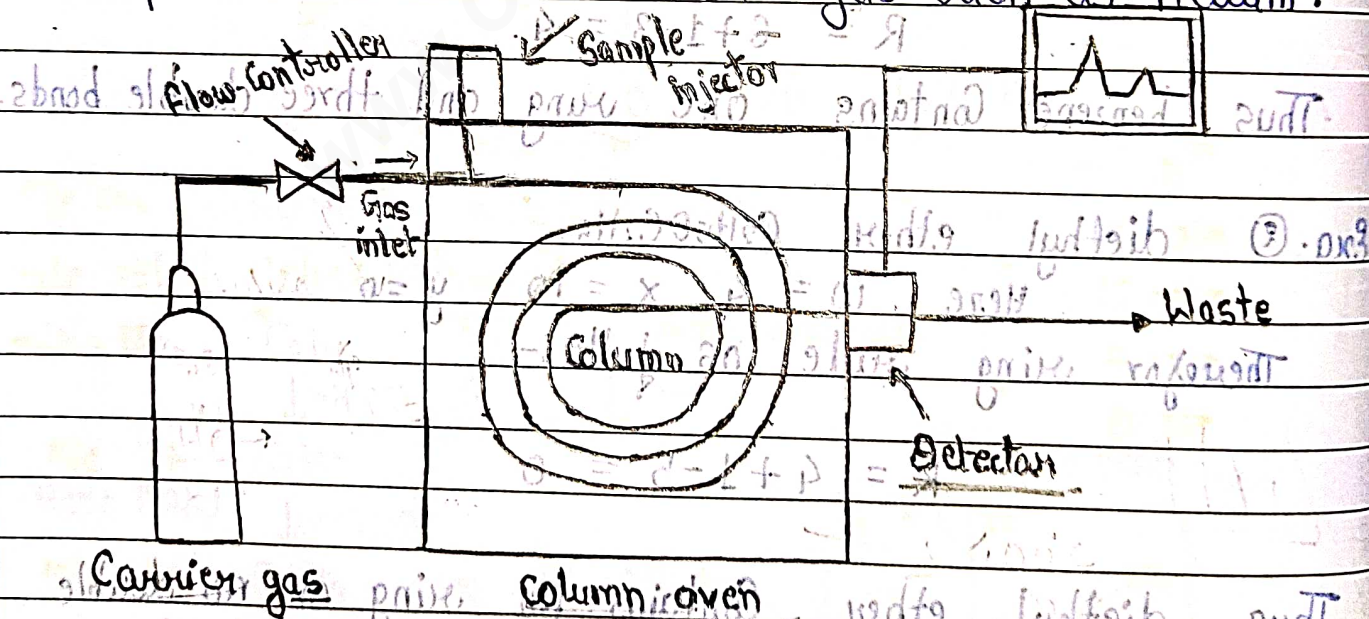
## ★ 1. GAS CHROMATOGRAPHY - MASS SPECTROMETRY

→ mass spectrometry, because of its high sensitivity and fast scan speed, is the technique most suited to provide definite structural information from the small quantities of material eluted from a gas chromatograph.

→ The association of GC-MS provides a powerful means of structure identification for the components of natural and synthetic mixtures.

→ This method is a known as a 'golden standard' for analysis.

→ In gas chromatography (GC), the mobile phase is an inert gas such as helium.





## MASS TO ANALYSIS \* ELECTROMETRY

- The sample enters a vacuum chamber through an inlet and is converted into gas phase ions.
- The ions are sorted according to their mass to charge ratios, usually with a quadrupole or ion trap.
- This data is converted into representative electrical signals and finally, a mass spectrum is created.

Advantage :- A great advantage to this method is that a researcher can take an organic solution, inject it into the instrument, separate the individual components and identify each of them.

Limitations :- if the GC instrument does not separate the samples compounds completely or correctly the MS feed is impure.

- ② AMS (Accelerator mass Spectrometry)
- ③ Liquid Chromatography
- ④ IRMS (Isotope Ratio Mass Spectrometry)
- ⑤ MALDI-ToF [Matrix Assistance Laser Desorption Ionisation]
- ⑥ SEDI-ToF [Surface Enhanced Laser Desorption Ionization]