

# Mass Spectrometry



Sandeep P. Netalkar

# Mass Spectrometry

## Contents

- ▶ Brief History of Mass Spectrometry
- ▶ Nobel prize pioneers
- ▶ Mass spectrometer: Instrumentation
- ▶ Structural analysis and Fragmentation Patterns
- ▶ Interpretation of mass spectrum
- ▶ Applications of mass spectrometry

# Mass Spectrometry

## Brief History of Mass Spectrometry

1897

J.J. Thomson. Discovered electrons by cathode rays experiment. Nobel prize in 1906.

1919

Francis Aston designed 1<sup>st</sup> mass spectrometer and measure  $z/m$  of ionic compounds.

1934

First double focusing magnetic analyzer was invented by Johnson and Neil.

1966

Munson and Field described chemical ionization.

1968

Electrospray Ionization was invented by Dole, Mack and others.

1975

Atmospheric Pressure Chemical Ionization (APCI) was developed by Carroll and others

# Mass Spectrometry

## Nobel prize pioneers



**Joseph John Thomson**

1906 Nobel Prize  
for Physics

*(theoretical and  
experimental  
investigations on the  
conduction of  
electricity by  
gases)*



**Francis William Aston**

1922 Nobel Prize for  
Chemistry

*(mass spectrograph,  
of isotopes, in a  
large number of non-  
radioactive  
elements)*



**Wolfgang Paul**

1989 Nobel Prize for  
Physics

*(for the development  
of the ion trap  
technique)*



**John Bennet Fenn**

2002 Nobel Prize  
for Chemistry

*(for the  
development of  
Soft Desorption  
ionization Method)*



**Koichi Tanaka**

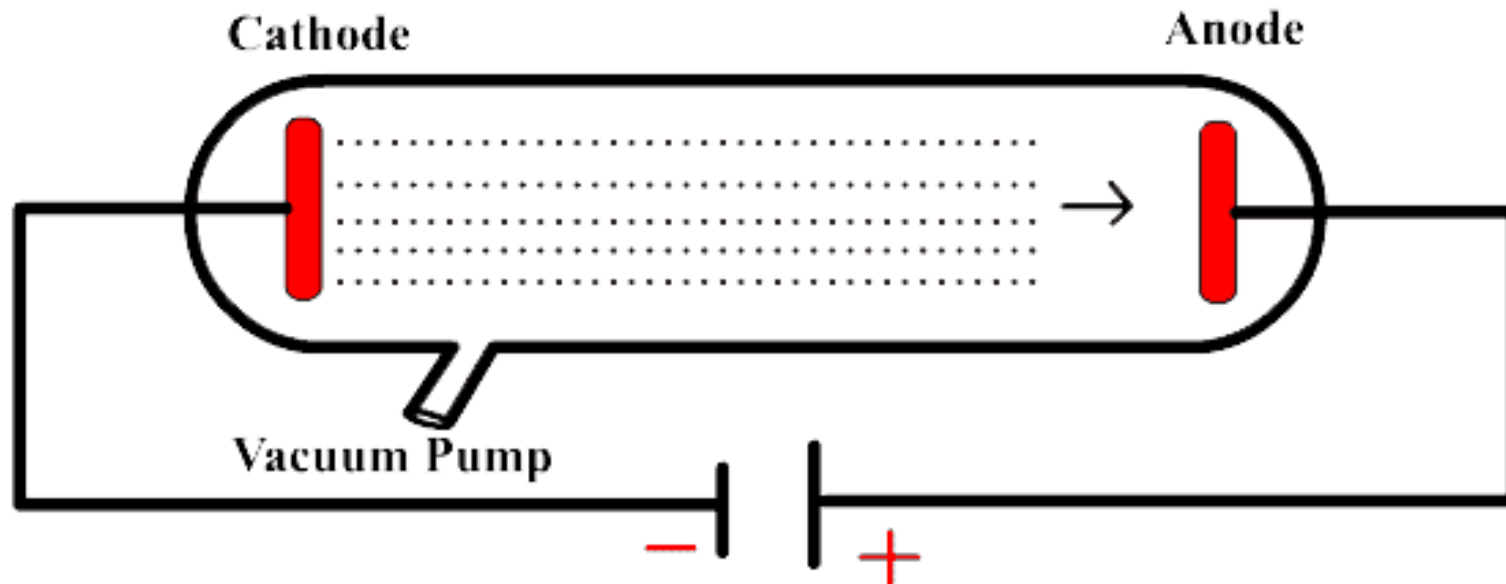
2002 Nobel Prize for  
Chemistry

*(mass spectrometric  
analyses of  
biological  
macromolecules)*

# Mass Spectrometry

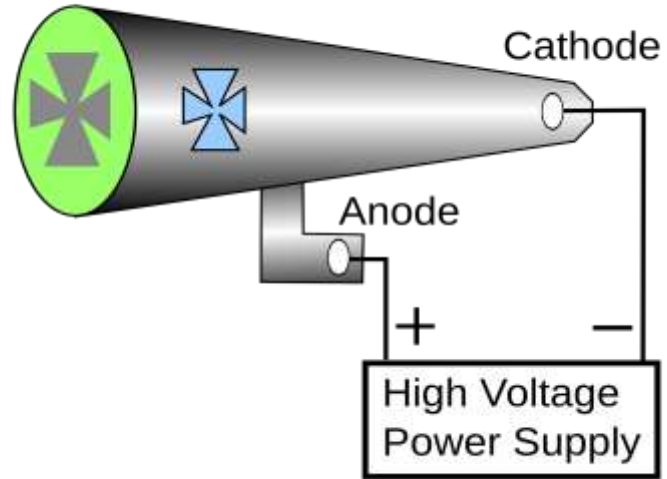
## Cathode rays

Discharge tube is also called "CROOCK TUBE". It is made of a glass tube which consists of two metallic plates. One plate is connected to positive terminal of high voltage power supply and the other to negative terminal. The plate connected to the positive terminal is called "ANODE" the other connected to negative terminal is called "CATHODE". The tube is filled with any gas and is partially evacuated

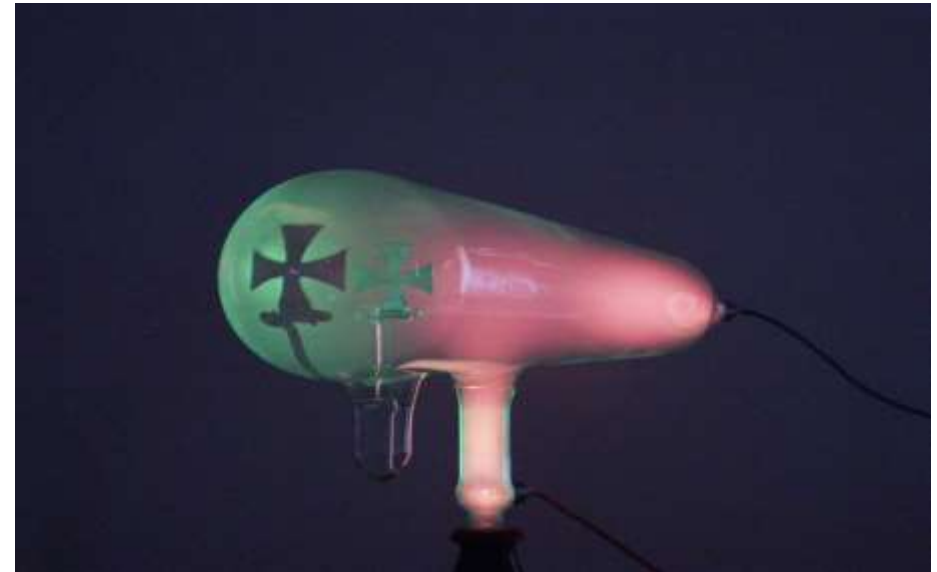


# Mass Spectrometry

## Cathode rays



Cathode ray tube. The cathode (negative terminal) is on the right. The anode (positive terminal) is in the base of the tube at bottom.



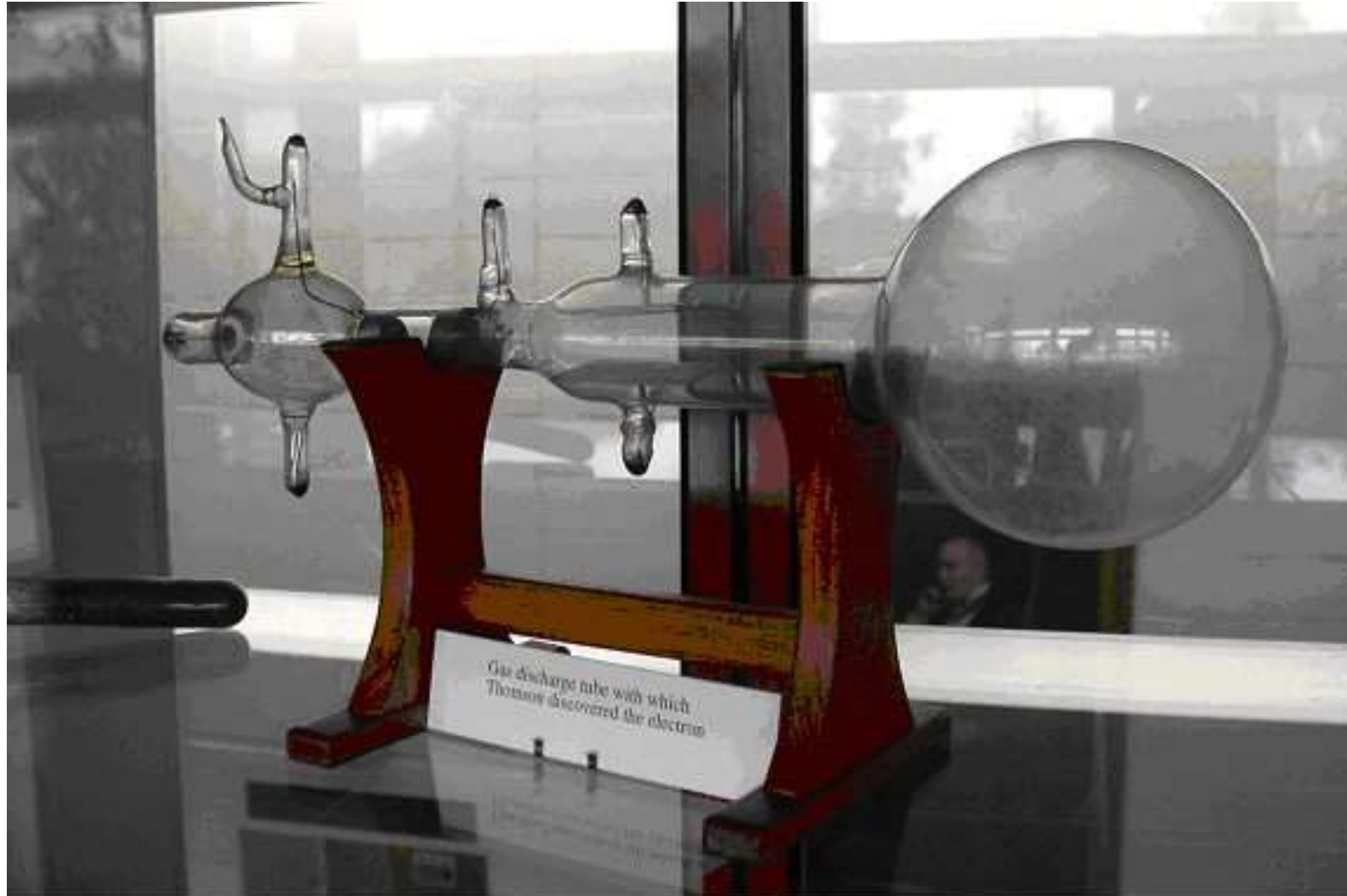
Cathode rays travel from the cathode at the rear of the tube, striking the glass front, making it glow green by [fluorescence](#). A metal cross in the tube casts a shadow, demonstrating that the rays travel in straight lines.



# Mass Spectrometry



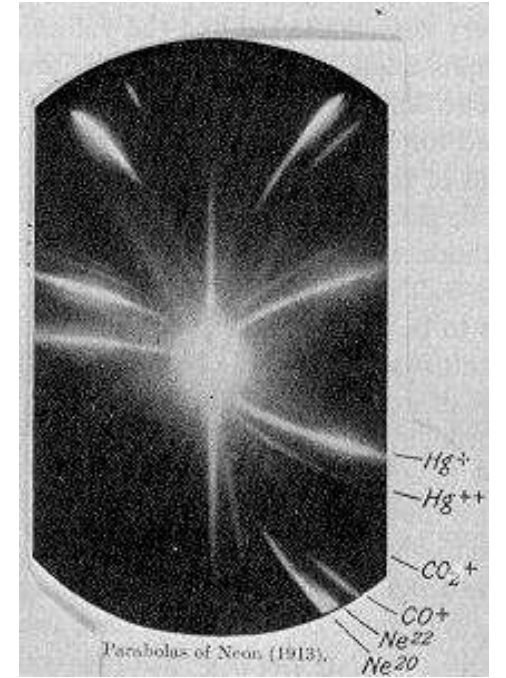
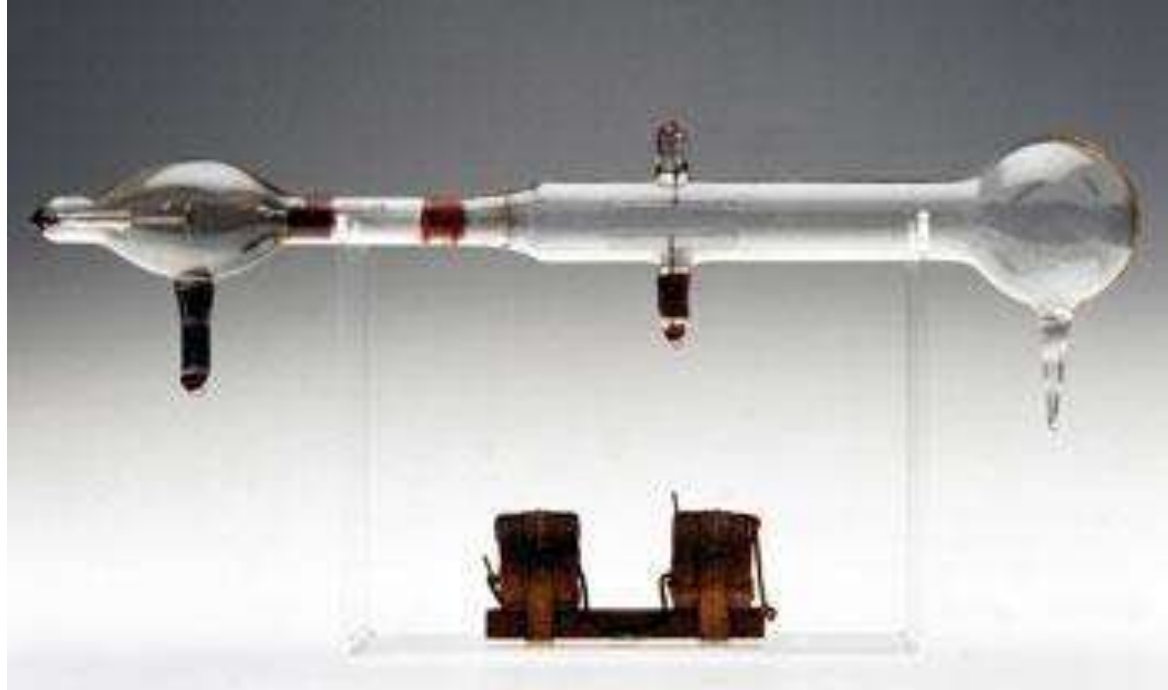
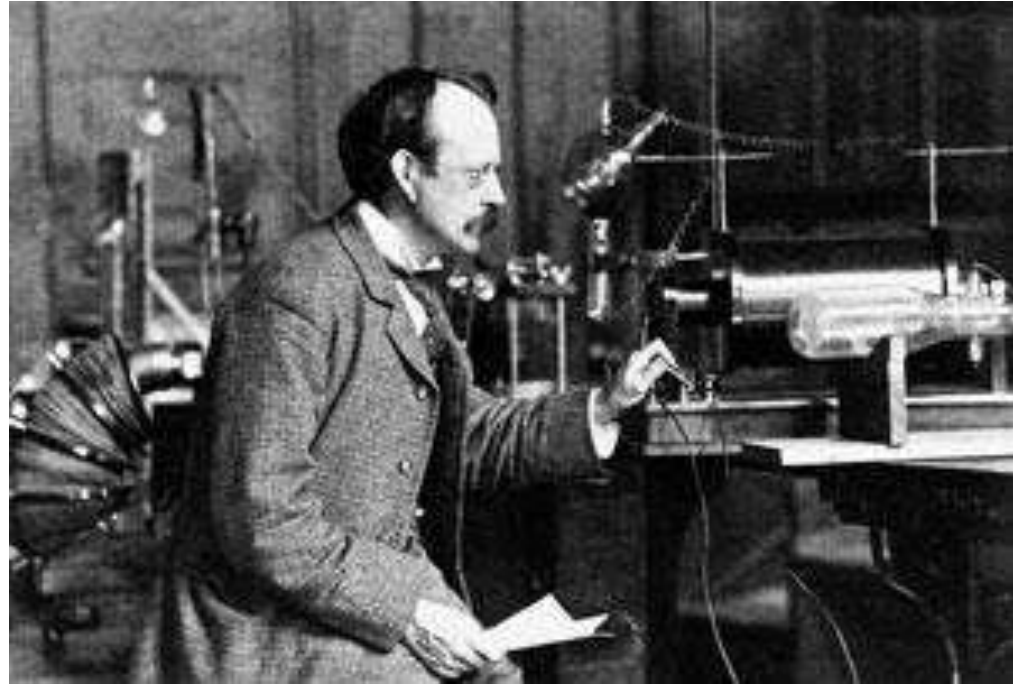
# Mass Spectrometry



Gas discharge tube with which J.J. Thomson discovered electron

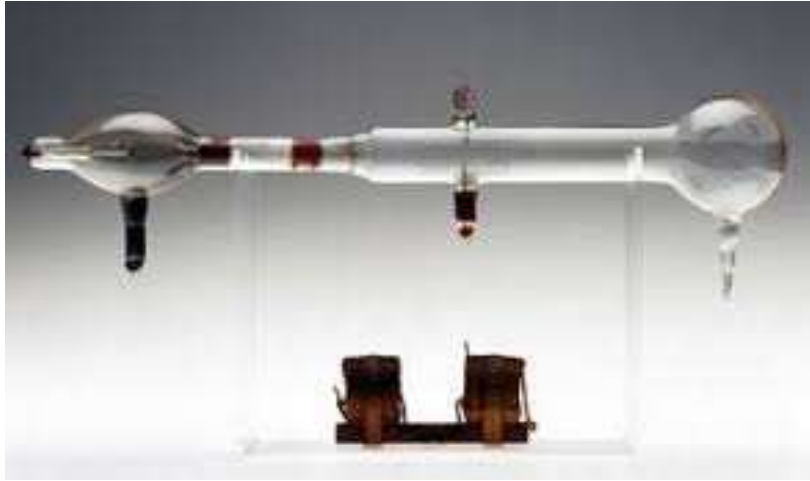


# Mass Spectrometry



# Mass Spectrometry

## Mass Spectrometer in its early days



# Mass Spectrometry



F. W Aston's first Mass Spectrograph 1919

# Mass Spectrometry

## Historical Instruments

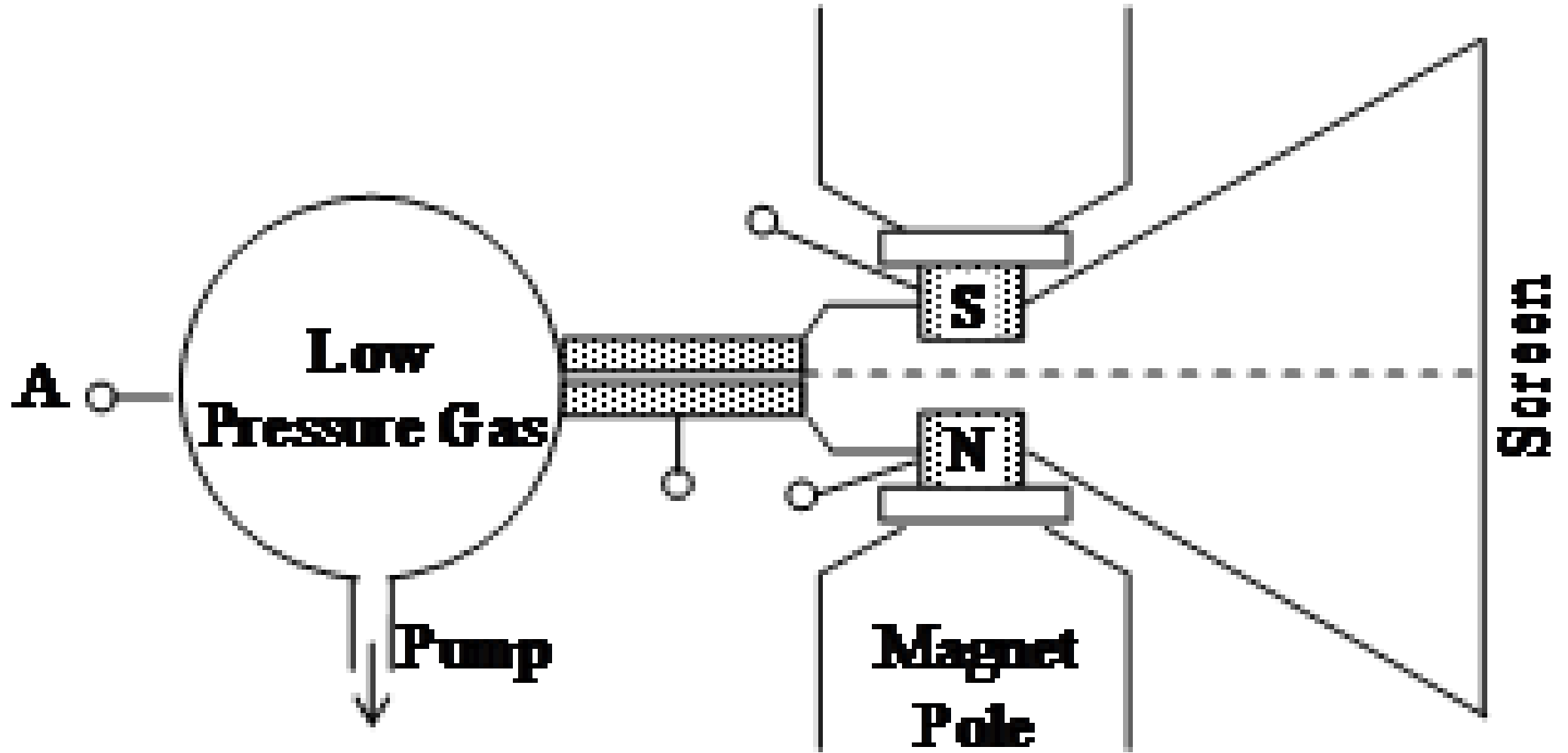
- Thomson's Parabola Mass Spectrograph
- F. W. Astons Mass Spectrograph
- A. J Dempster's Mass Spectrometer

## Thomson's Parabola Mass Spectrograph

A very significant investigation of Thomson were carried out using positive ray parabola instrument. The greatest interest in this instrument is of historical nature but certainly it is useful to learn the principal of operation of parabola mass spectrograph which was of great productivity in the hands of Thomson

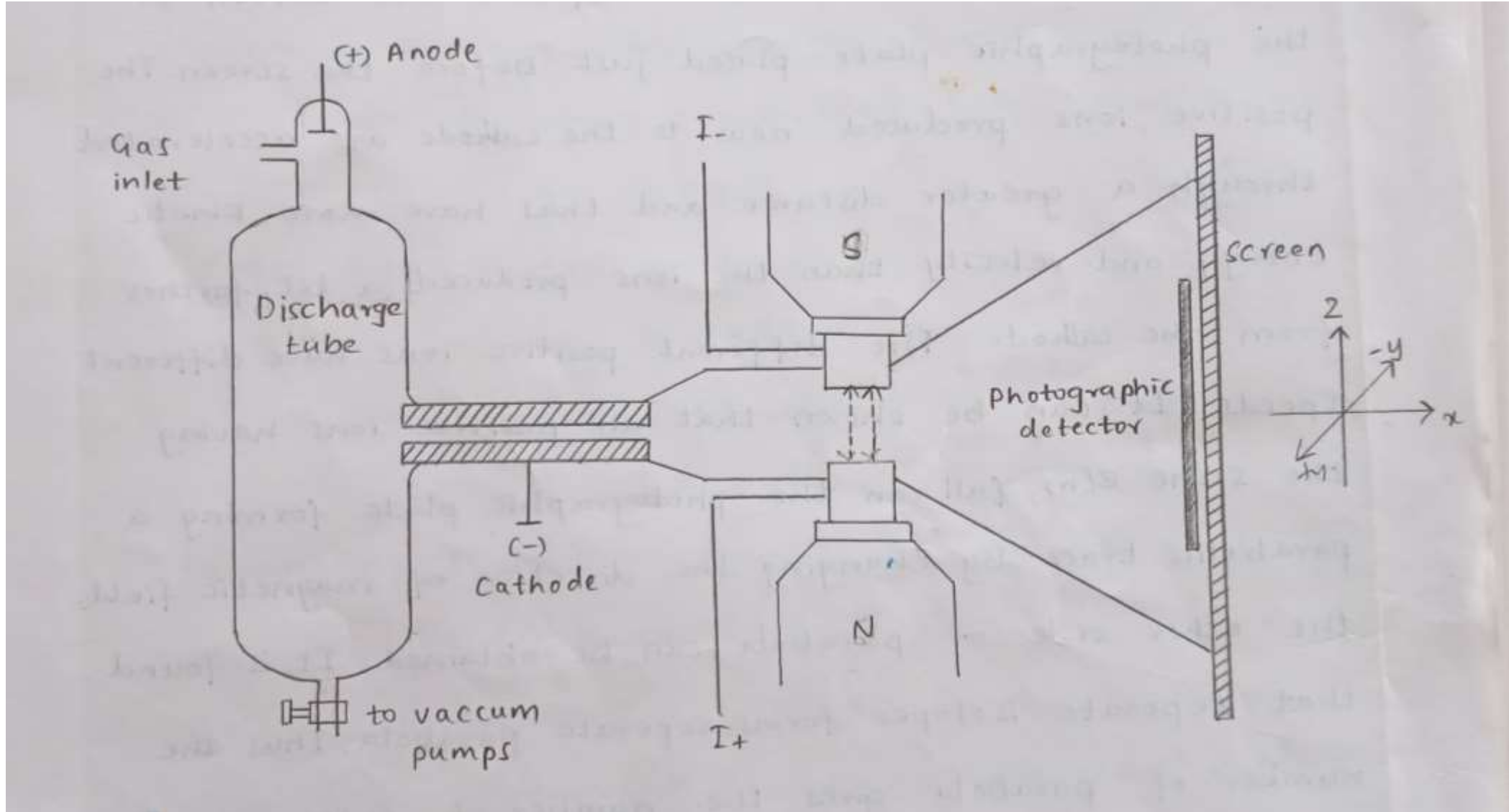
# Mass Spectrometry

Thomson's Parabola Mass Spectrograph



# Mass Spectrometry

## Schematic representation of Thomson's Parabola Mass spectrograph

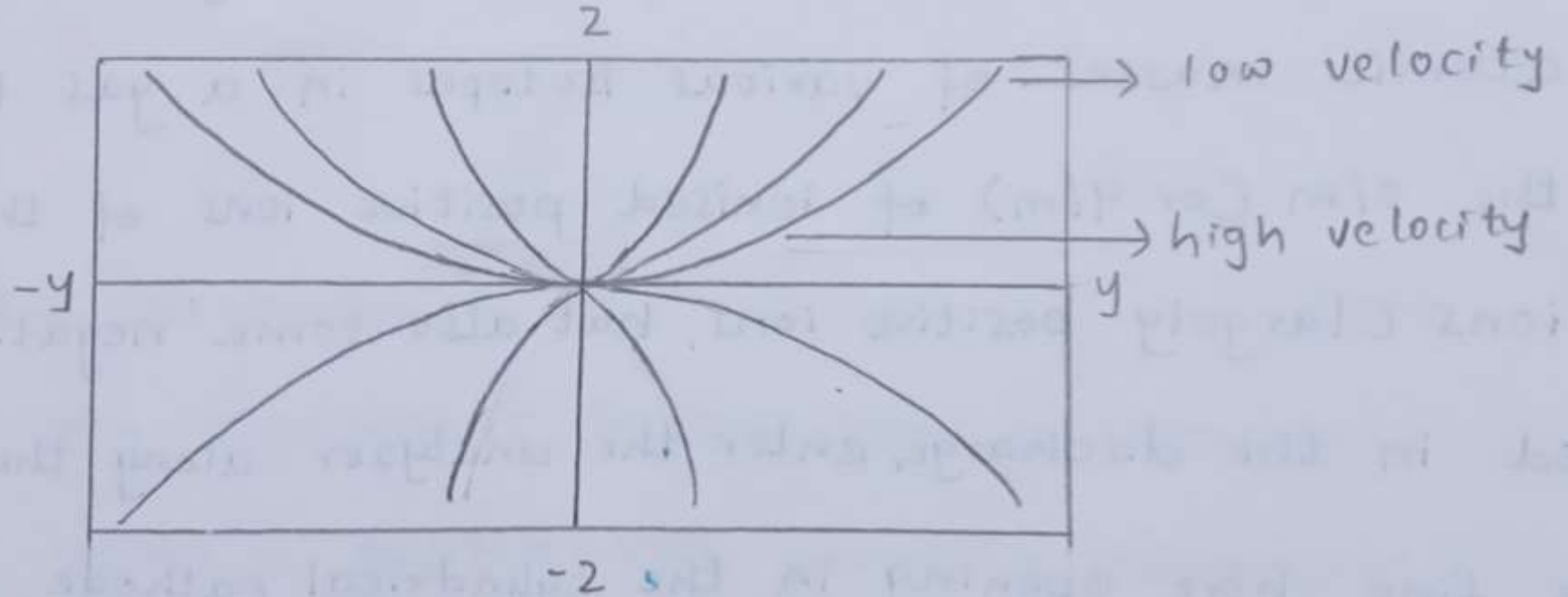




# Mass Spectrometry

## Photographic record of Thomson's Parabola Mass Spectrograph

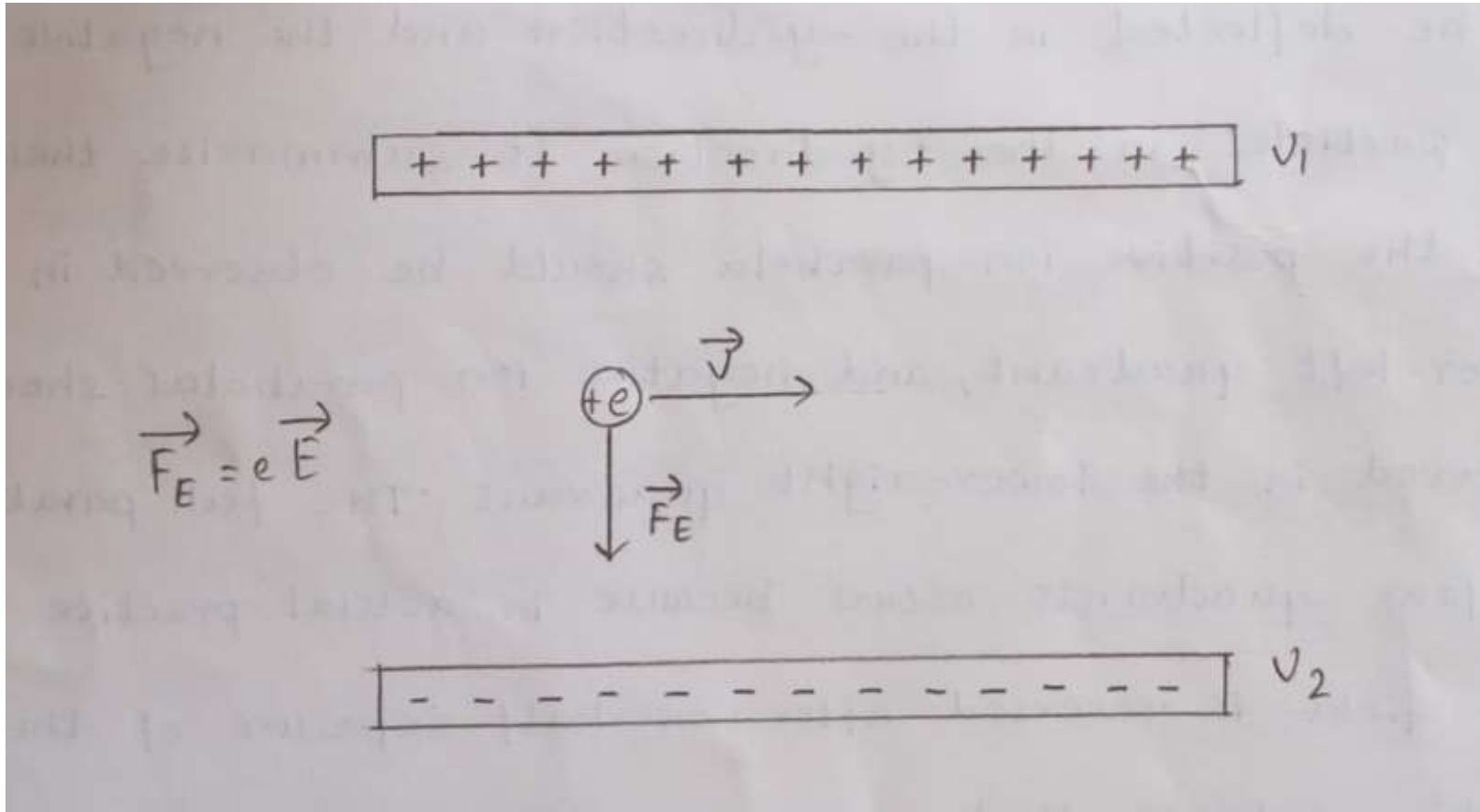
(Original record)



The photographic record of a parabola mass spectrograph (hypothetical)

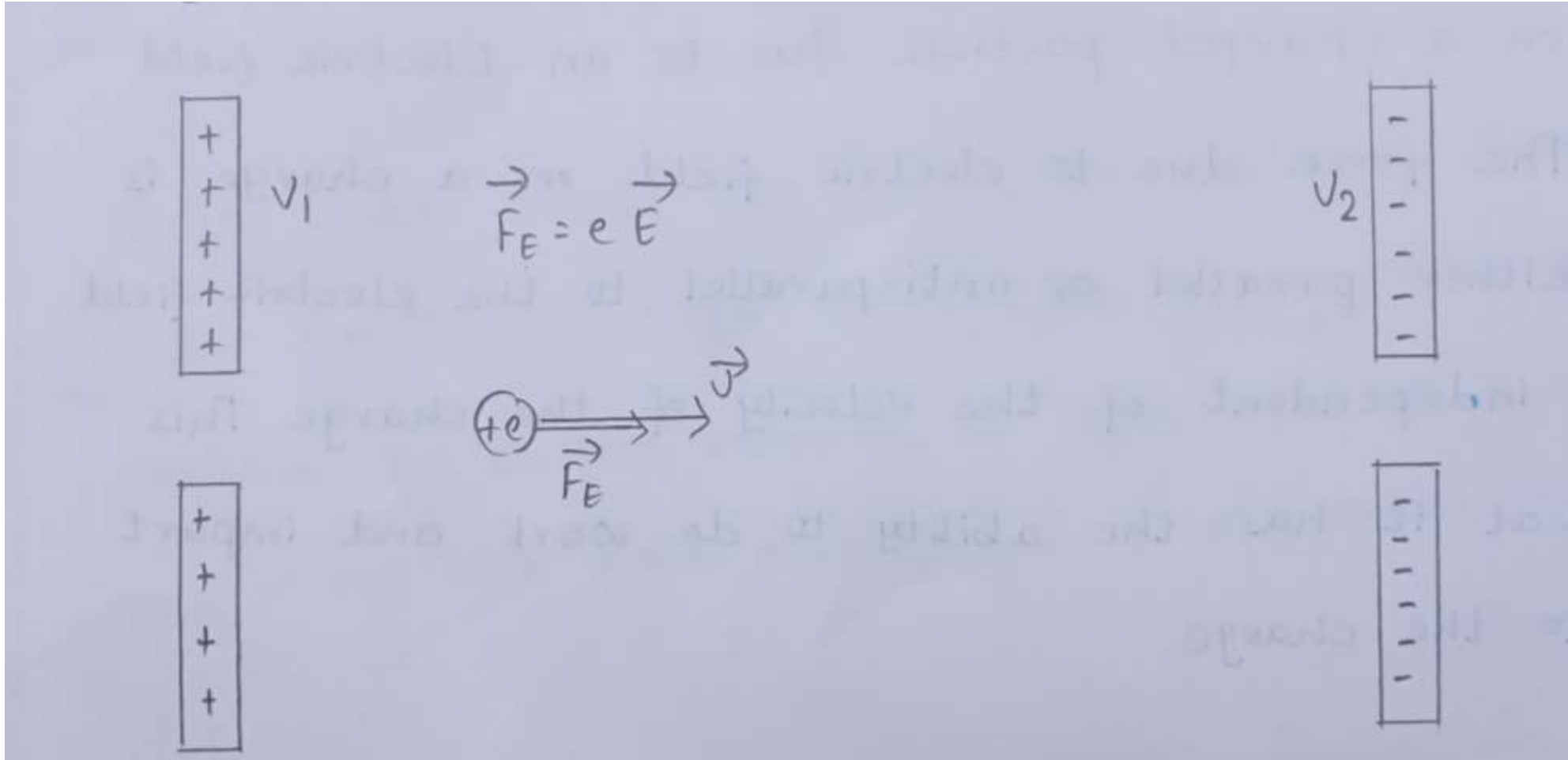
# Mass Spectrometry

## Force on a charged particle due to electric field



# Mass Spectrometry

## Force on a charged particle due to electric field



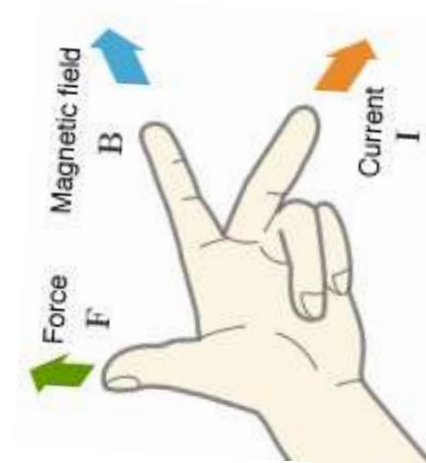
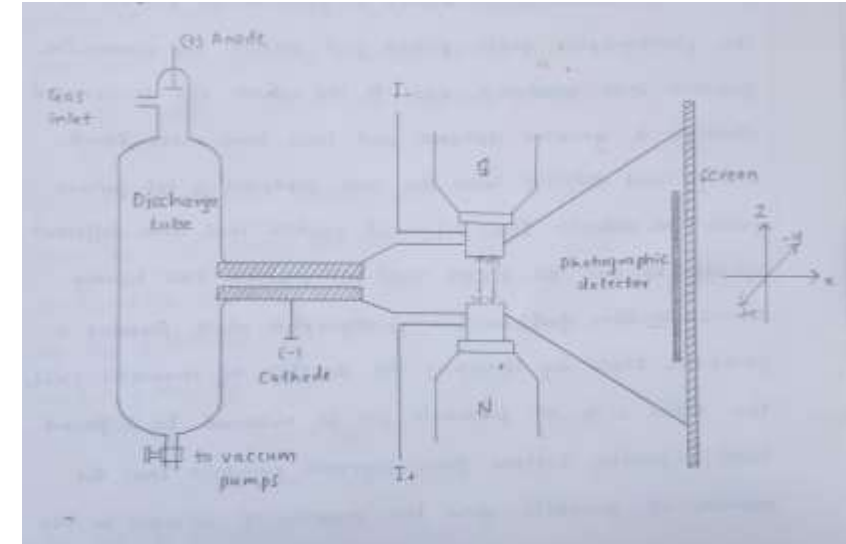
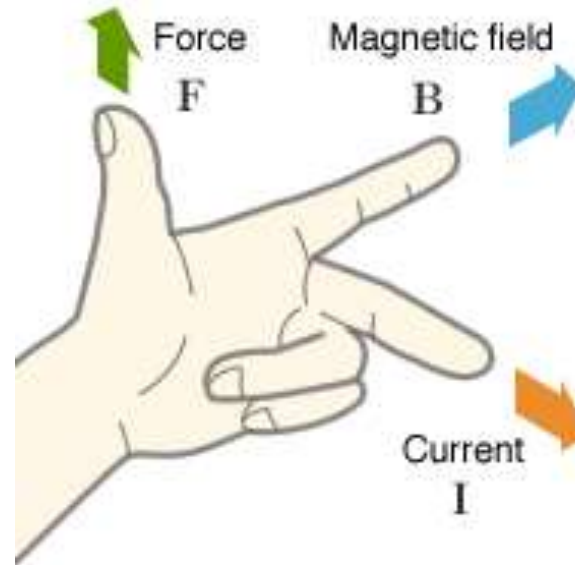
# Mass Spectrometry

## Force on a charged particle due to magnetic field

When a current-carrying conductor is placed in an external magnetic field, the conductor experiences a force perpendicular to both the field and to the direction of the current flow. A left hand can be held, as shown in the illustration, so as to represent three mutually orthogonal axes on the thumb, forefinger and middle finger.

The left-hand rule requires you to

“Hold out your left hand with the forefinger, second finger and thumb perpendicular to each other. If the forefinger represents the direction of the field and the second finger represents that of the current, then thumb gives the direction of the force.”



# Mass Spectrometry

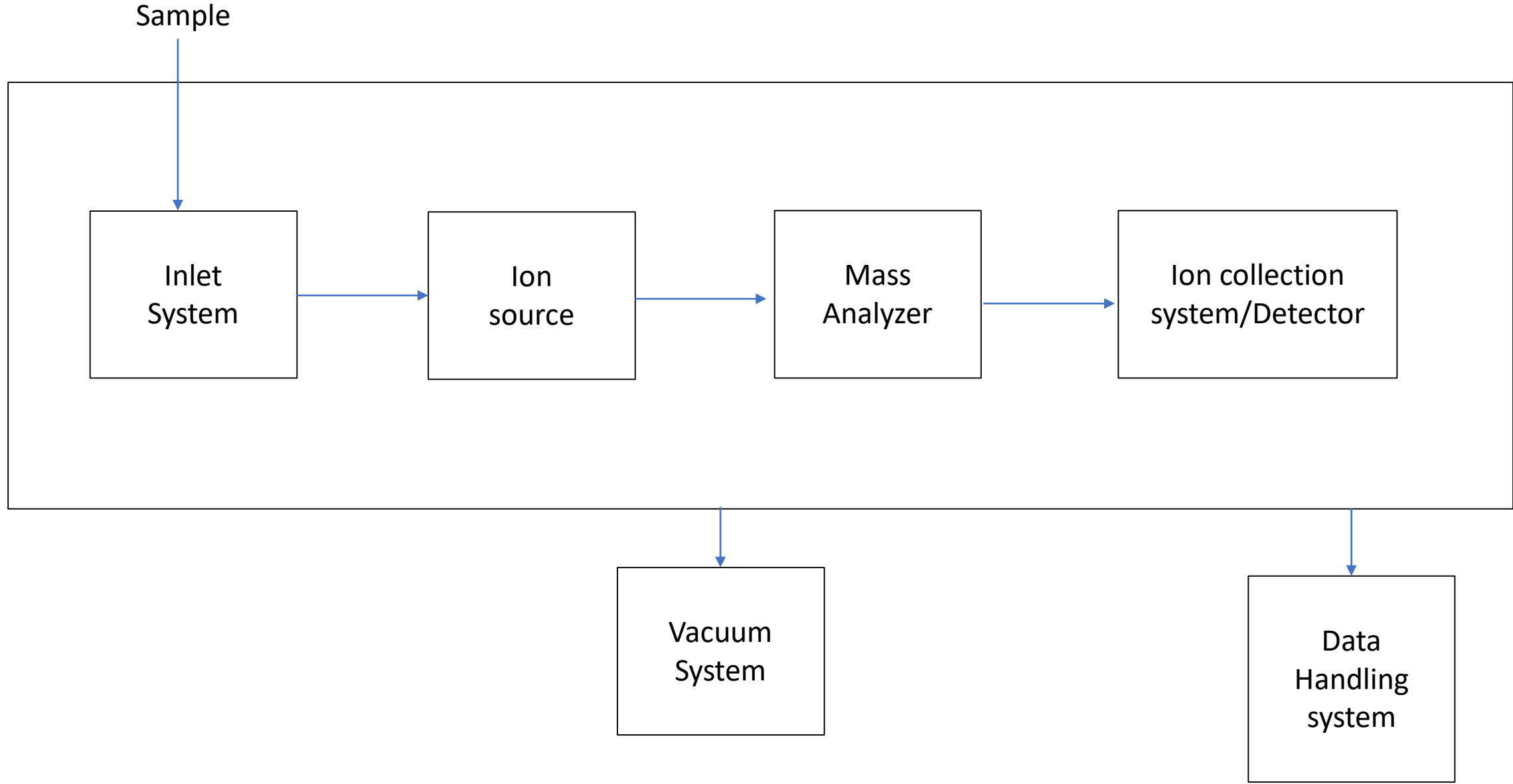
## Mass Spectrometry: Instrumentation and Theoretical Principle

There is no universal Mass Spectrometer. Certain design and configurations lend themselves to the solution of specific problems better than others. Functionally all Mass Spectrometers performs three basic task

- Creating gaseous ion fragments from the sample
- Sorting these ions according to their mass-to-charge ratio
- Measuring the relative abundance of fragment ions with different  $m/z$  values

# Mass Spectrometry

## Mass Spectrometer: Block Diagram





# Mass Spectrometry

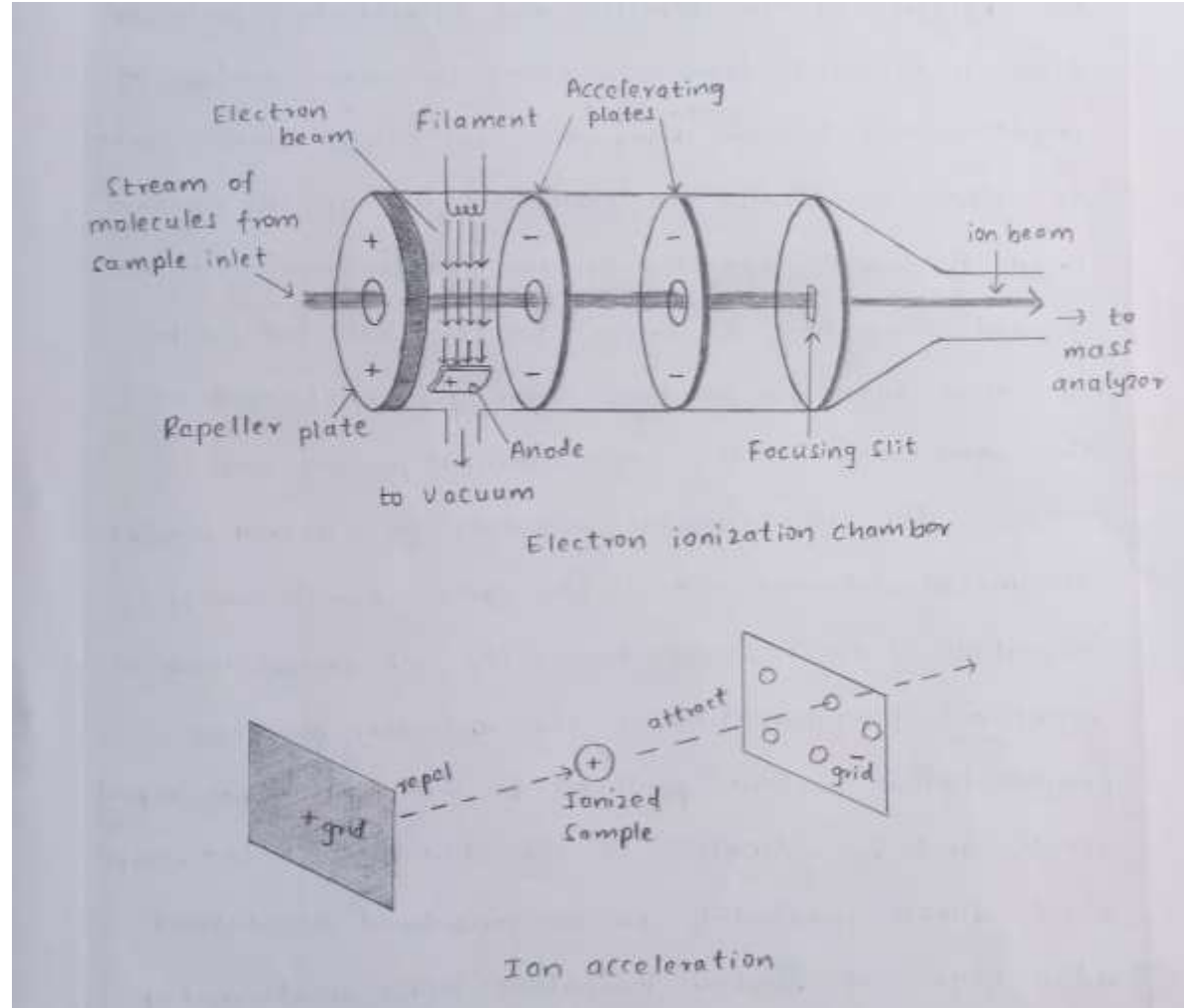
## Ion source

The methods available for ionization are summarized as follows

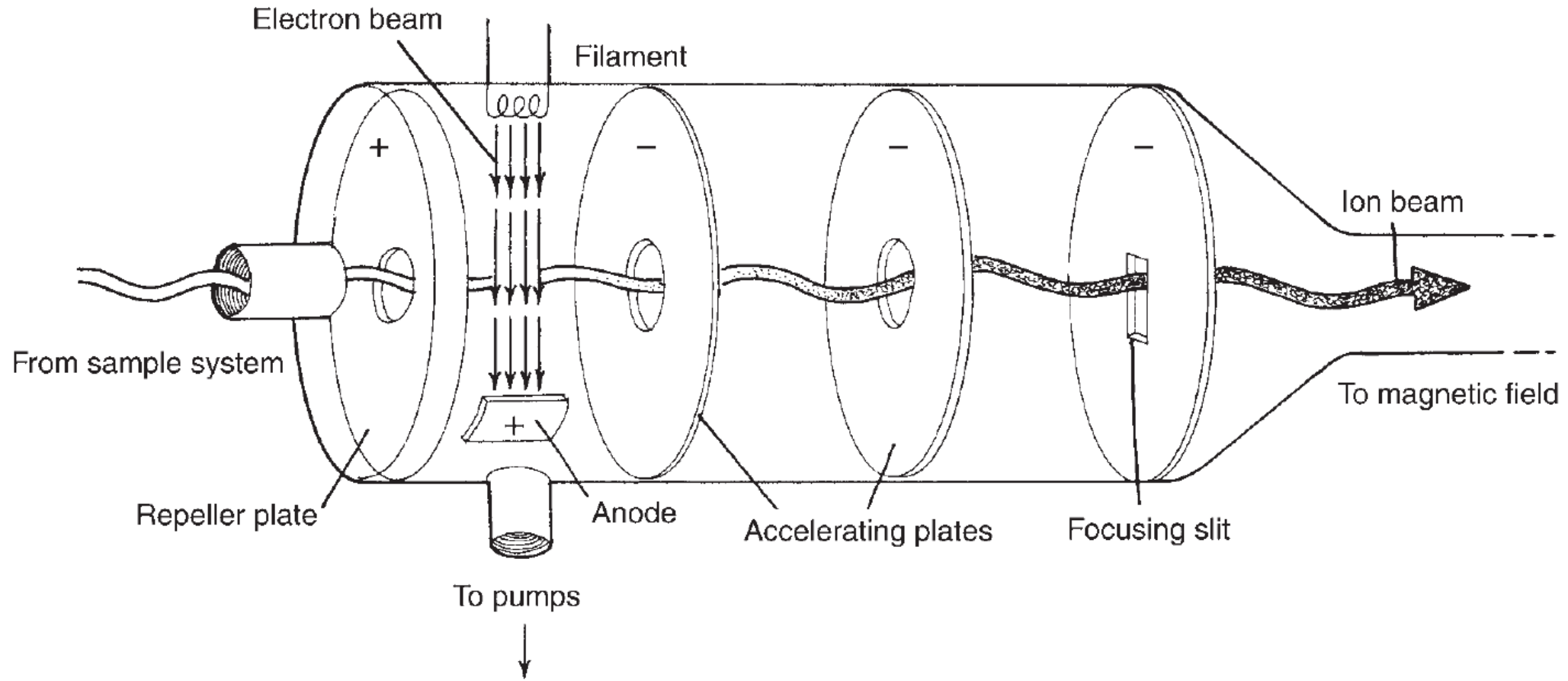
- Electron ionization or electron impact (EI)
- Chemical Ionization
- Desorption Ionization techniques
- Electron spray ionization

# Mass Spectrometry

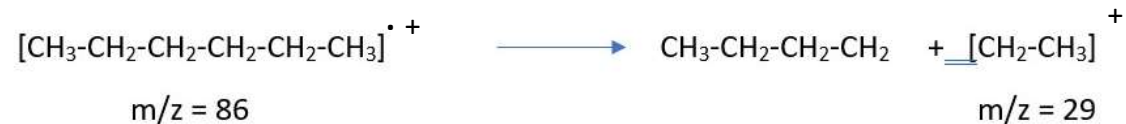
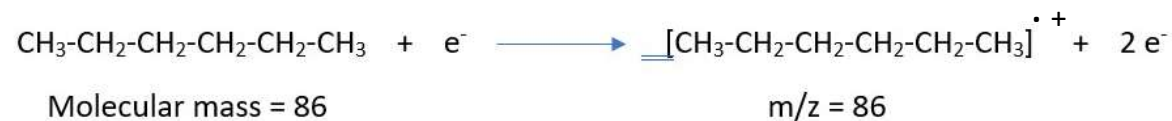
## Electron impact ionization chamber



# Mass Spectrometry



# Mass Spectrometry



# Mass Spectrometry

## Chemical Ionization (CI)

- In chemical ionization, the sample molecules are introduced into a stream of ionized reagent gas that is taken in large excess relative to sample.
- The sample molecules undergo collision with reagent ions and get ionized by various mechanism like proton transfer, hydride abstraction and adduct formation
- Any readily available gas or highly volatile liquid can be used as reagent gas for chemical ionization
- Common ionizing reagents for CI include methane, ammonia , isobutane and methanol

# Mass Spectrometry

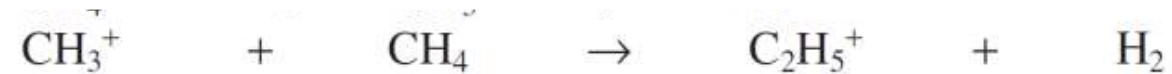
Primary ionization



Secondary ionization



Collision with neutral molecules, CH<sub>4</sub>



Collision with neutral molecules, CH<sub>4</sub>



# Mass Spectrometry

The sample molecules (M) introduced then get ionized by collision with reagent ions



## Advantages

- Selective production of intact quasi-molecular ion  
Which is particularly useful in the determination of molecular mass of sample under investigation

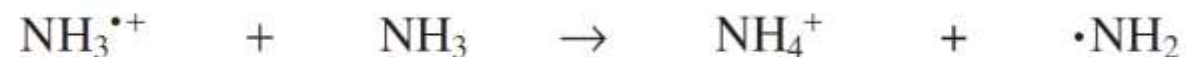
The quasi molecular ion fragments to little extent compared to molecular ion

# Mass Spectrometry

If ammonia gas is used as the reagent gas the reagent ion will be  $\text{NH}_4^+$  cation. The formation of ammonium cation reagent ion from ammonia can be depicted as follows



Collision with neutral ammonia molecules



The sample molecules (M) introduced undergo collisions with reagent ammonium ions and get ionized



Using iso-butane reagent gas produces t-butyl cations which readily protonate basic sites on sample molecules

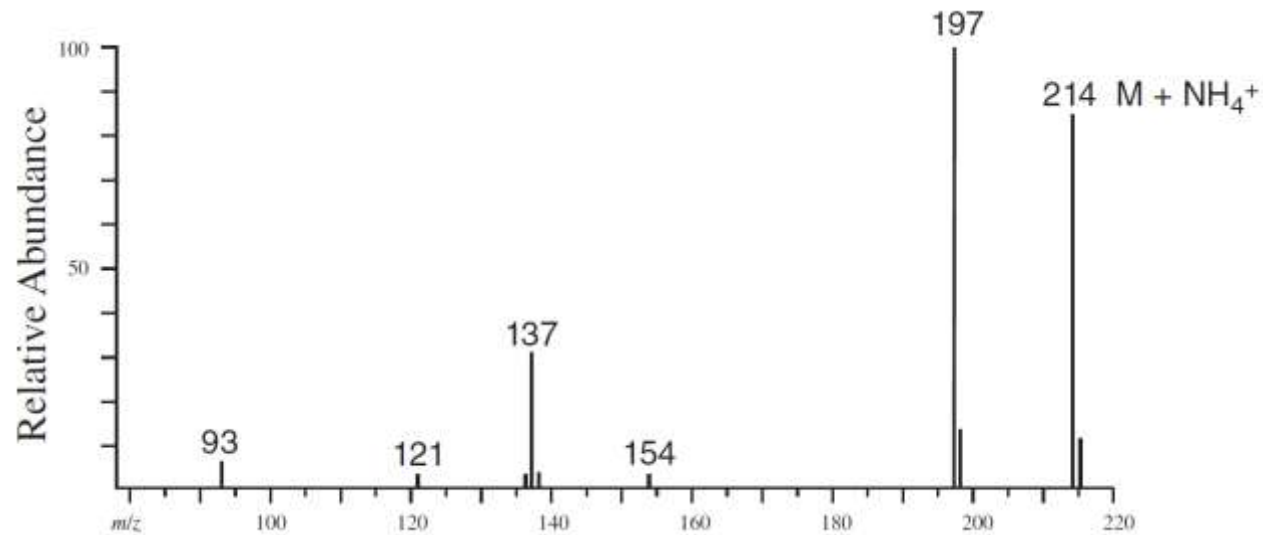
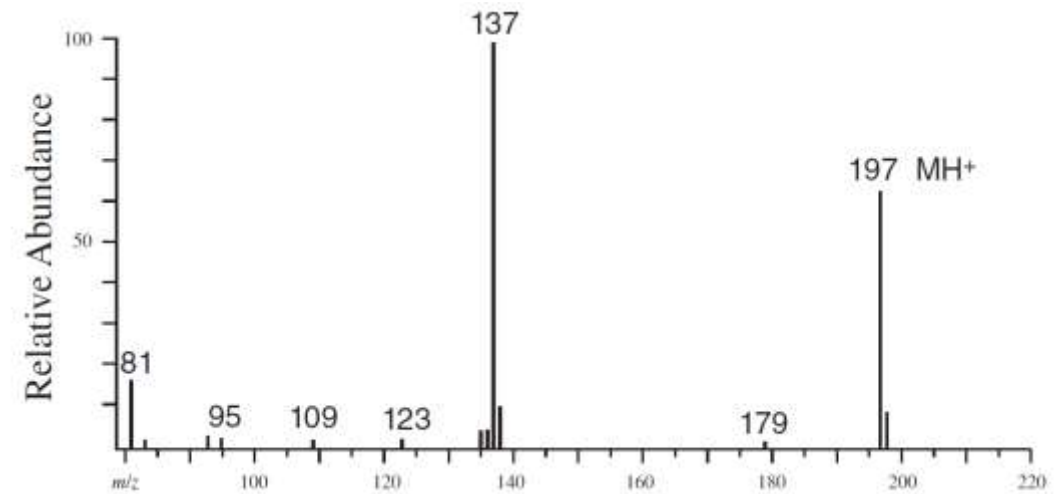
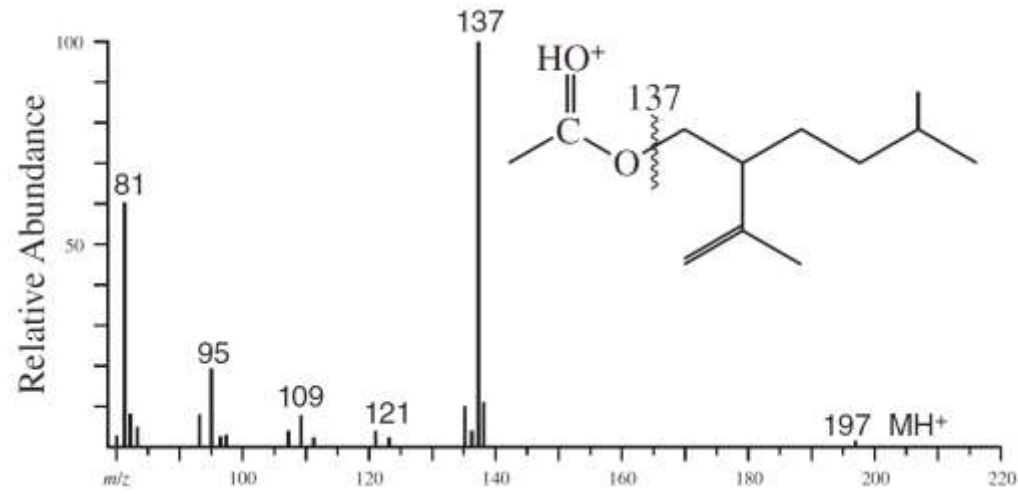


# Mass Spectrometry

## SUMMARY OF CHEMICAL IONIZATION (CI) REAGENT GASES

Reagent Gas	Proton Affinity (kcal/mole)	Reagent Ion(s)	Analyte Ion(s)	Comments
H <sub>2</sub>	101	H <sub>3</sub> <sup>+</sup>	(M + H) <sup>+</sup>	Produces significant fragmentation
CH <sub>4</sub>	132	CH <sub>5</sub> <sup>+</sup> , C <sub>2</sub> H <sub>5</sub> <sup>+</sup>	(M + H) <sup>+</sup> , (M + C <sub>2</sub> H <sub>5</sub> ) <sup>+</sup>	Less fragmentation than H <sub>2</sub> , can form adducts
NH <sub>3</sub>	204	NH <sub>4</sub> <sup>+</sup>	(M + H) <sup>+</sup> , (M + NH <sub>4</sub> ) <sup>+</sup>	Selective ionization, little fragmentation, some adduct formation
(CH <sub>3</sub> ) <sub>3</sub> CH	196	(CH <sub>3</sub> ) <sub>3</sub> C <sup>+</sup>	(M + H) <sup>+</sup> , [M + C(CH <sub>3</sub> ) <sub>3</sub> ] <sup>+</sup>	Mild, selective protonation, little fragmentation
CH <sub>3</sub> OH	182	CH <sub>3</sub> OH <sub>2</sub> <sup>+</sup>	(M + H) <sup>+</sup>	Degree of fragmentation observed between that of methane and isobutane
CH <sub>3</sub> CN	188	CH <sub>3</sub> CNH <sup>+</sup>	(M + H) <sup>+</sup>	Degree of fragmentation observed between that of methane and isobutane

# Mass Spectrometry

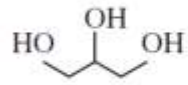


**FIGURE 3.3** Comparison of CI-MS data of lavandulyl acetate using methane (top), isobutane (middle), and ammonia (bottom) as reagent gases. (From McLafferty, F. W., and E. Tureček. *Interpretation of*

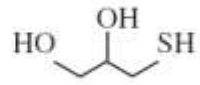
# Mass Spectrometry

## Desorption ionization techniques

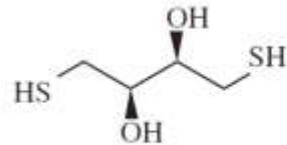
- ❑ The electron impact ionization (EI) and Chemical ionization (CI) require relatively volatile (low molecular weight) samples.
- ❑ The Desorption ionization technique allows the analysis of non volatile samples with high molecular weight
- ❑ In desorption ionization, the sample to be analysed is first dissolved or dispersed in a matrix like glycerol, thioglycerol, diethanolamine, nictotinic acid or 2,5-dihydroxybenzoic acid



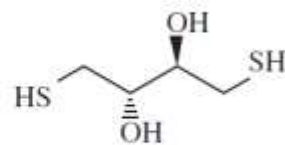
Glycerol



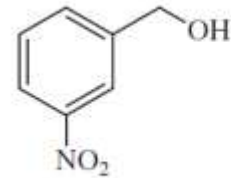
Thioglycerol



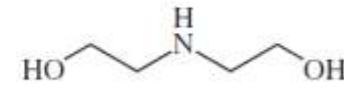
Dithiothreitol



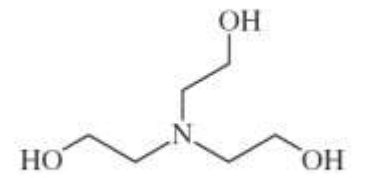
Dithioerythritol



3-Nitrobenzyl alcohol



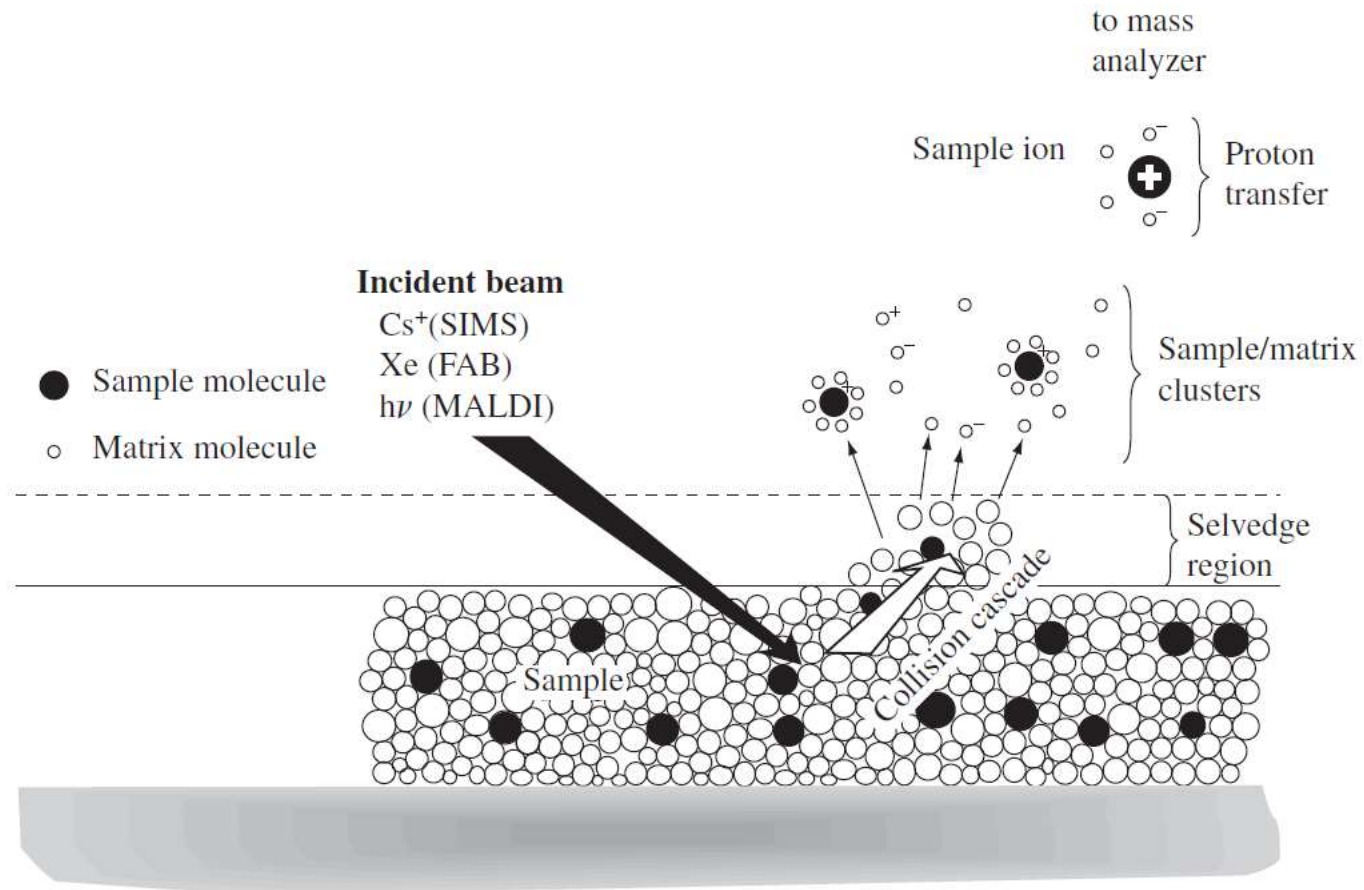
Diethanolamine



Triethanolamine

# Mass Spectrometry

- ❑ This is then allowed to undergo bombardment with high energy (1-10 KeV) neutral atoms like argon or xenon atoms, this is called fast atom bombardment (FAB)
- ❑ Or bombarded with beam of ions like Ar or Cs, this is called secondary ion mass spectrometry (SIMS)
- ❑ Or bombarded with high energy photons like nitrogen laser, this is called matrix assisted laser desorption ionization (MALDI)
- ❑ The collision of these atoms/ions/photons with the sample ionizes some of the sample molecules and ejects them from surface

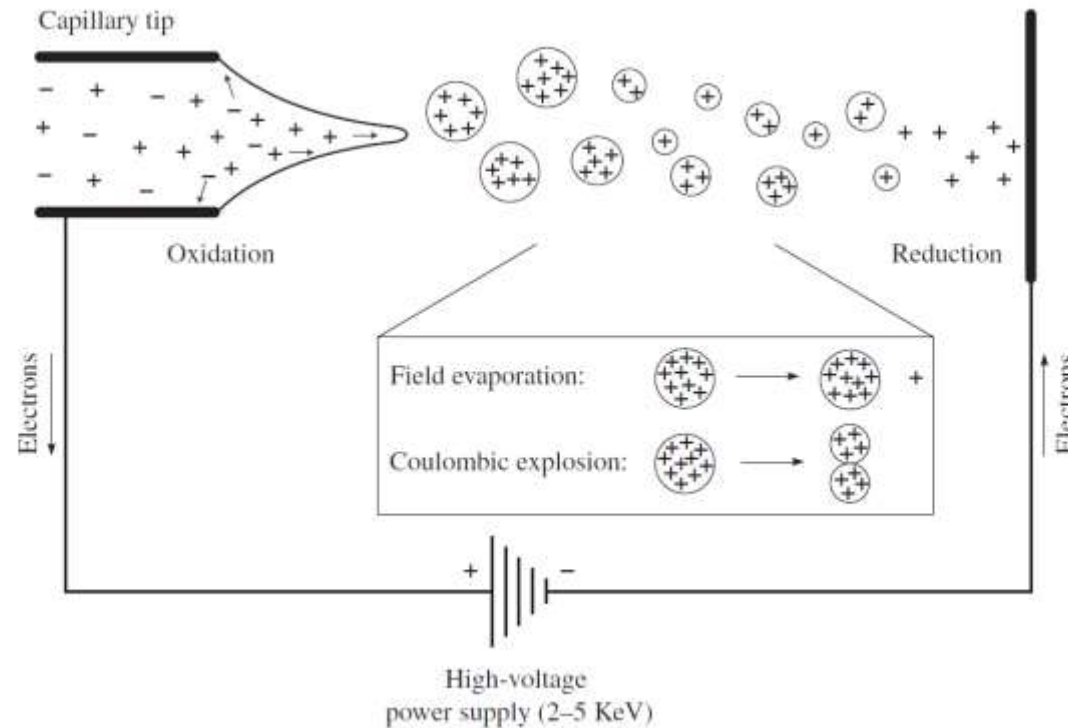




# Mass Spectrometry

## Electrospray ionization (ESI)

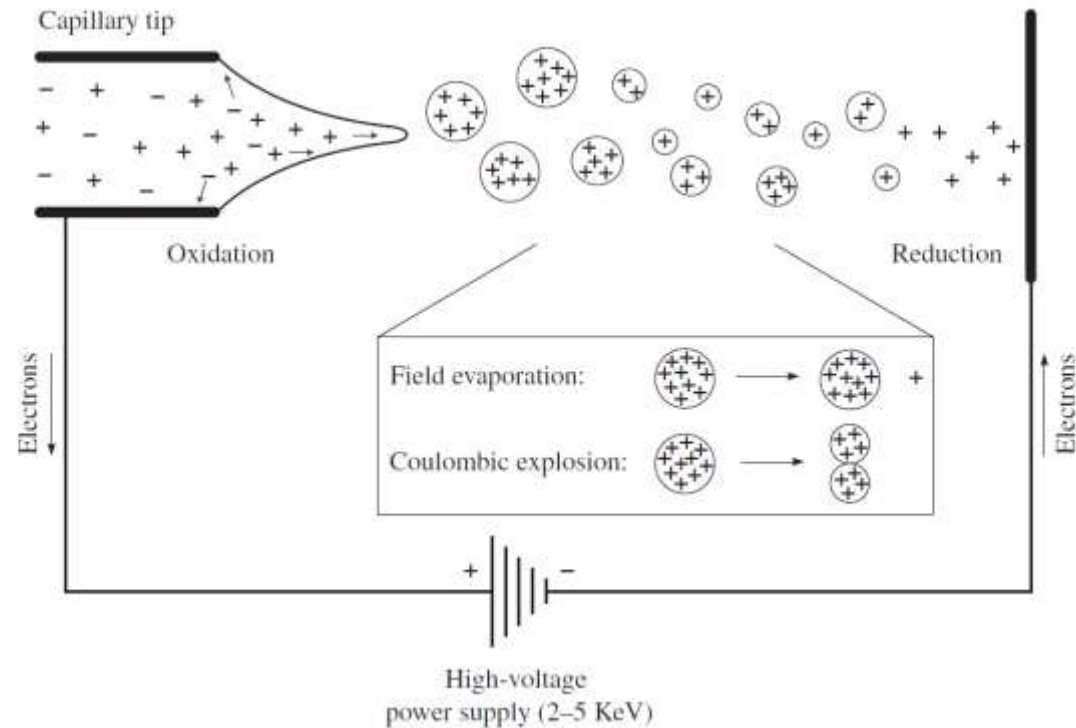
- ❑ Electrospray ionization (ESI) is another useful technique for studying high molecular weight biomolecules and other non volatile samples
- ❑ In electrospray ionization the sample solution is allowed to pass through fine capillary and to that capillary is applied high voltage across its surface



# Mass Spectrometry

## Electrospray ionization (ESI)

- ❑ As a result of application of high voltage, ions are produced and the solution containing ions is sprayed into heated chamber
- ❑ The charged droplets formed are subjected to counterflow of drying gas (usually Nitrogen) that evaporates solvent molecules from the droplets

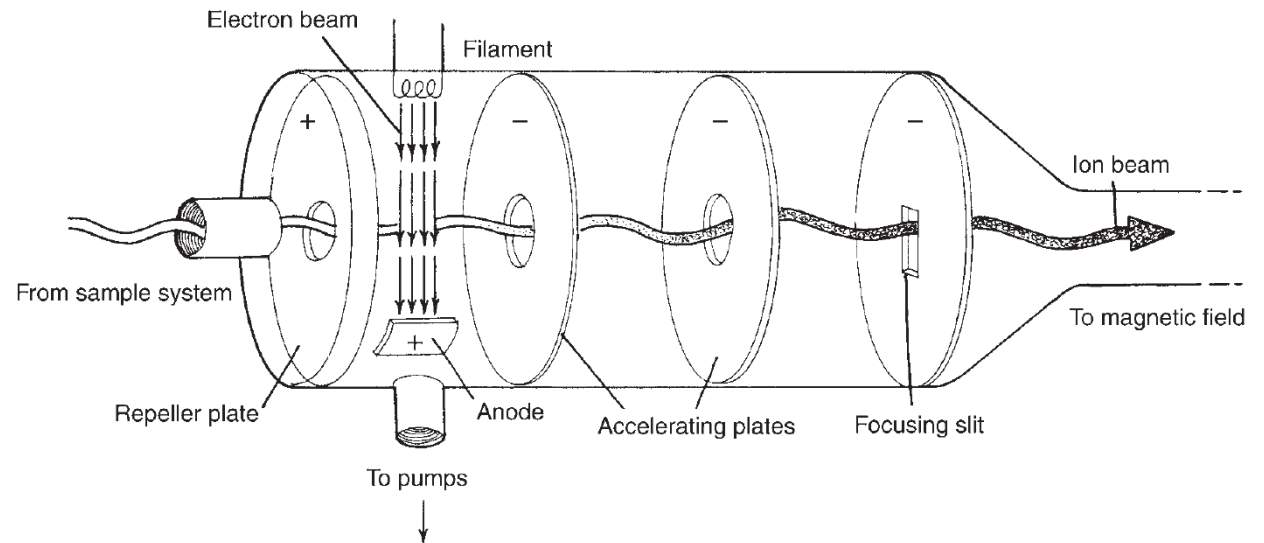


# Mass Spectrometry

## Mass Analyzer

Once the sample has been ionized the beam of ions is accelerated by an electric field and then passes into mass Analyzer, the region of the mass spectrometer where the ions are separated according to their mass-to-charge ( $m/z$ ) Ratios. Just like there are many different ionization methods for different applications, there are also several type of mass analyzers. While some mass analyzer are more versatile than others, none of the options are one size fits all.

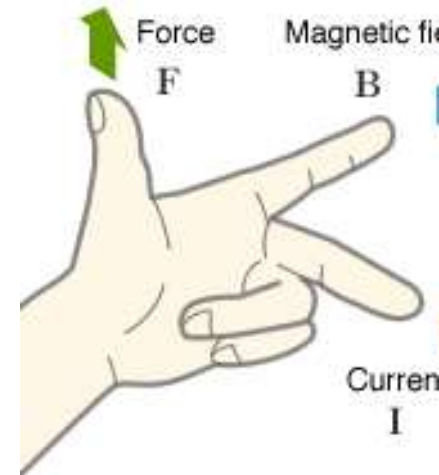
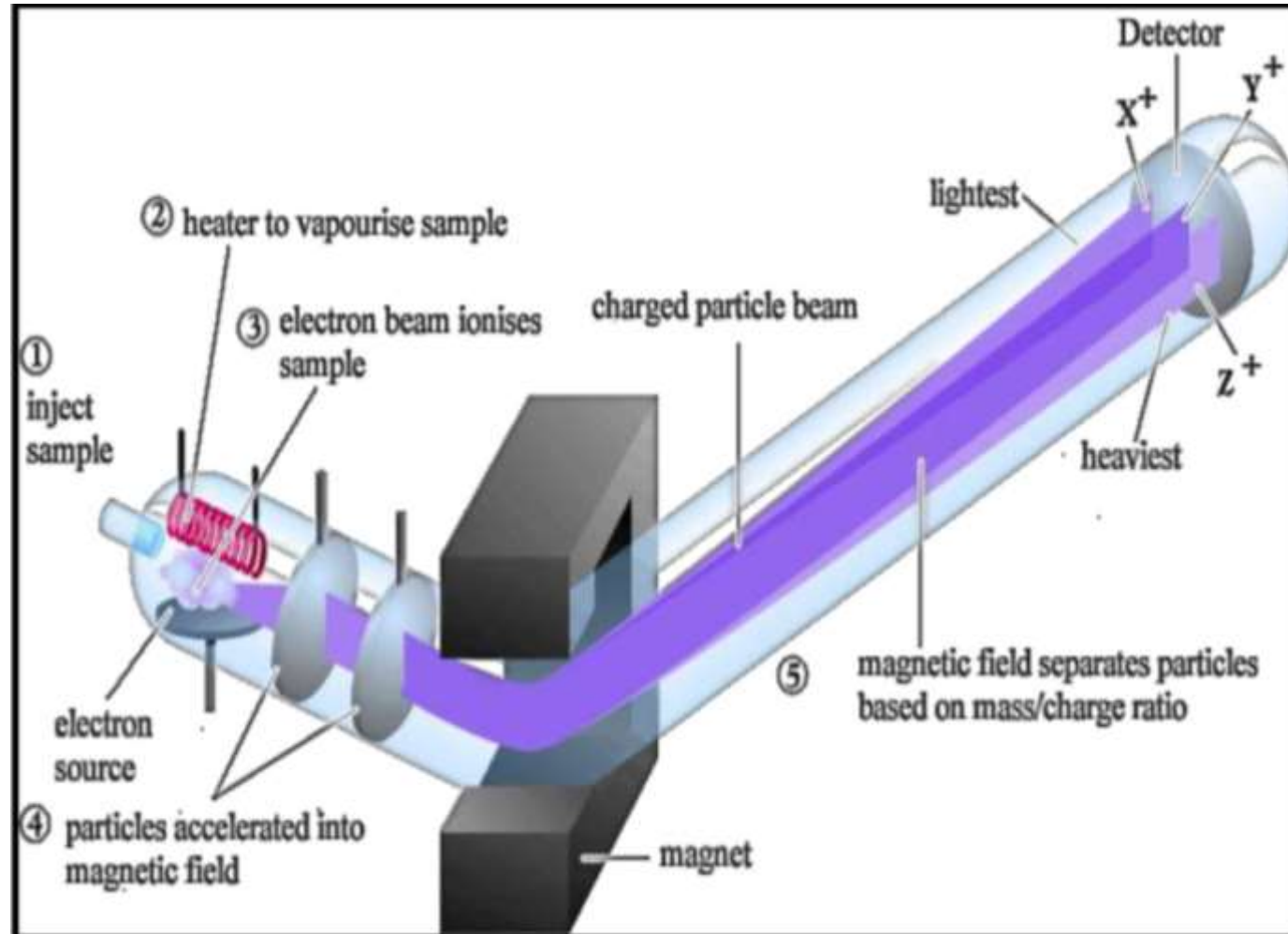
- Magnetic deflection or sector mass analyzer
- Double focusing mass analyzer
- Quadrupolar mass analyzer
- Time-of-flight mass analyzer



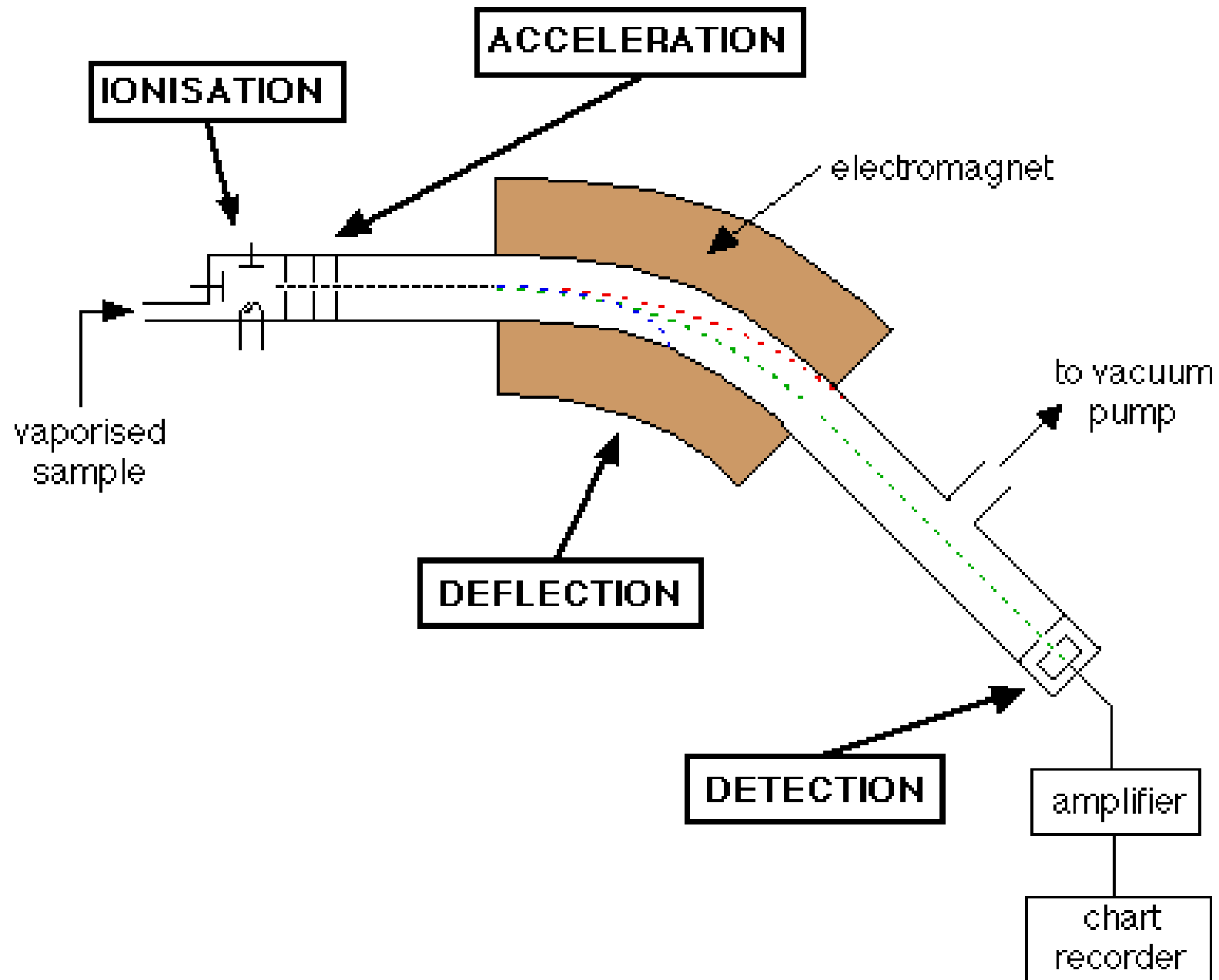
# Mass Spectrometry

## Magnetic deflection or sector mass analyzer

- ❑ The magnetic deflection mass analyzer is the most commonly used mass analyzer in mass spectrometry
- ❑ In this method the beam of ions coming out of the ion source unit is subjected to magnetic field that causes the ions to be deflected along the curved path.



# Mass Spectrometry



# Mass Spectrometry

Let us consider a positive ion of mass  $m$  and charge  $z$ , produced in the ion source, is accelerated by the applied electric field of potential  $V$ , to a velocity  $v$ .

The work done by the applied electric field of potential  $V$  on the positive ion of charge  $z$ , is given by,

$$W = zV \quad \text{-----} \quad (1)$$

The potential difference ( $V$ ) between the two points in an electric field is a measure of the work done ( $W$ ) in moving one coulomb of charge between the two points

$$V = \frac{W}{z} \quad \text{-----} \quad (2)$$

Where,

$V$  = potential difference between two points in an electric field expressed in Volts

$W$  = Work done in moving quantity of charge between two points in an electric field, expressed in joules

$z$  = quantity of charge expressed in coulombs

# Mass Spectrometry

The formula  $V = \frac{W}{z}$  defines the volt

If one joule of work is done by moving one coulomb of charge between two points in an electric field, the potential difference between two points is one volt.

When a charge particle moves in an electric field, the work done by the electric field on the charged particle is converted to kinetic energy of the charged particle.

The kinetic energy that the positively charged ion of mass  $m$  and charge  $z$ , accelerated to a velocity  $v$  by the applied electric field of accelerating potential  $V$  is given by

$$T = \frac{1}{2}mv^2 \text{ ----- (3)}$$

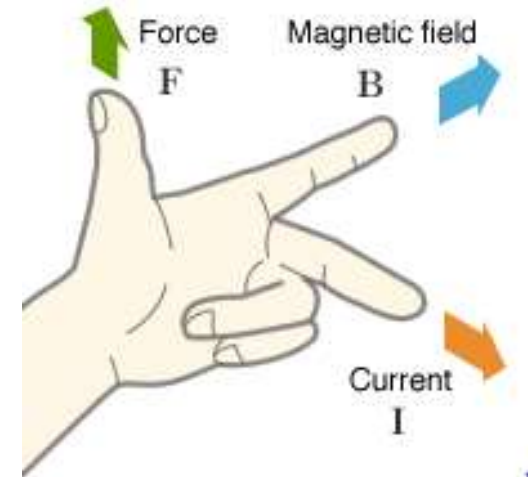
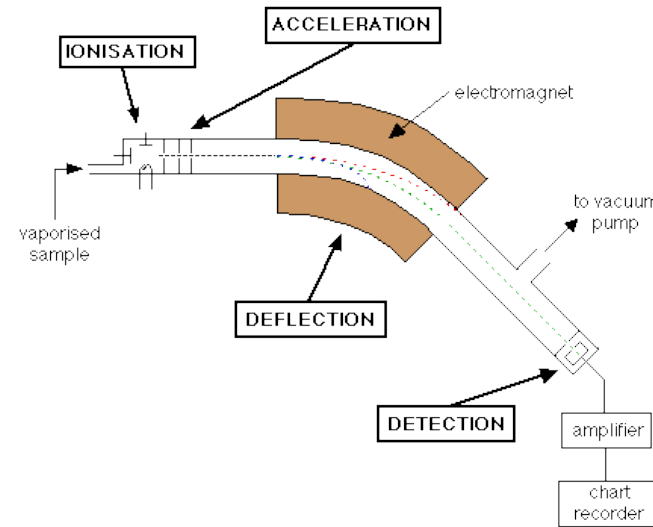
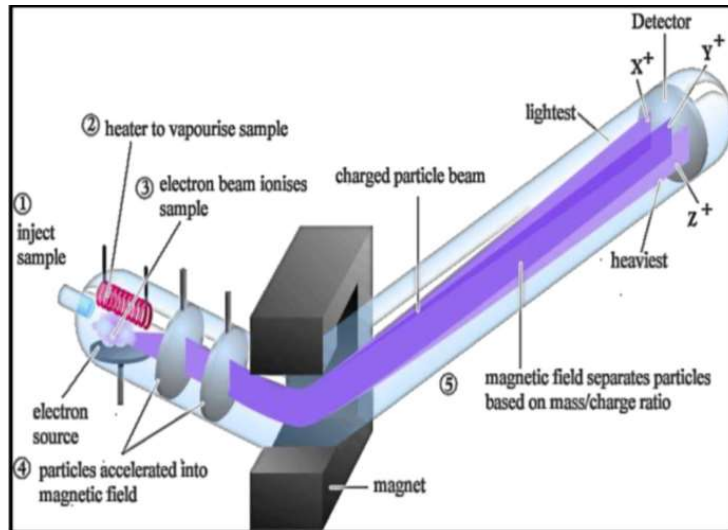
Since the work done on the charged ion by an electric field is equal to the gain in kinetic energy of the charged ion, we have from equation (1) and (3)

$$zV = \frac{1}{2}mv^2$$

or, 
$$v^2 = \frac{2zV}{m} \text{ ----- (4)}$$

# Mass Spectrometry

As the positively charged ion enters the magnetic field, B placed perpendicularly to their direction of motion, the positively charged ion experiences a force at right angle to both its direction of motion and the direction of magnetic field, thereby bending or deflecting the ion into a circular path of radius r



So in a magnetic field of strength B, a positively charged particle of mass m and charge z, moving with a velocity v experiences a force at right angle to both its direction of motion and direction of magnetic field, given by,

$$F_B = zv \times B \text{ ----- (5)}$$

The direction of the force can be easily realized by the use of Fleming's right hand rule



# Mass Spectrometry

The magnetic force always acts perpendicular to the direction of velocity, so that this force can never produce any work on the charged particle and hence cannot impart it any kinetic energy. The charged particles kinetic energy and speed thus remains constant, but the direction of motion is affected.

This is typical of uniform circular motion and the magnetic force supplies the centripetal force

$$F_{cp} = F_B = zvB \text{ ----- (6)}$$

For a charged particle of mass  $m$  and charge  $z$  moving with a velocity  $v$  in a circular path of radius  $r$ , the centrifugal force is given by

$$F_{cf} = \frac{mv^2}{r} \text{ ----- (7)}$$

As the positively charged ion moves through the magnetic field it follows a circular path when the centrifugal force becomes equal to the centripetal force.

Equating the centripetal and centrifugal forces from equation 6 and 7 we have,

$$\frac{mv^2}{r} = zvB$$

Or,

$$v^2 = \left( \frac{zBr}{m} \right)^2 \text{ ----- (8)}$$

# Mass Spectrometry

From equation 4

$$v^2 = \frac{2zV}{m} \text{ ----- (4)}$$

Equating equation 4 and 8 we have,

$$\frac{2zV}{m} = \left( \frac{zBr}{m} \right)^2$$

Therefore, 
$$\frac{m}{z} = \frac{B^2 r^2}{2V}$$

Where, m is the mass in atomic mass units and z is the number of electronic charge

# Mass Spectrometry

## Problems

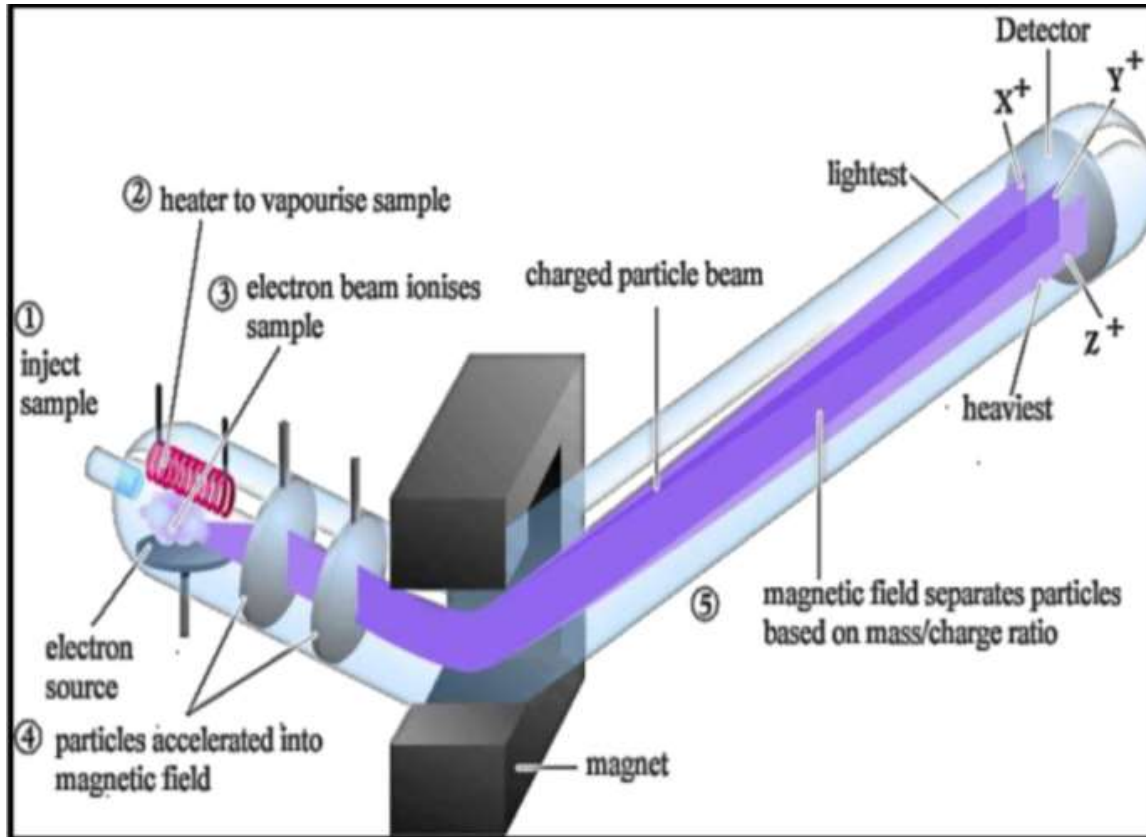
1. What must be the strength of the applied magnetic field in the magnetic deflection mass analyzer spectrometer with a radius of curvature of 30.48 cm and operating at an potential of 2500 Volts so that  $C_3H_5$  ion will be brought to the focus of the detector
2. For a magnetic deflection mass analyzer spectrometer the Xe ion at  $m/z$  131.29 was observed at magnetic field strength of 2085 gauss. What magnetic field would be necessary to focus the  $CCl_3$  ion at  $m/z$  118.361 if the accelerating potential were left unchanged

## Problems

1. What must be the strength of the applied magnetic field in the magnetic deflection mass analyzer spectrometer with a radius of curvature of 30.48 cm and operating at an potential of 2500 Volts so that  $C_3H_5$  ion will be brought to the focus of the detector

## Problems

- For a magnetic deflection mass analyzer spectrometer the Xe ion at  $m/z$  131.29 was observed at magnetic field strength of 2085 gauss. What magnetic field would be necessary to focus the  $\text{CCl}_3$  ion at  $m/z$  118.361 if the accelerating potential were left unchanged





# Mass Spectrometry

## Atomic Mass Units

- ❑ An atomic mass unit or amu is a physical constant equal to one-twelfth of the mass of an unbound atom of carbon-12. It is a unit of mass used to express atomic masses and molecular masses.
- ❑ When the mass is expressed in amu, it roughly reflects the sum of the number of protons and neutrons in the atomic nucleus (electrons have so much less mass that they are assumed to have negligible effect)

One mole of carbon =  $6.023 \times 10^{23}$  atoms

Molecular weight of carbon = 12g/mole

i.e, mass of one mole of carbon = 12 g

i.e, mass of  $6.023 \times 10^{23}$  atoms of carbon = 12 g

$$\begin{aligned}\text{Mass of one atom of carbon} &= \frac{12}{6.022 \times 10^{23}} \text{ g} \\ &= \frac{12}{6.022 \times 10^{23}} \times 10^{-3} \text{ kg}\end{aligned}$$

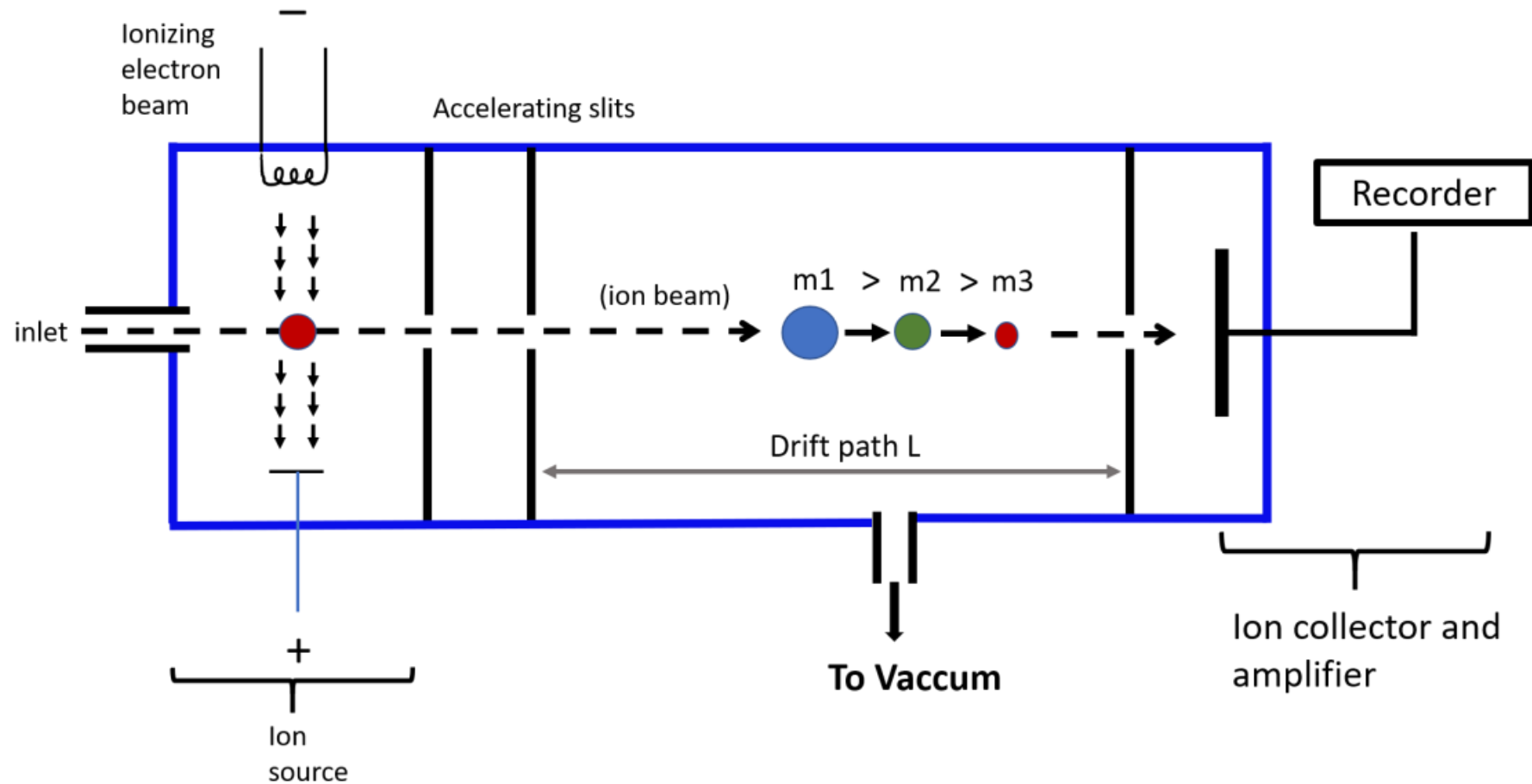




# Mass Spectrometry

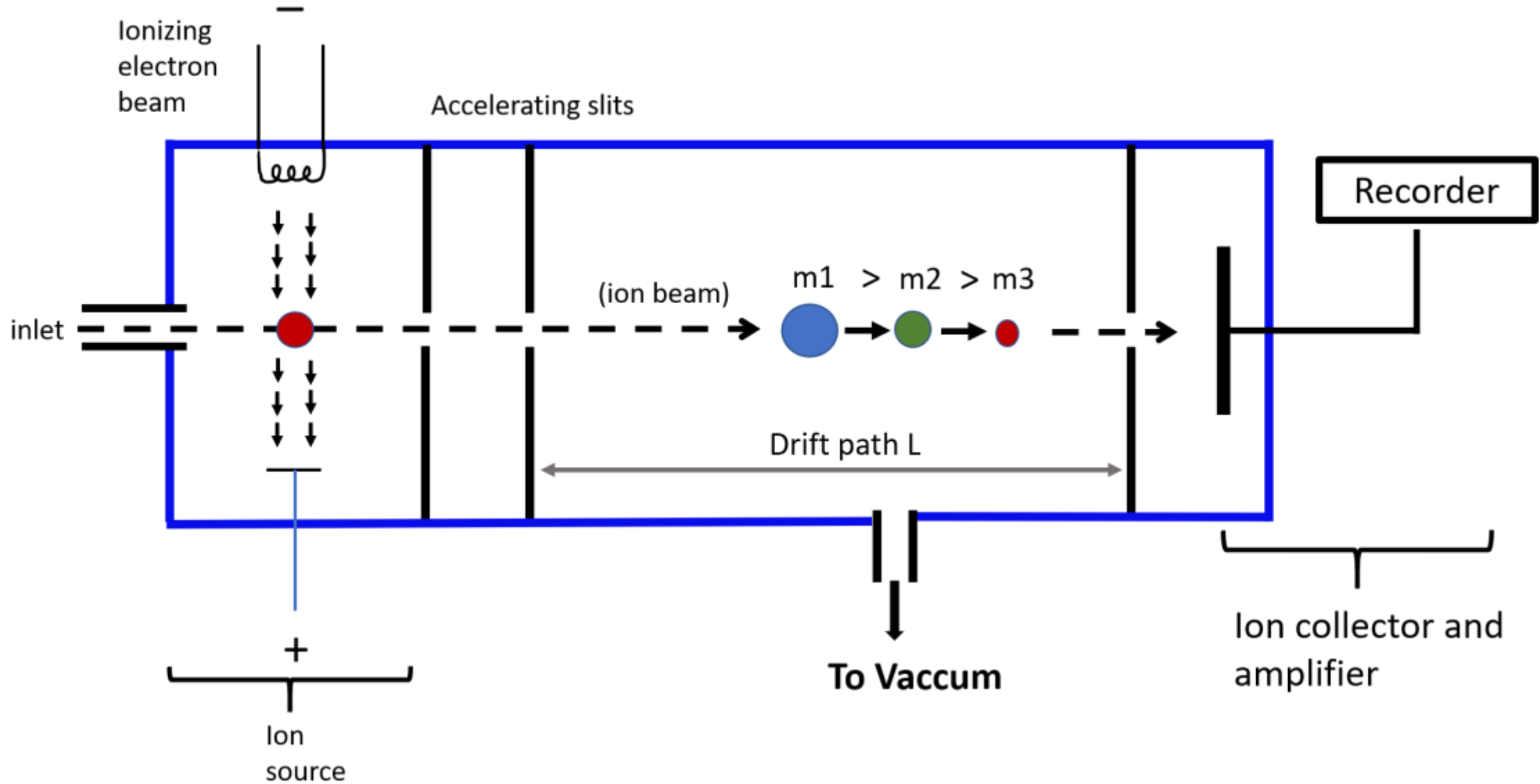
## Time of flight Mass analyzer

- Time of flight mass analyzer operates on the principle that if ions with different masses are all accelerated to the same kinetic energy, each ion acquires a characteristic velocity that depends upon its  $m/z$  ratio, i.e., on the mass of the ion.
- If there is fixed distance of travel of the ions to the ion detector, the time of their travel will vary with their mass, the lighter ions travelling faster will strike the detector in a shorter period of time



# Mass Spectrometry

- The time of flight mass analyzer separates the ions by time without the use of magnetic field



# Mass Spectrometry

Consider a positive charged ion of mass  $m$  and charge  $z$  produced in the ionization chamber and accelerated by electric potential  $V$  to a velocity  $v$ .

The work done by the electric potential  $V$  on the positive charged ion of charge  $z$  is given by

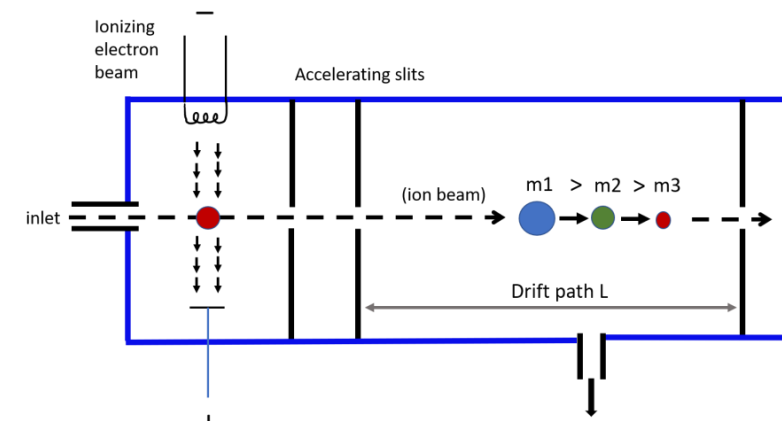
$$W = zV \text{ ----- (1)}$$

The kinetic energy of this positively charged ion of charge  $z$  and mass  $m$  accelerated to velocity  $v$  by the potential  $V$  is given by

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

Since the work done on the charged ion by an electric field is equal to the gain in kinetic energy of the charged ion, we have from equation (1) and (3)

$$zV = \frac{1}{2}mv^2 \text{ ----- (3)}$$



# Mass Spectrometry

The time of flight mass analyzer does not employ a magnetic field for the separation of ions of different  $m/z$ . Instead, the time it takes for the positive charged ion to reach the ion collector or detector and how this flight time depends upon the  $m/z$  value is determined.

It should be pointed out that the time of flight mass analyzer are the only type of mass analyzer that do not necessarily require a magnetic field/

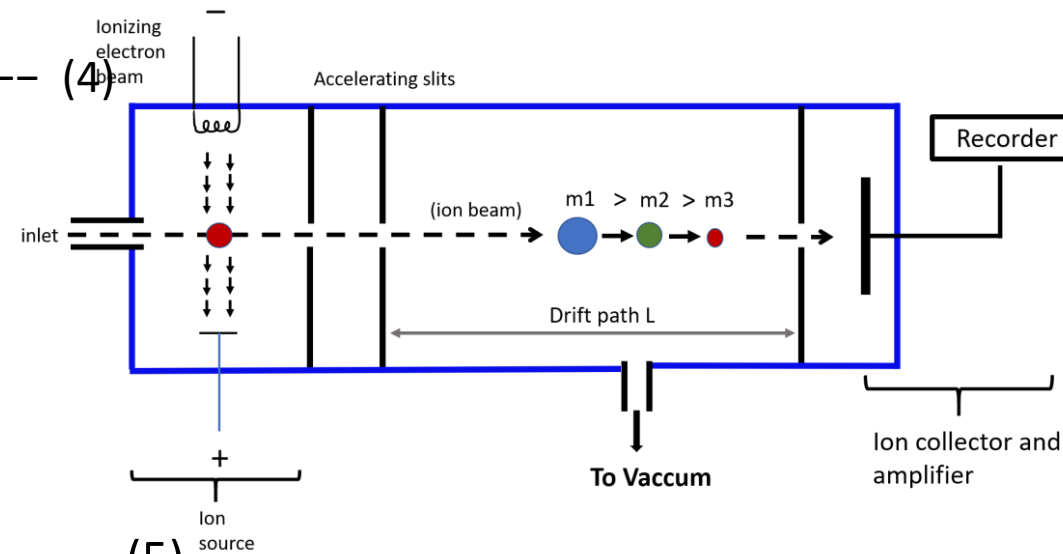
If  $L$  is the length of the flight path of the ions and  $v$  is the velocity of the ions, under the accelerating potential  $V$ , the time of flight  $t_f$  is given by

$$t_f = \frac{L}{v} \quad \text{Or} \quad v = \frac{L}{t_f} \quad \text{--- (4)}$$

Substituting equation 4 in equation 3 we get

$$zV = \frac{1}{2} m \left( \frac{L}{t} \right)^2 \quad \text{Or} \quad zV = \frac{mL^2}{2t_f^2}$$

$$\frac{m}{z} = \frac{2Vt_f^2}{L^2} \quad \text{--- (5)}$$



# Mass Spectrometry

Or

$$t_f = L \sqrt{\frac{1}{2V} \left( \frac{m}{z} \right)}$$

Thus the time of flight of various ions is simply proportional to the square root of the mass to charge ratio of the ions

# Mass Spectrometry

## Problems

1. A time of flight mass spectrometer has a flight length of 97.5 cm. The accelerating potential is 2845 volts. How long it will take PH<sub>3</sub> ion to traverse the spectrometer from ion source to detector
2. What is the difference in the times of arrival of PH<sub>2</sub> and PH<sub>3</sub> ions using the same instrument and operating conditions as given in question 1

## Problems

1. A time of flight mass spectrometer has a flight length of 97.5 cm. The accelerating potential is 2845 volts. How long it will take PH<sub>3</sub> ion to traverse the spectrometer from ion source to detector

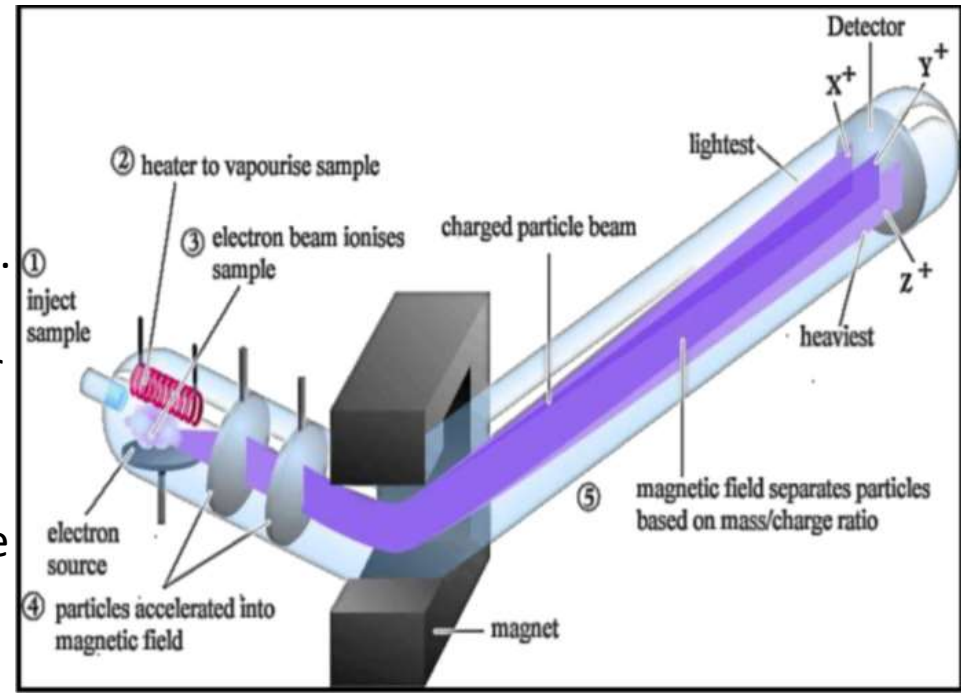




# Mass Spectrometry

## Detector, Amplifier and Data System

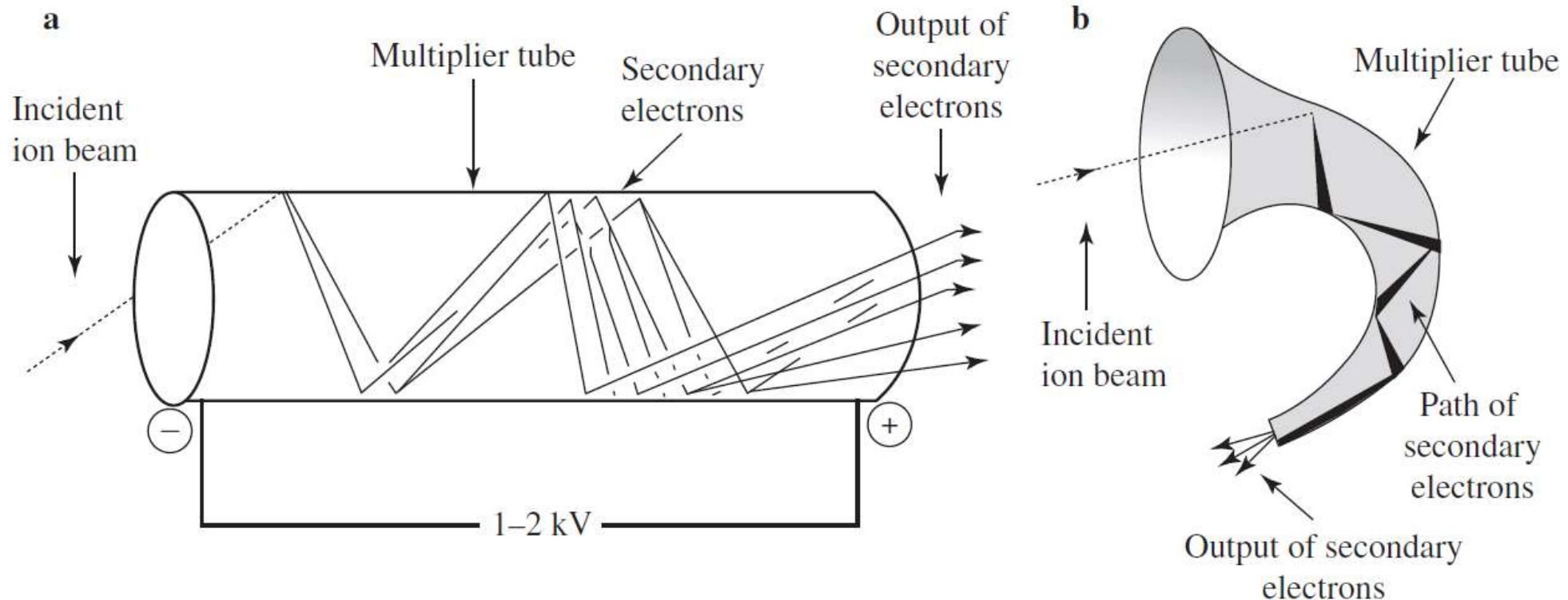
- The analyzer leads the resolved positive ions successively to the detection unit.
- Each type of ions with a particular  $m/z$  ratio strikes the counter of the detector produces an electric current.
- The produces electric current is proportional to the number of ions striking the counter.
- Thus the measurement of current produced by each type of ions is an indication of the relative abundance of ions of particular  $m/z$  ratio
- But the problem is that the number of ions of particular  $m/z$  value reaching the counter of detector is very less and hence the current produced is also low.
- This is because only very few molecules undergo ionization in the ion source unit and consequently the number of fragment ions will be still less.
- Besides not all the ions produced can reach the detector, in fact most of the ions never reach the detector in a scanning spectrometer
- Therefore the current produced when the positive ions strike the counter needs to be amplified



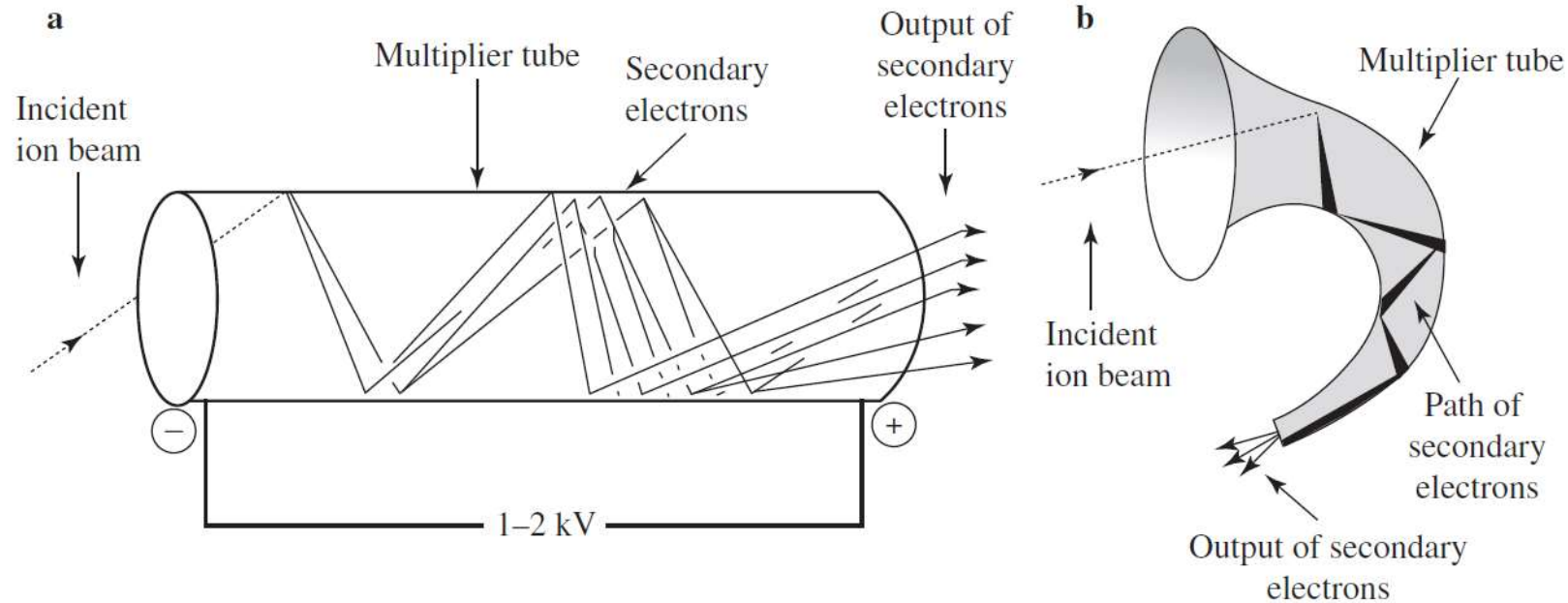
# Mass Spectrometry

- The detection with amplification is generally done through the use of electron multiplier detector which consists of lead doped glass coated with lead oxide. The amplified current corresponding to each type of ions with definite value of  $m/z$  reaches the data system from the detector

## Linear channel electron multiplier



# Mass Spectrometry

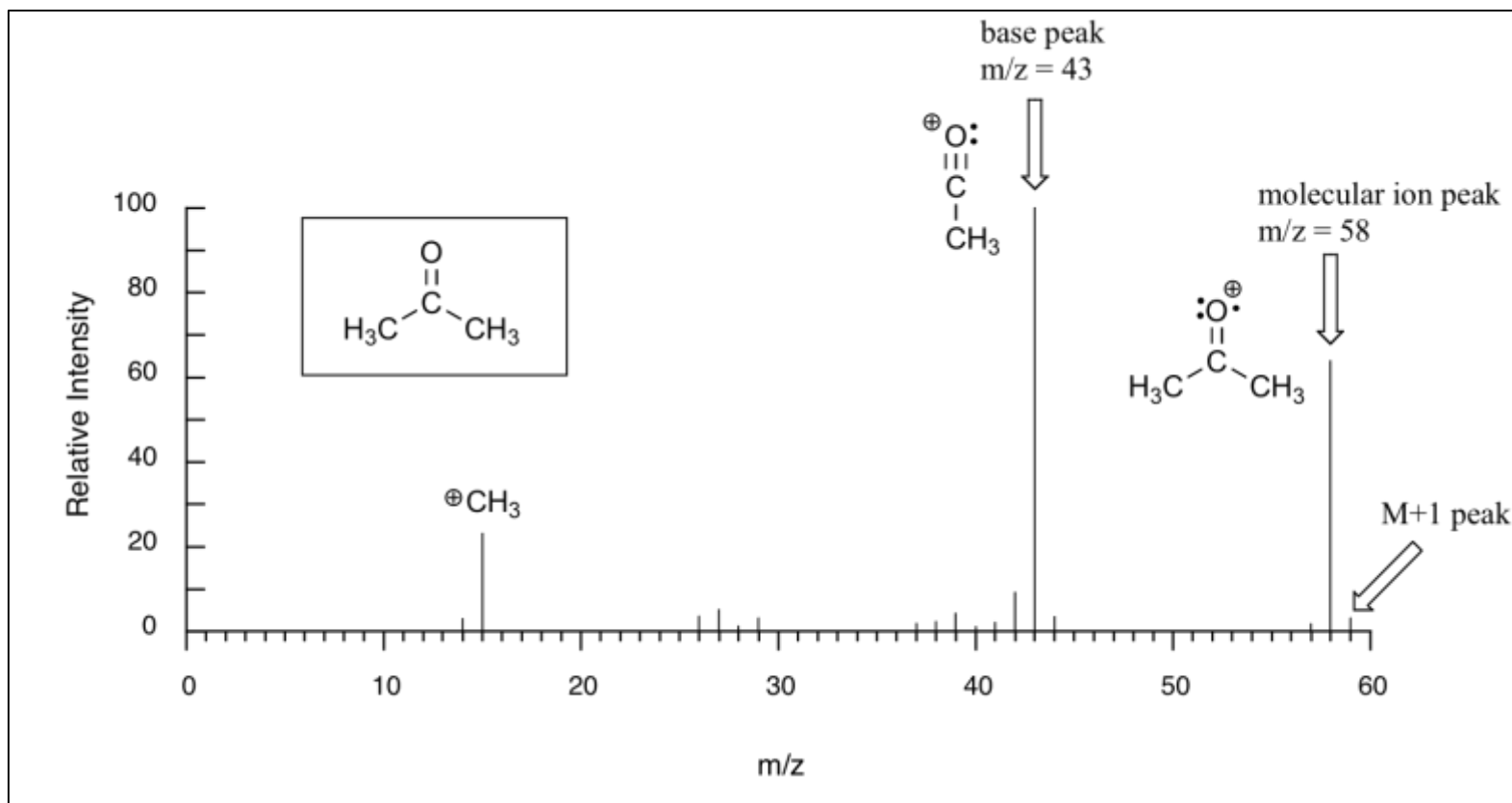


- ❑ When the ion strikes the surface of the electron multiplier(lead doped glass coated with lead oxide), two electrons are ejected.
- ❑ The approx. 2 KV potential difference between the opening and end of the detector draws the electrons further into the electron multiplier where each electron that strikes the surface again, each causing the ejection of two more electrons.
- ❑ This process continues until the end of the electron multiplier is reached and the electric current is analyzed and recorded by the data system
- ❑ The signal amplification just described will be  $2^n$  where  $n$  is the number of collision with the electron multiplier
- ❑ Typically electron multipliers provide a signal increase of  $10^5 - 10^6$  order.

# Mass Spectrometry

## Presentation of mass spectrum

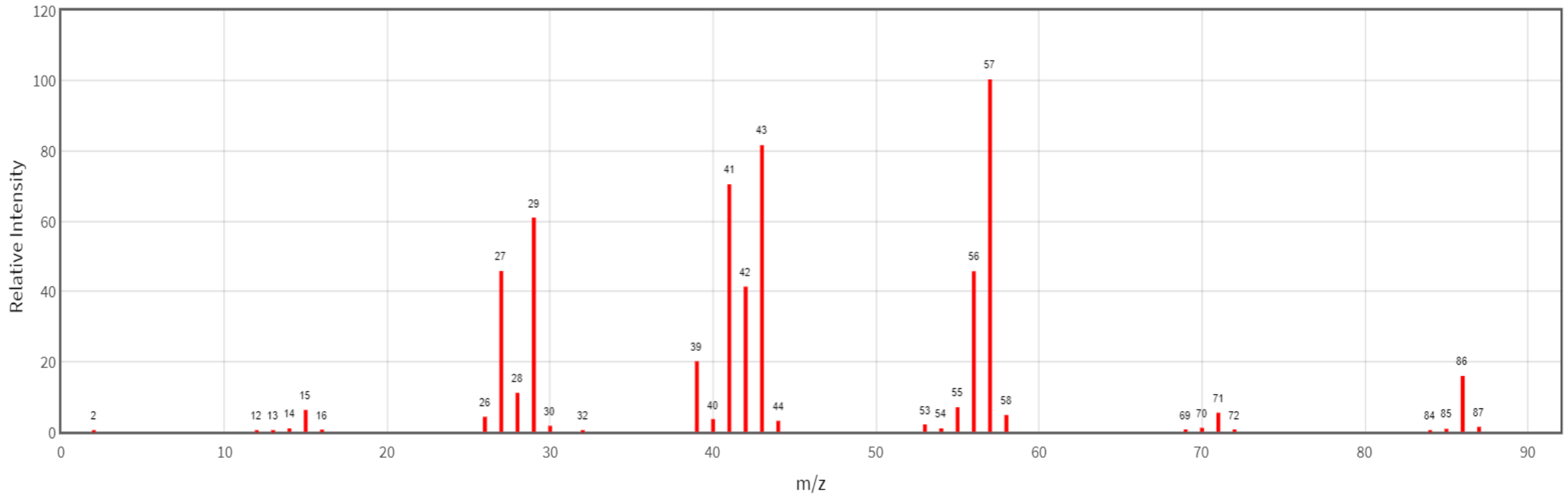
- ❑ A typical mass spectrum of a compound is obtained by plotting  $m/z$  values along x-axis and the corresponding ion abundance along the y-axis.
- ❑ The heights of the peaks in the spectrum indicate ion abundance and evidently the tallest peak will indicate the most abundant ion formed in the ionization process.
- ❑ The tallest peak representing the most abundant ion is called the **base peak**



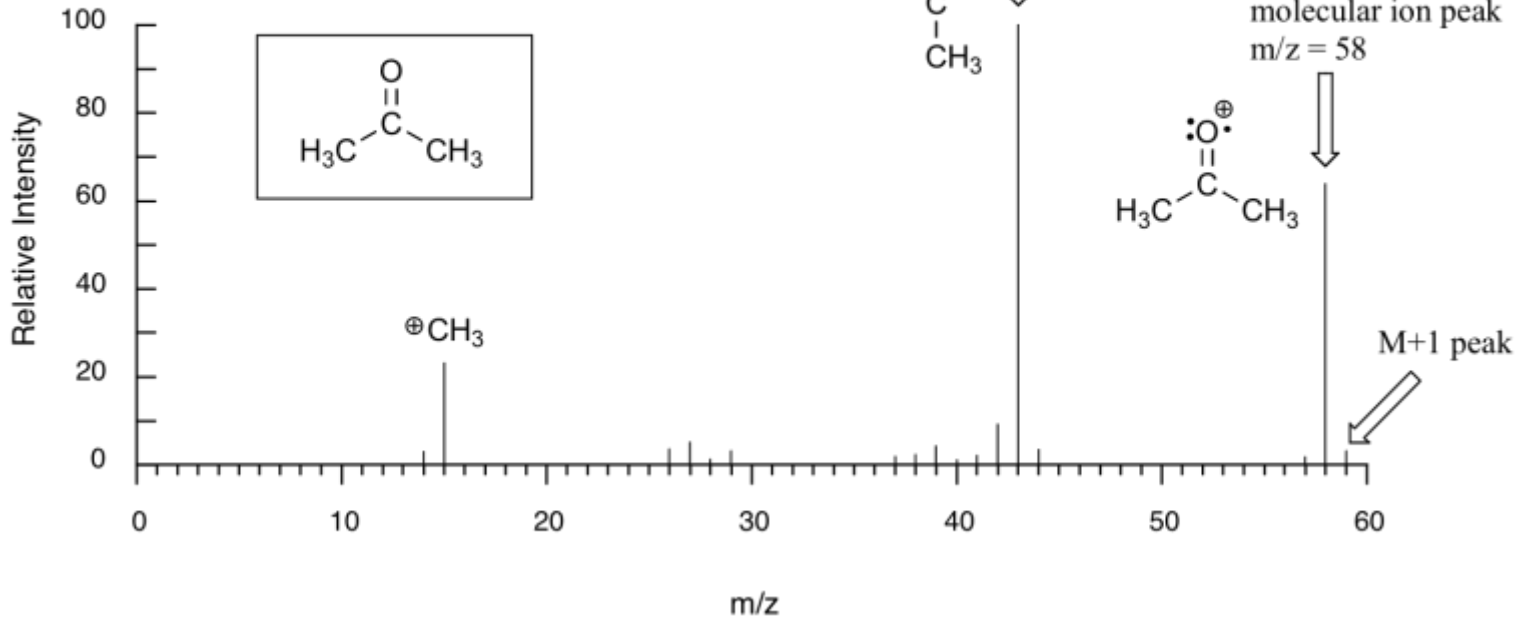
# Mass Spectrometry

n-hexane

Mass Spectrum



# Mass Spectrometry



# Mass Spectrometry

## Metastable ion peak

So far we have seen that all the molecular ions are not equally stable. Besides not all molecules acquire the same kinetic energy on collision with electron beam in the ion source unit. Therefore the life times of the molecular ions formed will be different.

The fragmentation processes were discussed on the basis of the positively charged fragments formed giving peaks in the spectrum, while the nature of the uncharged fragment not recorded in the spectrum was deduced from the difference between the molecular ion or primary fragment ion under consideration.

When a molecule becomes ionized on electron impact the positively charged molecular radical ion will under the influence of applied potential in the ion source begin to travel towards accelerating region. If the rate of decomposition of this molecular ion into fragment is very fast, all such ions will decompose before reaching the accelerating plates and only the fragment ions produced will be accelerated and deflected or focused into the detector

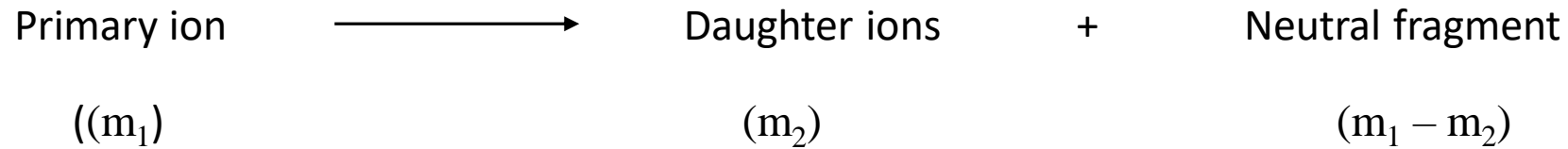
In other words metastable peaks arise from the ions which decompose after they are accelerated out of the ion source but before entering the analyzer

The result is that the spectrum will consist of fragment peaks with no peak for molecular ion.

# Mass Spectrometry

Thus there will be some primary ions which will decompose into fragments while traversing the accelerating region.

i.e.,



The ions will be first accelerated as of mass  $m_1$  (primary ion) and at the point of decomposition, part of the kinetic energy achieved will be carried off by the neutral fragment while the mass  $m_2$  (daughter ion) will continue to be accelerated and deflected/focused as such and the particle will be recorded neither at  $m_1$  nor as  $m_2$  but will give rise to a diffused peak of low intensity with a maximum at mass  $m^*$

$$\begin{aligned} m^* &= \frac{\text{mass of daughter ion}}{\text{mass of parent ion}} \\ &= \frac{(m_2)^2}{m_1} \end{aligned}$$



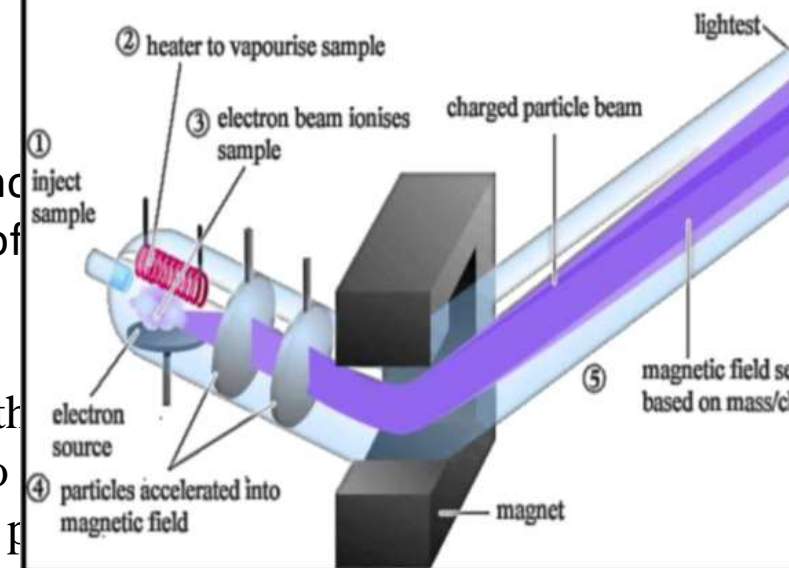
# Mass Spectrometry

# Mass Spectrometry

## Metastable ion peak

So far we have seen that all the molecular ions are not equally stable. Besides not all molecular ions receive the same amount of energy on collision with electron beam in the ion source unit. Therefore the life times of molecular ions are different.

Molecular ion ( $M^+$ ) or simply ions formed in the ionization chamber with life times of the order of  $10^{-6}$  s. Some of these ions may move to the accelerating plates and are accelerated before they have an opportunity to fragment. Some molecular ions ( $M^+$ ) or simply ions may disintegrate into fragments just after crossing the accelerating plates. This process occurs in the mass analyser region of the mass spectrometer to produce cations ( $A^+$ ) and a radical ( $B\cdot$ ).



These two species will then share the kinetic energy of the molecular ion. The fragments ions formed at this point have considerably lower energy than normal ions since the uncharged portion of the original ion carries away some of the kinetic energy that the ion received as it was accelerated.

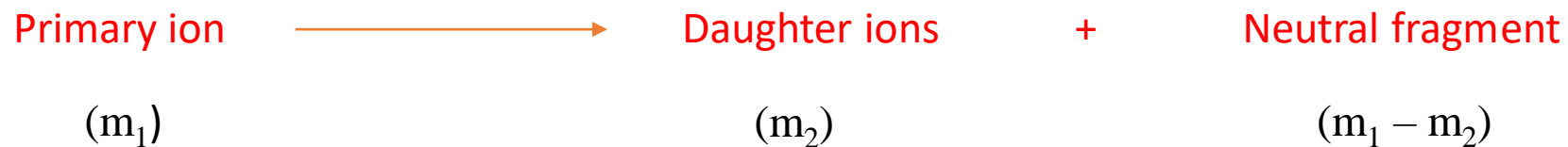
The same fragment cation ( $A^+$ ) may also be formed in the ion source unit and it may travel to the detector after being accelerated. This is the normal process of formation and detection of ions.

# Mass Spectrometry

But the same fragment ion ( $A^+$ ) formed after acceleration in the analyser region will be slightly energetically different from the ion ( $A^+$ ) though they have the same mass and this abnormal ion follows an abnormal flight path on its way to the detector. This ion appears at the  $m/z$  value that depends on its own mass as well as the mass of the original ion (molecular ion) from which it was formed. This ion ( $A^+$ ) with different kinetic energy is called the metastable ion and this type of ion give rise to metastable ion peak.

Meta stable ion are generally broad and they frequently appear at the non integral values of  $m/z$

The equation that relates the position of the metastable ion peak in the mass spectrum to the mass of the original ion is



$$\begin{aligned} m^* &= \frac{\text{mass of daughter ion}}{\text{mass of parent ion}} \\ &= \frac{(m_2)^2}{m_1} \end{aligned}$$



$$m^* = \frac{(m_2)^2}{m_1} = \frac{(A^+)^2}{M^+}$$

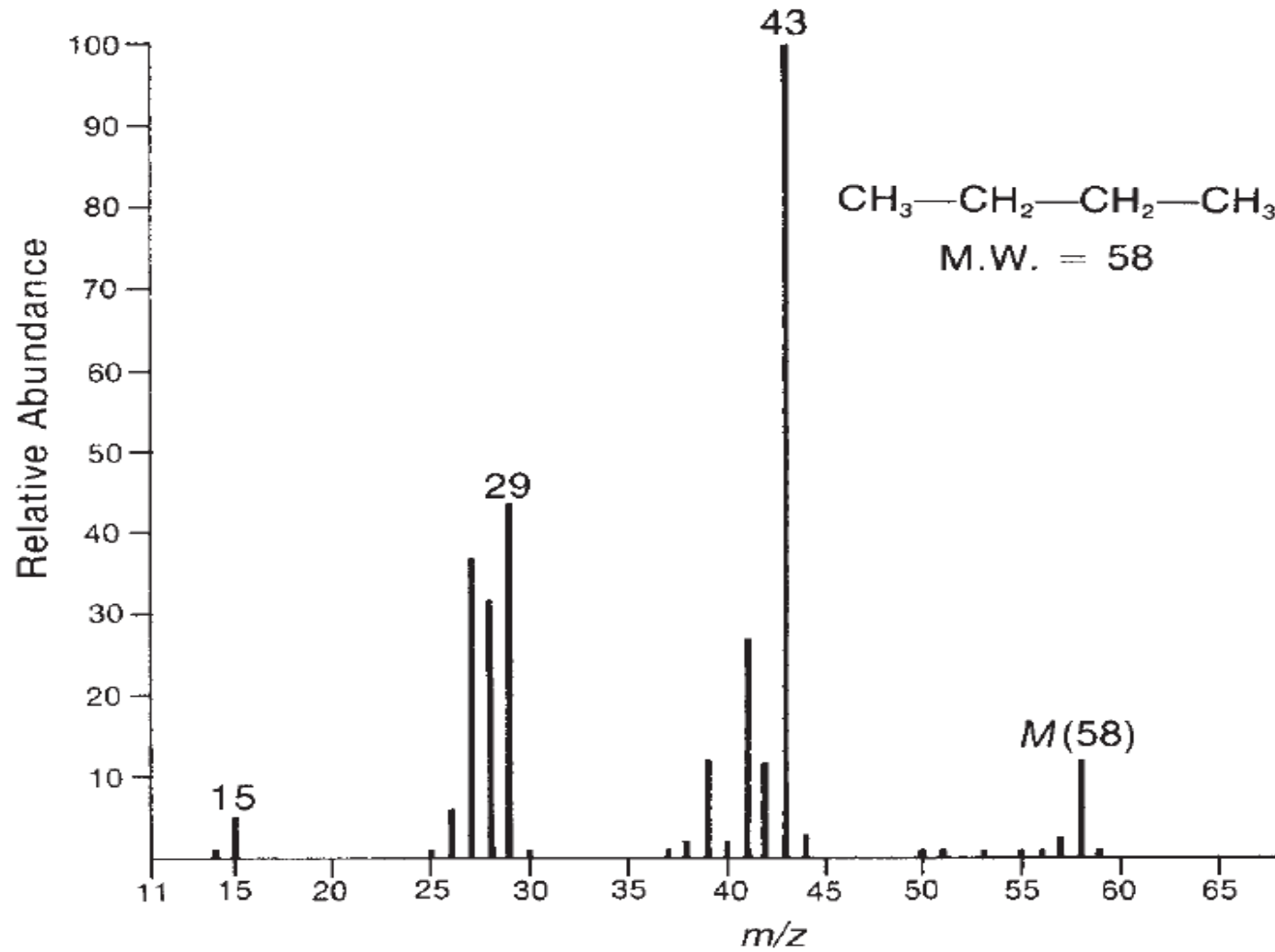
# Mass Spectrometry

# Mass Spectrometry

Calculate the expected apparent mass of the metastable ion produced when  $m/z$  decomposes by loss of  $\text{CH}_2$  to  $m/z$  51

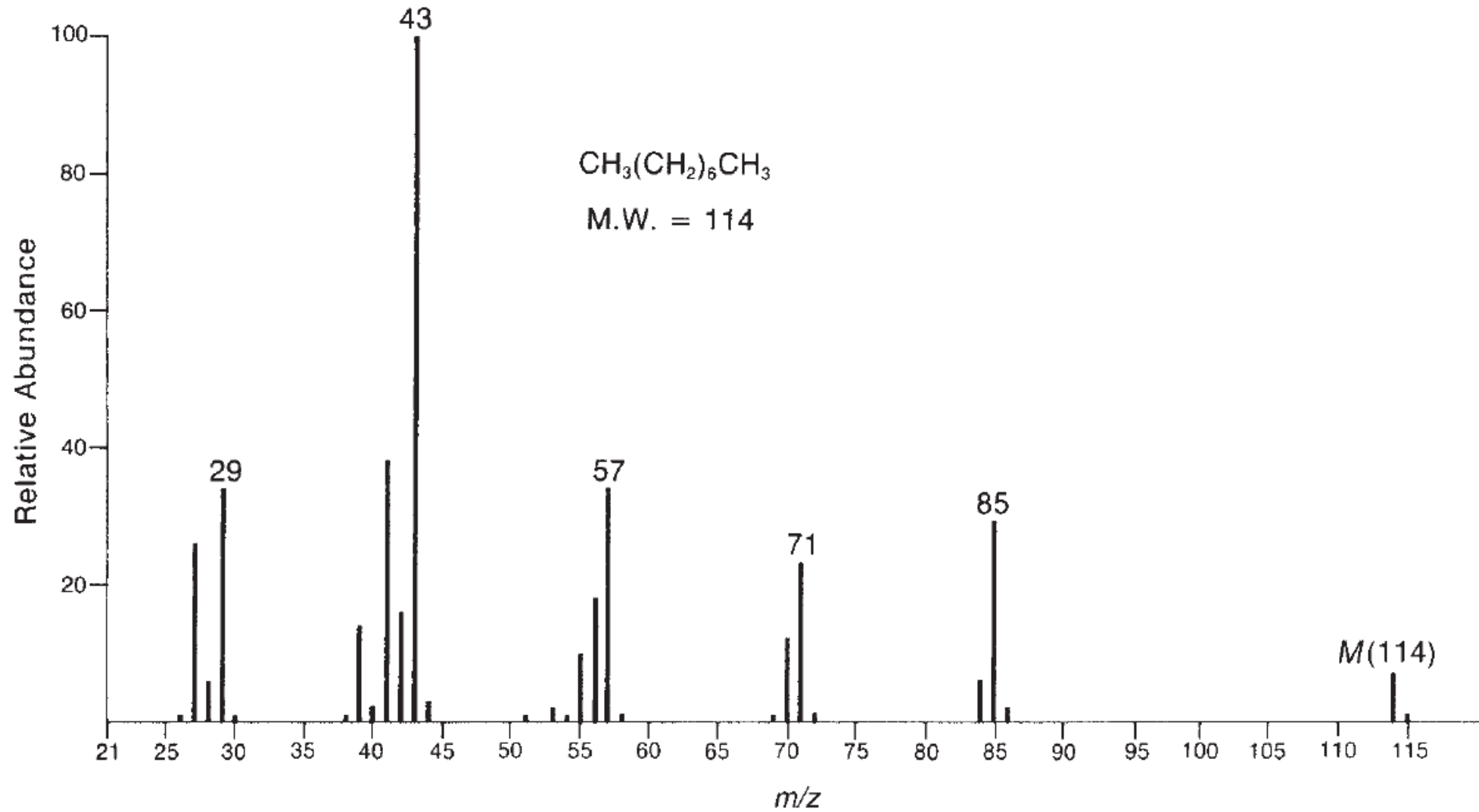
# Mass Spectrometry

Mass spectrum of butane.



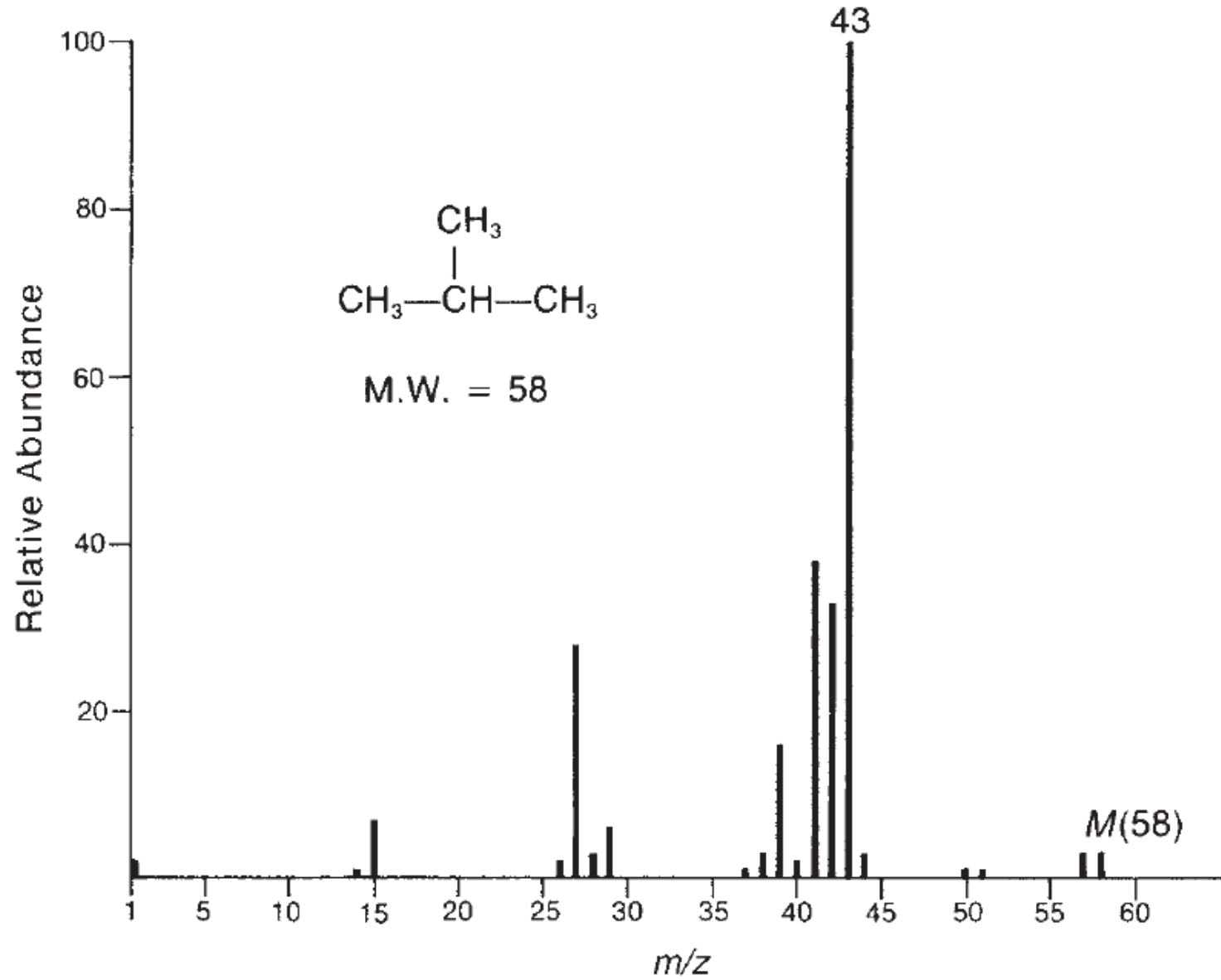
# Mass Spectrometry

Mass spectrum of octane.

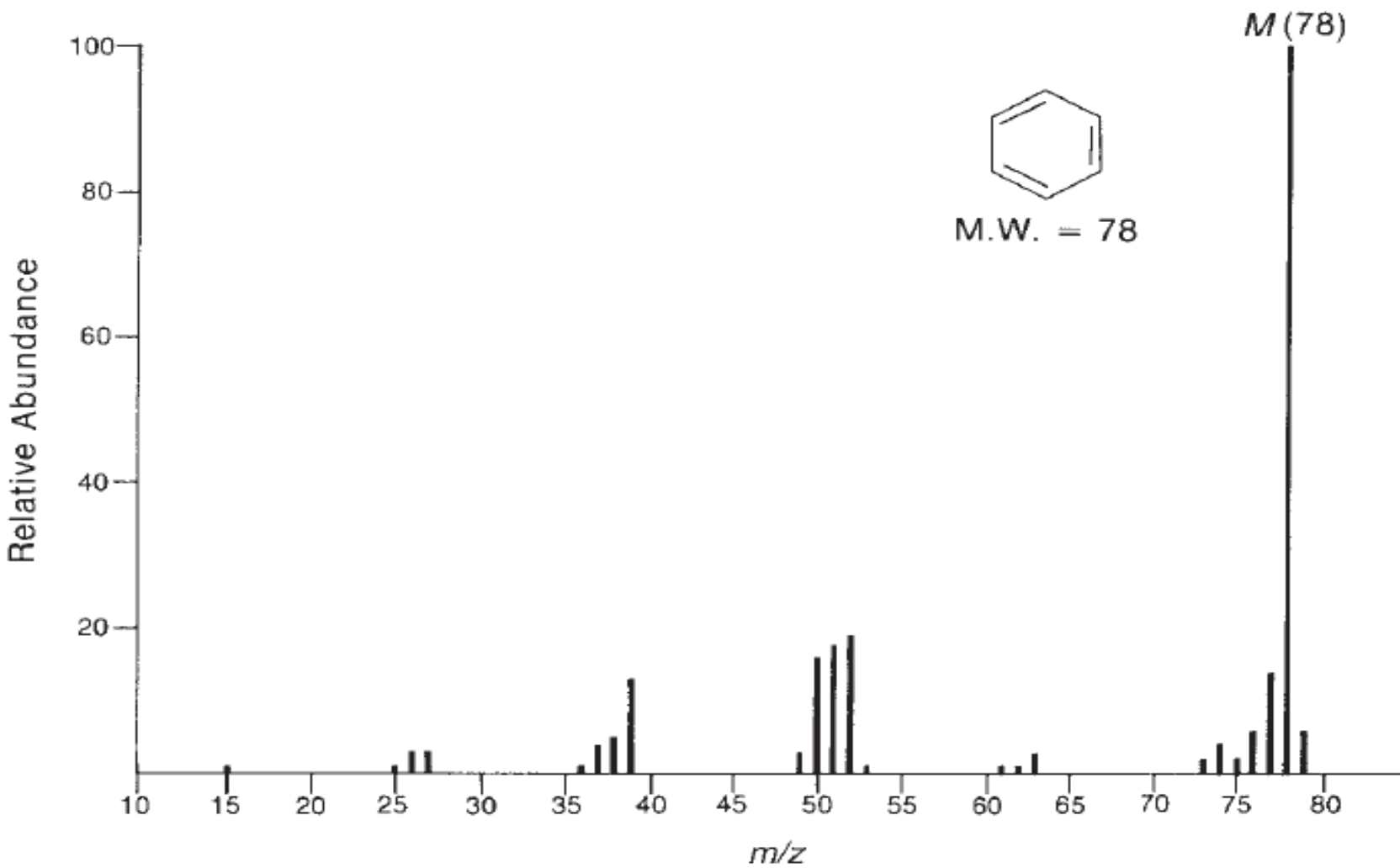




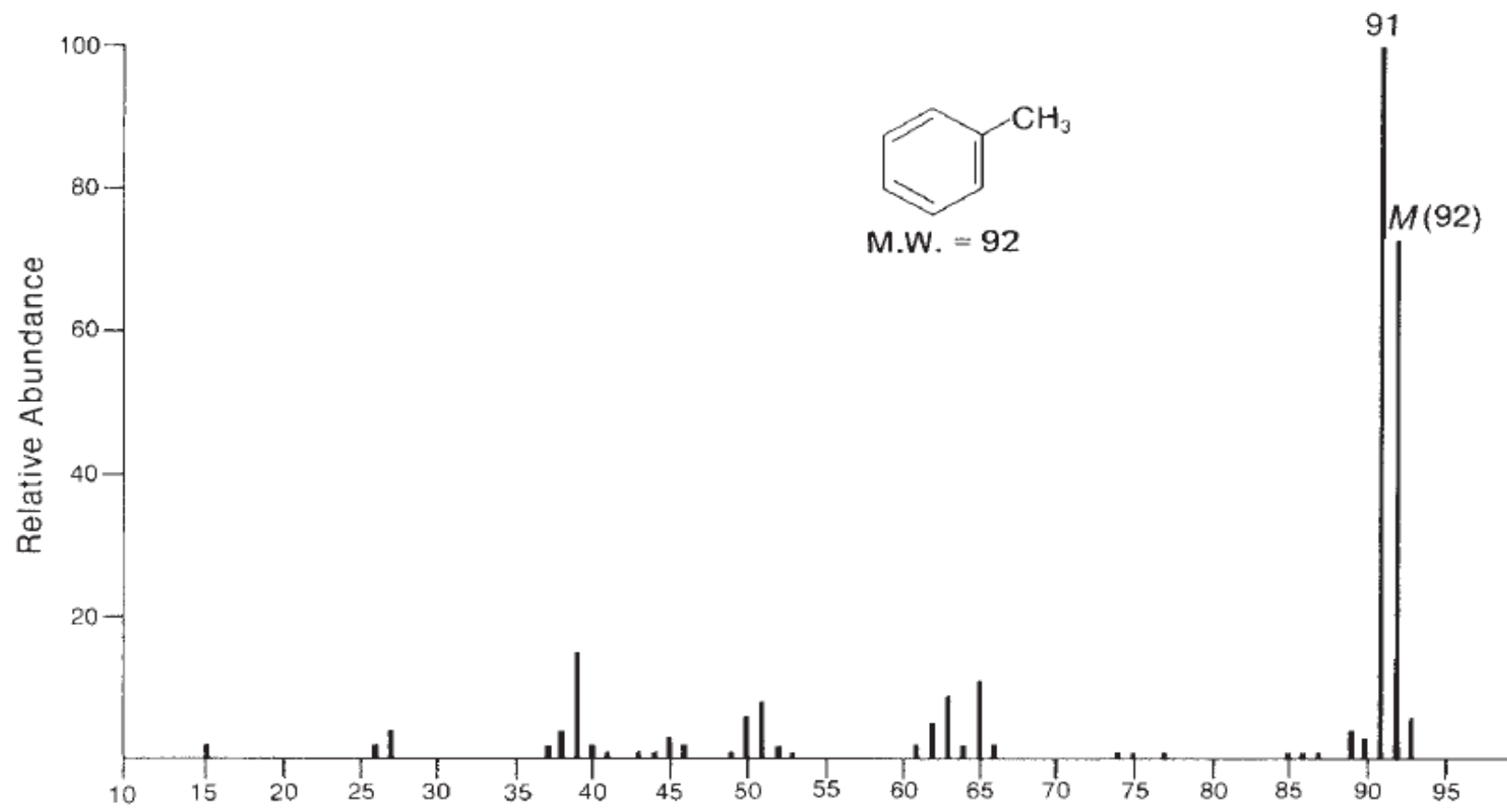
Mass spectrum of isobutane.



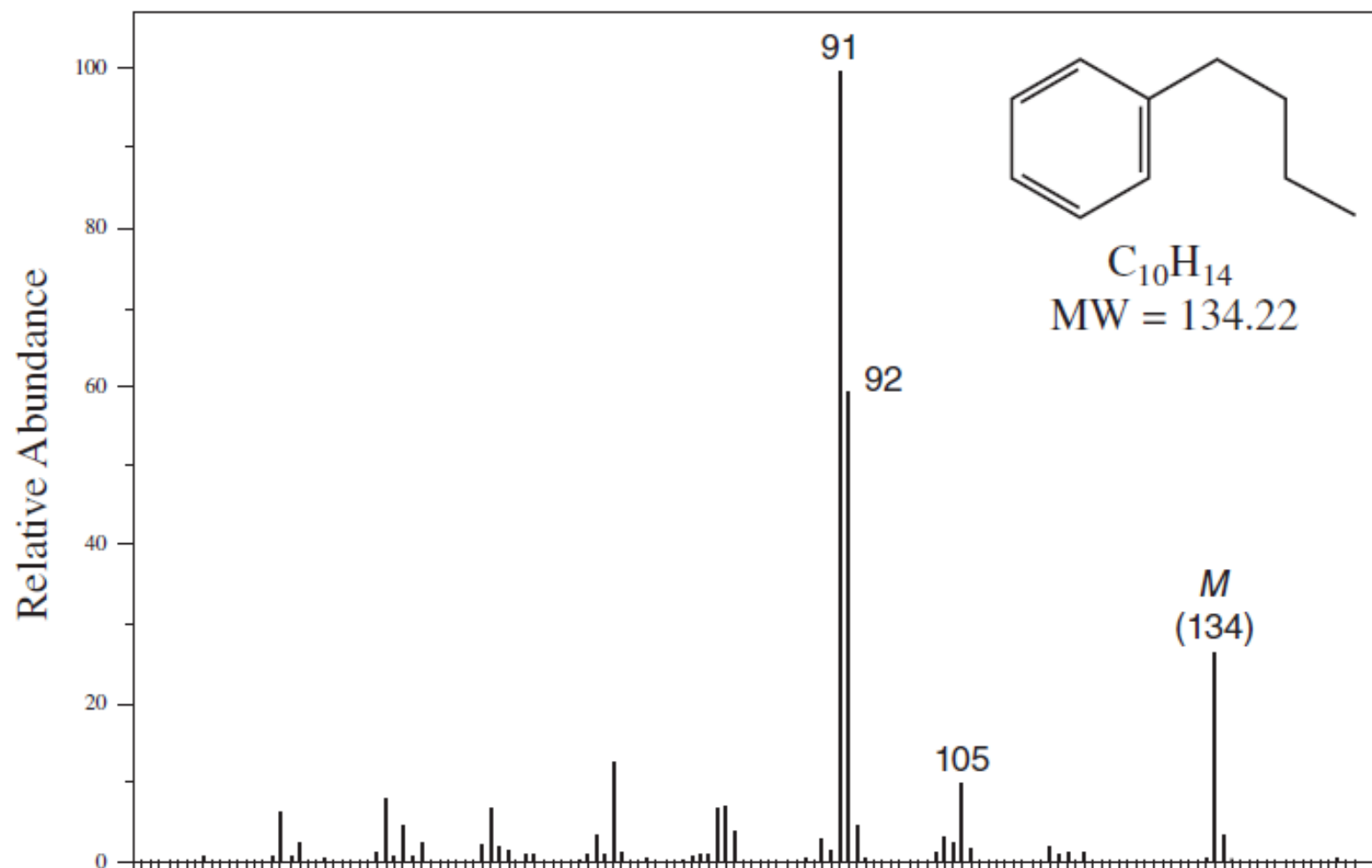
# Mass spectrum of benzene



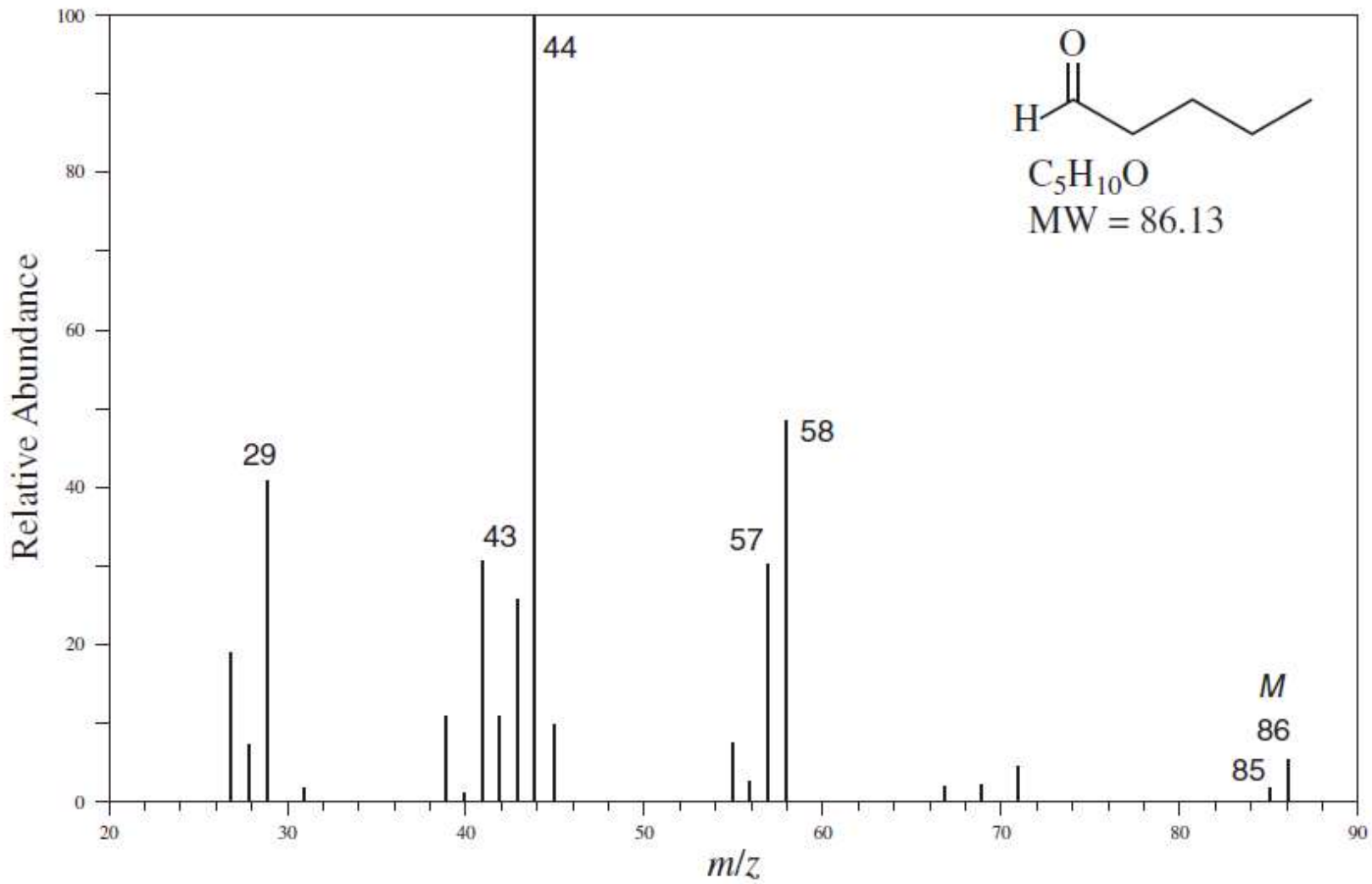
Mass spectrum of toluene.



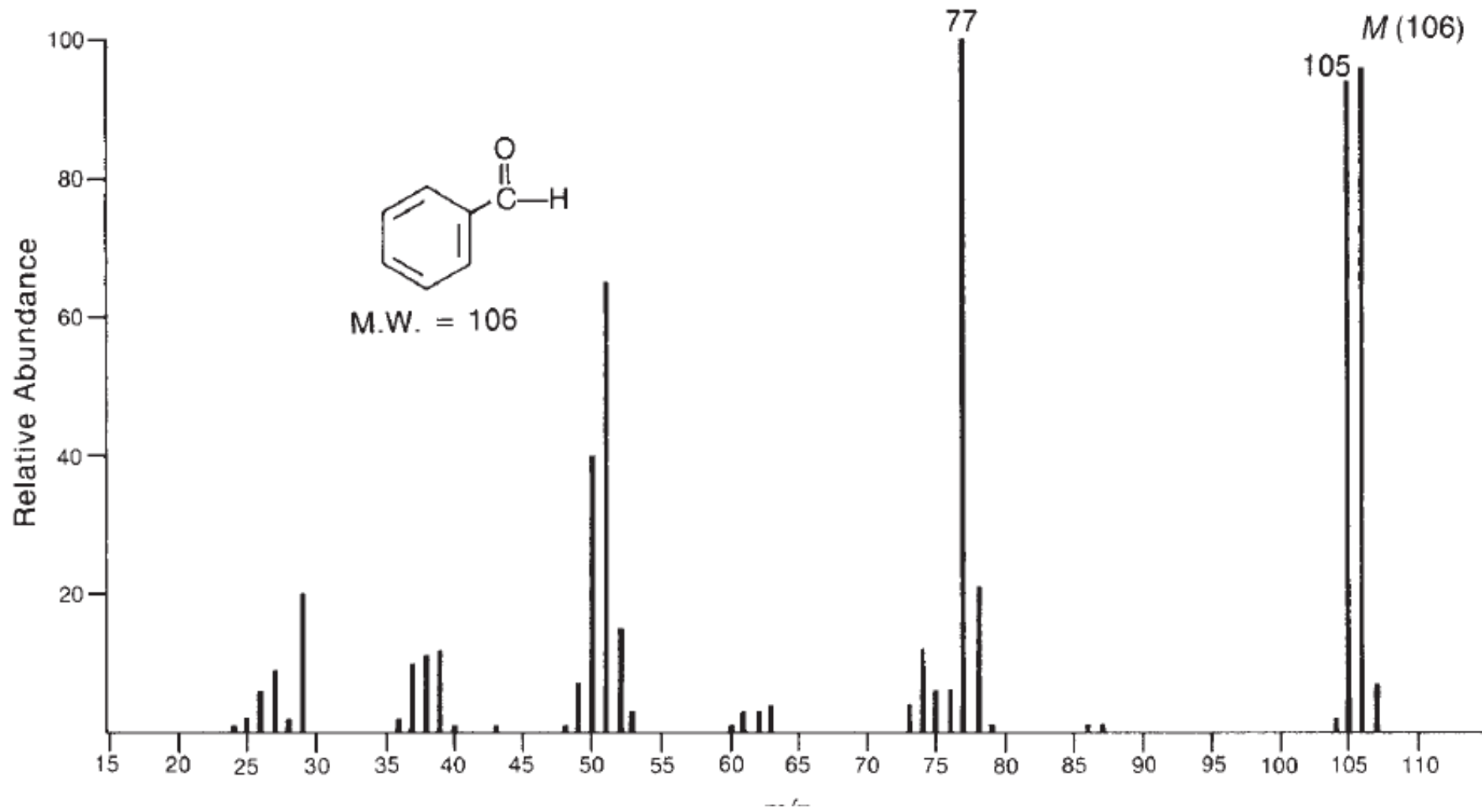
# Mass spectrum of butylbenzene



Mass spectrum of valeraldehyde.



# Mass spectrum of benzaldehyde.



# Mass spectrum of 2-butanone

