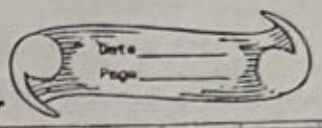
Mass Spectroscopy



⟹ " Analytical technique whose molecules are seperated ~~with~~ by their m/z ratio. "

⟹ molecular mass → measured as Da.

⟶ Mass Spectrometer :—

" An analytical instrument that first ionizes the analytes (molecules) & then seperates and measures the mass of a molecules or its fragments."

⟶ Ions undergoes fragmentn in mass spectrometer.

⟶ Molecular Ions :—

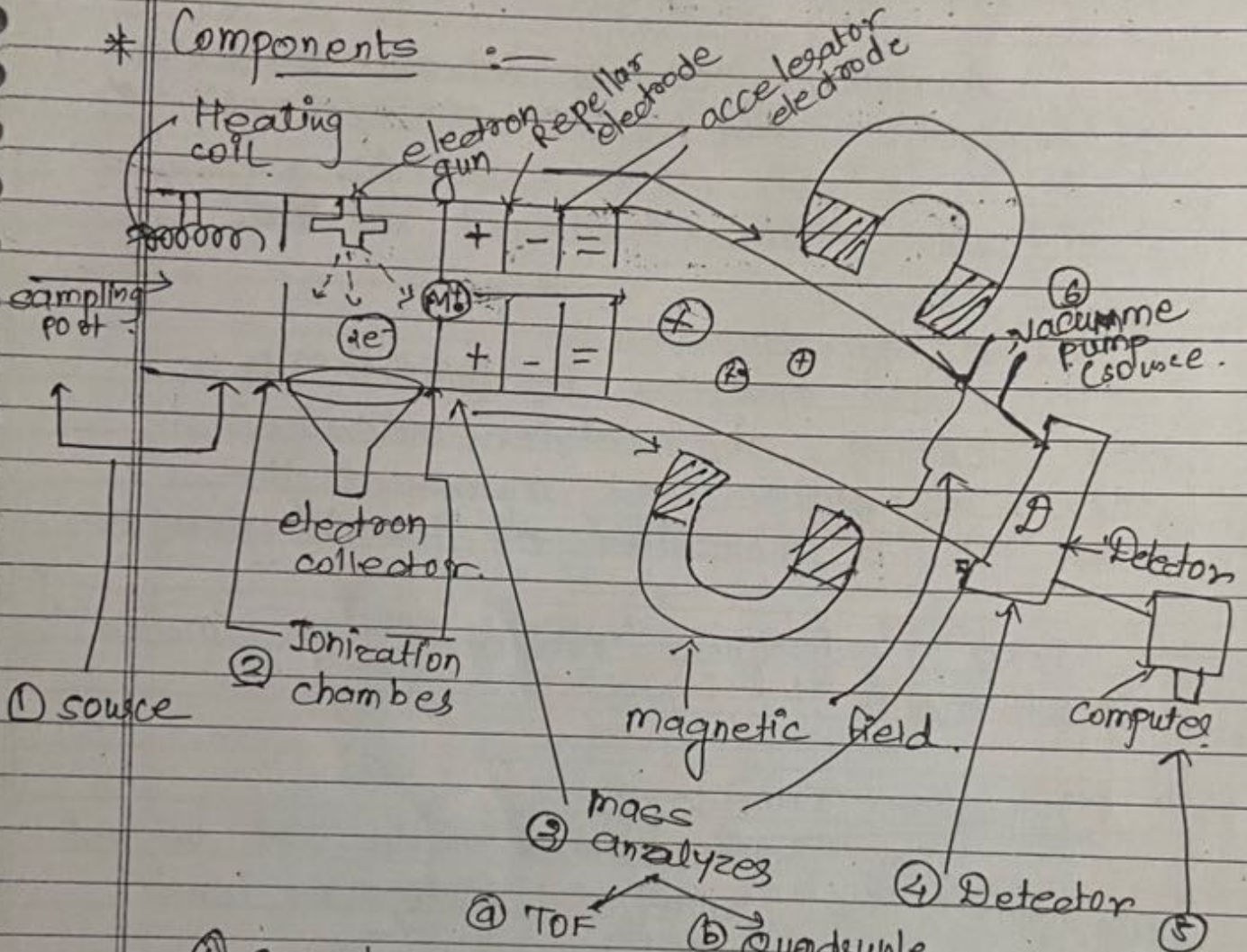
An unfragmented ions of original molecule is called " molecular ions "

↓

Ions that are formed By fragmentn of molecular ions ⟶ i/a " fragment ions ".

— : Instrumentation :—

* Components :—



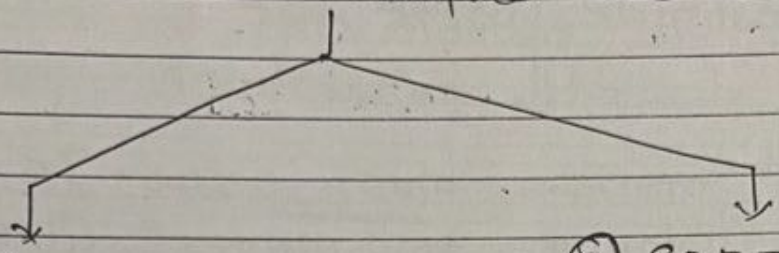
① Sample source
② Ionization chambes
③ Mass analyzes
④ Detector
⑤ computes
⑥ Vacuum source.

① Sample :—

→ Can be analyzed — solid, liquid, gas for
↓
But these have to vaporize first By Heating them

(2) Ionization Source :—

→ Ionization techniques are of 2 types



(A) HARD IONIZATION

→ produces extensive fragmentation ions.

→ (1) Electron Ionization
→ (2) ICP

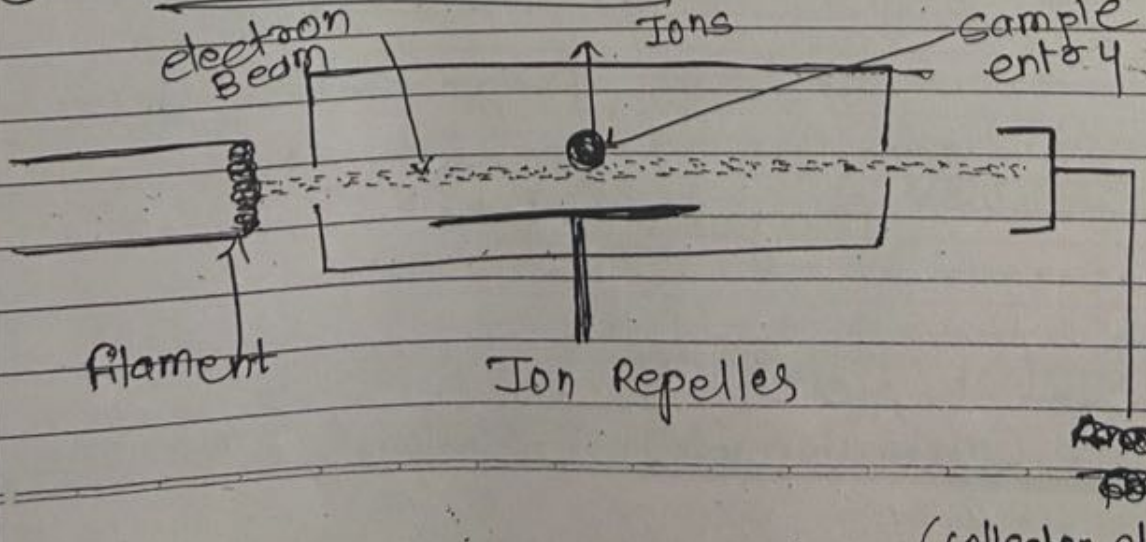
(B) SOFT IONIZATION

→ Very little fragmentation ions are produced.

(1) chemical ionization
(2) Electrospray ionization
(3) APCI
(4) APPI
(5) MALDI

(A) HARD IONIZATION :—

(1) Electron Ionization :—



→ Gas phase molecules are bombarded by electron emitted from a heated filament & attached to a collector electrode

↓

This process must occur in a vacuum to prevent filament oxidation.

↓

Potential difference will generate a electrons with high energy

↓

So these will be collision of electron & organic molecules

↓

produces radical cation (molecular ion)

↓

highly unstable

↓

Undergo fragmentation into cation ion & radicle - k/a "fragment ions"

↓

$AB^{+\bullet}$ (molecular ion) $\longrightarrow$ A^{+} (cation) + $B^{\bullet}$ (Radical)

↓

Cations are repelled out from the ionization chambes by an electrical field & introduced into mass analyzes by accelerating electrode.

→ Application :—

① LC- MS

② Inductive Coupled plasma :— ICP :—

→ ICP source converts the atoms or the elements in the sample to ions.

→ ICP - MS → determination of trace elements & Heavy metal analysis in tissue / Body fluids.

→ Extreme ~~to~~ sensitivity.

Mechanism :—

Sample moleaules are introduced in ICP ionizer in vapour form

↓

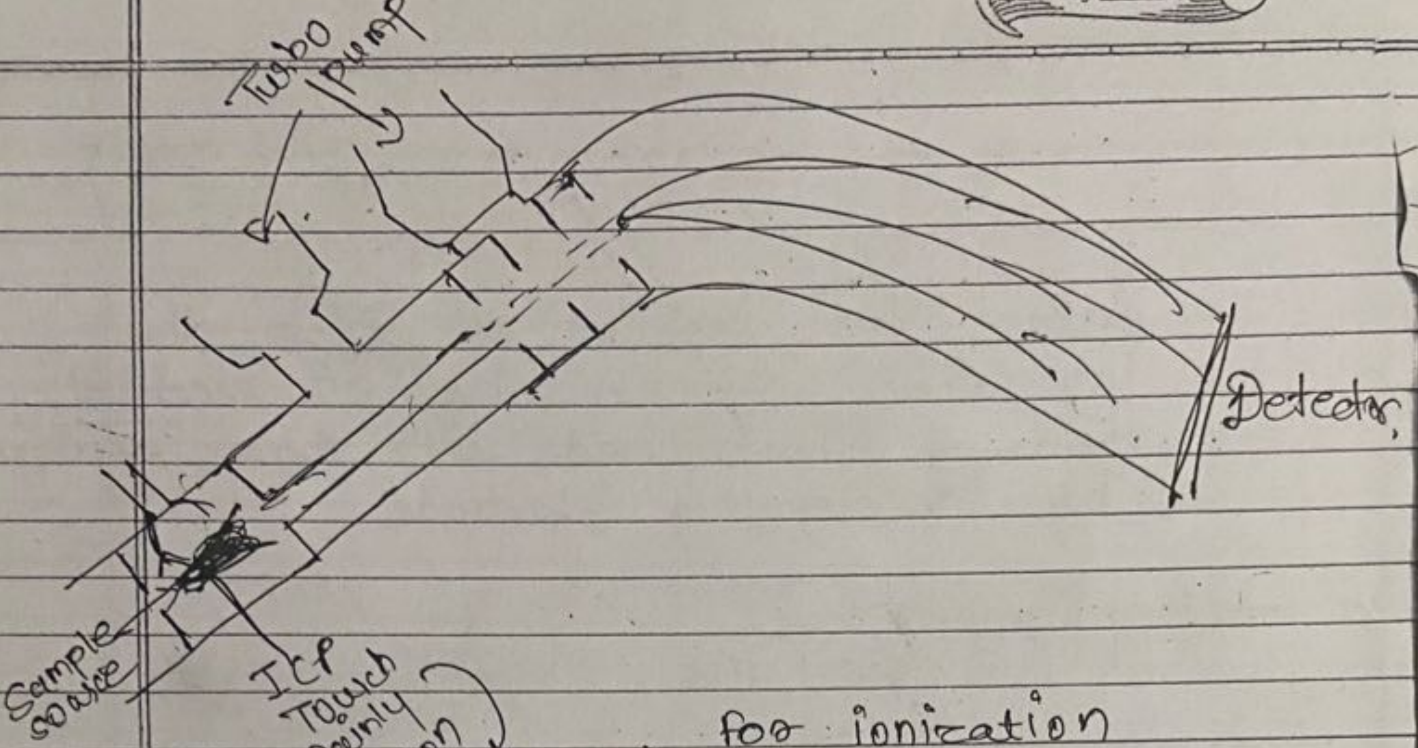
Breaks & ionizes the moleaules

↓

Seperated from neutral moleaules By sample cone

↓

Ions forms sharp beam & travels through analyzer



→ for ionization ↓

$$m + Ar^{+} \longrightarrow m^{+} + Ar^{\cdot}$$

- m ↓ molecule of interest
- Ar^{+} ↑ Argon
- m^{+} ↑ collides & gives electrone charge → Causes ionization.

→ Ar takes e^{-} from m & forms m^{+}

⟹ Plasma can be created by heating a gas or subjecting to a strong electromagnetic field applied with a laser or microwave generator.

B SOFT IONIZATION :-

① Chemical Ionization :-

→ In this technique, a proton is transferred/ gain from a gas phase analyte by a reagent gas molecule

Eg :- methan, Ammonia.

↓

This reagent gas is heated

↓

Generation of reactive gaseous species like $NH_3^{\bullet}$, $CH_3^{\bullet}$ (NH_4^+, CH_5^+)

↓

Interact with themselves

eg:- $NH_3^{\bullet} + NH_3^{\bullet} \longrightarrow NH_4^+ + NH_2^{\bullet}$

cation

$CH_4^{\bullet} + CH_4^{\bullet} \longrightarrow CH_5^+ + CH_3^{\bullet}$

↓

generation of cations

↓

They will interact with analytes (proton donor)

↓

converts the sample into tuely charged molecule

↓

These molecules (tuely charged) are more stable

↓

They undergoes less fragmentation

→ application : ① GC MS

② -ve electrone capture CI : for quantification of drugs like Benzodiazepins.

② Electrospray Ionization :—

→ Samples are ionized at atmospheric pressure before introduction into the mass analyzer.

↓

The sample typically an HPLC effluent, is passed through a narrow metal/ fused silica capillary under high voltage

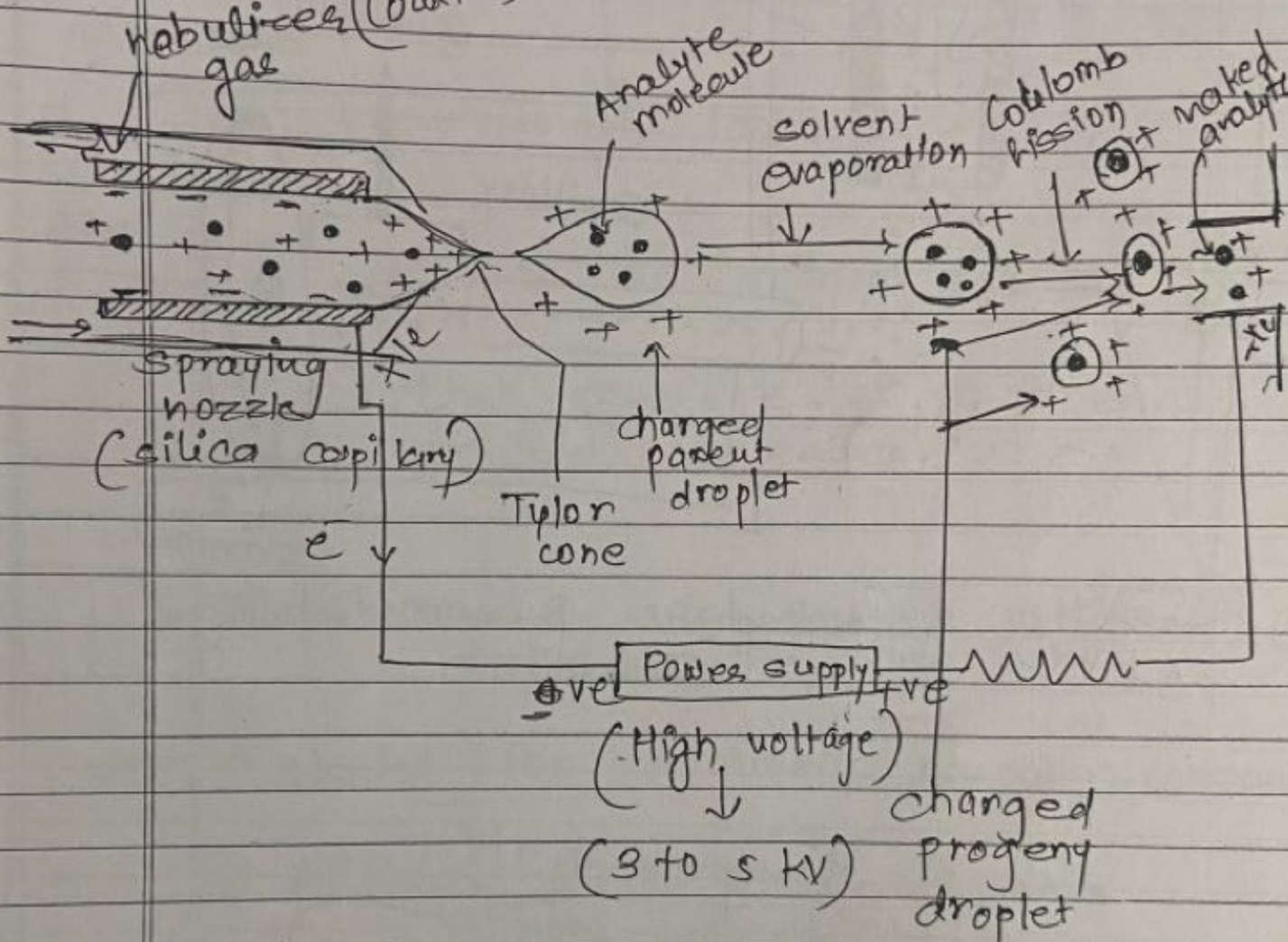
↓

The partial charge seperation b/w the liquid & capillary results in instability in the liquid

↓

Expulsion of a series of charged droplets from a "taylor cone" forms at the tip of capillary.

→ It produces multiple charged ions. Pesticidary from peptides & proteins.



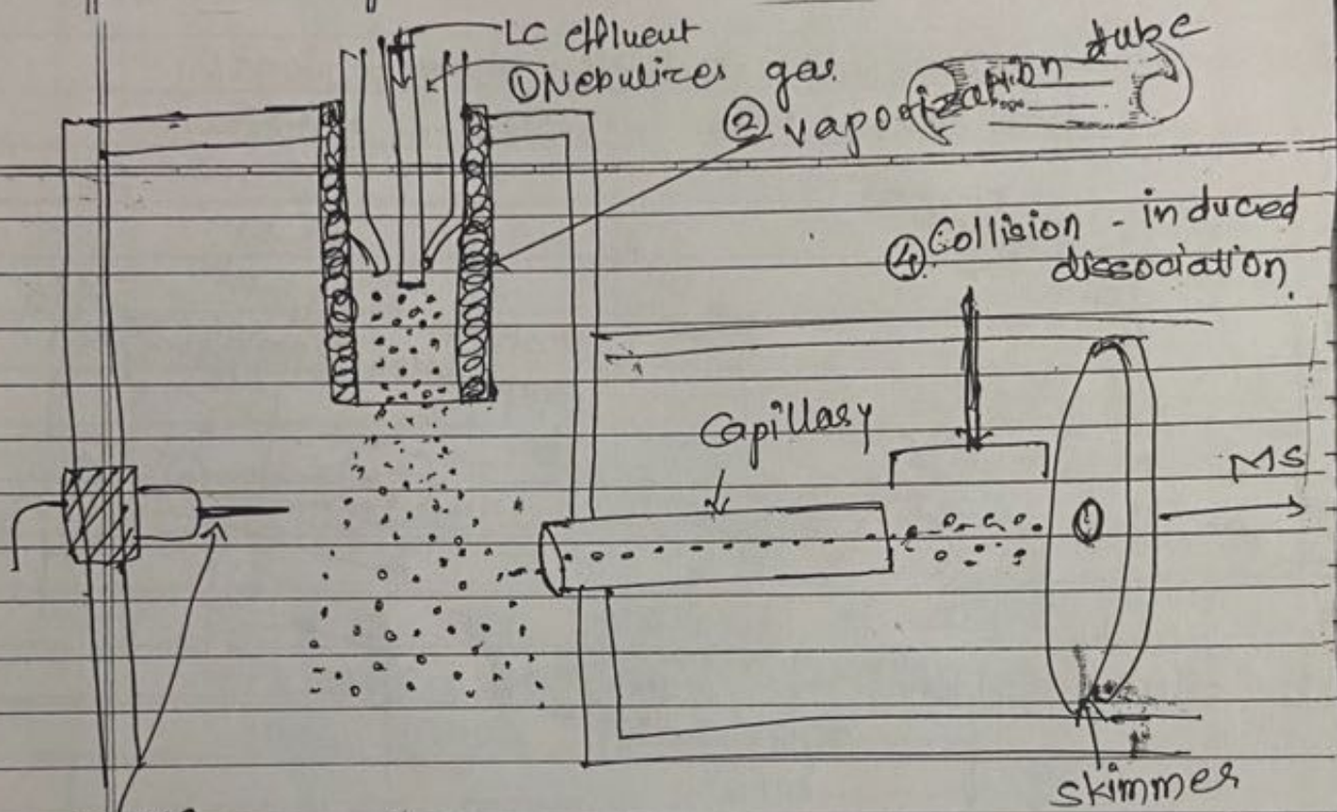
→ Useful for polar compounds

③ APCI :- Atmospheric Pressure Chemical Ionization :-

→ Same as ESI except no voltage is applied to the inlet capillary.

→ key Feature :- use of seperate corona discharge needle to genesate corona discharge.

→ Ions generated by corona discharge undergo - Ion : molecule reaction



[Atmospheric Pressure chemical Ionization]

→ $H_2O + H^+ \longrightarrow H_3O^+$

A (Analyte) $+ H_3O^+ \longrightarrow AH^+ + H_2O$

Cation

↓

Clusters on solvent + analytes.

→ Solvent molecules (eg. ~~use~~ H_2O) are put in excess relative to analytes in the sample

↓

predominatly ionize early.

↓

act as a reagent gas

↓

that reacts & e° to ionize analyte molecules.

→ Skimmes - act as a curtain to declusters the ions.

→ Useful for relatively nonpolar compounds

④ APPI :- Atmospheric Pressure Photo Ionization :-

→ Same as APCI except an ultraviolet photon flux is used instead of corona discharge needle to generate ions.

⑤ - MALDI (Matrix Assisted Laser Desorption / Ionization)