analytical chemistry

The branch of chemistry that deals with complete characterization of compound is called Analytical chemistry i.e qualitative & quantitative analysis.

qualitative: identification of substance (salt analysis, detection)

quantitative: amount of each component present in sample (% titration, volumetric analysis)

Classical method of qualitative analysis

Combustion Analysis

Used for:

This method is merely used for Organic Compounds

Purpose:

It's used to calculate empirical & molecular formulas for Organic Compounds.

Products:

The CO_2 & H_2O can only be detected & are separately collected.

drawback:-

Complexity: The Process can be complex & requires precise control of conditions to ensure accurate results.

Sample destruction: The sample is completely burned, so it can't be recovered or re-used.

Interefeence: Other elements or Compomds present in sample can interfere with analysis, leading to inaccurate results.

Cost: The equipment & materials needed for Combustion analysis can be expensive.

Time- Consuming:- The Process can be time-consuming, especially if multiple samples needed to be analyzed.

Application:- The Process is only applicable only to C, H & O atoms.

Empirical & molecular formula

• Empirical formula:

1) % of each element

$$\% C = \frac{\text{mass of C}}{\text{mass of Compomd}} \times 100 \times \frac{12}{44}$$

$$\% H = \frac{\text{mass of H}}{\text{mass of Compomd}} \times 100 \times \frac{2}{18}$$

$$\% O = 100 - (\% C + \% H)$$

2) Moles of each element

$$\text{Mole} = \frac{\% \text{ of element}}{\text{atomic mass}}$$

find mole ratio of each element

$$\text{atomic ratio} = \frac{\text{mole of element}}{\text{least value of moles}}$$

to find

$$n = \frac{\text{Molecular Molar mass}}{\text{empirical formula mass}}$$

find Molecular formula

Molecular formula = n(empirical formula)

Review Question #2

Give data:

mass of compound = 0.5439g

mass of CO_2 = 1.039g

mass of H_2O = 0.6369g

Required:

Empirical formula = ?

Solution:

% of C:

$$\%\text{ of } C = \frac{1.039}{0.5439} \times \frac{12}{44} \times 100 = 52.09\%$$

% of H:

$$\%\text{ of } H = \frac{0.6369}{0.5439} \times \frac{2}{18} \times 100 = 13.01\%$$

% of O:

$$\%\text{ of } O = 100 - (52.8 + 13.01).$$

= 34.89%

moles :-

C:

mole of C = $\frac{52.09}{12}$ = ~~4.4~~ 4.34 mol.

H:

mole of H = $\frac{13.01}{1}$ = 13mol

O:

mole of O = $\frac{34.89}{16}$ = 2.18 mol

mole ratio:

C :- $\frac{4.34}{2.18}$ = 2

H: $\frac{13.01}{2.18}$ = 6

O: $\frac{2.18}{2.18}$ = 1

empirical formula:

C_2H_6O

Question # 3.

Given data:

% C = 65.44%

% H = 5.50%

% O = 29.06%

molecular mass of compound = 110.15 g/mol.

Required:

empirical formula = ?

Molecular formula = ?

Solution:-

moles:

C:-

$$\text{moles of C} = \frac{65.44}{12.} = 5.45 \text{ moles}$$

H:-

$$\text{moles of H} = \frac{5.50}{1.008} = 5.45 \text{ mole}$$

O:-

$$\text{moles of O} = \frac{29.06}{16} = 1.815 \text{ mole.}$$

mole ratio:-

C:

$$\text{ratio} = \frac{5.45}{1.815} = 3$$

H:

$$\text{ratio} = \frac{5.45}{1.815} = 8$$

O :-

ratio = $\frac{29.06}{1.815} = 1$

Empirical formula:

C_3H_3O

molecular formula:

empirical formula = $12 \times 3 + 1 \times 3 + 16 \times 1$

$= 55\ g/mol$

$n = \frac{110.15}{55} = 2$

molecular formula:

$= 2 \times (C_3H_3O)$

$= C_6H_6O_2$

modern method of analysis

Spectroscopy

The Branch of Science which describes the interaction of electromagnetic radiation with matter is known as Spectroscopy

OR

Electromagnetic radiation is in form of energy Commonly known as Radiation energy such as Cosmic rays, Gamma rays, X-rays, UV, Visible light, Infra-red, Microwaves, Radiowaves

highest energy, frequency, wave no. & low λ.

→ **Principle :-**

Different molecules absorb different amount of radiation when they interact with them.

lower energy radiation causes :-

- molecular rotation
- Bond cleavage

High energy radiation causes:

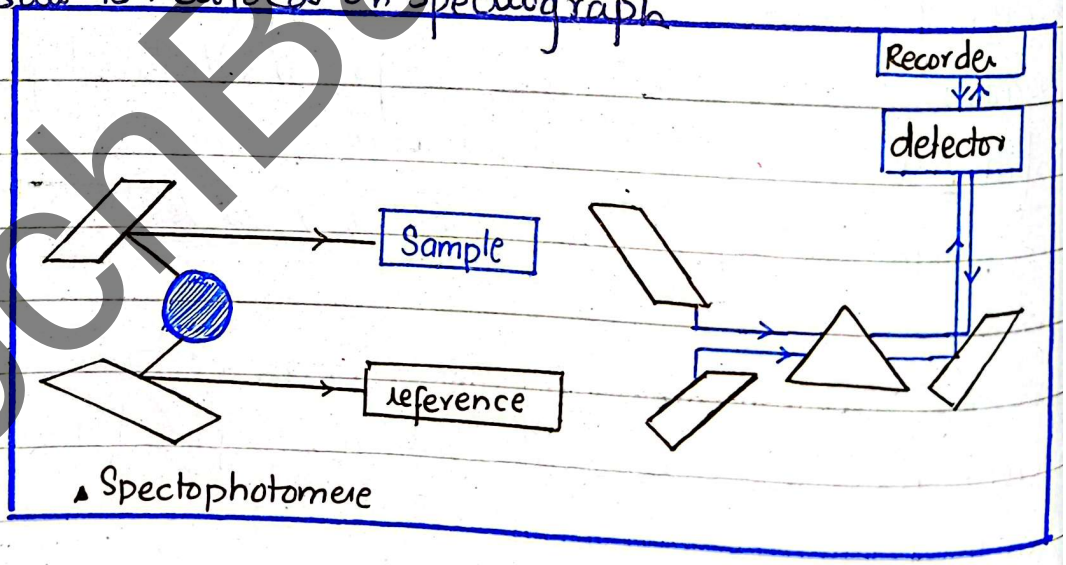
- electronic excitation.
- Bond cleavage.

Spectrophotometer:-

An instrument that is used to measure the amount of electromagnetic radiation absorbed or emitted by a compound.

Construction:

- A light source of radiation.
- A sample Cuvette.
- Prism (mono chromator).
- Detector
- Result is Recorded on Spectrograph



▲ Spectophotometer

Infrared Spectroscopy

The Spectroscopy that deals with the study of electromagnetic radiation of matter with IR region is called Spectroscopy.

range:

It's range lies in terms of wave no & wavelength.

Wave no: 4000 cm^{-1} to 625 cm^{-1}.

wavelength: 2.5 um - 16 um.

Principle / effect:

It's called Vibrational motion within Molecule.
(Vibrational Spectroscopy).

Basic Principle:-

- A molecule is made up of large number of atoms.
- These continuously undergo Vibration & rotation.
- Since IR have low energy So it only effect the Vibrational K.E of atoms causing a small displacement of atoms from mean position changing its dipole moment.

↳ validmostly for Polar Molecule.
They are IR active polarity will change.

Application / Use / Purpose :-

- Helps to identify bonds & functional groups.
- Identify structue of Organic Compound.

Types of Vibration :

→ 2 types :-

Stretching vibration :

- Bond length change
- Bond angle remains constant.

Bending vibration :

- Bond angle change.
- Bond length remains constant.

Types of Region :

Finger Print Region :

600 – 1500 cm^{-1}

- Shows characteristic of Compound.
- Different Compounds give diff peaks in this Region.
- This Region is used to Identify structural of Organic Compound.

Functional Grap Region :

1500 - 4000 cm^{-1}

- Diff functional Groups shows diff absorption in this Region.

ultra violent Spectroscopy

→ electronic Spectroscopy ←

The Spectroscopy that deals with study of interaction of electromagnetic radiation with matter in U.V region.

range:

UV region: 200 - 400nm

Visible region: 400 - 800 nm.

Principle/effect:

It involves transition of electrons within molecule or ion from lower energy level to higher energy level by absorbing UV or Visible Radiation.

Purpose/use:

- Helps to determine the presence of Unsaturation & extent of Conjugated in molecule

Principle of UV visible Spectroscopy:

The absorption of UV visible radiation causes the excitation of e^- from lower to higher energy levels.

(HOMO - LUMO).

highest occupied molecular orbital → lowest Unoccupied molecular orbital

Types of e⁻ present in molecule:

i. Sigma e⁻ (σ)
ii. $\bar{\pi}$ e⁻ ($\bar{\pi}$)
iii. Non-bonding e⁻ (n)

Types of electron transition:

- $\sigma \rightarrow \sigma^*$:

- Transition occur in saturated hydrocarbon (alkane & cycloalkane).
- The Sigma e⁻ are strongly held together & UV region is not so energetic to excite e⁻s.
- Thus Requires energy in range of 150nm.
- Occurs in Vaccum Region.

- $n - \sigma^*$:

- Transition occurs in saturated molecule containing heteroatom. ($CH_3-\ddot{O}H$).

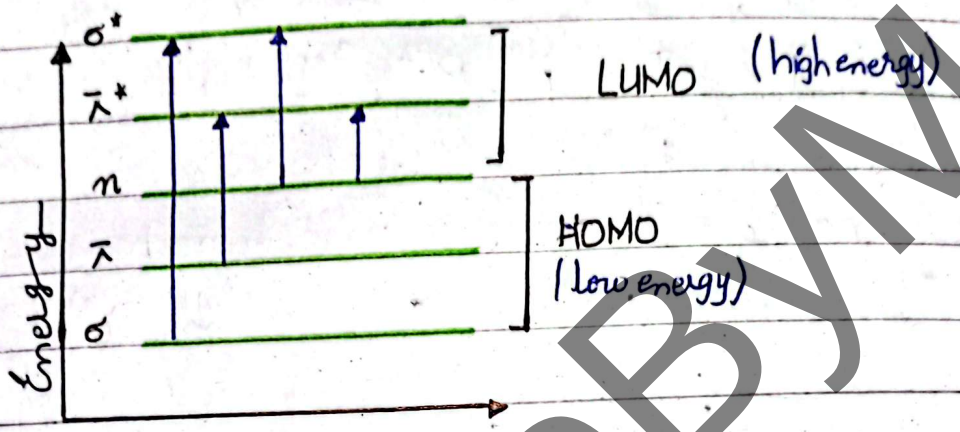
- $\bar{\pi} - \bar{\pi}^*$:

The Transition occurs in Unsaturated Compound = & ≡ bond.
(C=C), (C≡C), (C=O).
(1,3-butadiene).

- $n - \bar{\pi}^*$:

The Transition occurs in molecule where double bond or triple bond invdving heteroatom.

- Requires least energy
- Occur at longer λ.
  (aldehyde & Ketone).



order:

$n - \pi^* < \pi - \pi^* < n - \sigma^* < \sigma - \sigma^*$

unsaturated | saturated | lone pair heteroatom | saturated

Nuclear magnetic resonance

The Spectroscopy which deals with study of interaction of electromagnetic radiation with manner in radio frequency region (4MHz - 750MHz) is called NMR Spectroscopy.

Spin active :

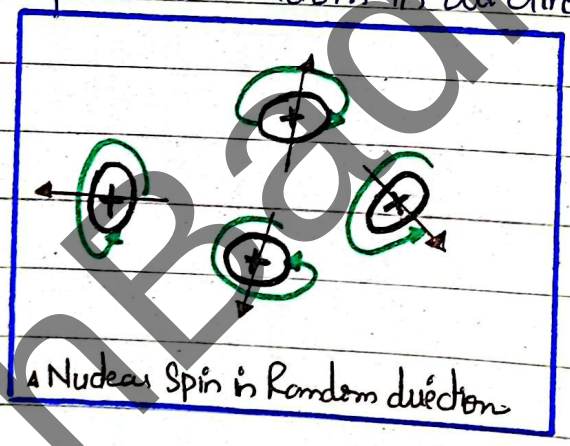
Nuclei which contain odd number of proton or neutrons or both are Spin active. like es these nucleus also spin about their own axis. & behave like tiny magnet. (F^{19}, P^{31}, ^{13}C, ^{1}H)

Spin in-active :

Nuclei having even no. of protons & neutrons are Spin in-active have zero Spin. (C^{12}, O^{16}).

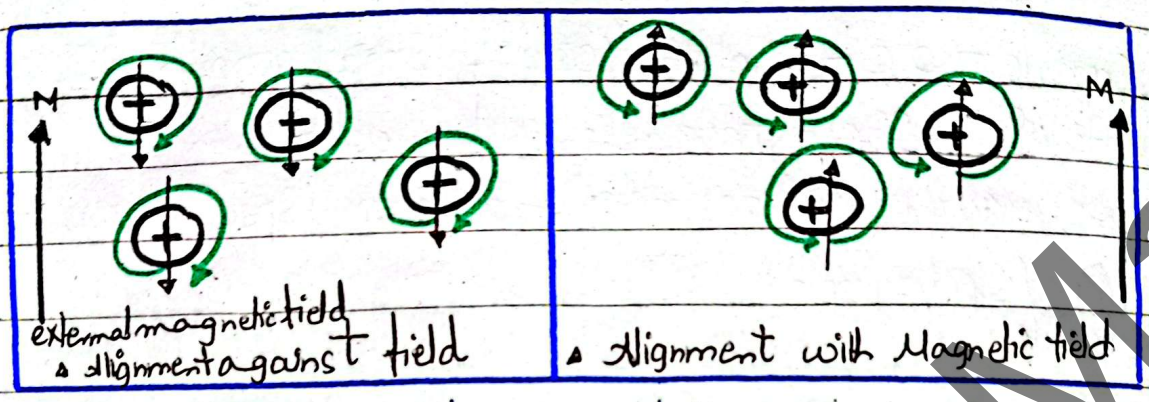
Basic Principle :

Without an external applied magnetic field, the nucleai Spin are random in all direction.



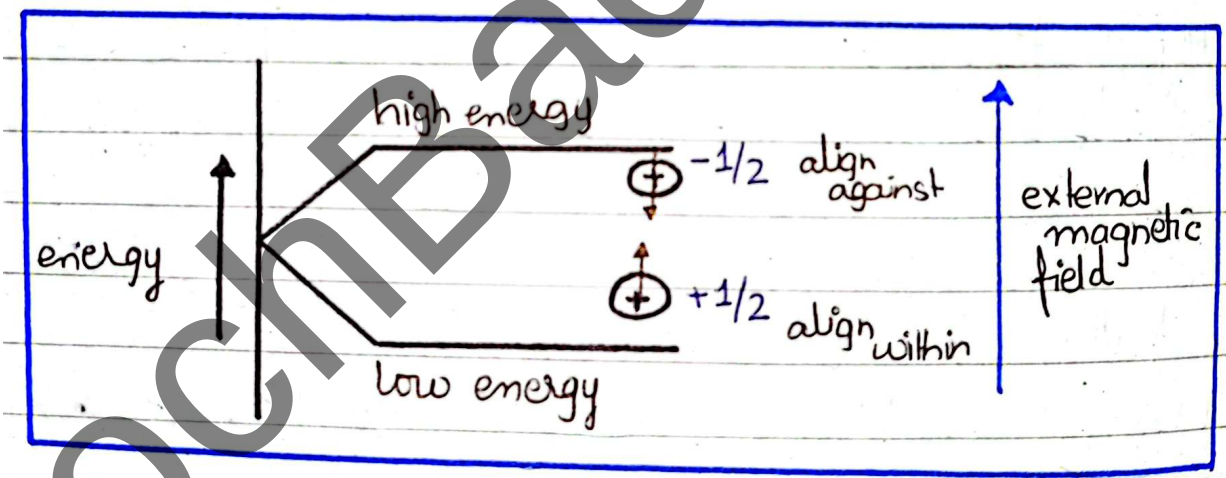
Nucleai Spin in Random direction

- When external Magnetic field is applied nuclei align themselves either ~~or~~ with or against field of external magnetic field. As a Result the Spin is split into 2 energy levels.
  - Low Energy $+1/2$ (Parallel)
  - high Energy $-1/2$. (Anti- Parallel)



- The energy difference b/w 2 spin state is very small & lies within Range of Radiowave.
- At Particular Combination of Magnetic field & frequency of Radiowaves, some nuclei change their spin state. this phenomena is called flipping.

$+1/2 \rightarrow -1/2$.
low high



Types:

- Proton NMR
- Carbon NMR
- Nitrogen NMR

Working:

Sample of o.c + Solvent (CCl_4) + Small amount of TMS ($(CH_3)_4Si$) + Strong magnetic field + radiowaves (rft: radiowaves transmitter) + detector (Spectrometer).

→ peaks (spectrograph)
→ fourier

Chemical shift: δ

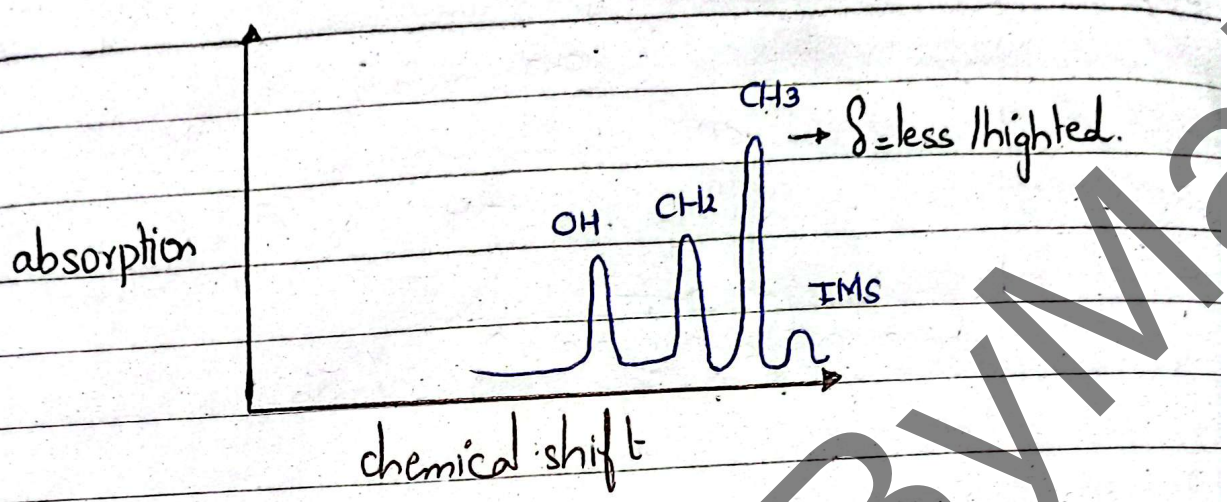
The Separation of absorption position of particular proton from absorption position of Reference is called chemical shift.

- ppm
- Common value for most of the Organic Compound is 0.0 - 10 δ.
- High shielded protons require lower frequency to resonate & low chemical shifts.

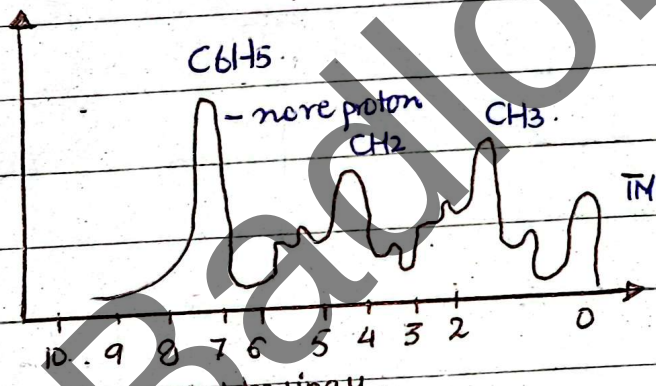
Proton NMR Spectra :-

- If all proton in a molecule are Similar as in CH_4, C_6H_6, their Spin state are equal & produce a Single peak.
- Proton in different environment requires slightly diff magnetic field to Resonate to show diff peak.
- Area under Peak $\propto$ no. of proton involved.
- Area under peak = height = No. of Proton.
- Value of chemical shift = how far away it's from E.N atom.

ethanol :



ethyl benzene :



$C_6H_5-CH_2-CH_3$

No. of peak = $n+1$ (CH_3)

= 2 + 1

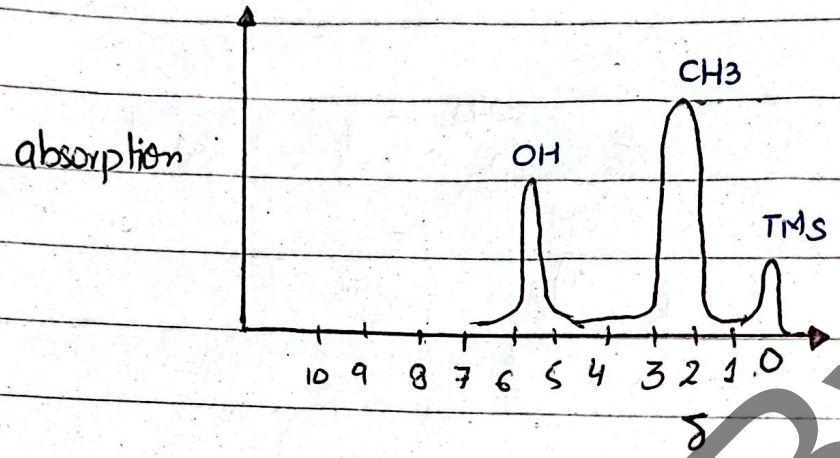
= 3 triplet

No. of peak = $n+1$ (CH_2)

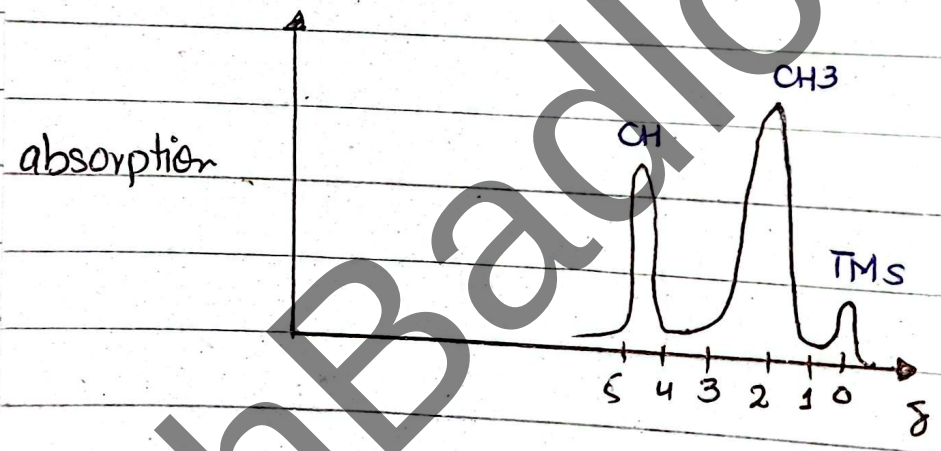
= 3 + 1

= 4 quadriplet.

methanol



2. Methyl Propane



Atomic Emission Spectroscopy

It is technique used to study the composition and structure of atoms by analyzing the light they emit.

Principle: 1

- When electronic transition occurs.
- When the energy is given to e^-, they become excited & moves to higher energy level. Due to unstability, it falls back to its original energy level by emiting photon at specific λ.
- Creating a Unique Spectrum for each element

Reading:

- In atomic Emission Spectroscopy, we read the spectrum via wavelength or frequency

Principle: 2

Excitation & Vapourization:

The Sample is introduced to any energy source i.e flame, inductively Occupied plasma (ICP) or an electrical discharge. They vapourizes the sample & provides sufficient energy to excite e^-s

Emission:

When atoms absorb energy, their e⁻s are promoted to higher energy level. As they return to ground state. They emit light at characteristic λ.

detection:

The emitted ~~sample~~ light is collected & passed through a Spectrometer, which separates light into components. The colored lines are separated by dark spaces.

Analysis:

The intensity of emitted light at each λ is measured.

The intensity ∝ Conc. of corresponding element in Sample.

The element is also detected by observing the spectrum

Colors: (line emission spectrum)

Each element has it's own color.

- Na → Yellow
- K → Violet
- Sr → red

] bunsen burner flame test

Each gase has it's own color.

- Ne → orange red
- H_2 → blue
- He → orange pink
- Cl_2 → yellow green / orange green

Differences:

Atomic Line Spectrum	Atomic Absorption Spectrum
Background	
• Dark	• light / Bright
Appearance	
• Bright lines on a dark background	• Dark lines on a bright background
Process	
• Emission of light by excited atoms.	• Absorption of light by ground-state atoms.
Energy Source	
• External energy source	• Continuous light source
Light interaction	
• Atoms emit light at specific λ.	• Atoms absorb light at specific λ.
Spectrum	
• Unique to each element, showing emitted λ.	• Unique to each element, showing absorbed λ.
Temp	
at high temp	at low temp
State	
substance in gaseous state.	Substance in liquid state.

Application of emission Spectroscopy:

- Used to detect 40- element
- Trace major Constituents in ceramics
- Traces of Co, Ni, Mo & V in Graphite
- Trace metal impurities in analytical reagents.
- Trace of Ca, Cu, Zn in blood
- Zinc in pancreatic tissue.

Application of absorption Spectroscopy:

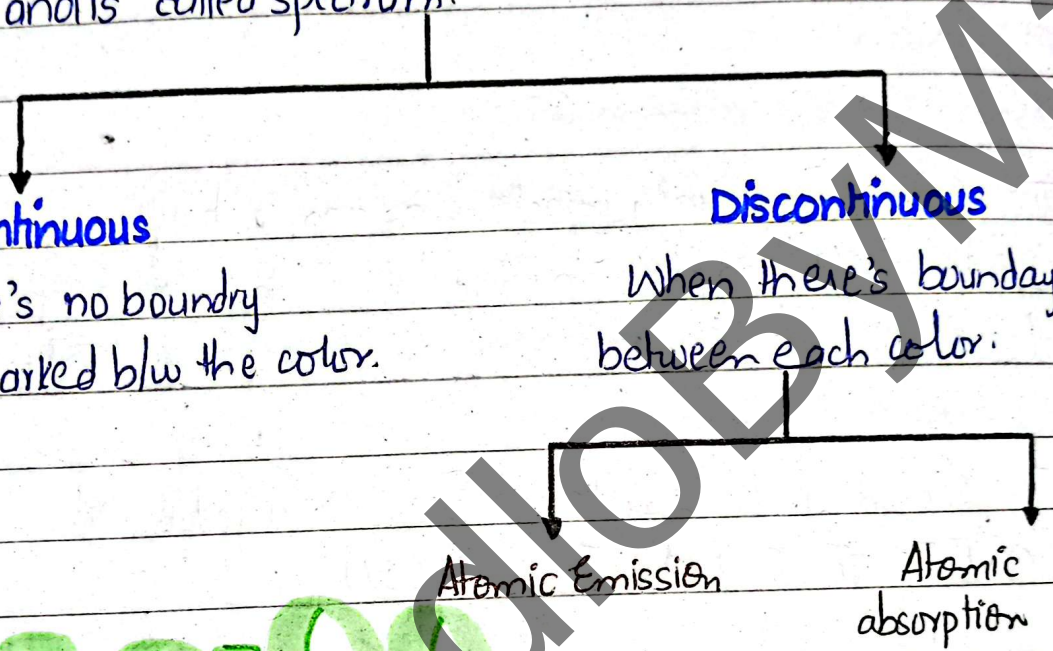
- Small conc of Sample is used
- highly Specific
- analysis of a metal from a complex mixtue is possible & a high energy source needs tnot be employed.
- Analysis of substance including ceramics mineralogy, biochemistry, metallurgy, water Supplies & soil analysis.

merits & demerits

merit	demerits
• Results are accurate & fast • Acurate than flame test • High Sensitivity • Multi-element analysis.	• Costly instrument • Maintenance is expensive. • Need experienced ppl

Spectrum & it's types :

When white light is passed through prism it's splitted into diff λ, each λ coresponds to diff color. This band is called spectrum.



mass Spectroscopy

The technique in which mass Spectrometer is used to detect mass spectroscopy

used to determine:

- isotope of an element
- relative abundance of isotope
- Relative atomic mass
- Molecular mass
- Molecular structure of molecule

mass Spectrometer:

An instrument which is used to measure the exact mass of isotopes & their relative abundance.

Principle:

Vapourization:

The Sample is usually injected as gas but if liquid or solid sample is introduced then it may be evapaurated in evaporation chamber (10^{-6}-10^{-7} torr)

Ionization:

The Sample is ionized to produce charged particles via EI, ESI, MALDI (70eV)

acceleration:

The ions are accelerated by an electric field, which imports them K.E (500-2000 V) → -ve

deflection:

The ions are then passed through a magnetic field which deflects them based on their mass-to-charged ratio. The angle of deflection $\propto \frac{1}{\text{charge to mass ratio}}$

- Lighter ions with o higher charged are defleted more than heavier ions with low charge

$$m/e = \frac{H^2 r}{E}$$

H → strength of M.F
r → radius of circular path
E → strength of E/F

detection: ion collector electrometer.

They are detected which measures the intensity of ions at diff m/e ratio. It displays their corresponding intensities.

mass Spectrum:

- It's a graph b/w mass no or m/e ratio taken on x-axis (abscissa) & relative abundance taken on y-axis (ordinate)
- No. of peak = possible isotopes
- height $\propto$ abundance

numerical of relative atomic mass

$$\frac{(\text{mass of isotope} \times \text{Natural abundance}) + (\text{mass of isotope} \times \text{Natural abundance})}{100}$$

How to identify structure.

Taking example of Propane.

$CH_3 / CH_2 / CH_3$

- break into fragments.
- Then convert into possible ions.

CH_3^+, CH_2^+, $CH_3^+ - CH_2$, $CH_3^+ - CH_2 - CH_3$

peak = 15 peak = 14 peak = 17 peak = 44.

detector :-
- Ions having definite m/e ratio is collected ion collector.
- produce diff current value for diff ion.
- heavy ions have more current value & higher peak
amplifier :- ^{12}C standard
- increase value of current

Recorder :-
graph b/w relative abundance & m/e ratio.

...ometer.

...es the intensity of

...ys their corresponding

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Review Q/S

iii- Q2.

Data:

a) $\lambda max = 223\,nm$

b) $\lambda max = 178\,nm$

Find:

Structure of the isomers = ?

Solve:

a) 1,3- Pentadiene.

Conjugated alkene → stable

$$CH_2 = CH - CH = CH - CH_3$$

b) 1,4- Pentadiene

isolated alkene → less stable

$$CH_2 = CH - CH_2 - CH = CH_2$$