

CHAPTER 24

ANALYTICAL CHEMISTRY

COMBUSTION ANALYSIS

- Burning of an organic compound in the presence of oxygen is called combustion.
- Combustion is an exothermic process
- Combustion analysis is used to find percentage of C, H and O.
- Take weighed organic compound.
- Mix with CuO in platinum boat.
- Place in furnace heated to about **850°C**
- Oxygen gas is passed over the sample
- Hydrogen oxidize into H_2O and absorbed in $Mg(ClO_4)_2$
- Carbon oxidize into CO_2 and absorbed in 50% KOH
- From the masses, percentages are calculated by using formulas.

$$\% \text{ age of carbon} = \frac{\text{mass of } CO_2 \text{ obtained in experiment}}{\text{mass of organic compound}} \times \frac{12}{44} \times 100$$

$$\% \text{ of hydrogen} = \frac{\text{mass of } H_2O \text{ obtained in experiment}}{\text{mass of organic compound}} \times \frac{2}{18} \times 100$$

$$\% \text{ of oxygen} = 100 - (\% \text{ of carbon} - \% \text{ of hydrogen})$$

→ Percentage of oxygen cannot be found directly through this method.

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EMPIRICAL FORMULA

1. Find out percentage of each element

2. Find the number of moles.

eg Moles of C = $\frac{\% \text{ of C}}{\text{Atomic mass of C}}$

3. Find the atomic ratio

(The simplest ratio b.w. the number of moles is found out by dividing the number of moles of each element by the smallest number of moles)

4. If atomic ratio is not in whole numbers then multiply with suitable number.

MOLECULAR FORMULA

Molecular Formula = $n \times$ Empirical formula

$n = \frac{\text{Molecular mass}}{\text{Empirical mass}}$

DETERMINATION OF STRUCTURAL FORMULA

For structural formula of a compound mainly three aspects are considered:

1. Physical properties of compound
2. Chemical properties of compound
3. Instrumental methods of analysis

1. PHYSICAL PROPERTIES OF COMPOUND

Physical properties are dependent on the structure and provides enough information about structural formula of the compound. e.g C_2H_6O is the molecular formula of both ethanol and diethyl ether.

Ethanol at room temp is liquid and its boiling point is 341 K, while dimethyl ether is a gas at room temp having boiling point of 248 K.

2. CHEMICAL PROPERTIES

Different compounds having same molecular formula but different functional groups behave differently to the same reactants. e.g ethanol reacts with sodium metal liberating hydrogen, while dimethyl ether do not react with it.

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3. INSTRUMENTAL METHODS OF ANALYSIS

- i) Spectroscopy
- ii) Nuclear Magnetic Resonance (NMR)
- iii) Atomic emission and absorption spectra
- iv) Mass spectrometry

1. SPECTROSCOPY

Spectroscopy is the study of the interaction b.w. matter and electromagnetic radiation.

- Organic compounds absorb energy on interaction with electromagnetic radiations.
- During the interaction of organic compounds with electromagnetic radiations certain wavelengths are absorbed, which excites the molecules / atoms to higher energy level.
- In atoms the transition results due to changes in distribution of electrons; while in molecules, along with changes in electronic distribution, changes in molecular rotations and bond vibration (stretching, bending) also occurs.
- The bond vibration and rotation of molecules need less energy i.e. in IR region, than the electronic excitation i.e. in uv/vis region.

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SPECTROPHOTOMETER

The instruments used to record the wavelengths absorbed and the concentration of the absorbing species is called spectrophotometer.

SPECTROPHOTOMETRY

Technique used to identify different substances as a result of their interaction with electromagnetic radiations.

→ Spectrophotometry is used for qualitative as well as quantitative analysis.

TYPES OF SPECTROSCOPY:

Some common types include

- i) Atomic spectroscopy
- ii) UV and visible spectroscopy
- iii) infrared spectroscopy
- iv) Nuclear magnetic Resonance (NMR)

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INFRARED SPECTROSCOPY

- organic compounds are exposed to weak radiations in the range $5000 - 667 \text{ cm}^{-1}$ (wave number $\bar{\nu}$)
- Increase in vibration of bonds and rotation of molecules takes place.
- Bonds undergo stretching and bending vibrations about the average value of interatomic distance.
- Such vibrations are particularly important with bonds involving H atoms, bcz of its low atomic mass.

BENDING VIBRATIONS

Bending vibrations do not change the interatomic distance (bond length) but change the angles b.w the atoms.

Four Types:

1. SCISSORING:

The movement of two atoms towards and away from each other

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2. ROCKING

It is like the motion of a pendulum on a clock but an atom is a pendulum and there are two instead of one

3. WAGGING

It is like the motion in which we make a \angle

sign with our fingers and bend them back and forth from our wrist.

4. TWISTING:

It is a motion as if the atoms were walking on a treadmill. (the same V shape but one is going back and the other is coming forth)

STRETCHING VIBRATIONS

The bond angle does not change but only the distance b/w the atoms change.

Stretching vibrations may be symmetric or anti-symmetric.

1. SYMMETRIC STRETCHING

Two or more bonds vibrate in and out together

2. ASYMMETRIC STRETCHING

Some bonds are getting shorter while others are getting longer.

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NOTE:

Stretching vibrations change bond length. Bending vibrations change bond angles.

→ IR spectrum is usually expressed in microns (μ) or in the form of wave number (cm^{-1})

→ Wave number is plotted on x-axis and % transmittance on y-axis.

→ Each dip in a spectrum is called band or peak.

→ A 100% transmittance means no absorption.

→ IR spectrum of organic compound is characteristic of structure of compound, and is of great assistance in establishing its identity.

→ IR-Region is divided into two regions:

1. Finger print region

2. Functional Group Region

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1. FINGER PRINT REGION

The region b/w $600 - 1500 \text{ cm}^{-1}$ is called finger print region. bcz the absorption in this region is characteristic of a compound. This region is used to identify a compound.

2. FUNCTIONAL GROUP REGION

The region b/w $1500 - 4000 \text{ cm}^{-1}$ is called functional group region. Different functional groups show absorption at different frequencies.

USES OF IR SPECTROSCOPY

1. identification of unknown compounds (through functional groups)

2. For Detection of impurities. The presence of absorption peak

at positions where the compound does not absorb indicates presence of impurities e.g. presence of cyclohexanone is readily detected in cyclohexanol by intense carbonyl band.

3. The progress of most reactions can be followed by examining the infra red spectra of aliquots withdrawn from the reaction mixture.

Aliquots: a portion of a larger whole, esp a sample taken ~~from~~ ^{for} chemical analysis.

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UV AND VISIBLE SPECTROPHOTOMETRY

- wavelength in range 200-800nm are used
- can change the distribution of loosely bonded (π -bond) and non-bonded electrons in molecules / ions.
- Almost all substances absorb certain wavelength in this range
- The absorption is according to Beer-Lambert's law

$$A = Ecl$$

A = absorbance

c : concentration of solution in mole per litre.

l : path length of sample solution in cm.

E : molar absorptivity or molar extinction coefficient, a constant characteristic of the solute at given wavelength.

- uv-vis spectrophotometry is used both for qualitative and quantitative analysis.
- For quantitative analysis we use Beer-Lambert law. The absorption of uv-vis light by a solution kept in a quartz cell of known path length is directly proportional to concentration of solution. Solutions of different concentration are prepared and are introduced into the uv-vis spectrophotometer in order to record their absorbances.

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WORKING CURVE

A graph is constructed by plotting the concentrations on x-axis and absorbances on y-axis. This graph is called working curve. During this experiment a selected wavelength at which maximum absorption occurs is used throughout the study.

FINDING CONCENTRATION OF UNKNOWN SOLUTION

We can find out the concentration of unknown solution through the graph of known solution (or working curve)

When a solution of unknown concentration is placed in the spectrophotometer, its concentration is displayed on the screen.

UV light : 10 - 400 nm

visible light : 400 - 800 nm

The electronic transition that are associated with the absorption of uv/vis radiation, are of four types:

1. $\sigma \rightarrow \sigma^*$ Transition

- occur in saturated HCs (which contain only σ -bonds)
- requires greater energy
- C-C bond absorbs 135 nm
- C-H bond absorbs about 125 nm
- bond breaks
- free radicals are formed

2. $n \rightarrow \sigma^*$ TRANSITION

→ occur in saturated molecules containing hetero atoms such as Oxygen, Sulphur, Nitrogen or halogens. e.g. $R-O-H$, $R-Cl$

→ requires slightly less energy than required for $\sigma \rightarrow \sigma^*$ transition

3. $\pi \rightarrow \pi^*$

→ occur in molecules containing double or triple bonds or aromatic rings.

→ Ethylene absorbs at 171 nm

→ Butadiene absorbs at 217 nm

4. $n \rightarrow \pi^*$

→ occur in molecules containing double or triple bonds involving hetero atoms e.g. $>C=O$, $-C \equiv N$ etc

TRANSITION METAL COMPLEXES

Transition metal complexes are usually colored due to d-d transition. Such compounds absorb radiations in the visible region.

When a compound absorb radiations in the violet region, it reflects all the remaining (six) colours which electively appear as a single colour (complementary colour). Complementary colour of violet is yellow green.

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Colour absorbed

Colour of complex
(complementary colour)

Violet

Yellow Green

Blue

Yellow

Blue Green

Red

Green

Purple

Yellow

Blue

Orange

Green Blue

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NUCLEAR MAGNETIC RESONANCE (NMR)

- NMR used for determining the content and purity of a sample as well as its molecular structure.
- Like electrons atomic nucleus also spin about an axis.
- Atomic nuclei behave like tiny magnets, as the spinning charged bodies produce magnetic field.
- As nuclear spin is quantized, therefore, magnetic moment of nucleus is also quantized.
- In a Proton the spin quantum number is $\frac{1}{2}$.
- Nuclei containing odd number of protons or neutrons or both also have a spin quantum number = $\frac{1}{2}$ e.g. C^{13} , N^{15} , F^{19} , P^{31}
- Nuclei having even number of protons and neutrons have zero spin and zero magnetic moment e.g. C^{12} and O^{16} . Such nuclei are invisible in NMR spectrometry.

APPLYING MAGNETIC FIELD TO NUCLEUS

- The spin states of a nucleus have equal energies, in the absence of applied magnetic field
- If a magnetic field is applied, the spin states are no longer of equal energy.

Lower energy: $+\frac{1}{2}$

High energy: $-\frac{1}{2}$

- Proton with magnetic field alligned with applied field is at a lower energy than that which aligns against the field.

FLIPPING

Nuclei with magnetic field aligned with applied field can absorb energy and change their spin state (high energy state). The phenomenon is called flipping.

The quantity of energy absorbed depends on the energy gap b/w the two states.

$$E_{\text{absorbed}} = E_{(-1/2)} - E_{(+1/2)}$$

In this case energy absorbed belongs to radio frequency region of the electromagnetic spectrum. (We keep the spins of photons similar by radiofrequency)

→ The difference in energy b/w the two spin states is dependent on the external magnetic field strength, and is always very small.

CHEMICAL SHIFT

Chemical shift is the resonant frequency of a nucleus relative to a standard in a magnetic field.

Often the position and number of chemical shifts are diagnostic of the structure of a molecule.

EQUIVALENT AND NON-EQUIVALENT PROTONS

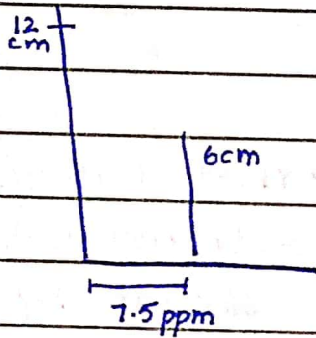
→ NMR spectrophotometer can differentiate b/w protons of different environments.

→ Protons of the same environment are called equivalent protons (represented by same letter)

→ Protons of other type are indicated by other letter.

BENZENE

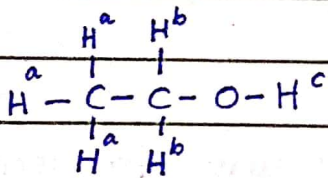
All the six protons of benzene are equivalent, therefore NMR spectrum of benzene shows a single peak.



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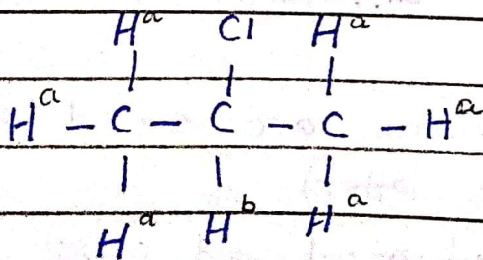
ETHANOL

Ethanol has three different types of protons and its spectrum contains 3 peaks



ISOPROPYL CHLORIDE

Isopropyl chloride has six equivalent protons which gives a single peak. The remaining proton, gives a peak at a different position



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- No. of peaks tells us kinds of protons
- Height of peaks tells about number of equivalent protons.
- The area under the peak is directly proportional to the number of protons.

TETRAMETHYL SILANE, TMS

For taking NMR spectrum of a substance a little amount of TMS, Tetramethylsilane $(\text{CH}_3)_4\text{Si}$ is added to it. It has been chosen as a standard.

- NMR spectrum is a plot of absorption (y-axis) and chemical shift (frequency) on x-axis.
- For TMS the value of chemical shift (δ) has been chosen as zero arbitrary.
- Chemical shifts of other compounds are compared with this reference value.
- All other compounds have chemical shift (δ) values higher than zero
- TMS has been chosen as a standard because its all protons are equivalent and show absorption at lowest δ value.
- TMS is highly volatile and can be separated from the compound after its spectrum has been recorded.
- Chemical shift is expressed as delta (δ) or Tau (τ) scale.
- NMR spectrum is rectangular chart paper with a linear scale of δ (delta) usually arranging from 0 to 12 ppm, the TMS signal is taken as $\delta = 0$

$$\delta = \frac{\text{Observed shift from TMS in (Hz)}}{\text{Operating frequency of spectrophotometer (Hz)}} \times 10^6 \text{ ppm}$$

* Relation B.w δ and Tau scale

$$\tau = 10 - \delta$$

usually ppm scale is used, where TMS signal is at 10 ppm.

* SHIELDED PROTONS

- Different protons give peaks at different δ value.
- Protons with greater electron clouds are called shielded protons and they require lower frequency for flipping from lower energy to higher energy states.
- Such peaks appear as upfield (lower δ value)

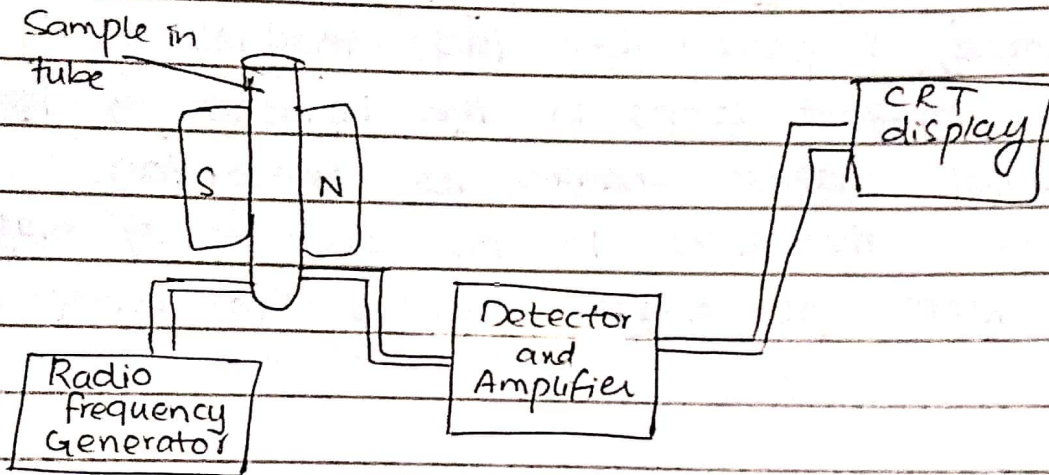
* DESHIELDED PROTONS

- Protons in the vicinity of higher electronegative atoms (like Cl, F, O etc) have lower electron densities around them and acquire higher energy for flipping are called deshielded protons.
- Such protons show peak at higher δ value (downfield)

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NMR

→ H-NMR : Analyzing compound on basis of Hydrogen atom.



→ The H-atom in sample absorb radiowaves and goes to high energy state.

→ The H-atom release back energy to come back to its original (low-energy) state

→ Detector detects the released energy.

→ Graph (spectrum) forms on display.

→ Interpreting the graph gives information about molecule.

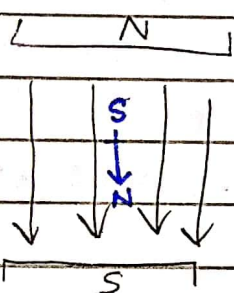
→ To perform NMR, NMR active atom must be used.

→ Due to even number of protons and neutrons both, overall spin of nucleus = zero.

→ The atoms having zero spin are NMR inactive atoms.

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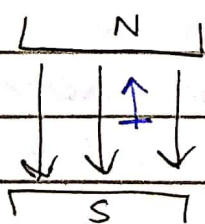
- The proton spin around its axis due to which it behaves as a magnet in which direction of magnetic field is from north to south.
- The proton acts as a small magnet.
- The proton (sample) is placed b/w large magnet.
- Whenever small magnet comes in the influence of large magnet, the small magnet changes its orientation.
- Mostly they orient themselves in the direction of magnetic field and are known as α -spin state or low energy state.



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α -spin state
(Low energy state)

- Some protons align opposite to external magnetic field.

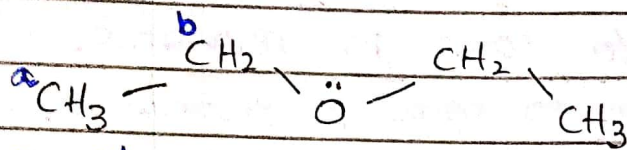


β -spin state
(High Energy state)

- In molecules, the hydrogen having more electron cloud when comes in influence of external magnetic field; they do not rotate completely in the direction of magnetic field due to the induced magnetic field of electrons. Such protons are shielded protons.

→ In some molecules the protons (H) are surrounded by electronegative atom which attract the electrons more towards itself and hence ~~deshielded~~ deshielding the protons. Such protons orient themselves in direction of external magnetic field...

e.g



a: shielded atoms

b: deshielded atoms

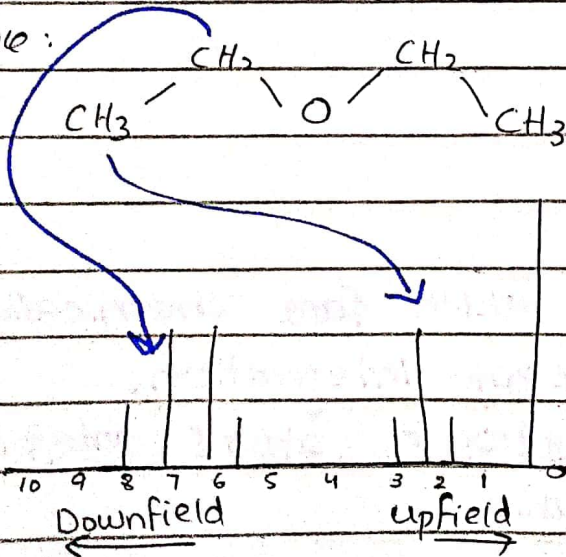
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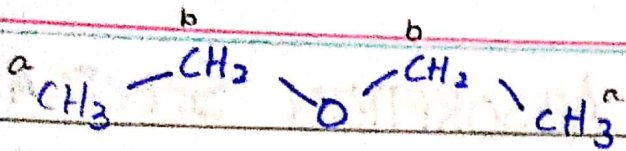
→ When radio waves fall on sample, they absorb energy and comes to high energy state (β-spin state). In this state the atoms are said to be in resonance.

→ The shielded protons require less energy to go into high energy state while the deshielded protons require more energy (more frequency)

→ The sample then release energy which is detected by detector and analyzed to form a graph.

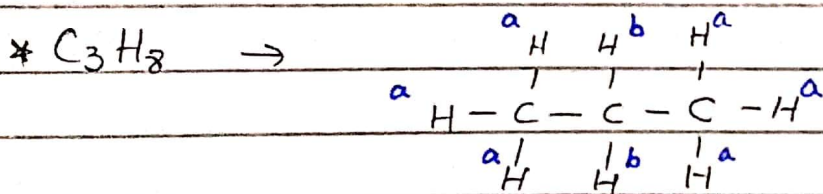
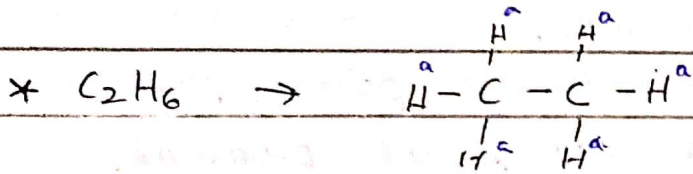
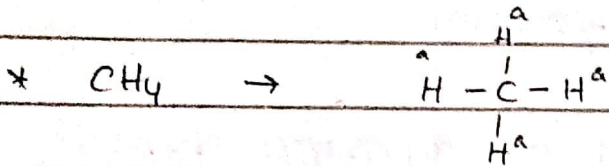
Example:





→ The 'a' molecules i.e 6 hydrogen face same environment

→ Similarly 'b' molecules i.e 4 hydrogen face same environment



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ATOMIC EMISSION AND ABSORPTION SPECTRA

* Solid \rightarrow Heated \rightarrow Light Emission \rightarrow Passed through spectrum \rightarrow Continuous Spectrum

* Gaseous state atom $\xrightarrow{\text{heat}}$ Line Spectrum

\rightarrow When hydrogen gas is taken in a discharge tube under low pressure it emits blue light.

\rightarrow When this blue light is passed through prism, four bright lines against a dark background are produced.

The colours are:

1. Red
2. Blue Green
3. Blue Violet
4. Violet

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\rightarrow These lines of hydrogen spectrum are collectively called Balmer series.

\rightarrow In invisible part of H-spectrum four more series are also obtained

Lyman (uv-region)

Paschen (^{near}IR-region)

Brackett (^{mid}IR-region)

Pfund (far IR-region)

\rightarrow To calculate wavelength of different bright lines of Balmer series:

$$\frac{1}{\lambda} = R_H \left[\frac{1}{2^2} - \frac{1}{n^2} \right]$$

R_H : Rydberg Constant

$$R_H = 2.18 \times 10^{-18} \text{ J}$$

- Red, blue green, blue violet and violet lines of Balmer series actually correspond to electronic transition from 6th, 5th, 3rd orbit to 2nd orbit respectively.

EMISSION SPECTRUM OF SODIUM

- Emission spectrum of sodium can be obtained when sodium salt is added to the Bunsen flame, yellow flame is produced.
- Yellow light when passed through prism, two closely spaced yellow lines called D_1 and D_2 are produced.
- For every element there is a unique emission or absorption spectrum

FLAME PHOTOMETER Koracademy.com

- emission Spectroscopic technique
- used to find conc. of Ni, Na, K etc in biological samples.
- An aqueous analyte is introduced into flame.
- Analyte : substance whose chemical constituents are being identified
- Water evaporates and solid salt is left behind.
- * Salt → Atoms → Vapours → Excitation of electrons → Loss of energy → Prism → Detected in spectrophotometer
- The intensity of light emitted by atoms is directly proportional to concentration of analyte

ATOMIC ABSORPTION SPECTROMETRY

- * Sample \rightarrow Vapours
 - * Some atoms get excited but majority are in ground state.
 - * When a light of particular wavelength from the hollow cathode lamp is passed through these atoms, they absorb light for excitation from ground state to high energy state.
 - * Absorbance of light by atoms is directly proportional to conc. of atomic vapours in the flame.
 - * For analysis of different elements different types of ~~elements~~ lamps are used which produce light of different wavelengths.
 - * Each element shows absorption of particular wavelength.
- \rightarrow Working Curve is constructed from the absorbances shown by solution of known concentrations.
- \rightarrow Sample of unknown concentration is aspirated into flame and its conc. is read from instrument

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MASS SPECTROMETRY

- To determine atomic and molecular mass.
- Positive ions are produced in ionization chamber.
- Different ions separate on the basis of m/e ratio.
- In magnetic field ions deflect in circular path.
- Lighter ions (low m/e) deflect to large extent than heavier ions.
- At a time only one kind of ions strikes the detector
- Intensity of electric signal is directly proportional to no. of ions striking the detector.
- Magnetic field is kept constant while accelerating voltage is continuously change ; one kind of ions after other will reach detector and thus more peaks are produced on chart.

→ Mass Spectrum:

x -axis → m/e ration

y -axis → relative abundance.

Higher the peak, higher the abundance

→ Mass Spectrum helps in finding the number of isotopes of an element and also their relative abundance.

* NEON

1. Ne-20 : 90.92%. (Most Abundant)
2. Ne²¹ : 0.57%. (Least Abundant)
3. Ne²² : 8.82%.

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* CHLORINE

Cl^{35} : 75%.

Cl^{37} : 25%.

* In mass spectrometer:

- Molecular ions (M^+) are produced due to loss of electron
- More ions are produced^{due} to fragmentation of molecule.
- Fragmentation occurs due to rupture of chemical bonds.
- Fragmentation pattern give idea of structure of molecule.

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