

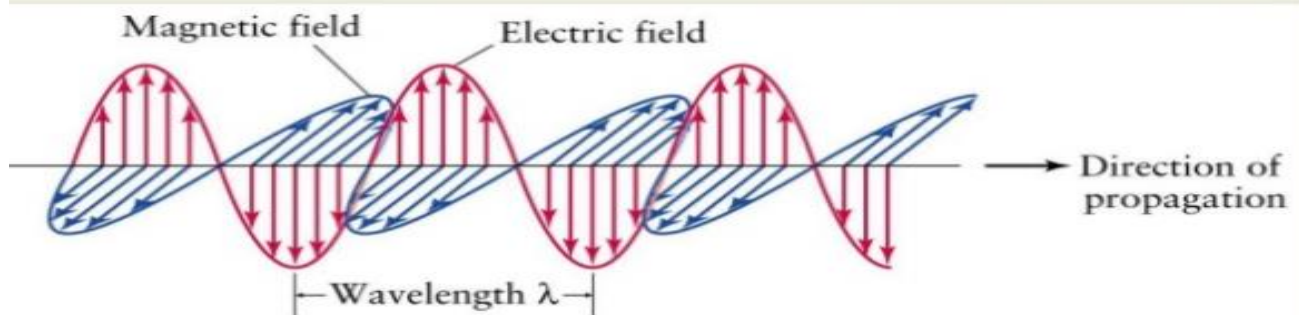
## Spectroscopic Techniques

### Introduction to electromagnetic radiation

Electromagnetic radiation is energy that is propagated through free space or through a material medium in the form of electromagnetic waves, such as radio waves, visible light, and gamma rays.

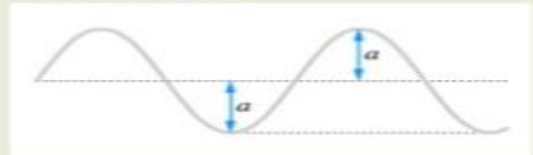
An electromagnetic wave is a transverse wave in that the electric field and the magnetic field at any point and time in the wave are perpendicular to each other as well as to the direction of propagation.

The two fields are at right angles to each other and are perpendicular to the direction of propagation



The parameters that characterize a wave motion are “amplitude (a), wavelength ( $\lambda$ ) and frequency ( $\gamma$ )”

**1) Amplitude** - this is “how high” the wave is:



**2) Wavelength ( $\lambda$ )** - this is the distance between two corresponding points on the wave and is measured in metres:



**3) Frequency** - number of cycles of a wave passing a fixed point per unit time and is measured in Hertz (Hz)

Wave Number: Number of waves per centimeter ( $\text{cm}^{-1}$ )

Velocity: velocity is the product of frequency and wavelength ( $\text{ms}^{-1}$ )

### Relation between frequency, velocity and wavelength

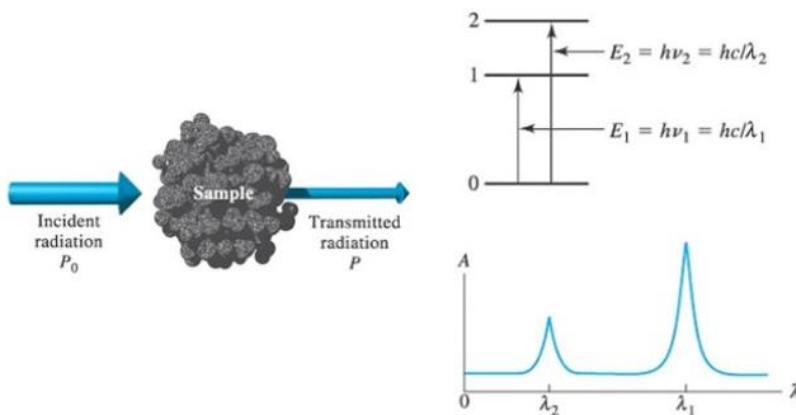
$$v_w = f\lambda$$

**Dual nature of electromagnetic radiations:** The phenomena of refraction, reflection, interferences are examples of wave properties. But the wave nature of electromagnetic radiation fails to explain many phenomenon like photoelectric effect, propagation of light in vacuum etc., To explain such phenomena, it is assumed that the electromagnetic radiation consists of a stream of discrete packets of energy called photons or quanta with energy  $E=h\nu$ , Where  $E$  is the energy of the photon  $\nu$  is the frequency of the electromagnetic radiation and  $h$  is Planck's constant ( $6.624 \times 10^{-34}$  Joule-second).

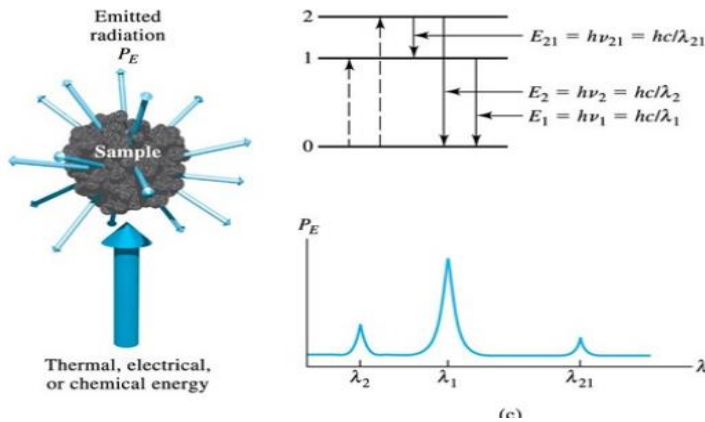
### Interaction of electromagnetic radiation with matter

#### (3) Energy transition process illustrate

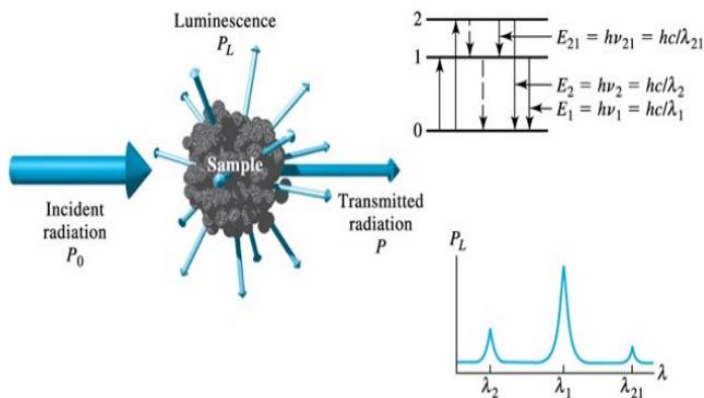
##### i) Absorption process



## ii) Emission or Chemoluminescence process

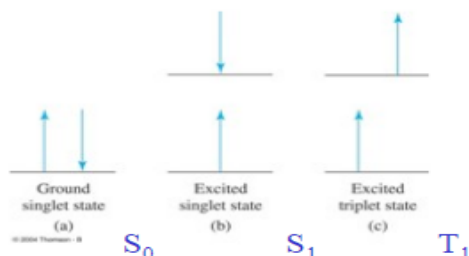


## iii) Photoluminescence process



- iv) **Photoluminescence** : Exciting atom/molecule by **light**, then, the emitted quantized energy is measured.
- a) **Fluorescence**: The ground state with the **same spin** as excited state.
  - b) **Phosphorescence**: The ground state with the **opposite spin** as excited state.
  - v) **Chemoluminescence (chemiluminescence)** : The luminescence (emission light) is the result of a chemical reaction.

### e) Fluorescence versus phosphorescence



- (1) **Fluorescence** : Emission of a photon when the analyte returns to a lower-energy state with the **same spin** as the higher energy state, i.e.,  $S_1 \rightarrow S_0$ , in which the electron life time in the excited state is  $\sim 10^{-5} - 10^{-8}$  s.
- (2) **Phosphorescence** : Emission of a photon when the analyte returns to a lower-energy state with the **opposite spin** as the higher-energy, i.e.,  $T_1 \rightarrow S_0$ , in which the electron life time in the excited state is  $\sim 10^{-4} - 10^4$  s.

### Energies corresponding to various kinds of radiations and the types of spectroscopy

Type of radiation	Wavelength Range(m)	Frequency Range(Hz)	Energy		Type of transition	Type of spectroscopy
			kJ/mol	eV		
Gamma ( $\gamma$ ) rays	$<10^{-12}$	$10^{20}-10^{24}$	$3.95 \times 10^8$	$4.1 \times 10^6$	Nuclear transitions	$\gamma$ -ray spectroscopy or Mossbauer spectroscopy
X-rays	1nm-1pm	$10^{17}-10^{20}$	$3.95 \times 10^6$	$4.1 \times 10^4$	Inner core electrons transitions	X-ray spectroscopy & X-ray diffraction
Ultra violet rays	400-1nm	$10^{15}-10^{17}$	$3.95 \times 10^4$	$4.1 \times 10^2$	Outer shell electron transitions	UV or Electronic spectroscopy
Visible rays	750-400nm	$4-7.5 \times 10^{14}$	$3.95 \times 10^2$	4.1	Outer shell electron transitions	Electronic spectroscopy, emission spectroscopy and fluorescence spectroscopy
Infrared rays	2.5 $\mu$ m-750nm	$10^{13}-10^{14}$	3.95	$4.1 \times 10^{-2}$	Vibrational transitions	Vibrational or Infrared spectroscopy
Microwave rays	1mm-25 $\mu$ m	$3 \times 10^{11}-10^{13}$	$3.95 \times 10^{-2}$	$4.1 \times 10^{-4}$	Rotational transitions	Rotational or Microwave spectroscopy
Radio waves	$>1$ mm	$3 \times 10^{11}$	$3.95 \times 10^{-6}$	$4.1 \times 10^{-8}$	Magnetically induced spin transitions	NMR and ESR spectroscopy

## Energies associated with the molecules

Total energy of the molecule is the sum of rotational, vibrational and electronic energy.

$$E_{\text{total}} = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}}$$

- i) **Translational energy:** The energy associated with the translational motion of the molecules along x,y and z-axis is called translational energy. It is given by

$$E_t = \frac{h^2}{2M} [ (n_x/a)^2 + (n_y/b)^2 + (n_z/c)^2 ]$$

- ii) **Rotational energy :** The atoms within a molecule rotate about an imaginary axis which is  $\perp$  to the line joining the nuclei of two atoms. This causes the rotation of the molecule. The expression for rotational energy of the molecule is given by:

$$E_{\text{rot}} = J(J+1) \frac{h^2}{8\pi^2 I}$$

where  $I$  = Moment of inertia of the molecule where  $J$  = rotational quantum number with values 0,1,2,3,4

- iii) **Vibrational energy:** This type of energy is associated with the vibrations of atoms in a molecule about equilibrium positions. The expression for vibrational energy on the basis of quantum mechanical approach is given by

$$E_{\text{vib}} = (v + \frac{1}{2}) h\nu$$

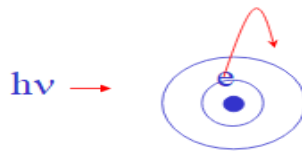
where  $\nu$  is the vibrational frequency and  $v$  is the vibrational quantum number having value 0,1,2,3,.....

- iv) **Electronic energy:** It is the energy associated with the motion of the electrons with respect to the nuclei of atom (of a molecule) as fixed points. The vibrational and rotational energy of the molecules are added to the electronic energy.

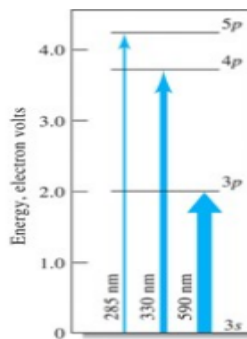
## 2) Absorption Spectra

### i) Atomic Absorption (line spectra)

When an atom absorbs specific quantized UV/Vis radiation, it undergoes a change in its **valence electron** configuration:



\* Transitions between two different orbital are termed **electronic transitions**.

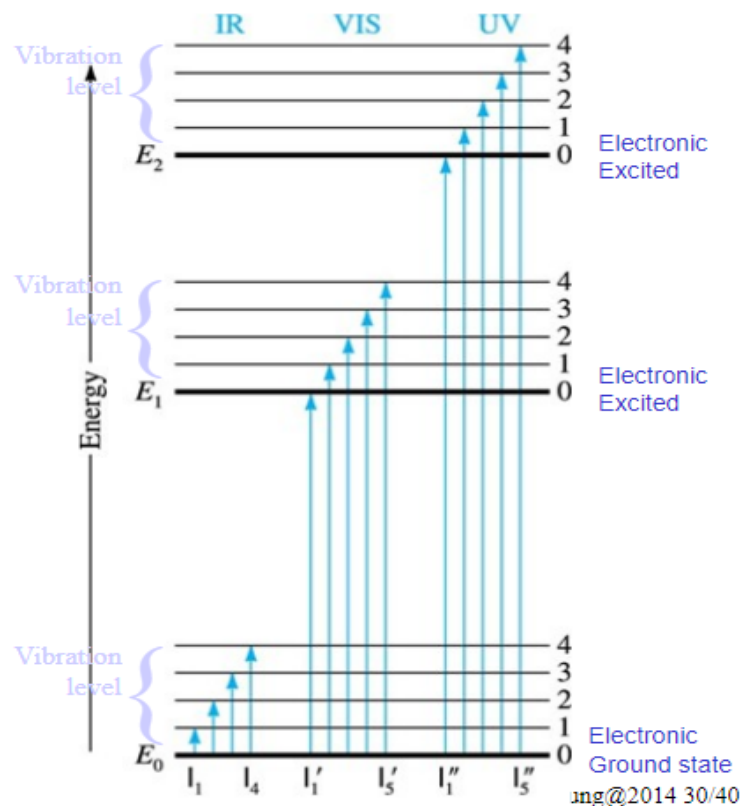


For example, Na consists of a few, discrete absorption lines corresponding to transitions between  $3s \rightarrow 3p$ ,  $3s \rightarrow 4p$  etc.

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### ii) Molecular Absorption (band spectra)

\* Molecular absorptions spectra are generally broad band (**band spectra**) because **vibrational** and **rotational** levels are "superimposed" on the electronic levels.



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## Factors affecting the position and intensity of spectral lines

### 1. Amount of sample

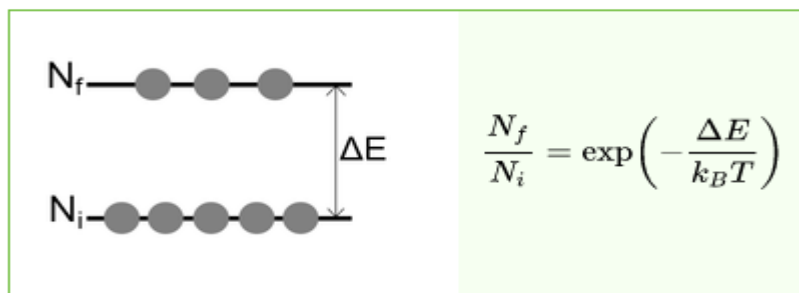
The intensity of lines on the spectrum will be affected by the amount of sample which light passes through. The intensity of this transmitted light depends on the sample concentration and path length. Ex. Beer-Lambert Law

### 2. Population of energy states

The continuous thermal agitation that molecules experience at any temperature (greater than zero Kelvin) ensures that they are distributed over all possible energy levels.

Population of a state = the average number of molecules in a state at any given time.

The Boltzmann distribution defines the relative population of energy states (usually the ratio of excited states to ground state).



$k_B$  = Boltzmann constant (=  $R / N_A$ ) =  $1.381 \times 10^{-23} \text{ J K}^{-1}$

$T$  = temperature (Kelvin)

A system can undergo a transition from one level,  $i$ , to another level,  $f$ , but only if it is in the first level  $i$  to begin with.

### 3. Spectroscopic selection rules

A selection rule is a statement about which potential transitions are allowed and which are forbidden. **Allowed transition** are those that obey the selection rules and gives intense bands in the spectra. **Forbidden transitions** are those that do not obey the selection rules, however they do take place but give weak bands in the spectra. Each spectroscopy has its own selection rules (see later lessons). Not all transitions are allowed even though energy conservation is obeyed.

Selection Rule: (i) In rotational spectroscopy during a transition, the rotational quantum number must change by 1 unit only, i.e.  $\Delta J = \pm 1$

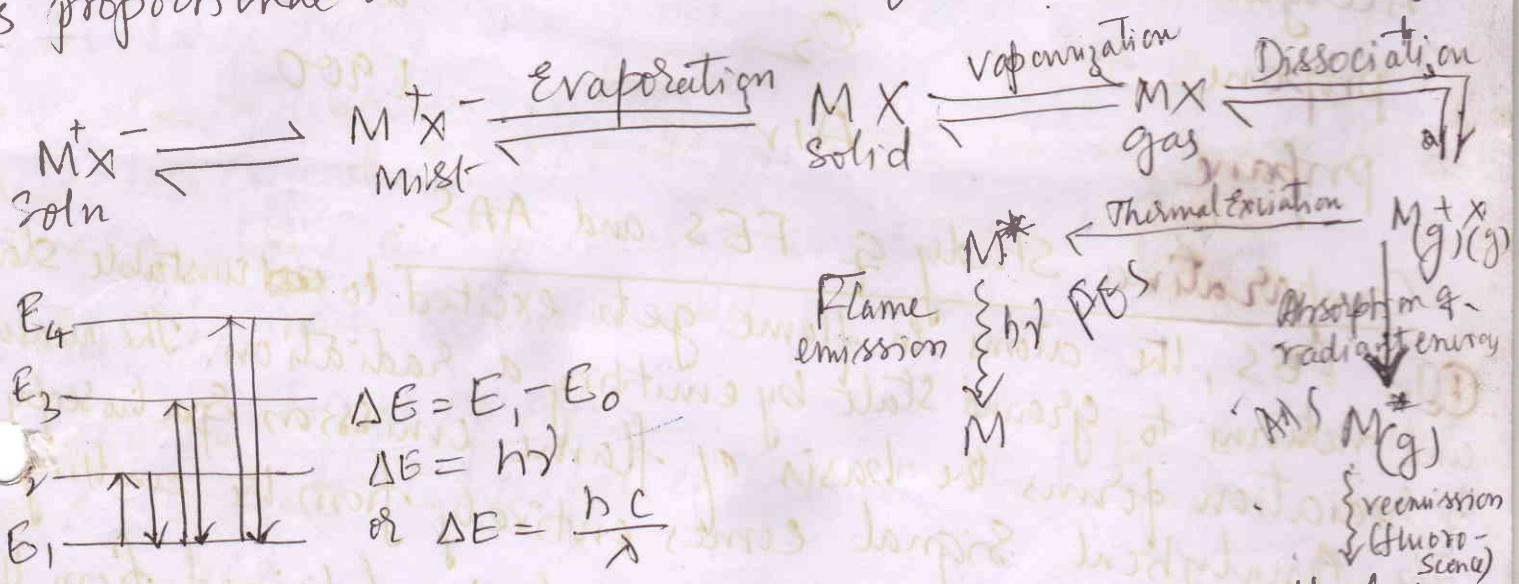
(ii) In vibrational spectroscopy, only transitions allowed are those which change the vibrational quantum number by 1 unit, i.e.  $\Delta v = \pm 1$ .



# FES and AAS

Principle of FES: When a soln containing a metallic salt is aspirated into the flame, some of the gaseous metal atoms get raised to an energy level & revert back to their ground state by emitting the absorbed energy in the form of radiation characteristic of the metal under investigation.

Principle of AAS: When a soln containing metallic salt is aspirated into the flame, only few atoms get excited & most of the atoms are in ground state. When a characteristic radiation is passed into the flame, the metallic atoms in the ground state absorb the radiation, and the extent of absorption is proportional to the concentration of the metal under investigation.



The relationship between the ground state and excited state populations is given by Boltzmann equation

$$\frac{N_1}{N_0} = \left( \frac{g_1}{g_0} \right) \cdot e^{-\Delta E / KT}$$

$N_1$  = No. of atoms in the excited state  
 $N_0$  = No. of ground state atoms  
 $g_1/g_0$  = ratio of statistical weights for ground & excited states  
 $\Delta E$  = energy of excitation =  $h\nu$   
 $K$  = Boltzmann Constant  
 $T$  = temp in Kelvin.



## Types of Flames used in AAS:

The temp<sup>r</sup> of the fuel is controlled by the type of the fuel and oxidant used.

Fuel	Oxidant	Flame temp <sup>r</sup> (°C)
H <sub>2</sub>	O <sub>2</sub>	2800
H <sub>2</sub>	Air	2100
H <sub>2</sub>	Ar	1600
H <sub>2</sub>	O <sub>2</sub>	3000
Acetylene	Air	2200
Acetylene	N <sub>2</sub> O	3000
Acetylene	O <sub>2</sub>	2800
Propane	Air	1900
Propane		

## Comparative Study of FES and AAS.

① In FES, the atoms in flame get excited to ~~an~~ unstable state and return to ground state by emitting a radiation. The measurement of radiation forms the basis of flame emission spectroscopy. The analytical signal comes entirely from the emitting atoms.

In AAS the signal, the signal is obtained from the difference between the intensity of the source in the absence of metallic elements present in the liquid and the decreased intensity of the source in the absence of obtained when metallic atoms are present in the optical path.

② In FES, the emission intensity is dependent upon the no. of exciting atoms and is therefore greatly influenced by temperature variations.



On AAS, atomic absorption depends upon the no. of unexcited atoms & the absorption intensity does not depend upon the temp<sup>o</sup> of the flame. intensity.

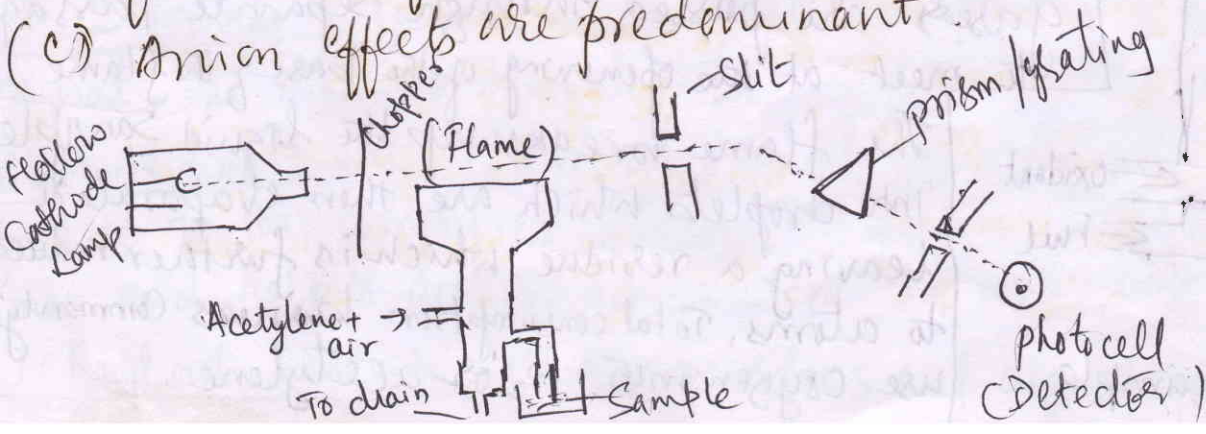
③ In AAS, the relation between absorbance & concentration is nearly linear, that is Beer's law is obeyed over a wide concn range. This is not true in cases of flame emission spectroscopy.

### Advantages of AAS over FES.

- ① The atomic absorption technique is specific, because the atoms of a particular element can only absorb radiation of their own characteristic wavelength.
- ② As large no. of atoms are involved in contributing an atomic absorption signal, variation in the temp<sup>o</sup> has less effect in AAS than FES where in smaller no. of atoms are producing emission signal.
- ③ AAS is more sensitive and accurate.

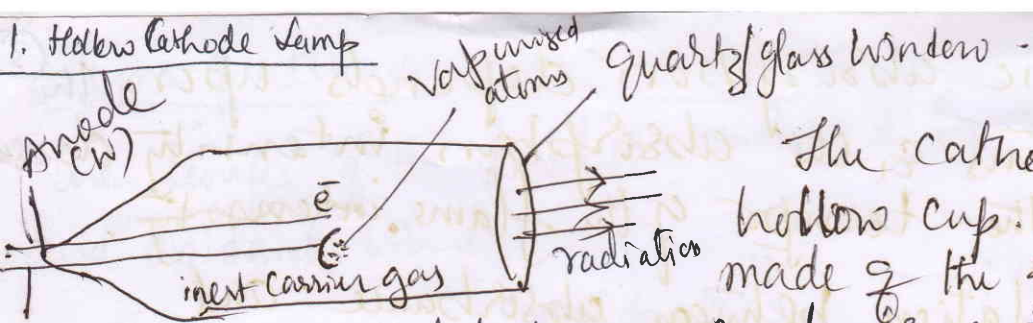
### Disadvantages of AAS

- (a) A separate lamp for each element to be determined is required.
- (b) Not very successful for the estimation of elements like Al, Ti, W, Mo, Si etc. as these elements give rise to the formation of oxides in the flame.
- (c) Anion effects are predominant.





### 1. Hollow Cathode Lamp



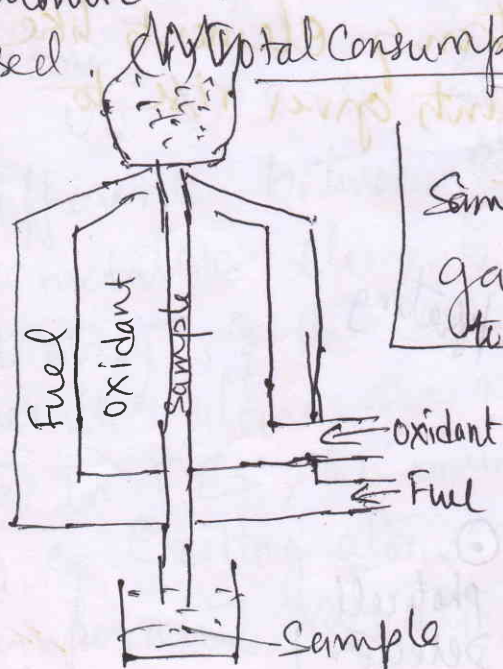
Cathode Hollow Cathode Lamp

The cathode tube consists of a hollow cup. ~~in~~ the cup ~~the~~ is made of the element to be determined. Anode is a tungsten filament.

The two electrodes are housed in a tube containing an inert gas. The window of the tube is made of glass/quartz/silica. When the potential difference is applied between two electrodes, the inert gas near the anode gets ionized & these ions are attracted to cathode at high velocity. The cathode material gets vaporised, excited to higher energy and upon returning to the ground state gives rise to emission of radiation.

2. Chopper: A rotating wheel between the hollow cathode lamp and the flame is called as Chopper. Chopper breaks the steady radiations from the lamp into pulsating light which gives pulsating current in the detector. Only pulsating current due to pulsating radn is amplified and recorded whereas the continuous radn emitted from the flame is not detected, hence absorption of light is measured without interference from the radiation emitted by the flame.

3. Atomizers To Convert the sample into very ~~small droplets~~ atomic state. Two types of flame atomizer are commonly used. (i) Total Consumption burner (ii) premix burner.

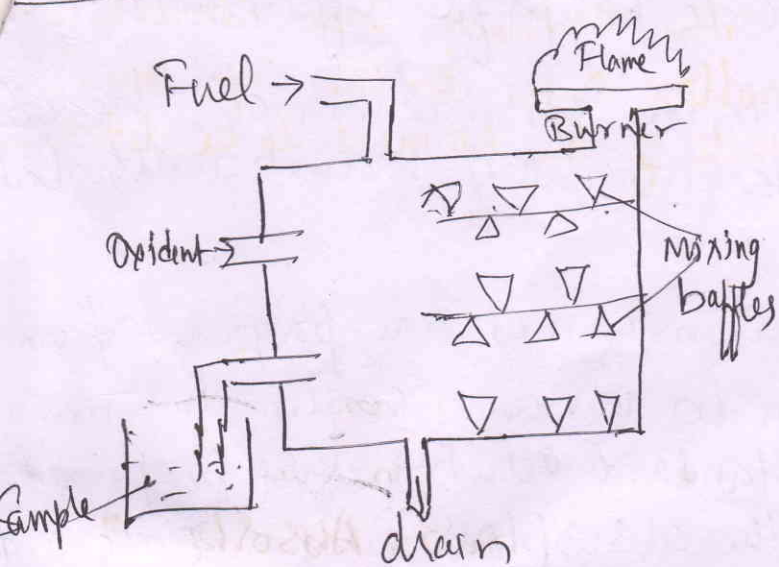


In Total Consumption burner, the sample solution, the fuel & oxidizing ~~gas~~ gases are passed through separate passages to meet at the opening of the base of the flame.

The flame breaks up the liquid sample into droplets which are then evaporated leaving a residue which is further reduced to atoms. Total consumption burners commonly use oxygen with  $H_2$  or acetylene.



## 1. premix burner



In premix burner, a mixture<sup>⑤</sup> of the sample (liquid), and fuel and oxidant are allowed to enter into a mixing chamber which is provided with baffles. Sample, fuel and oxidant are mixed thoroughly and fed on to the top of the burner, where the mixture gets atomized and further process takes place.

## Comparison of total consumption burner with premix burner.

Total Consumption burner	Premix burner
1. Amount of sample in the flame is large which enhances sensitivity	1. Only small drops reach the flame
2. No explosive hazard	2. long path provides sensitivity
3. Large droplets not entirely decomposed.	2. Quiet operation.
4. Noisy & hard to use	3. Rate of sample introduction is low.
	4. possibility of explosion

4. Monochromators: The most common monochromators are prisms & gratings. The function of monochromator is to select a particular absorbing line from the spectral lines (radiation) emitted from hollow cathode lamp.

5. Detectors: Convert the absorbed radiation into an electrical signal. The most common detector is photomultiplier tube.

6. Amplifier: The electrical signal from the detector is fed to the amplifier which amplifies the electric signal many times and help to achieve an excellent signal-to-noise ratio.

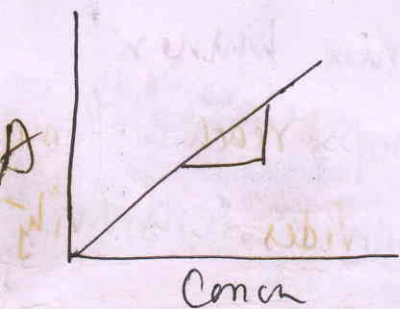
7. Read out Devices: Chart recorders and digital readout devices are used.



Qualitative Analysis : very limited for this as it- (6)  
requires different hollow cathode lamps for different metals.

Quantitative analysis : Quantitative estimations are based upon the determination of the amount of radiation absorbed by the sample.

Calibration Curves : Calibration curves are prepared from soln of the sample metal ion in known concn. A series of corresponding metal ion standard solutions are prepared and are atomized to get the absorption. Absorbance and concns are linearly related between  $E_i$  will give a straight line. Now the sample metal ions are also atomized and measured the absorbance  $E_i$  hence concn can be determined from the calibration curve.



$$\text{Absorbance} = \text{Slope} \times \text{Concn}$$

$$A = m \cdot c$$

### 1. Determination of Na, K, Ca & Mg in blood serum

The procedure consists of prepn of diluted solution of serum in the presence of  $\text{LaCl}_3$ . The test solns are then aspirated in AA spectrometer and absorbances are measured. These are compared with those noted for aqueous std. solutions. This Ca & Mg can be estimated in the presence of  $\text{LaCl}_3$ . Na & K can be determined in dilutions of 50 or 100:1.

2. Determination of lead in petrol. Standard solutions containing tetraethyl lead are prepared in cyclohexanone. The aspiration of standards is done at 283nm using air acetylene mixture. Response curves of TEL are prepared by plotting absorbance against concn. Then the sample petrol is diluted with cyclohexanone and concn of additive determined from the response curves.

3. Detmn of Vanadium in Lubricating oil; oil dissolved in White Spirit

4. Detmn of Mg in tap water