# X –RAY FLUORESCENCE SPECTROMETRY

**X- rays are short wavelength electromagnetic radiations produced by the deceleration of high energy electrons or by electronic transitions of electrons in the inner orbitals of atoms.**

**X- rays have a wavelength range of $10^{-5}$ $\overset{0}{\text{Å}}$ to 100 $\overset{0}{\text{Å}}$ . Conventional X- ray spectroscopy is largely confined to 0.1 $\overset{0}{\text{Å}}$ to 25 $\overset{0}{\text{Å}}$ .**

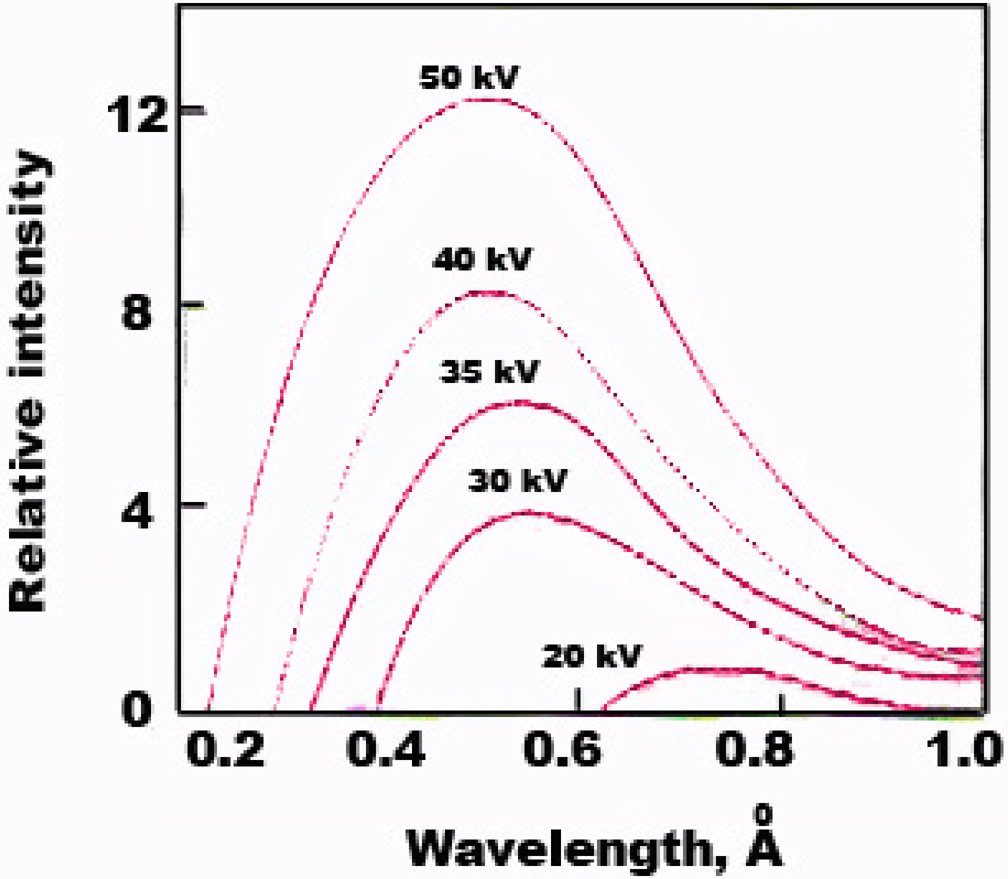
X- rays are generated by:

1. Bombarding a metal target with a beam of high energy electrons.
2. Exposing a substance to a primary beam of X–rays to generate a secondary beam of X–rays of lower energy.
3. Using a radioactive source emitting X–rays during its decay process and
4. From a synchrotron radiation source.

**In an X–ray tube both continuum and line spectra are emitted. Electrons are produced at a heated cathode and accelerated toward a metal anode (target) by a potential difference of 100 kV. Upon colliding with the anode, part of the energy of the incident beam is converted into X–rays.**

**The continuum X–ray spectrum exhibits a well defined short wavelength limit ($\lambda_0$) which is a characteristic of the applied voltage, irrespective of the nature of the target.**

# CONTINUUM RADIATION FROM AN X - RAY TUBE WITH A TUNGSTEN TARGET



**The continuum radiation results from collisions between the electrons and atoms of the target. Each collision results in the emission of a photon. The energy of the photon is equal to the energy loss of the electron. A number of collisions with decreasing energy may occur for each electron as it bounces from one atom into another . The maximum photon energy generated corresponds to the instantaneous deceleration of the electron to zero kinetic energy in a single collision.**

**The kinetic energy of all the electrons can be expressed as the Duane – Hunt law,**

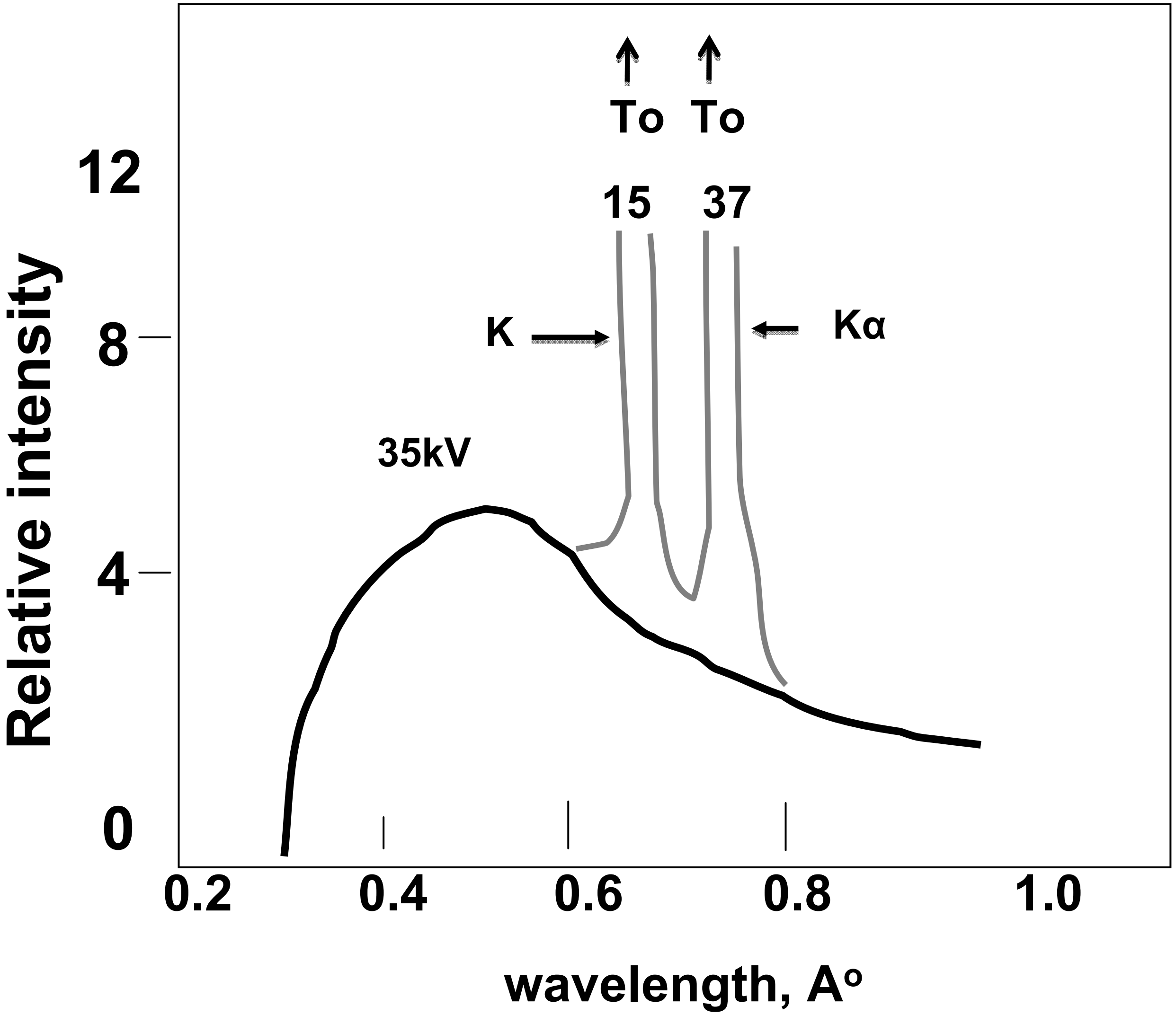
$$Ve = h\,\nu_0 = hc / \lambda$$

**where v is the applied potential, $\nu_0$ is the frequency.**

**Thus the kinetic energy is the product of accelerating voltage and the charge on the electron and $\nu_0$ is the maximum of the radiation that can be produced.**

**X–ray line spectra result from electronic transitions in the innermost atomic orbitals. They occur in the longer wavelength range of 4 – 6 $\overset{0}{\mathrm{\AA}}$ . The line spectra occur for all the elements having atomic numbers of 12 and above. Elements having atomic numbers less than 23 show only two lines called as K series and designated as $K_\alpha$ and $K_\beta$. These are of short wavelengths. For example K series for tungsten target appear at 0.18 and 0.21$\overset{0}{\mathrm{\AA}}$.**

# LINE SPECTRUM WITH A MOLYBDENUM TARGET



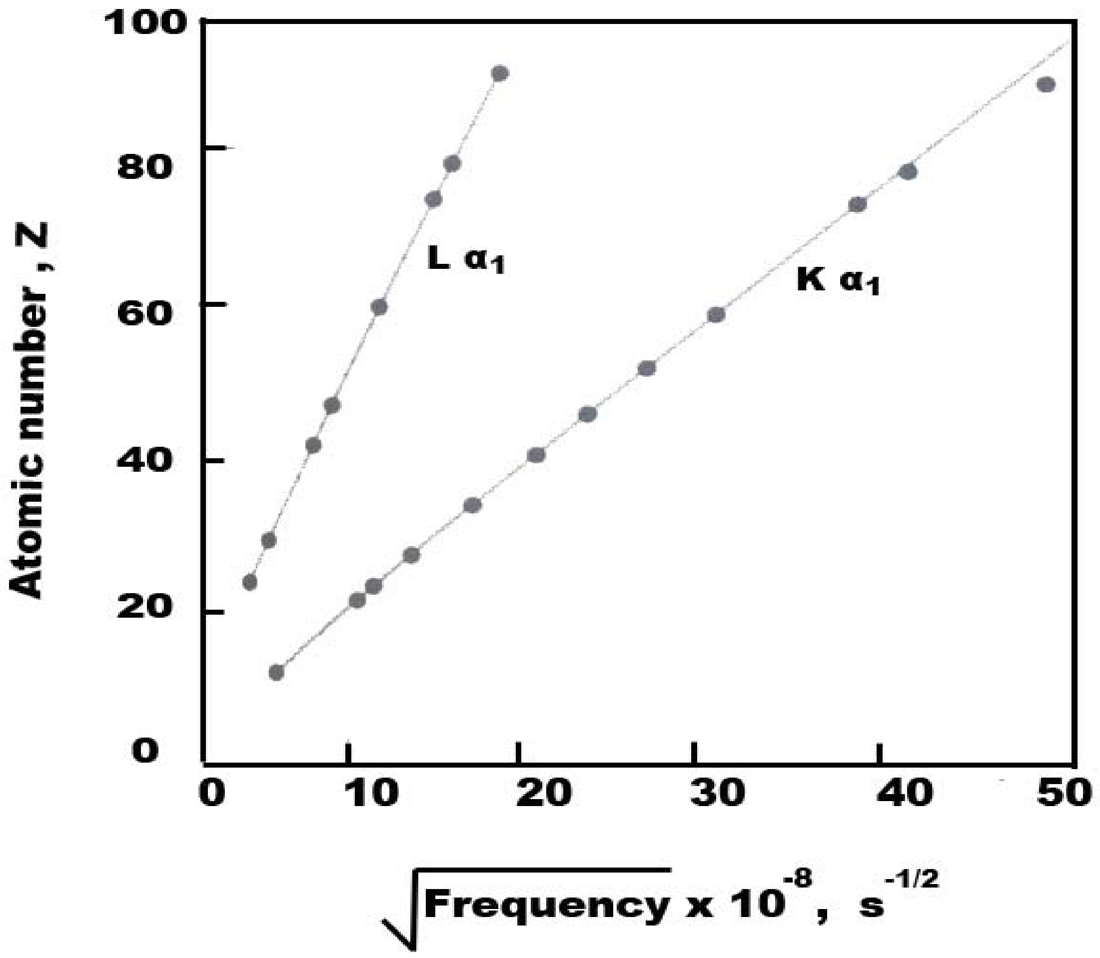
**Elements having atomic numbers more than 23 show L series which are also designated as $\alpha_1$ , $\beta_1$. There is a threshold voltage for each element below which line spectra do not appear. For example, below 50 kV , no line spectra is obtained for molybdenum. However above 70 kV it produces line spectra.**

# X–ray emission lines for some typical elements

| Element | Atomic number | K – Series | | L – Series | |
|---|---|---|---|---|---|
| | | $\alpha_1$ | $\beta_1$ | $\alpha_1$ | $\beta_1$ |
| Na | 11 | 11.909 | 11.617 | - | - |
| K | 19 | 3.742 | 3.454 | - | - |
| Cr | 24 | 2.290 | 2.085 | 21.714 | 21.323 |
| Rb | 37 | 0.926 | 0.829 | 7.318 | 7.075 |
| Cs | 55 | 0.401 | 0.355 | 2.892 | 2.683 |
| W | 74 | 0.209 | 0.184 | 1.476 | 1.282 |
| U | 92 | 0.126 | 0.111 | 0.911 | 0.720 |

**Mosley showed that there is a linear relationship between the square root of frequency for a given K or L line and the atomic number as shown below.**

$$c/\lambda = a(Z - \sigma)^2$$

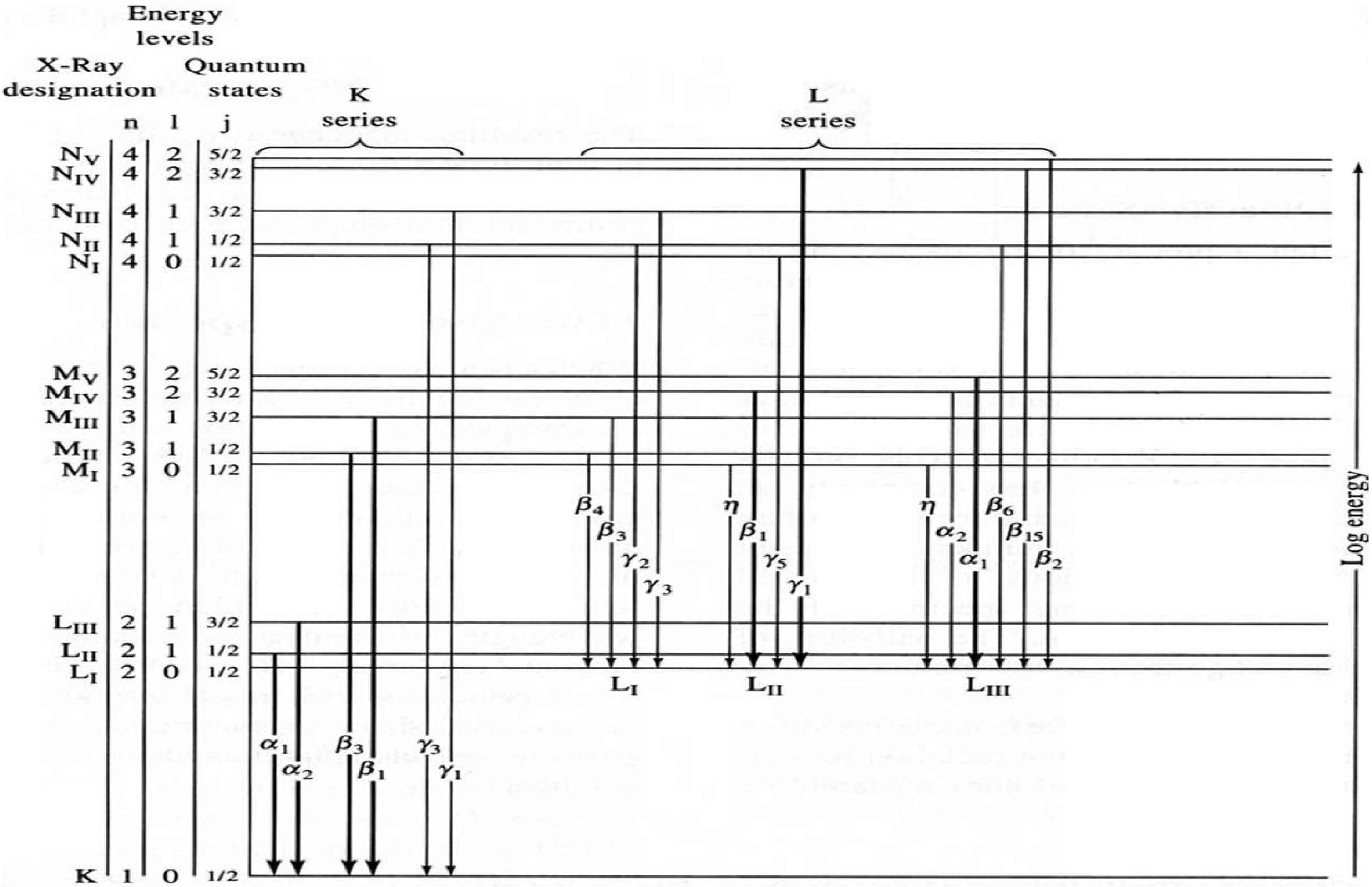


The short wavelength K series is produced when the high energy electron beam removes an electron from those orbitals nearest to the nucleus of the target atom. This produces an excited ion which emits a quanta of radiation as electrons from outer orbitals undergo transitions to fill the vacancy.

K series lines arise from transitions between higher energy levels and the K shell.

L series of lines results when an electron is lost from the second principal quantum level directly or from the transition of an L electron to the K level.

# PARTIAL ENERGY LEVEL DIAGRAM CAUSING X–RAYS PRODUCTION



**In this figure, the atomic energy levels are in the logarithmic scale. The energy difference between $\alpha_1$ ,$\alpha_2$ and $\beta_1$, $\beta_2$ are so small that they appear as single lines.**

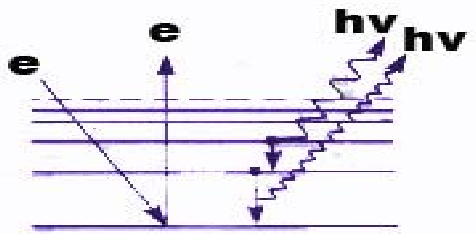
**This energy level diagram is applicable to any element with sufficient electrons to permit the number of transitions shown.**

**The wavelengths of characteristic X–ray emissions are independent of the chemical state of the element as the transitions do not involve bonding or nonbonding electrons. Thus the position of $K_\alpha$ line for tungsten or any element is same whether it is an oxide, sulphide or pure metal or an organic complex.**

**Based on the properties of X–rays, a number of analytical methodologies have been developed over the years. These include :**

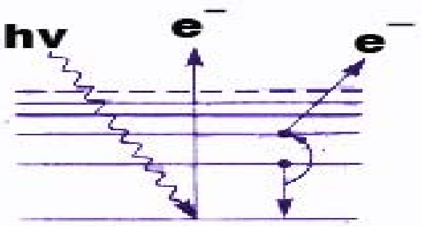
- **a) X–ray emission spectroscopy (XES)**
- **b) Auger emission spectroscopy (AES)**
- **c) X-ray fluorescence spectroscopy (XFS)**
- **d) Electron spectroscopy (ESCA)**
- **e) X–ray absorption**
- **f) X–ray diffraction**

# X–RAY ANALYTICAL METHODS



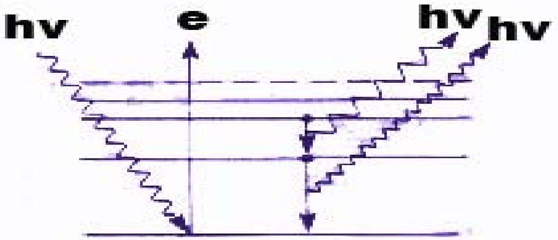
(a)

**X – ray emission**



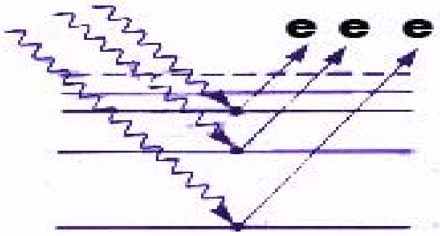
(b)

**Auger emission**



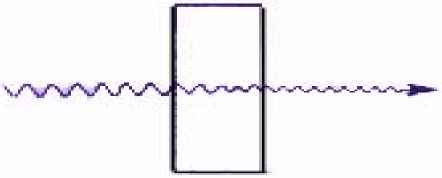
(c)

**X–ray fluorescence**



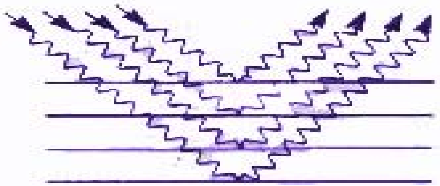
(d)

**Electron spectroscopy**



(e)

**X–ray absorption**



(f)

**X – ray diffraction**

**X–ray absorption and emission spectra are quite simple because they consist of very few lines. X–ray emission spectrum of an element may be obtained by using the sample itself as the target element. However this approach is not very convenient for all types of samples.**

**Instead, excitation can be accomplished by irradiating the sample with a beam of X–rays from an X–ray tube or a radioactive source. In this method, all the elements in the sample are excited by the absorption of the primary beam which emit their own characteristic fluorescence X–rays.**

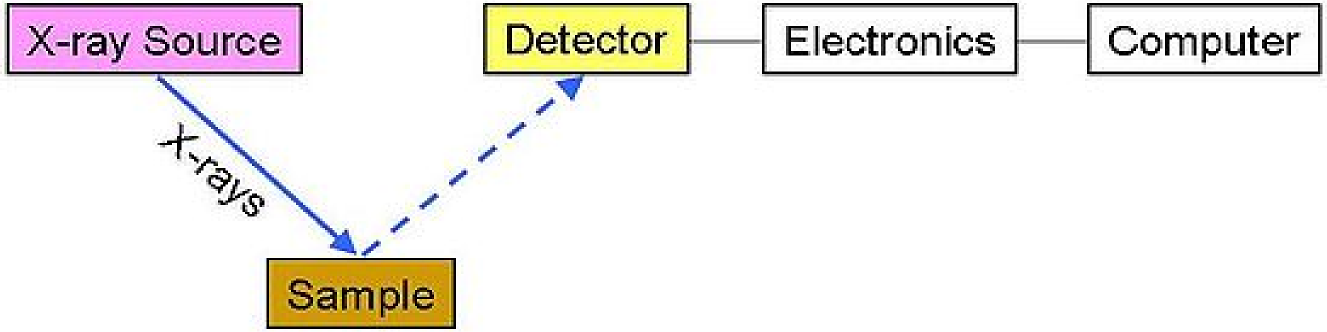
**Thus XRF is a powerful tool for the qualitative (pass fail test) and quantitative estimation of all but the lightest elements having atomic numbers greater than that of oxygen (>8).**

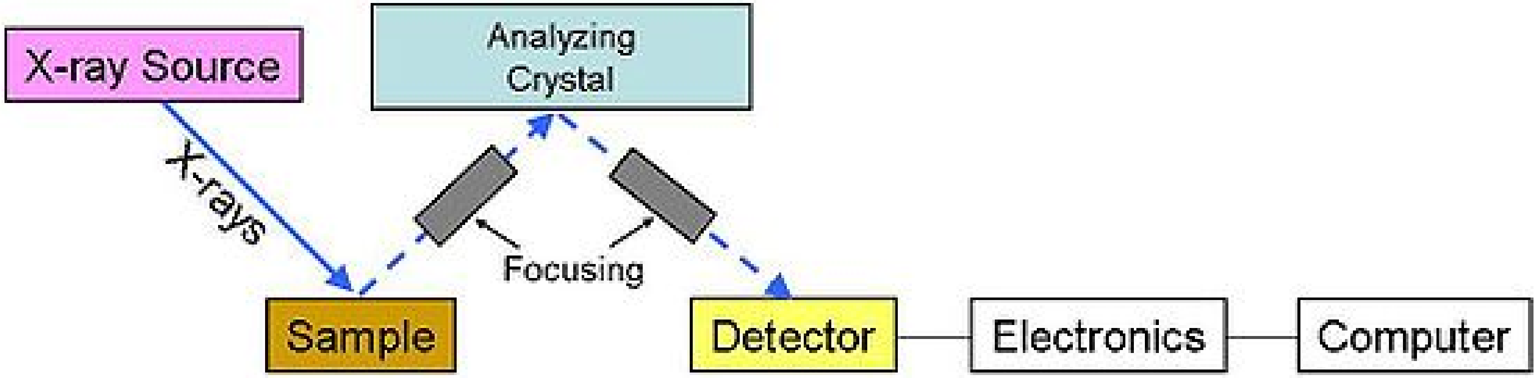
**XRF is a non destructive technique as against most of the other elemental techniques.**

**There are two types of X-ray fluorescence spectrometers : wavelength dispersive X–ray fluorescence (WDXRF) and energy dispersive X–ray fluorescence (EDXRF) spectrometers.**

**Important instrument components of XRF include a source, a transducer, a signal processor and read out.**

# INSTRUMENTATION FOR XRF





# SOURCES

## 1. Coolidge tube

An X–ray tube is a high vacuum, sealed off tube containing a heated filament cathode (W) and a 5 x 10 mm heavy block of copper with a metal target plated or embedded on its surface. Target materials include tungsten, chromium, copper, molybdenum, rhodium, scandium, silver, iron and cobalt.

Separate circuits are used to heat the filament and to accelerate the electrons to the target. The heater circuit controls the intensity of the emitted X–rays and the accelerating voltage determines their energy or wavelength. Both current and voltage must be stable up to 0.1%.

**X–ray generation by this method is basically an inefficient process and much energy is wasted as heat. Hence cooling of the anodes is necessary.**

**Modern equipments employ highly sensitive transducers and hence cooling is not necessary.**

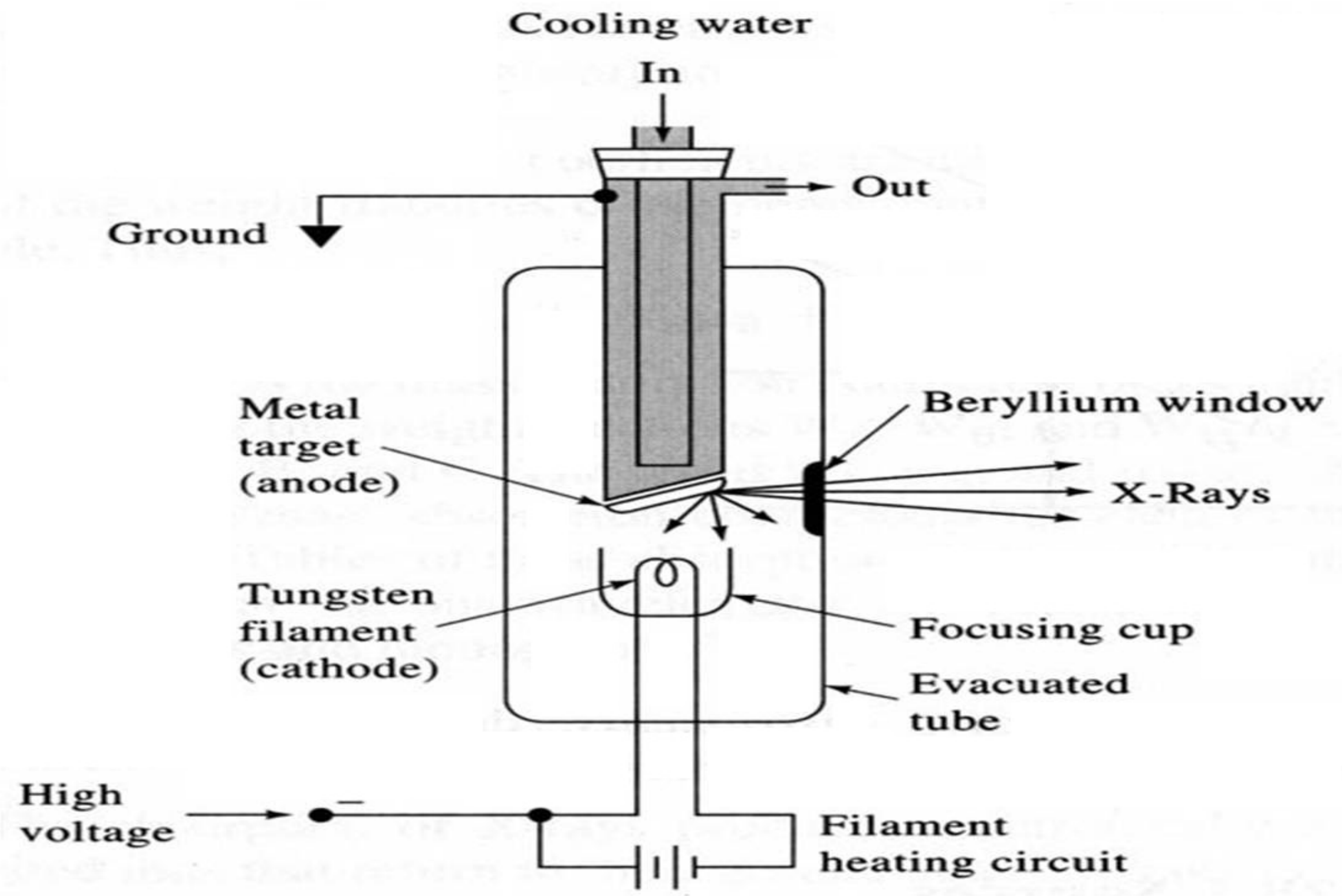
**The X–ray beam passes out of the tube through a thin beryllium window or a special glass. For wavelength of 6 – 70 $\overset{0}{\text{Å}}$ , ultra thin (1µm) aluminum or parlodion films are used to isolate the tube.**

**The current is regulated by monitoring the X–ray tube DC current and controlling the filament voltage. When the full wave is rectified, the voltage reaches its peak value 120 times per second and persists for only a small fraction of time.**

**When the tube is operated at 50kV, the gain is two fold for elements up to At. Number 35 (Br) and increases to four fold at At. Number 56 (Ba).**

**Normally X–ray tubes are operated between 50 – 60 kV but now a days tubes with 100 kV are available.**

# SCHEMATIC OF AN X-RAY TUBE



# RADIOISOTOPES

**A variety of radioactive substances such as $^{3}_{3}H$, $^{55}_{1}Fe$ , $^{57}_{27}Co$ , $^{109}_{48}Cd$ , $^{125}_{53}I$ , $^{147}_{61}Pm - Al$; $^{210}_{82}Pb$ etc., are used as sources in XRF. Some elements produce simple line spectra and others produce a continuum. A given radioisotope will be suitable for exciting a number of elements. For example a source giving X–ray in 0.30 – 0.47 $\overset{0}{\mathrm{A}}$ is suitable for XRF studies for all elements up to silver. The sensitivity improves as the wavelength of the source line approaches the absorption edge.**

# SECONDARY FLUORESCENCE SOURCES

**In some applications an X–ray tube with tungsten target is used to excite Kα and Kβ lines of MO.**
**The resulting fluorescence spectrum would contain only line spectra which can be used for the excitation of the analyte.**

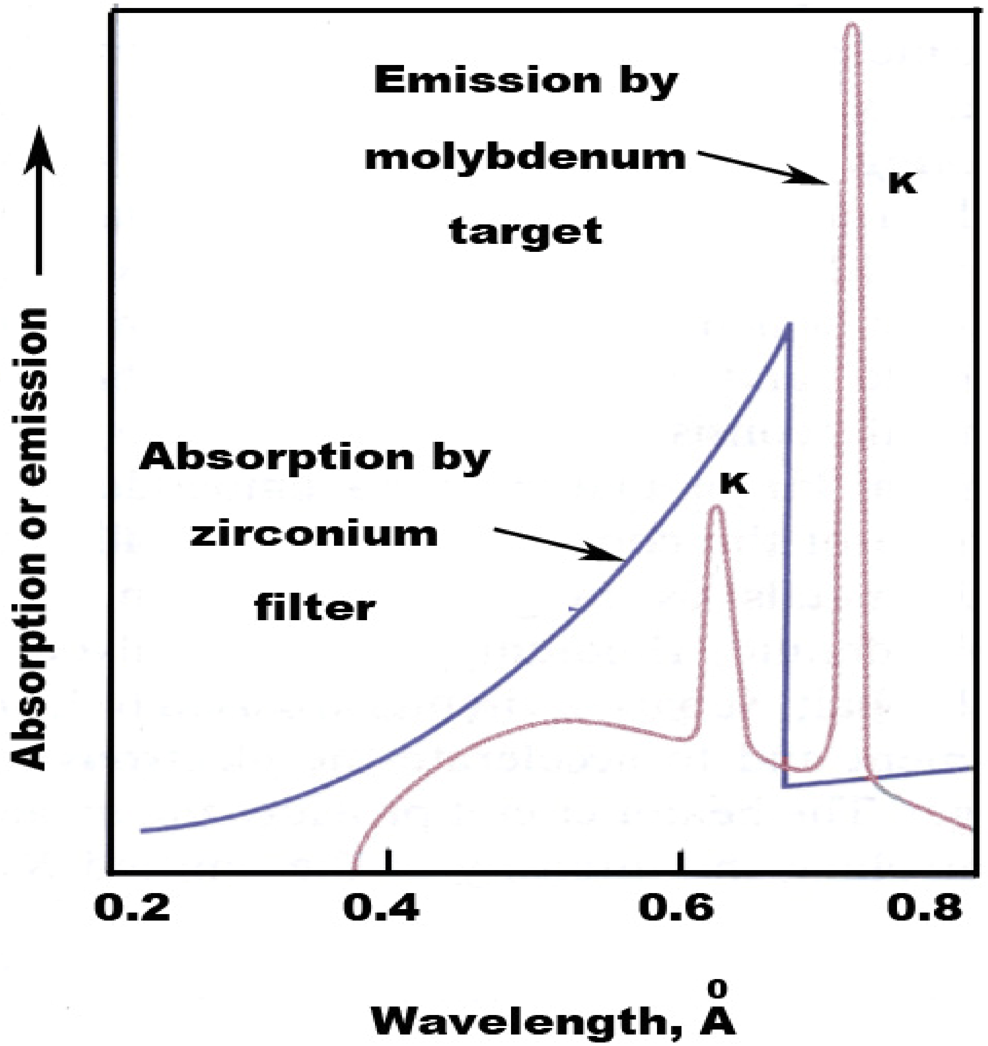
# X–RAY FILTERS

In some applications, x–ray tubes with narrow wavelength range are required. Both filters and monochromators are used for this purpose.

Zirconium filters of 0.01 cm thickness are suitable to isolate $K_\alpha$ line. It filters most of the continuum and $K_\alpha$ line.

Several other filters have also been developed for this purpose. Quite often, thin strips of other metals are also employed for this purpose.

# FILTERS FOR X-RAYS



# X–RAY MONOCHROMATORS

**X–ray monochromators consist of a pair of beam collimators. One serves as a slit and the other serves as the dispersing agent.**

**The latter is a single crystal mounted on a goniometer or a rotating table that permits the determination of the angle θ between the crystal face and the collimated incident beam.**

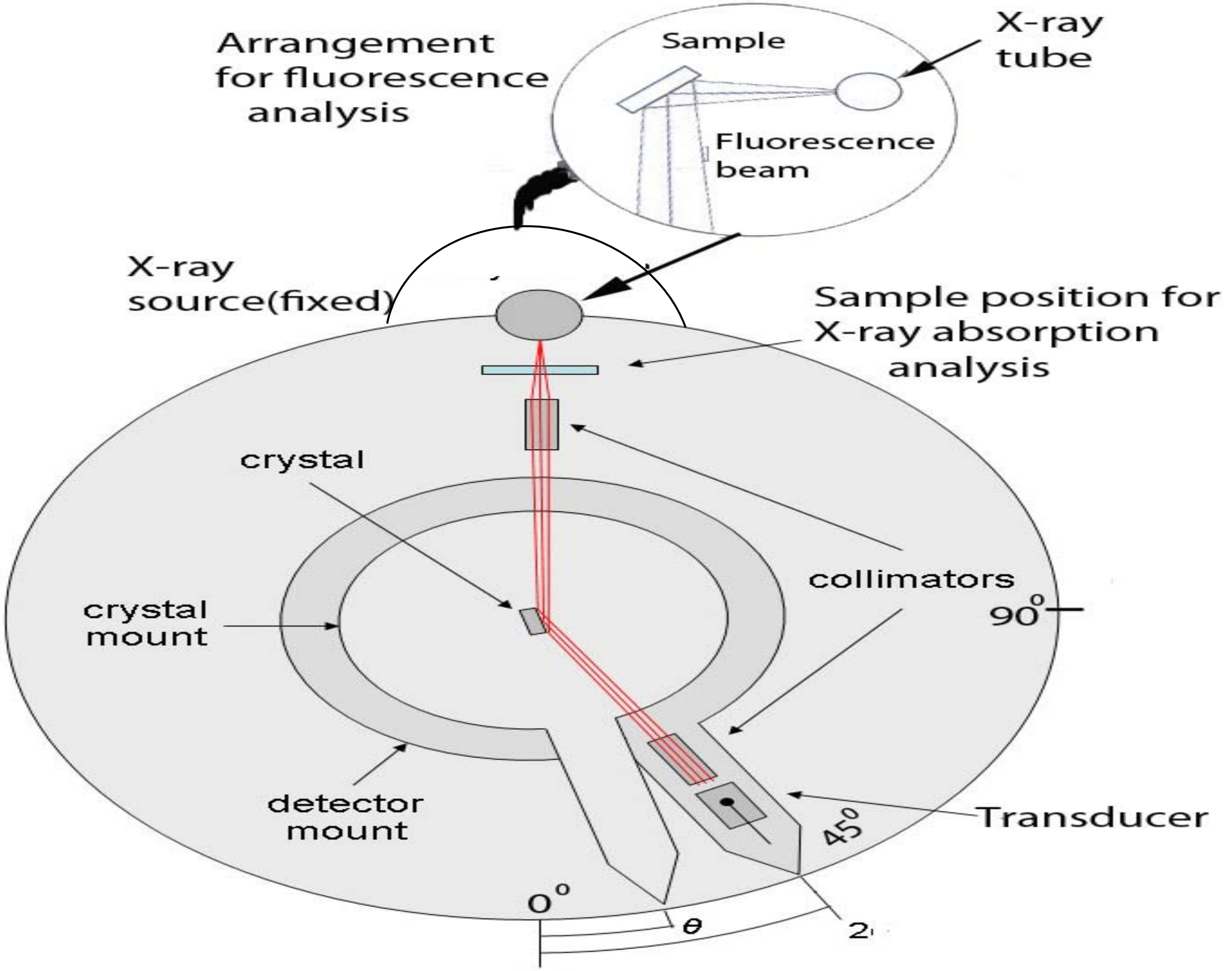
**Bragg's equation shows that for any given angular setting of the goniometer only a few wavelengths are Diffracted according to the equation,**

$$n\lambda = 2\, d \sin\theta$$

**To produce a spectrum, the exit beam and the detector must be mounted on a second table that rotates at twice the rate of the first. Hence when the crystal rotates by an angle θ the detector rotates by 2θ.**

**Modern X-ray monochromators have microprocessor controlled motors to drive the crystal and the detector independently without a gear based mechanical connection. Hence they can scan rapidly at the rate of $240^0$/min.**

# AN X-RAY MONOCHROMATOR AND DETECTOR ARRANGEMENT



**The collimators in an X-ray monochromators consist of a series of closely spaced metal plates that absorb all the radiations except the parallel beams.**

**X-radiation longer than 2A is absorbed by the atmospheric gases. Therefore if longer wavelength X-rays are required, the sample compartment must be flushed with helium or it must be evacuated by pumping.**

**With flat crystals, up to 99% of the X-radiation is divergent which is absorbed by the collimators. The loss can be minimized further by 10% using a curved crystal surface. The curved surface also accomplishes the focusing of the divergent beam from the source on the exit collimator.**

# DIFFRACTING CRYSTAL PROPERTIES

| Crystal | Lattice Spacing | Wavelength range, a $\overset{0}{A}$ | | Dispersion, $^0/\overset{0}{A}$ | |
|---|---|---|---|---|---|
| | d, $\overset{0}{A}$ | $\lambda_{max}$ | $\lambda_{min}$ | at $\lambda_{max}$ | at $\lambda_{min}$ |
| Topaz | 1.356 | 2.67 | 0.24 | 2.12 | 0.37 |
| LiF | 2.014 | 3.97 | 0.35 | 1.43 | 0.25 |
| NaCl | 2.820 | 5.55 | 0.49 | 1.02 | 0.18 |
| EDDT[b] | 4.404 | 8.67 | 0.77 | 0.65 | 0.11 |
| ADP[c] | 5.325 | 10.50 | 0.93 | 0.54 | 0.09 |

[a] **Based on the assumption that the measurable range of $2\theta$ is from $160^0$ for $\lambda_{max}$ to $10^6$ for $\lambda_{min}$**

[b] **EDDT = Ethylenediamine d-tartrate**

[c] **ADP = Ammonium dihydrogen phosphate**

The useful wavelength range for a crystal is determined by its lattice spacing ‘d ’ and the detector problems when $2\theta$ is much less than $10^0$. This happens when $\theta$ is approaching zero or $180^0$. Under these conditions, polychromatic radiation scattered from the crystal surface becomes very high. Therefore only up to $160^0$ ($2\theta$) are employed in X-ray work.

Crystals with large crystal lattice spacing (d), such as ammonium dihydrogen phosphate offer better control over the scatter control but it results in lower dispersion also.

Differentiating Bragg's equation, we get,

$$\frac{d\theta}{d\lambda} = \frac{n}{2d \cos \theta}$$

Hence dθ/dλ the measure of dispersion is inversely proportional to d. Hence low dispersion prohibits the use of shorter wavelengths. Here topaz or LiF must be substituted.

# X-RAY DETECTORS

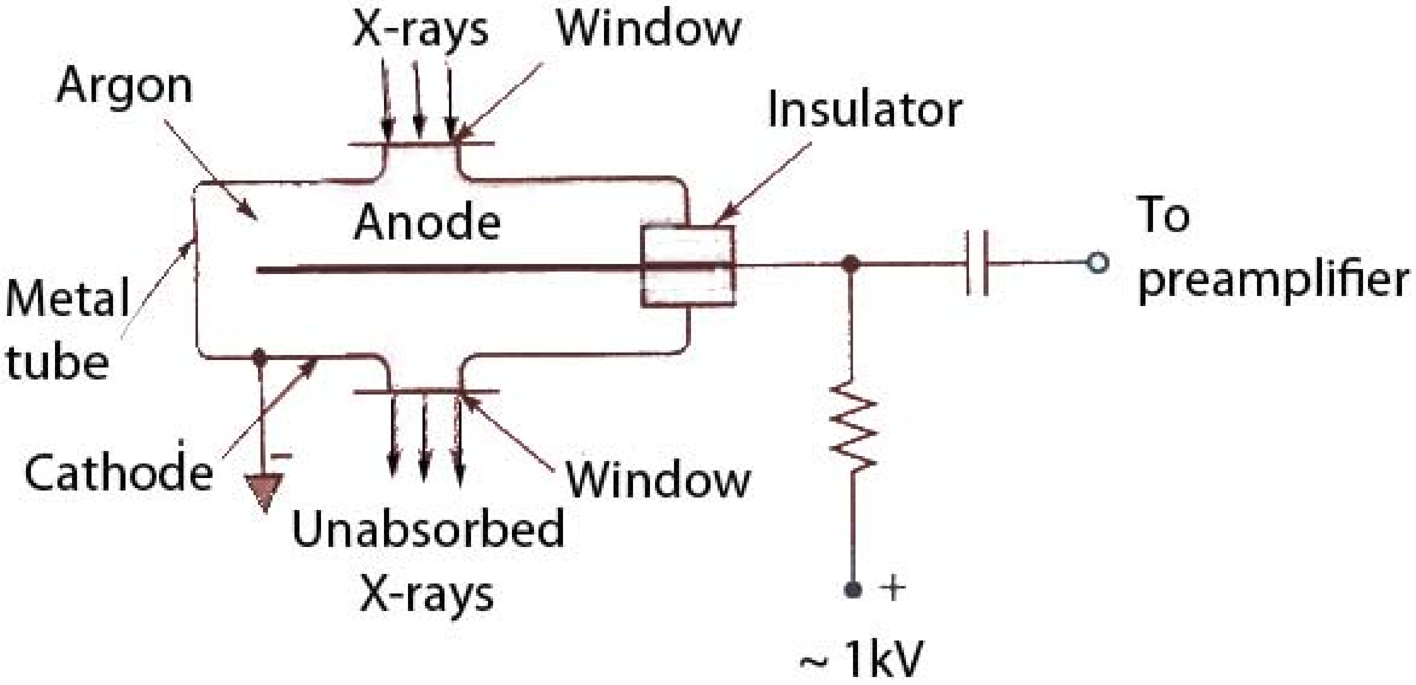
X-ray detectors are usually operated as photon counters. In this mode, individual pulses of the charge are produced as quanta of radiation which are absorbed by the transducer and counted. This requires rapid response times for the transducer as well as the signal processor. This technique is useful for low intensity X-ray beams.

# GAS FILLED TRANSDUCERS

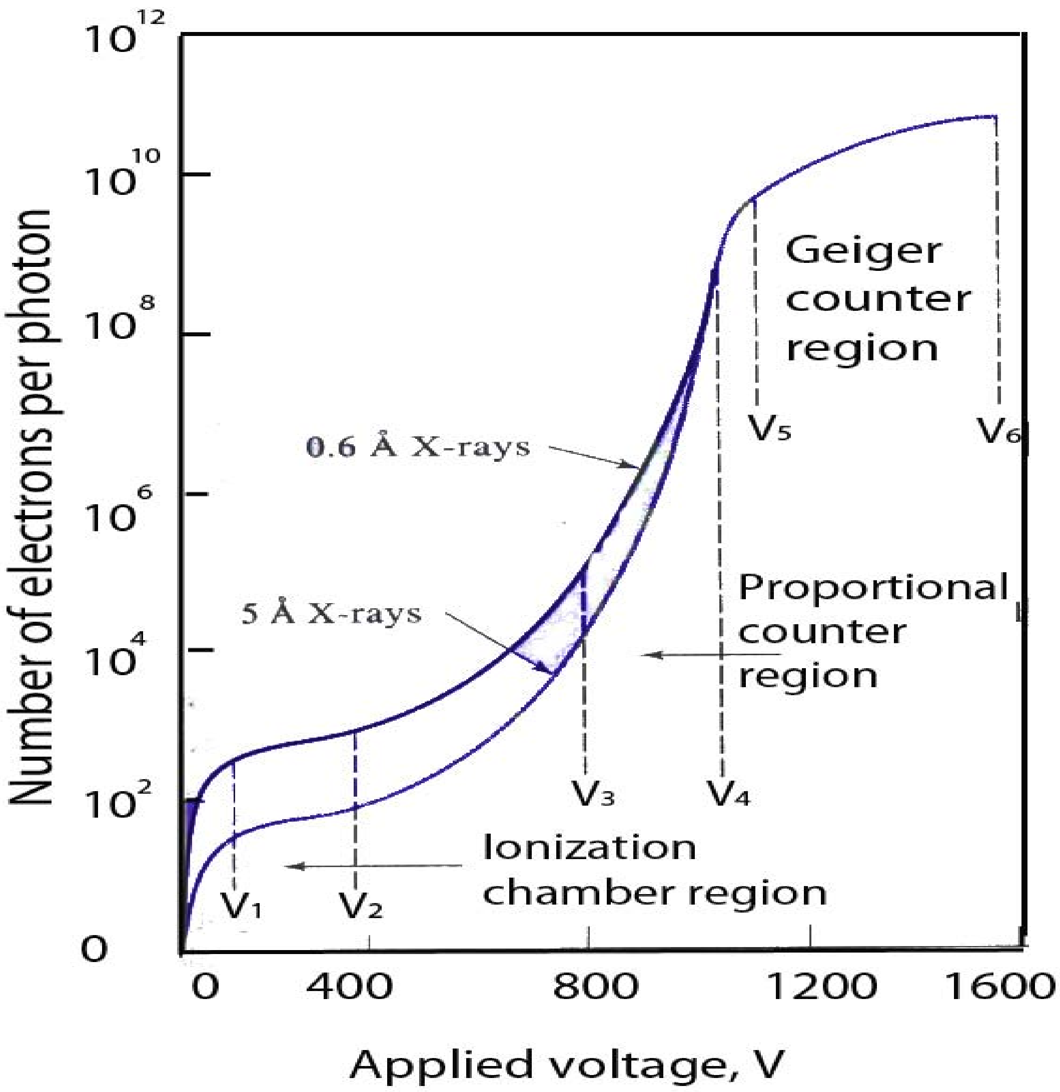
When X-rays pass through an inert gas such as argon, xenon or krypton, a large number of positive ions and electrons are produced for each X-ray quantum. Therefore, conductivity of the gases increases from this phenomenon. Ionization chambers, proportional counters and Geiger tubes are used to measure this enhanced current.

A typical gas filled transducer is shown here. The radiation enters the chamber through a transparent window of mica or beryllium or aluminum or mylar sheet. Each photon of X-radiation interacts with one atom of argon and causes it to loose one of its outer electrons. The photo electron loses its kinetic energy by ionizing several hundred additional argon atoms. The electrons move toward the central wire anode and argon cations move towards the cylindrical metal cathode.

# GAS FILLED DETECTOR



# AMPLIFICATION OF DETECTOR SIGNALS



This figure shows the effect of applied voltage on the number of electrons reaching the anode for each photon.

The region $V_1 – V_2$ ,shows the number of electrons reaching the anode which is fairly constant for each photon.

In the region $V_3$-$V_4$ ,the number of electrons increases rapidly with applied voltage. Here secondary ion pair production occurs due to the collisions between the accelerated electrons and gas molecules. Therefore, under these conditions amplification of the current occurs.

The region $V_5$-$V_6$ shows that amplification of the electrical impulse is enormous but the current is independent of the type and energy of the incoming radiation. The current is actually governed by the geometry and gas pressure of the tube. This region is known as the Geiger region.

# SCINTILLATION COUNTERS

**A scintillation counter consists of a transparent crystal of sodium iodide containing 0.2% thallium iodide shaped in the form of a cylinder shaped 3x4 inch in each dimension. One surface is plane which faces the cathode of a PMT. As the incoming radiation passes through the crystal, its energy is lost to the scintillator which is subsequently released in the form of photons of fluorescence radiation.**

**The flashes of light produced are transmitted to the photocathode which in turn produce an electrical pulse that can be amplified and counted.**

# X-RAY FLUORESCENCE METHODS

As explained earlier there are two types of XRF instruments: Wavelength dispersive (WDXRF) and energy dispersive (EDXRF).

In WDXRF an X-ray beam from a radioactive source is collimated and dispersed into its component wavelengths. Both single channel (sequential) or multichannel (simultaneous) detection systems are employed.

In single channel instruments, the crystal and the transducer are set at specific angles (θ & 2θ respectively) and the counting progresses until sufficient counts are obtained for precise measurements. The instrument can be automated to cover the entire $360^0$ C. In such instrument the movement of the crystal and detector are synchronized and the output is connected to the data acquisition system.

The X-ray sources use chromium for long wavelengths and tungsten target for short wavelengths. Such instruments cost around 25 lakh Rupees.

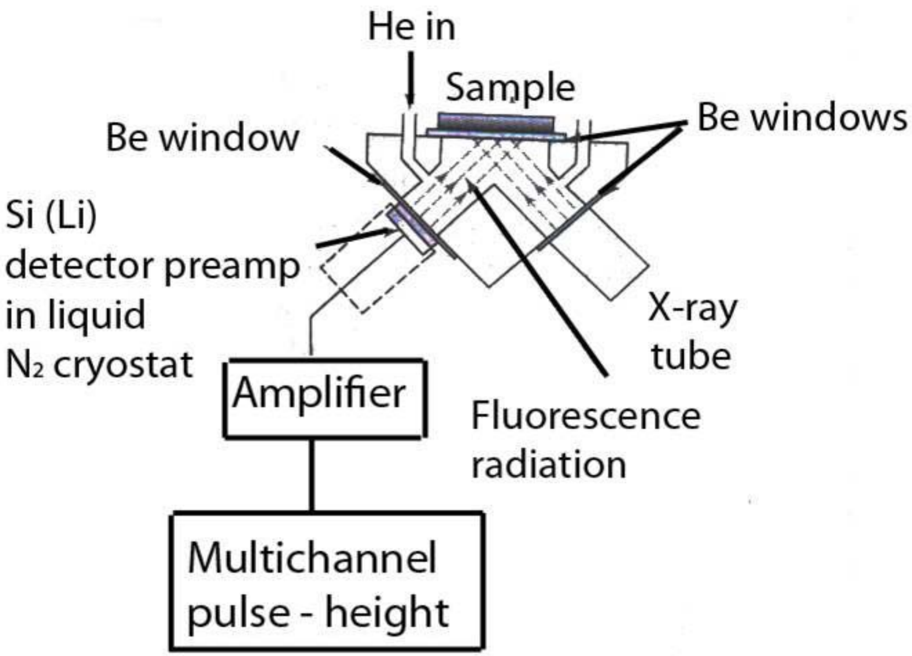
**Multichannel instruments are costlier (> 150,000$). They are useful for the determination of up to 24 elements simultaneously. In these instruments, individual channels of an appropriate crystal and a detector are arranged radially around an X-ray source and sample holder . The crystals for most of the channels are fixed at an appropriate angle for a given analyte line.**

**For every element to be determined there will be a dedicated transducer, amplifier, pulse height detector and counter or integrator. These instruments are equipped with a computer for precise instrument control, data processing and display of analytical results. The analysis is usually completed within a few seconds to a few minutes.**

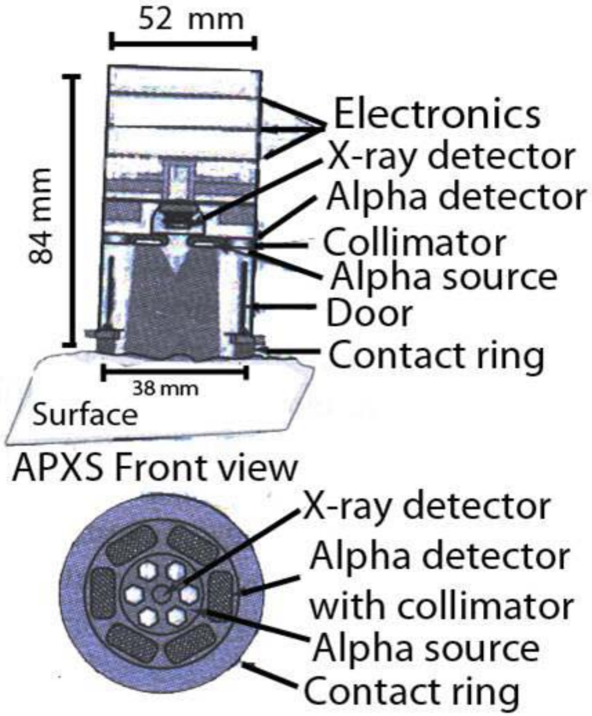
# ENERGY DISPERSIVE XRF

**EDXRF has a polychromatic source such as an X-ray source or a radioactive material, a sample holder, a semiconductor detectors and various electronic components for energy discrimination.**

**The analytical methodology is very simple. There are no moving parts and no collimators or crystal diffractor. Therefore the energy reaching the detector is 100 times more than WDXRF instruments. Hence low power X-ray tubes or weaker radioactive materials can be used as radiation sources which are cost effective and more safer to use .**



**(a) Schematic design of EDXRF**

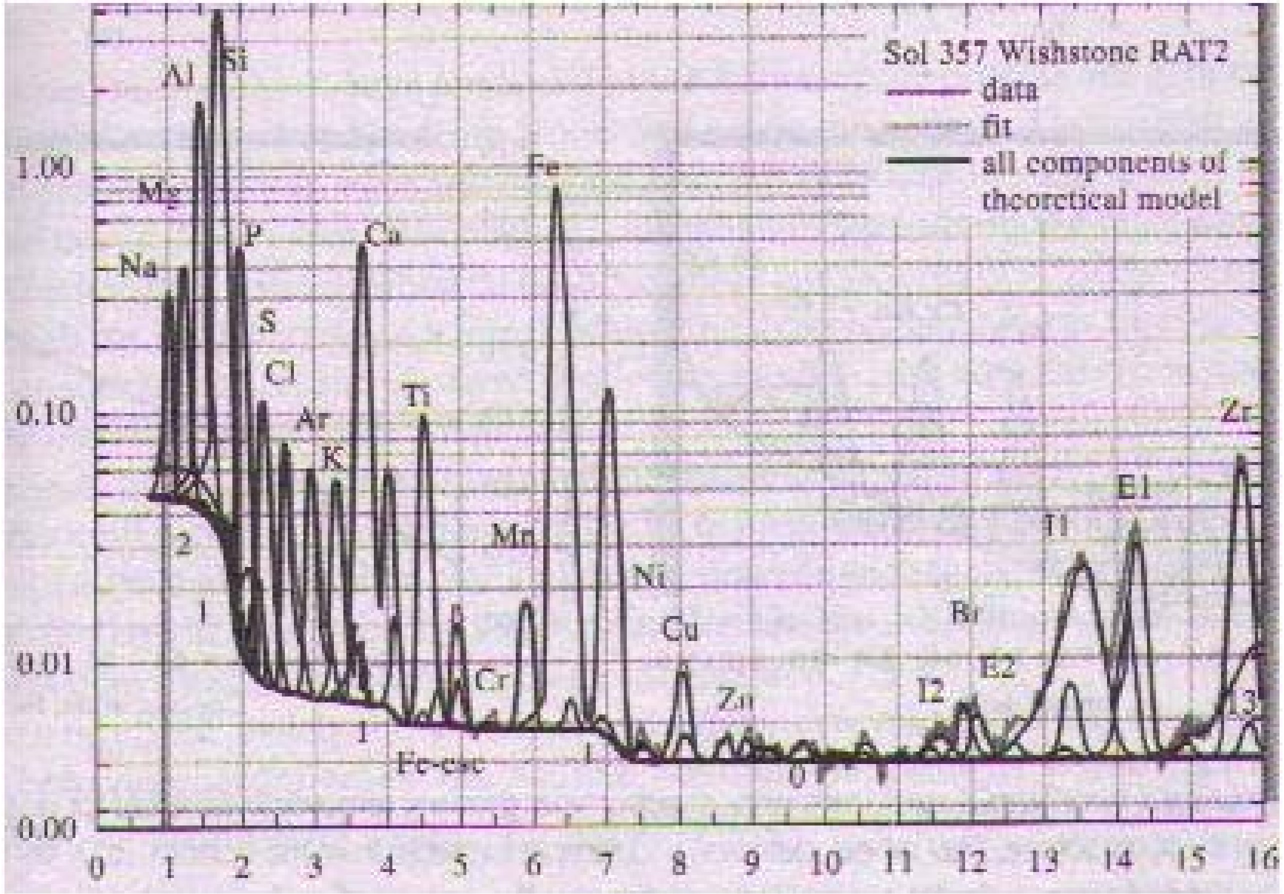


**(b) Mars Mission Rover head**

The sensor head in the rover contains 6 curium-244 sources that emits X-rays and 5.81 MeV α particles. X-ray emission is stimulated by bombardment by α and other subatomic particles such as protons to produce Particle Induced X-ray Emission (PIXE).

The X-ray detector is a new room temperature type that exhibits low noise and high signal to noise ratio for most of the elements.

# XRF DETERMINATION OF MARTIAN ROCKS



Intensity counts per second

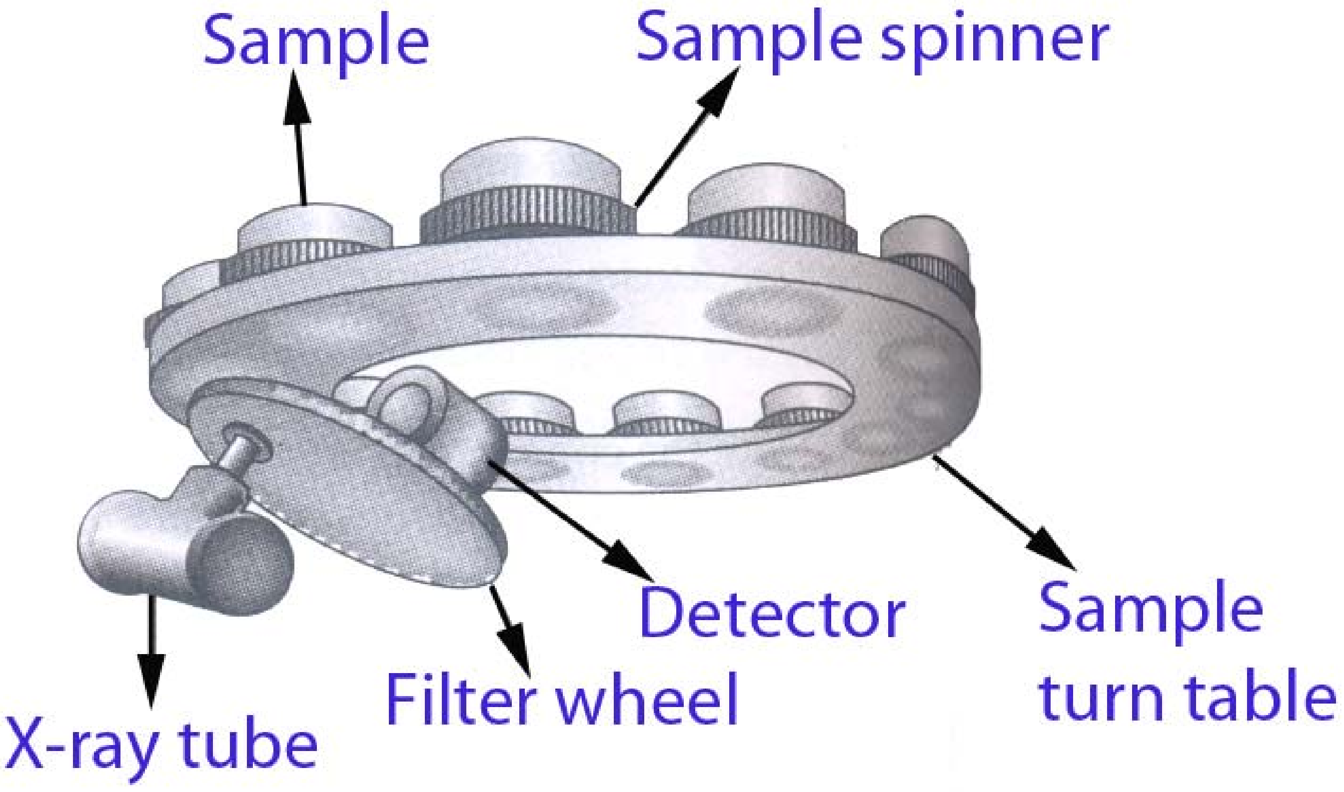
Energy, keV

**In multichannel EDXRF, all the emitted X-ray lines are measured simultaneously. Therefore increased sensitivity and improved signal to noise ratio are obtained (Fellgett advantage). Improved resolution at shorter wavelengths is another advantage.**

**A bench top EDXRF is available for the routine determination of up to 12 elements ranging from sodium to uranium in industrial samples. In this Instrument, the radiation from an X-ray tube passes through an appropriate filter and strikes the bottom of the rotating sample. The fluorescence signal passes on to the sample detector (silicon) which provides signals to the multichannel counting system.**

**The system uses a rhodium anode X-ray tube , five programmable filters, a helium purge system, a twelve positive sample changer and a spinner to rotate each sample during the data acquisition processes to reduce sample in homogeneity.**

# A BENCH TOP XRF MODEL



EDXRF plots energy vs intensity (cps). The energy is in keV. Quantitative analysis can be obtained by measuring the peak heights. A rough estimate of the concentration can be obtained by,

$$P_X = P_S \cdot W_X$$

where $P_X$ is the relative line intensity measured in terms of number of counts per fixed time , $W_X$ is the weight fraction of the desired element in the sample and $P_S$ is the relative intensity of the line under identical conditions if $W_X$ were unity. The value of $P_S$ is determined with a standard sample of known composition or pure element.

# ANALYTICAL METHODOLOGY

Matrix effects: Absorption of the X-rays from atoms well below the surface. The extent of attenuation depends upon the mass absorption coefficient of the medium and its composition. Signal decreases.

Enhancement of fluorescence may occur due to the secondary excitation of the analytical line-signal increases.

This effect can be minimized by using a closely matched standards except the added element.

**Alternately, an internal standard is introduced in all the standards and samples.**

**One can also dilute the sample and standards that absorb X-rays only weakly. Water, organic solvents, starch, lithium carbonate, alumina, boric acid, borate glass etc., Here matrix effects become essentially constant.**

# APPLICATIONS

When X-ray absorption and enhancement effects are minimal, the XRF line intensity and element concentration curves are linear. NIST standards provide such materials which can be used to calibrate the instruments. Typical application include:

(i) Analysis of rock samples for 22 elements.
(ii) Alloy composition control during manufacture.
(iii) Lead and bromine, in aviation fuels, Ca, BA, zinc in lubricating oils, pigments in paint samples.
(iv) Determination of chlorine, sulphides and sulphur dioxide on O-toluidine, silver nitrate and sodium hydroxide impregnated micropore filter papers.
(v) Determination of Fe, Cu, Zn in rice samples.

# ADVANTAGES OF XRF

(i) The spectra are relatively simple and not subject to much interference.

(ii) Non destructive technique. Hence useful for analysis of paintings, archeological specimens, jewellery , antique items etc.,

(iii) Speed and convenience of the procedure.

(iv) Precision and accuracy are comparable to established methods in classical techniques.

# DISADVANTAGES OF XRF

(i) The concentration range varies from 0.01 – 100%.

(ii) Not useful for light elements (less than 23 At. Numbers).

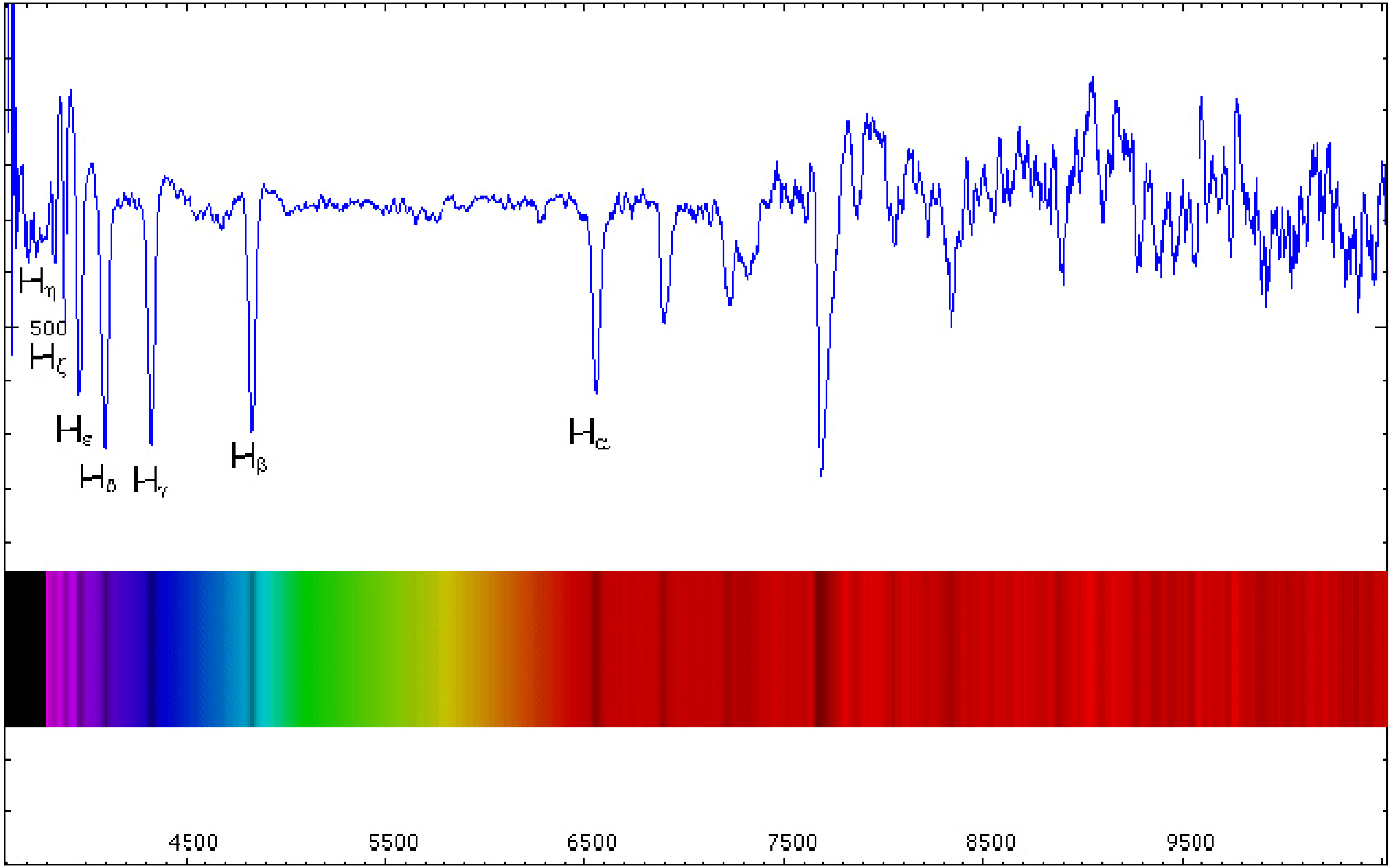
(iii) High cost of the instruments.

# ATOMIC ABSORPTION SPECTROMETRY

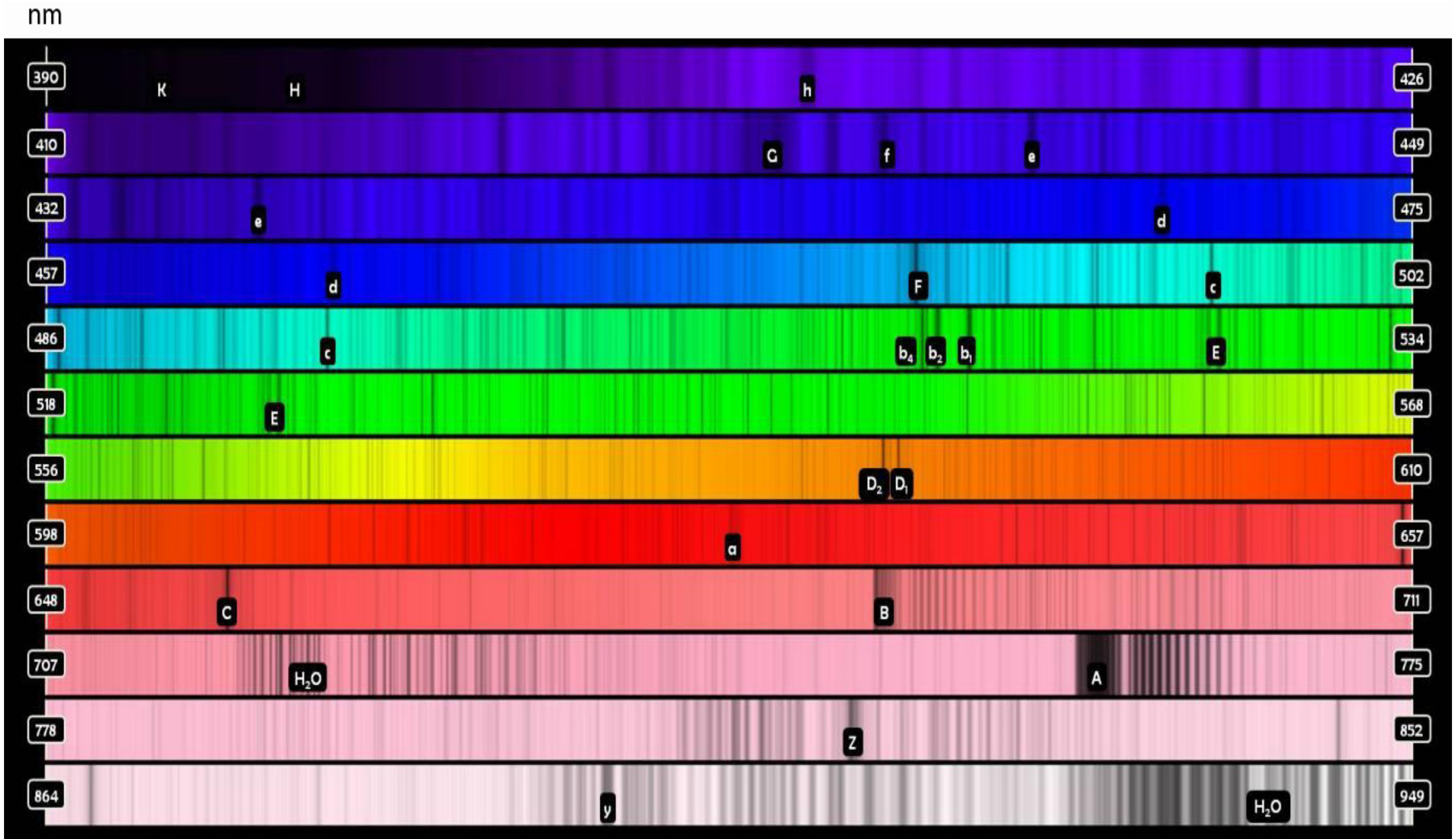
**The phenomenon of atomic absorption was first discovered by Woolaston  in 1802 in the spectrum of sunlight. Till then thought to be a continuous spectrum, Woolaston made a remarkable observation that the solar spectrum was in fact interrupted by “dark lines” which was later confirmed by Fraunhofer in 1814. However, Brewster put forward the idea that these dark lines denoted till then by alphabetical markers are in fact due to the presence of vapors of certain elements in the sun’s atmosphere. Therefore, it follows that substances emitting specific radiations are also capable of absorbing the same, causing the spectrum of dark lines in the bright background.**

This phenomenon generally known as Kirchoff’s law was used to deduce the presence of oxygen, hydrogen, sodium, iron, calcium etc., in the solar spectrum. The experimental confirmation for this came from electric arc or spark, when the spectral source surrounded by atomic vapors also showed dark lines because of absorption of the emitted radiations. Foucalt in France also demonstrated the reversal of spectral lines.

# FRAUNHOFFER LINES



# FRAUNHOFFER LINES



| K | H | h | G | | f | e | d | F | c | $b_4$ | | $b_2$ | $b_1$ | E | $D_2$ | $D_1$ | a | C | B | | A | Z | y | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ca+ | Ca+ | Hδ | Ca | Fe | H | Fe | Fe | Hβ | Fe | Mg | Fe | Mg | Mg | Fe | Na | Na | $O_2$ | Hα | $O_2$ | $H_2O$ | $O_2$ | $O_2$ | $O_2$ | $H_2O$ |
| 393.368 | 396.847 | 410.175 | 430.774 | 430.790 | 434.0 | 438.355 | 466.814 | 486.134 | 495.761 | 516.733 | 516.891 | 517.270 | 518.362 | 527.0 | 588.995 | 589.592 | 627.661 | 656.281 | 686.719 | 720.0 | 759.370 | 822.696 | 898.765 | 940.0 |

In 1902, Wood repeated the experiments of Kirchoff and Foucalt and proved conclusively that by introducing sodium vapor in the optical path of sodium emission lines (589.0 and 589.6 nm), a reduction in the intensity of radiation occurs. By analogy with acoustic resonance lines, he also showed the possibility of using these resonance effects to detect traces of mercury. The potential of this technique was not recognized by analytical chemists and spectroscopists till 1924.

**Angerer and Joose published the atomic spectra of iron group metals, followed by Frayne and Smita for indium, aluminum, gallium and tantalum. Muller and Pringshiem in 1930 published the first atomic absorption method of measuring the mercury content in air. Even this did not evoke interest in the analytical chemists for the determination of other elements.**

**Walsh, in 1955 developed the first real application of atomic absorption to chemical analysis. In the same year Alkamade and Miatz described a double beam method of spectral selection with two flames, the first being the source and the second as atomizer. Since then the atomic absorption spectrometry is in the forefront of chemical analysis. The first commercial atomic absorption instruments appeared in 1960s.**

**Spectacular advances in instrumentation, electronics, automation and computers over the years have made atomic absorption spectrometry, one of the most reliable analytical techniques of modern times perhaps equalled only by atomic emission spectrometry in terms of simplicity, sensitivity, specificity and speed of operation.**

The development of electrothermal atomization by L’vov and Massmann pushed the detection limits of atomic absorption technique to nanogram and picogram and sometimes even up to femtogram levels.

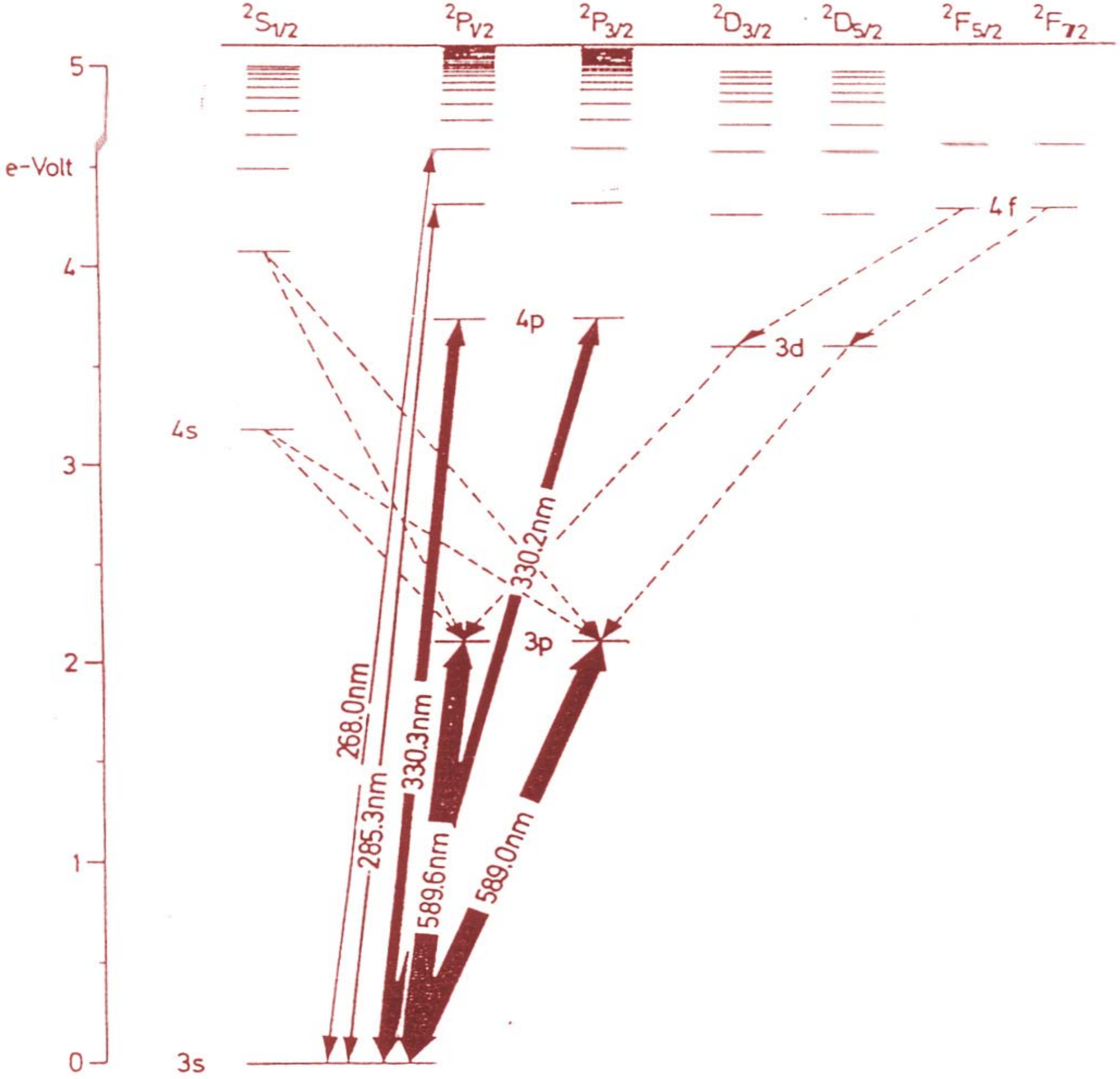
Hydride generation atomic absorption spectrometry for arsenic, antimony, bismuth, selenium, tellurium, germanium, lead and cold vapor mercury determination have proved attractive accessories for atomic absorption technique to make it the first choice of analytical chemists throughout the world.

**The popularity of the atomic absorption spectrometry can be gauged by the fact that more than 100 books, 10,000 publications and 5000 symposia and conferences till date have appeared with applications in biological, chemical, nuclear, industrial products, soils, environment etc.,**

# THEORETICAL CONCEPTS OF ATOMIC ABSORPTION

**The simplest concept of atomic structure is that of the positively charged nucleus containing protons and neutrons surrounded by an equal number of electrons orbiting in space in the electric field created by the protons. According to quantum mechanics, such a system can exist in a stable state only if its energy is quantized even at the lowest energy level or ground state. All other levels are excited levels, which can be induced by mechanical or electromagnetic means. The energies associated with these atomic states are in the range of a few electron volts represented by Grotian diagram. Such a diagram for sodium is shown in the next slide.**

# ENERGY LEVEL DIAGRAM FOR SODIUM



**Emission of light occurs when an atom reverts to a state of lower energy. Bohr's equation expresses the conservation of energy by the relation:**

$$\nu = E_1 - E_2 / h \qquad (1)$$

$$\text{or } \lambda = c / \nu = hc / E_1 - E_2$$

**where c is the velocity of light (2.99793 x 108 m/s), h is the Plank's constant (6.62 x $10^{-34}$ in SI Units), v is the frequency, λ is the wavelength and $E_1$, $E_2$ are the energy levels of excited and ground states.**

**Inserting the numerical values, we get:**

$$\lambda = 1.23978 / \Delta E$$

**Thus a transition from the resonance level of sodium (2.102 electron volts) to ground state would correspond to the emission of:**

$$\lambda = 1.23972 / 2.102 = 0.5986\ \mu m \text{ or } 589.6\ nm$$

**When a photon of frequency $\nu$ interacts with an atom of energy $E_2$, the atom may be able to absorb the photon thus raising it s energy to $E_2$ + h$\nu$, provided the new energy level is equal to one of the excited energy levels of that atom, Then we can write:**

$$\nu = E_1 – E_2 / h \qquad (2)$$

**Comparison of equations 1 and 2 shows that “An atom can only absorb the radiations that it is able to emit”. This forms the basis of spectrometry.**

The fundamental difference between emission spectrometry and absorption spectrometry may be defined as:

(i) For emission to occur, a number of atoms must be in the excited state.

(ii) For atomic absorption to occur, a number of atoms must be in the ground state.

The second condition is easily attained compared to the former in that, free atoms in the ground state can be easily generated in flame compared to the excited state, by flame emission.

**The characteristic absorption wavelengths for an atom can be calculated once the energy levels are experimentally determined. But several wavelengths are never observed which proves that some sort of selection rules be developed. These rules were evolved empirically at first, and subsequently confirmed by applying quantum mechanical principles to the concept of transition probabilities.**

**The probability of a spontaneous emission by transition between energy levels $E_1$ and $E_2$ is defined as the fraction of number of atoms that drop to lower level per unit time.**

**Mathematically,**

$$dN_{1\rightarrow 2} = AN_1\, dt \qquad (3)$$

**where A is the coefficient of proportionality termed as Einstein emission coefficient. Higher the probability of transition, the greater is the intensity of emission. The strongest emission lines correspond to values of A in the range of $10^8$ to $10^9$ / sec.**

**Similarly if $N_2$ atoms in the lower transition state are irradiated by a radiation of frequency $\nu$ derived from equation (1) and the volume flux density $\rho(\nu)$, the number of d $N_{2\text{-}1}$ of atoms that will absorb the radiation in time dt is proportional to $N_2$, $\rho(\nu)$ and dt. Hence,**

$$dN_{2\rightarrow 1} = B_{2\text{-}1}\,,\ N_2\ \rho\ (\nu)\ dt \qquad (4)$$

The term $B_{2\rightarrow1}$ is known as **Einstein's absorption coefficient.** Now a days, the term oscillator strength is being used to denote the relationship between B and the total number of electrons.

$$B_{2\rightarrow1} = \pi e^2 \lambda / m h c f_{2,1} \qquad (5)$$

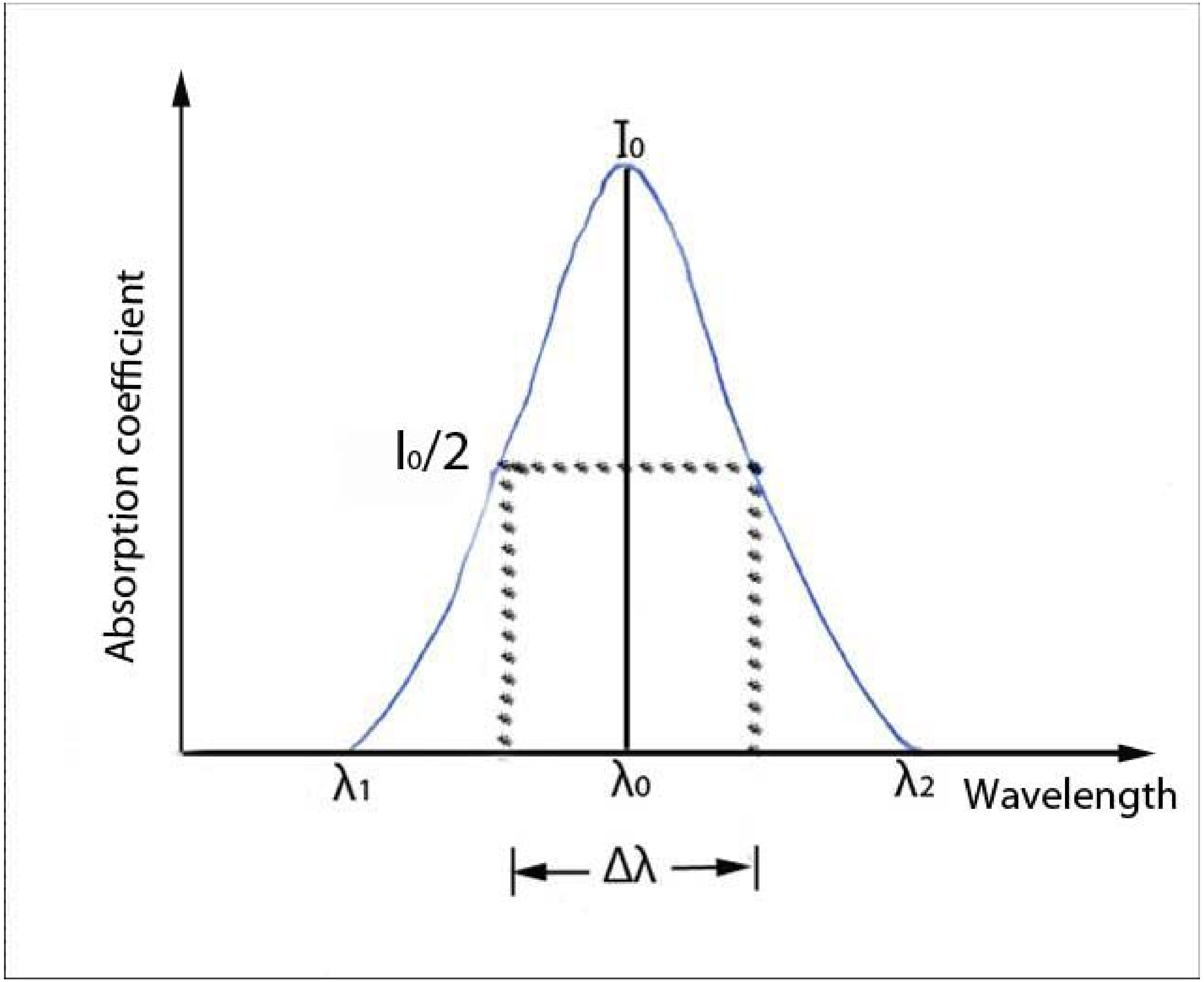
where, e and m are the electronic charge and mass. Thus for sodium D lines, oscillator strength is 0.23 and 0.47 and for potassium they are 0.35 and 0.70.

**The emission lifetime of any transition is approximately $10^{-8}$ sec. However, if there are sufficient numbers of atoms, steady state emission or absorption phenomena can be observed within the experimental time frame. For atomic absorption to occur , intense emission of the desired element must be generated first. The radiations generated from electric dipole, magnetic dipole, electric quadrupole interactions give rise to such lines among which electric dipole are most important. Both Einstein emission (A) and absorption coefficients (β) are non-zero, only if the levels involved are of opposite parity and if $\Delta J = \pm 1$.**

**Using these selection rules, resonance level of an atom may be defined as that of lowest excited energy level that can interact with the ground state by a transition of electric dipole type. The corresponding wavelength is known as the resonance line. Therefore, it follows that for a particular atom the resonance line is the most intense of highest oscillator strengths and only this line is useful for analysis provided the wavelengths are in the 200-600 nm range.**

In practice, it is impossible to get a truly monochromatic line, but the energy is distributed symmetrically over a narrow waveband. The width of a spectral line is defined as the value of Δλ where the intensity is 50 percent of the total. This is called as **half width.** The shape and size of an absorption or emission band is affected by several factors such as natural broadening, Doppler broadening, pressure broadening and electric or magnetic field broadening etc.,

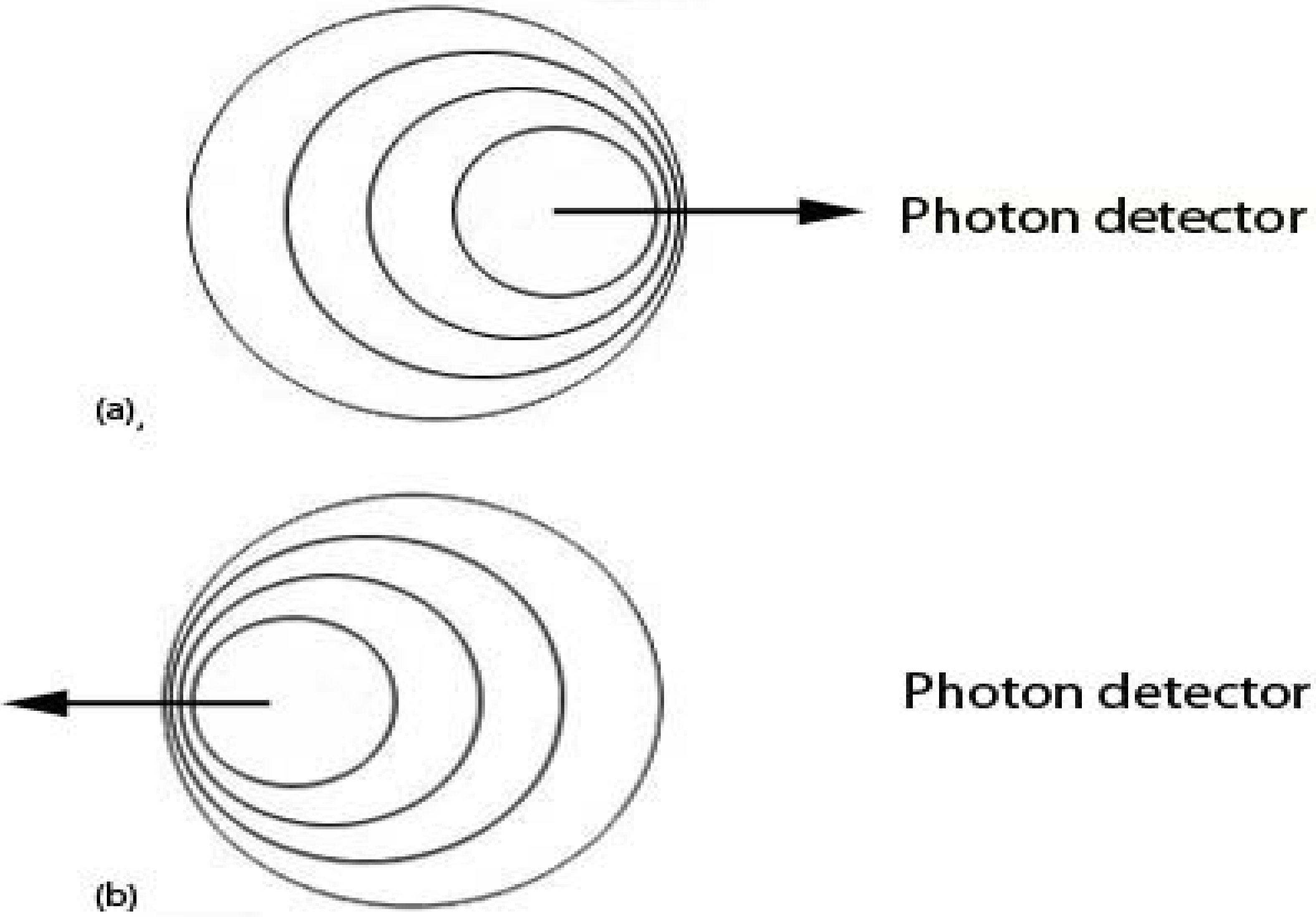
# PROFILE OF A RESONANCE LINE



# NATURAL BROADENING

Due to the short lifetime of energy states, Heisenberg's uncertainty principle is applicable for all transitions. Thus a small broadening effect of the order of a few millionth of a nanometer at 250 nm occurs rising to about $10^{-4}$ nm at 1µm. This natural width is influenced further by a variety of factors, chief among them being the disordered thermal motion of the atoms and various types of collisions of atoms.

# DOPPLER BROADENING



**If an atom emitting a radiation $\lambda_0$ moves with a velocity $v$ relative to the observer, the observed wavelength $\lambda$ is given by,**

$$\lambda = \lambda_0 + \lambda_0 v / c \qquad (6)$$

**where c is the velocity of light in the vacuum. Further, if the atoms are in thermal equilibrium at temperature T, their velocities will have a Maxwellian distribution.**

**The monochromatic absorption coefficient K as a function of λ may be expressed as:**

$$K(\lambda) = K_0 \exp \{ [ -(\lambda - \lambda_0) / \Delta\lambda_d \, 2 \, (\ln 2)^{½} ]^{2} \} \qquad (7)$$

**where $\Delta\lambda_d$ is the Doppler halfwidth related to T and the atomic mass M by the equation:**

$$\Delta\lambda_d = 7.16 \times 10^{7} \lambda_0 \, ( T/M )^{1/2} \qquad (8)$$

**The line is thus shown to have a Gaussian profile. It is possible to calculate the values of $\Delta\lambda_d$ at 2000, 2500 and 3000 K and the line widths for these temperatures are of the order of 30-50 $\mathrm{m}\overset{0}{\mathrm{A}}$.**

# PRESSURE BROADENING

Since the atoms in the vapour state are in a perpetual state of motion, collision of atoms is inevitable causing radiation quanta of slightly differing frequencies to be absorbed or emitted. Several types of particles  may be involved in the collisions. Interaction of electrically charged particles causes line broadening known as ‘Stark effect’.  Collisions with uncharged atoms lead to van Der waal’s effect. Collisions between atoms of the same type leading to resonance broadening effect is referred as ‘Holtsmark’ effect. Since it is difficult to differentiate between these three effects they are collectively referred as ‘Lorentz’ broadening.

The broadening of spectral lines reduces the lifetime of the excited state of the atoms. It also increases the line profile of the radiation. The monochromatic absorption coefficient of the em radiation at a wavelength λ is given by:

$$K(\lambda) = K_0 / 1 + [2 (\lambda - \lambda_0) \Delta L]^2 \qquad (9)$$

where $K_0$ is the maximum absorption coefficient and ΔL is the half width. The profile of this distribution is flatter than Doppler broadening but both are almost of the same order. The half width ΔL is thus a fraction of the frequency of collision (Z), which in turn is a function of the temperature and the effective cross section defined by:

$$\Delta \lambda = Z \lambda_0^2 / \pi C \qquad (10)$$

**It may be noted that both Doppler and Lorenz broadening occur simultaneously resulting in a similar but broader profile known as Voigt profile (Kλ) which may be mathematically expressed as:**

$$K(\lambda) = \mathrm{K_o}\ \mathrm{a} / \pi \int_{-\infty}^{+\infty} \mathrm{e}^{-\mathrm{y}2} / \mathrm{a}^2 + (\mathrm{w} - \mathrm{y})^2\ \mathrm{dy} \qquad \textbf{(11)}$$

**Where** **a = $\Delta\lambda_L$ / $\Delta\lambda_D$ ( ln 2 )$^{1/2}$ ,**

**w = λ – $\lambda_0$ / $\Delta\lambda_D$ 2 (ln 2 ) $^{1/2}$ ,**

**y = 2δ / $\Delta\lambda_D$ (ln 2 ) $^{1/2}$ and**

**δ = distance to the point λ at which K(λ) and $K_0$ are the calculated and the maximum value of the coefficient.**

The curves are symmetrical with a maximum at $\lambda_0$. Apart from Doppler and Lorenz effects, line broadening also occurs due to hyperfine structure exhibited by many resonance lines due to nuclear spin. Isotope shift of the resonance lines also contributes additionally to the line broadening. These effects are also significant but not as prominent.

In essence, the sum total of all these line broadening effect is of the order of 0.0005-0.005nm, which increases with increasing temperature and pressure. The significance of peak width at half the peak height has a profound effect on the emission characteristics of radiation sources, (especially hollow cathode lamps) which will be discussed later.

# MEASUREMENT OF ABSORPTION

**Based on quantum physical description given earlier, rigorous mathematical expressions have been derived to determine the absorption coefficient, its variation with N.f.l, effect of monochromator band width and also of optical density. However, for practical analytical purposes a physical understanding of these phenomena is more relevant which may be Interpreted as follows.**

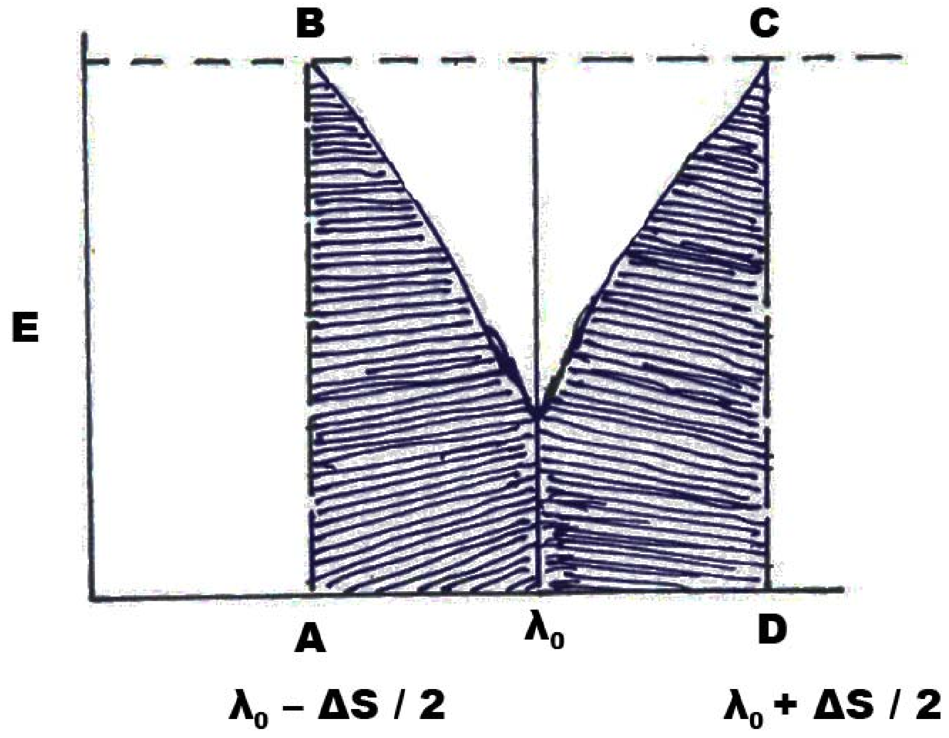
**A very narrow frequency interval is essential for the absorption of resonance radiation. However, it is impossible to isolate and obtain high intensity of illumination in the range of 0.0005 – 0.005 nm from continuum radiation sources. It would be too weak to be of any practical use. To overcome this difficulty, Walsh recommended that the radiation source should be made of the analyte element only. Therefore only the resonance line need to be separated from other spectral lines by a monochromator.**

**Assuming that a monochromator isolates a spectral band ΔS covering the absorption line $\lambda_0$ (resonance line), the total spectral energy received by the detector is :**

$$I_0 = \int_{\lambda_0 - \Delta S/2}^{\lambda_0 + \Delta S/2} \mathrm{I}_0 \mathrm{d}\lambda \qquad \textbf{(13)}$$

$$= \mathbf{I_0 \, \Delta \, \lambda_S} \qquad \textbf{(14)}$$

**= Area of the rectangle ABCD**



**Now if a homogeneous gas having an absorption K(λ) is interposed in a length of the radiation beam, the energy within the band λ will decrease by the same amount but the spectral profile will have the same shape.**

Instead of considering the radiation per unit volume, if the total radiant flux (Φ) is considered, then it may be proved that the absorption factor and hence optical density is proportional to the concentration of the free atoms and to the path length in the absorbing medium provided that the concentration is low and the spectral bandwidth is narrow. This is nothing but Beer – Lambert’s law which can be expressed as:

$$\Phi_{tr} = \Phi_0 \, e^{-x_v N l} \qquad (16)$$

Where $\Phi_0$ and $\Phi_{tr}$ are the radiant fluxes before and after absorption in the path length l, $x_v$ is the spectral absorption coefficient and N is the number of atoms.

This expression may be rearranged in the familiar form,

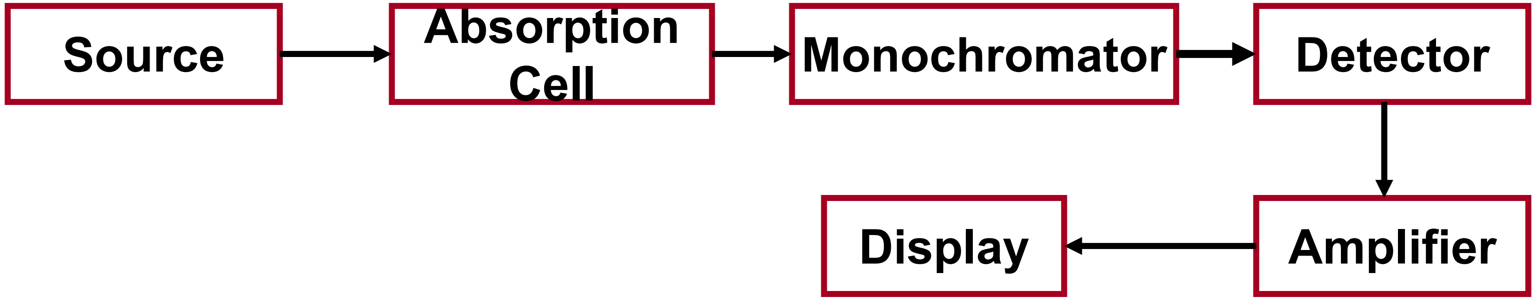
$$\text{Absorbance} = A = \text{Log}\ \Phi_0 / \Phi_{tr} = 2.303\ x_v\ N\ L \qquad (17)$$

The total number of free atoms in optical path cannot be determined but it is not necessary for routine applications, as atomic absorption is a relative technique like any other spectroscopic techniques.

**The physical conditions for highest sensitivity may be summarized as follows:**

- **The absorption line should have lowest energy state and highest population of the atoms in the ground state.**
- **If several resonance lines are there, the one with highest oscillator strength has to be chosen.**
- **Employing a source of radiation, that emits a line of the same wavelength but with lower half width.**
- **Path length may be increased within practical limits in the absorbing medium since B-L law states that the absorption also increases according to the path length.**

Employing these conditions, we can in principle, construct an atomic absorption spectrometer using a hollow cathode lamp made of the same element as the analyte, an atomizer to produce a population of ground state atoms, a monochromator with an entrance and exit slit for collection, dispersion and selection of resonance line, a detector for the measurement of radiation intensity followed by an amplifier and a read out device.  A schematic diagram of such a system is shown here.



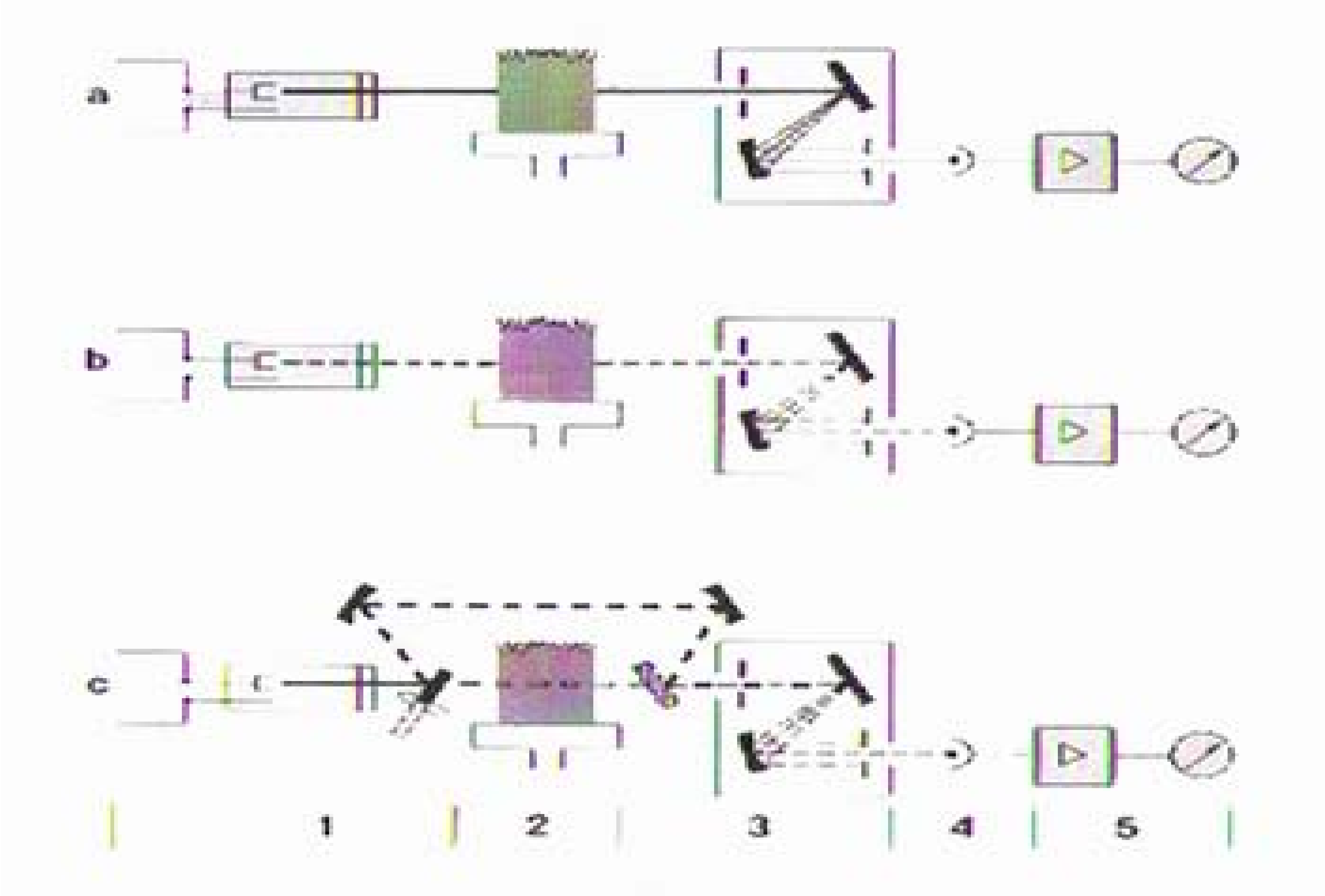
**Depending upon the choice of the components and method of operations several variants of atomic absorption spectrometers result, which are enumerated below,**

1) **Single beam DC instrument – This is the simplest arrangement. The earliest AAS instruments were of this type.**

2) **Single beam AC instrument – By applying the pulsed current to the radiation source or by mechanically chopping the radiation before it enters the absorption cell.**

3) **Double beam AC instrument – By using a rotating mirror/chopper arrangement, the radiation is passed alternately through the flame and around the flame. Then it is possible to construct a double beam instrument. Both beams are recombined by a semitransparent mirror placed behind the flame. The electronics of the system is designed to yield directly the ratio of the transmitted radiation flux to that of the incident radiation. The stability is also better.**

# SCHEMATICS OF ATOMIC ABSORPTION SPECTROMETERS



4) **Multi element Simultaneous AAS – Use of radiation sources containing resonance lines of several elements focused in to the absorption cell permits simultaneous determination of several elements. However the optics and electronics need to be suitably modified to handle various signals readout and printouts.**

5) **Electrothermal AAS – By substituting the absorption cell (i.e flame) with an electrically heated graphite furnace, very efficient means of producing atomic vapor can be achieved. This technique has gained wide popularity since last 15 years permitting the quantitative determination in ppb levels ($10^{-9}$ g).**

6) Hydride Generation AAS – Arsenic, antimony, bismuth, selenium, tellurium, germanium, lead etc, are capable of forming their respective hydrides in acidic medium. These compounds easily dissociate into their metallic and non-metallic components which, when introduced into the flame (absorption cell ), permit not only their separation but also estimation in ppb levels ($10^{-9}$ g).

7) Mercury cold vapor AAS – Mercury has a unique property of being reduced to metallic form directly from its combined state and also has a significant vapor pressure which permits its determination at room temperature. It only needs to be transported to the absorption cell. This technique is known as cold vapor technique.

Over the years atomic absorption spectrometry as an analytical technique has been accepted as a standard method of analysis all over the world. An enormous amount of literature on the instrumentation, radiation, sources, atomization techniques, optics, signal handling and data presentation has been developed. The advent of computers has made it possible for maximum use of automation, instrument control and statistical data evaluation. On an average, more than 500 research papers are being published on the application of AAS to various matrices every year.

Now we shall discuss the detailed aspects of atomic absorption spectroscopy.

**AAS is the measurement of the absorption of em radiation by the atoms in the gaseous state.**

**Free atoms do not undergo vibrational & rotational transitions but only electronic transitions. Such excited electron may return to ground state by atomic emission, atomic fluorescence or atomic absorption phenomena.**

**The various energy states of an atom are described by $n,l$ and inner quantum number $J$.**
**Selection rules permit $L = \pm 1$ and $n =$ any number.**

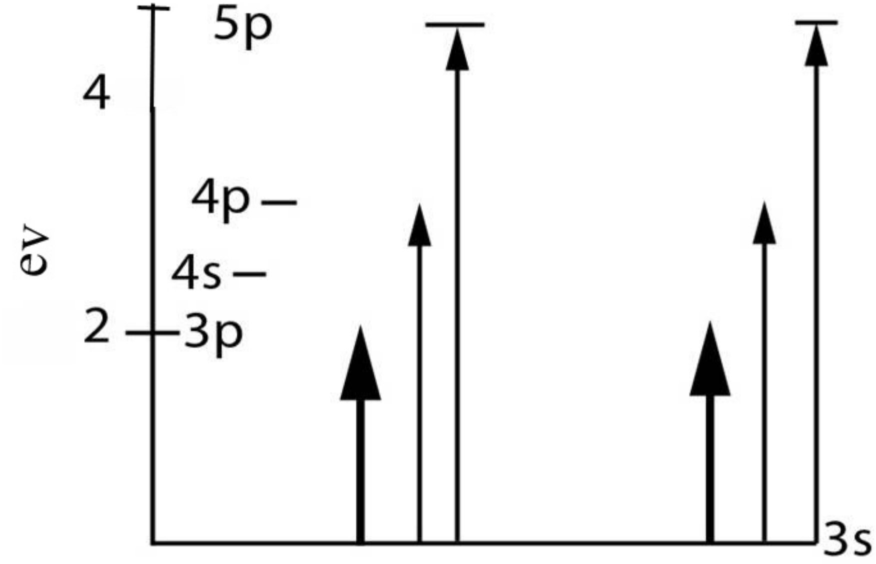
For sodium atom the most loosely bound electron is designated by,

$3s^2\ S^{1/2} \rightarrow 3\ p^2\ p^{1/2\ ,3/2}$ 589.593 nm / 588.996 nm

$4\ p^2\ p^{1/2,3/2}$ 330.294 nm / 330.234 nm

$n\ p^2\ p^{1/2,3/2}$

In emission spectrum all possible lines are obtained.



**Since all elements can be excited to their next higher energy level ,in theory any element can be determined by atomic absorption spectrometry.**

**However, below 200 nm, analysis of As, Se, I, S , P etc., is difficult owing to the incipient absorption by oxygen and hot flame gases. Cerium ,Thorium and other refractive elements also present difficulty. Artificial and radioactive elements can not be analyzed by atomic absorption spectrometry.**

# THERMAL EXCITATION

It must be appreciated that for atomic absorption to occur , we have to produce a population of atoms in the ground state. This can be achieved by exposing a sample of the analyte to high temperatures. At high temperatures prevailing in the flames, compounds decompose into ions, which in turn pick up electrons to produce atoms.

The ratio of number of atoms $N_j$ in an excited state j to the number of atoms in the ground state $N_0$ is given by,

$$\frac{N_j}{N_0} = \frac{P_j}{P_0} . e^{-Ej/KT}$$

where $P_j$ & $P_0$ are the statistical weights of the excited and ground states , k is the boltzmann's constant and T is the absolute temperature .