Modern Instrumental Methods of Analysis

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Lecture No. # 17

Atomic Absorption Spectrometry - 1 Theoretical Aspects

We were discussing that both emission and absorption coefficient must be non-zero, only if the levels involved are of the opposite parity and if delta J is equal to plus or minus 1.

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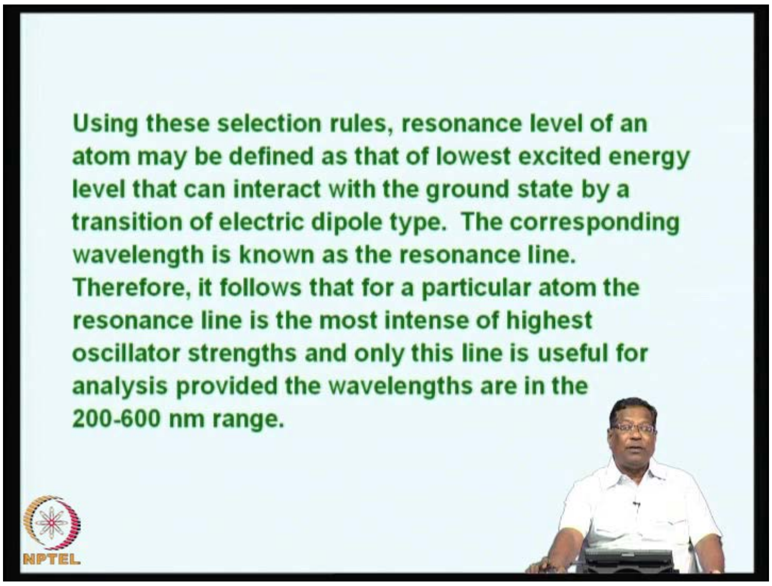

Using these selection rules, resonance level of an atom may be defined as that of lowest excited energy level that can interact with the ground state by a transition of electric dipole type. The corresponding wavelength is known as the resonance line. Therefore, it follows that for a particular atom 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.

So, using these selection rules, resonance level of an atom may be defined as that of the lowest excited energy level that can interact with the ground state by transition of the 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 the highest oscillator strengths and only this line would be useful for analysis provided the wavelengths are in the 200 to 600 nanometer range, that is were most of the spectrophotometric as well as atomic absorption wavelength lines, resonance lines will occur.

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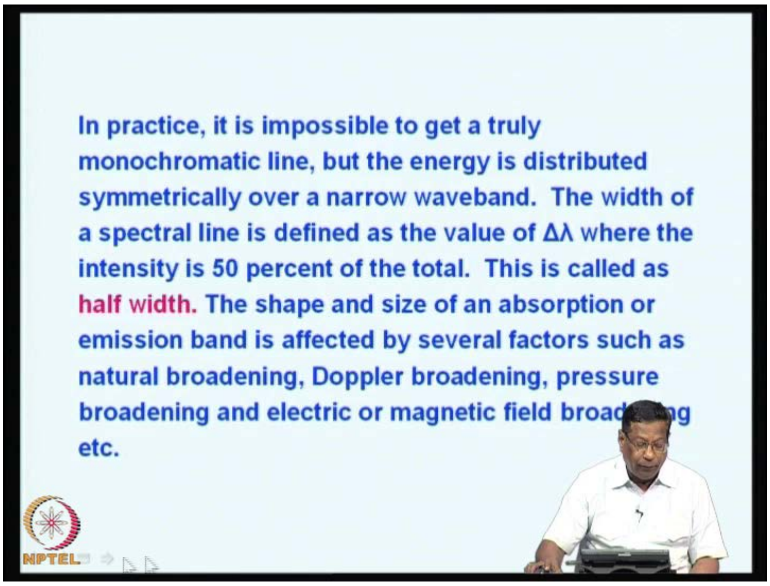

In practice, it is impossible to get a truly monochromatic line, but the energy is distributed symmetrically over a narrow waveband. The width of a spectral line is defined as the value of Δλ where the intensity is 50 percent of the total. This is called as half width. The shape and size of an absorption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

So, in practice, it is impossible to get a truly monochromatic line. And what do we mean by monochromatic line, truly monochromatic line means, a electromagnetic radiation of the exact wavelength, only one wavelength. So, it is almost impossible to get a truly monochromatic line, but the energy is distributed over a narrow waveband.

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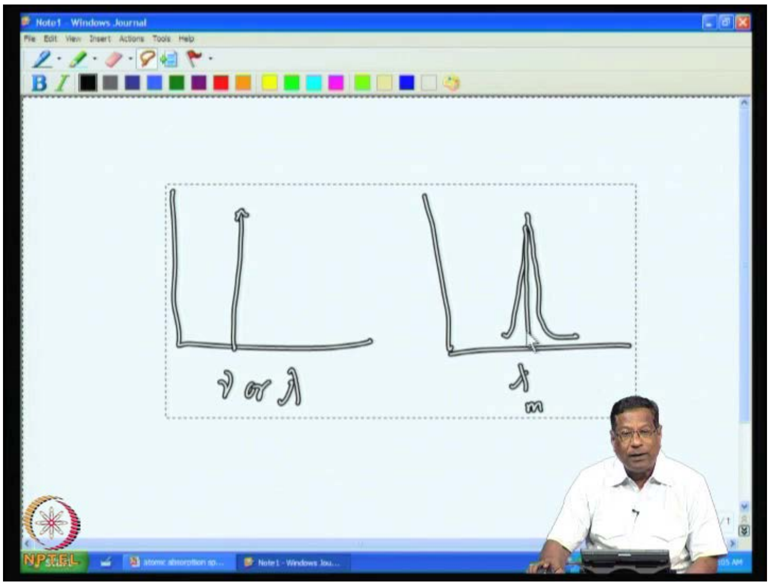

For example, if you if you look at this spectrum of a of a monochromatic radiation, the frequency or wavelength should be of single wavelength like this. So, what actually you get is a small band of radiation, where the lambda max corresponds to the same as same as the line resonance resonance line, but you would also see some amount of other radiations creeping into the radiation along with this. Now, you can imagine that, the energy also is distributed symmetrically over a small narrow waveband. The width of a spectral line is defined as the value of delta lambda; that means, the range of frequencies what you are getting, 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 etcetera, these are the causes for a line spectrum to be converted into a band spectrum. And band spectrum is always associated with half width that is what we are discussing.

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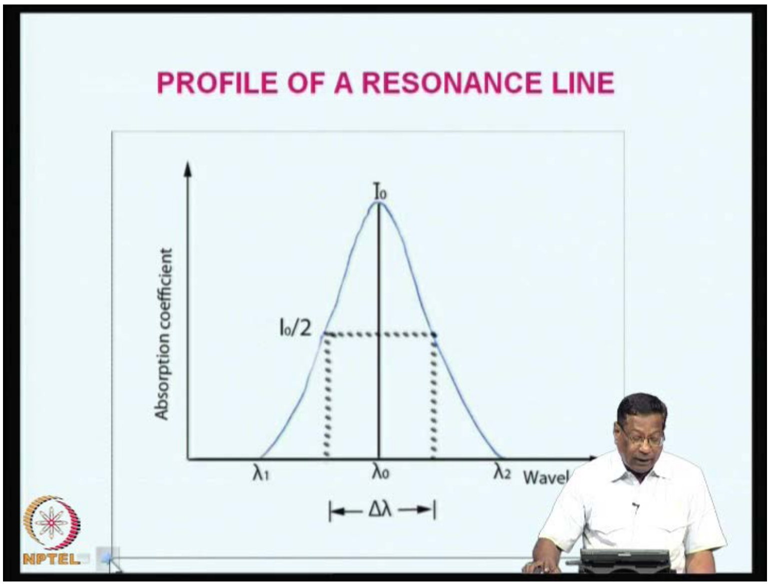

PROFILE OF A RESONANCE LINE

So, a like this, in this figure what you are seeing is, I 0 is the wavelength what you need, that is the resonance line, but what you are getting is, a group of wavelengths starting from lambda 1 to lambda 2 of which the midpoint corresponds to lambda 0, this also happens to be the maximum intensity line in this case. So, the half width is, half the height of I 0 corresponds to this I 0 by 2 and the wavelengths corresponding to this, is known as band pass width, this we have discussed earlier in molecular absorption also.

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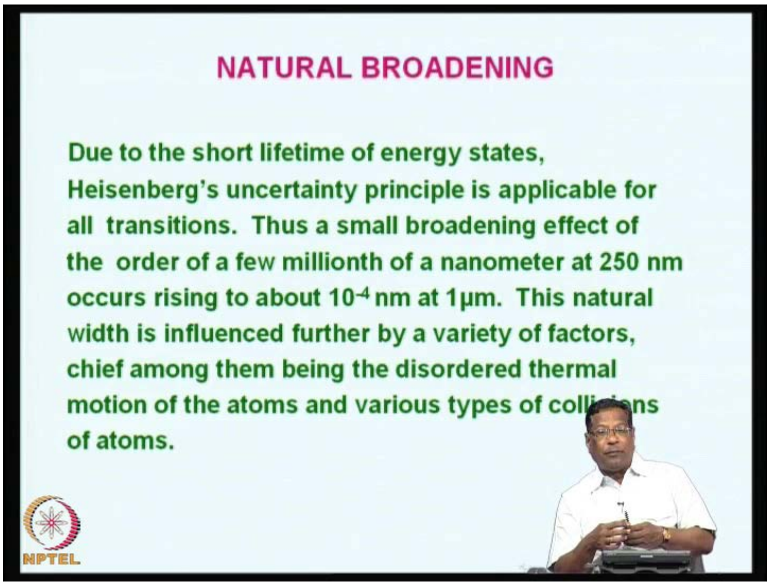

NATURAL BROADENING

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.

So, the reasons for this to occur as we have seen in the in this slide is that (Refer Slide Time: 05:26), there is a broadening effect taking place, and these are the causes are due to natural broadening, Doppler broadening, pressure broadening, electric or (( )) field broadening etcetera.

So, let us discuss about natural broadening due to the short lifetime of the energy states, Heisenberg principle uncertainty principle is applicable for all transitions. Therefore, a small broadening effect of the order of few millionth of a nanometer nanometer is 10 rise to minus 9 meters and a few millions of the nanometer, broadening occurs around 250 nanometers, it rises up to 10 rise to minus 4 nanometer around 1 micrometer.

This natural width is further influenced by a variety of factors, chief among them being the disordered thermal motion of the atoms and various types of collisions. For example, if you want to imagine that, the the transition occurs due to number of atoms present in a confined space and the atoms being so small, they are always in a perpetual state of motion.

So, this perpetual state of motion is always referred as, the disordered thermal motion of the atoms, it is due to the temperature as well as, various types of collisions, because the atoms in a confined space are not stationary, but they keep on moving here and there and they can heat also each other and then, there could be elastic and inelastic collisions taking place. So, this is due to natural broadening.

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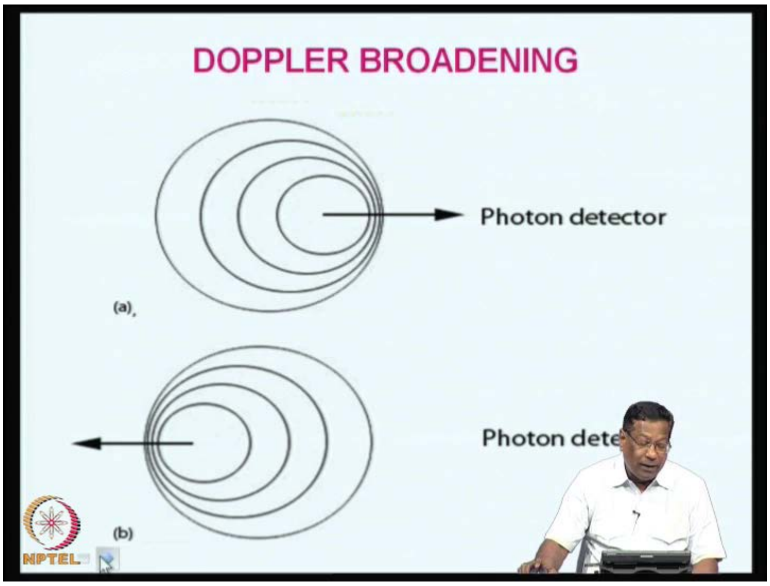

DOPPLER BROADENING

And then, we have Doppler broadening, Doppler broadening is essentially the broadening occurring due to the movement of the source of the signal with respect to the observer. Now here, I have shown you can image simple conditions like, if you are standing on a railway platform, if a train is coming towards you, you will be hearing the sound, increasing sound, until it reaches you, but after it reaches after the train passes you, the sound will keep on diminishing; and this effect can be schematically shown like this, that train is moving like this (Refer Slide Time: 08:26), you are you are standing here, where photon detector is returned. So, the sound keeps on increasing and you will be feeling more sound. When it is going away from you, the sound intensity decreases, same thing happens with respect to the radiation also.

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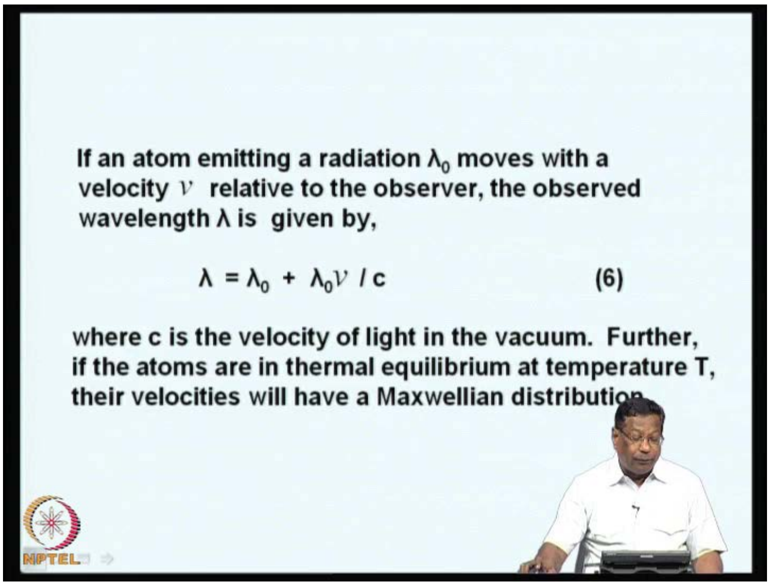

If an atom emitting a radiation λ_0 moves with a velocity v relative to the observer, the observed wavelength λ is given by,

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

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.

If an atom emitting a radiation lambda 0 moves with a velocity v relative to the observer, the observed wavelength is given by a simple expression like this, lambda is equal to lambda 0 plus lambda 0 into velocity divided by the (( )) velocity of the light in the vacuum. Further, if the atoms are in thermal equilibrium at temperature T, their velocity will also have a Maxwellian distribution that is, they will be distributed around the central frequency.

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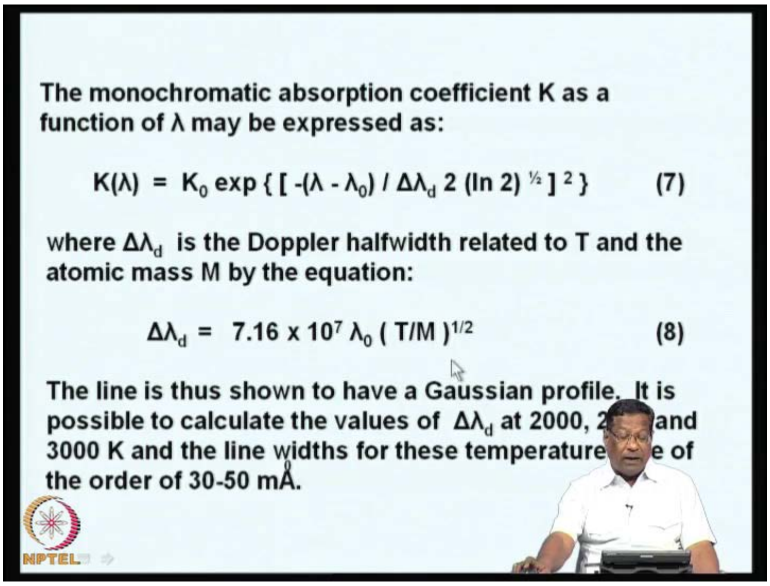

The monochromatic absorption coefficient K as a function of λ may be expressed as:

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

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, 2 and 3000 K and the line widths for these temperature e of the order of 30-50 mÅ.

So, the monochromatic absorption coefficient K as a function of lambda may be expressed as, K lambda is equal to K 0 exponential of minus lambda minus lambda 0 that is the difference in frequency divided by delta lambda into 2 ln into rise to 1 by 2 whole square, where delta lambda d (Refer Slide Time: 10:15), this one is the Doppler half width related to the temperature related to T and the atomic mass M by the equation like this, 7.16 into 10 rise to 7 lambda 0 into T by M whole rise to half. The line is thus shown to have a Gaussian profile. Now, what you have understand by Gaussian profile?

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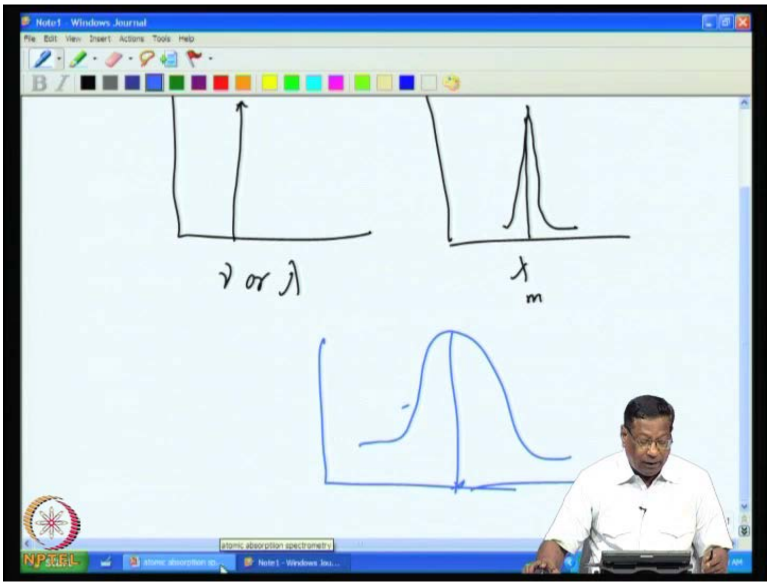

The Gaussian profile is essentially a curve like this, which shows a lambda max and equal distribution on the other side I am I have not been able to draw it properly, but you should imagine that, both sides are both sides in this on the left side of this line and right side of this line are uniform, so this is Gaussian profile.

And this Gaussian the line is thus shown to have a Gaussian profile, it is possible to calculate the value of delta lambda d that is the distribution at different temperature 2000, 2500, 3000 degree Kelvin and the line widths for these temperatures are of the order of 30 to 50 milliangstroms, that is about 1000 th of angstrom unit.

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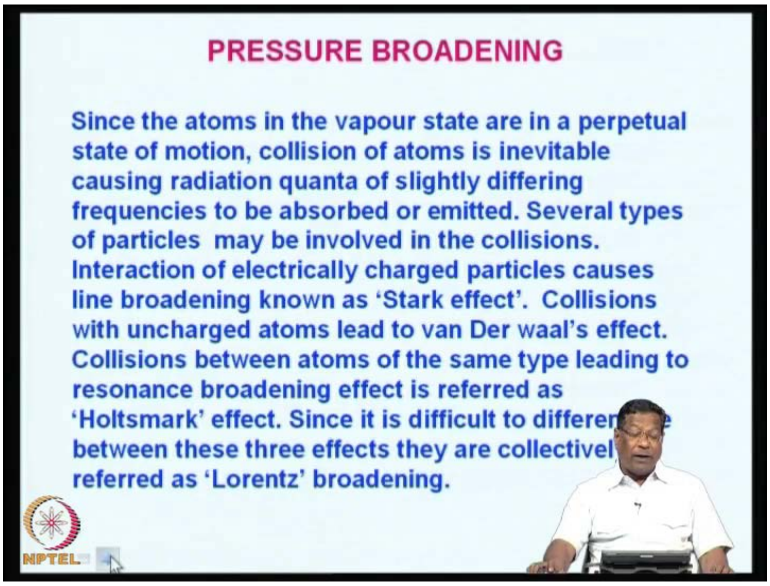

PRESSURE BROADENING

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 differen e between these three effects they are collectivel referred as 'Lorentz' broadening.

So, other types of broadening occurs in the, when the atoms are in the vapour state, they are in because they are in a perpetual state of motion and collision among the atoms is inevitable. Therefore, it causes radiation quanta of slightly differing frequencies to be absorbed or emitted; that means, again the absorption does not occur at the exact wavelength, but slightly to the left or right of the frequency graph.

And several types of particles may be involved in the collisions for example, interaction of electrically charged particles causes line broadening known as stark effect; that means, the atoms are not neutral, but electrically charged particles. So, you would know that, positively charged particles would get attracted to negatively charged particles and start collisions etcetera, and this kind of transition collisions are known as stark effect. Then, sometimes collisions between uncharged atoms also can, because of their thermal motion, but no chemical reaction, they lead to van Der waal's effect, these are very weak collisions and van Der waal's forces are also very weak, but collisions nevertheless.

So, collisions between atoms of the same type lead to leading to a resonance broadening is known as Holtsmark. Suppose, you have a matrix of number of elements, then cadmium, titanium, thorium, cerium etcetera, if you take a sample of water sea water then, you will have calcium, magnesium and many other elements. So, the collision between calcium and calcium atoms, that is of the same type leading to resonance broadening is known as Holtsmark effect.

Since, it is difficult to differentiate between these three effects, they are collectively refer to as Lorentz broadening. So, we have Doppler effect and then, natural broadening and then, Lorentz effect occurring all the time whenever you have produce a group of atoms in the ground state.

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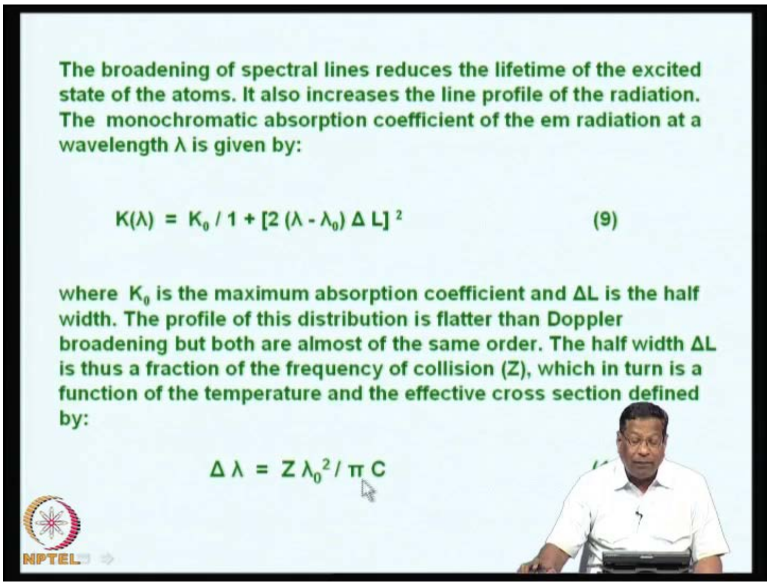

The broadening of spectral lines reduces the lifetime of the excited state of the atoms. It also increases the line profile of the radiation. The monochromatic absorption coefficient of the em radiation at a wavelength λ is given by:

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

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:

$$\Delta \lambda = Z \lambda_0^2 / \pi C$$

Now, the broadening of spectral lines actually reduces the lifetime of the excited state of the atoms. It is also it also increases the line profile of the radiation, because of the Gaussian distribution. The monochromatic absorption coefficient of the electromagnetic radiation at a wavelength lambda; that means, if this radiation is to be absorbed by a group of atoms, the absorption coefficient is given by this equation (Refer Slide Time: 15:42), that is K lambda is equal to K 0 divided by 1 plus 2 into lambda minus lambda 0 into delta L whole square. Now here, K 0 is the maximum absorption coefficient and delta L is the half width.

The profile of this distribution is slightly flatter than Doppler broadening, but both are almost of the same order. Therefore, the half width delta L in this equation is thus a fraction of the frequency of collision that is numbers Z, number of collisions which in turn is again a function of the temperature. Higher the temperature, more is the number of collisions, lower the temperature, less is the number of collisions. And for collisions to occur and cause broadening we also need to effective collisions; that means, the the atoms should not just grace each other, but they should hit each other squarely and this is known as effective cross section, that is defined by delta lambda is equal to effective number of collisions Z and lambda 0 square divided by pi into C.

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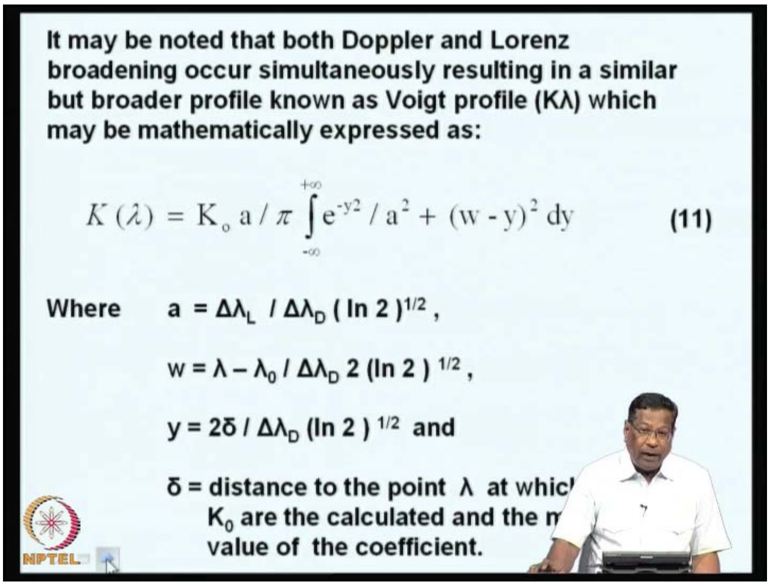

It may be noted that both Doppler and Lorenz broadening occur simultaneously resulting in a similar but broader profile known as Voigt profile (Kλ) which may be mathematically expressed as:

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

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

$w = \lambda - \lambda_0 \,/\, \Delta\lambda_D\, 2\, (\ln 2)^{1/2}$,

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

δ = distance to the point λ at whic
K_0 are the calculated and the m
value of the coefficient.

So, it may be noted that, both Lorentz broadening and Doppler broadening occurs simultaneously resulting in a similar profile, but broader profile, both of them put together we get what is known as a Voigt profile. And it is not just a Gaussian profile, but it is a slightly different Voigt profile, K lambda which may be mathematically expressed as, K lambda is equal to K 0 into a divided by pi and an integral of e to the power of minus y square divided by a square plus w minus y whole square d y, where a is given by these expressions (Refer Slide Time: 17:57).

Now, this is slightly complicated expression derived from several other considerations we will not go into the details of these derivations, but we will understand that, the profile of a resonance line is never a single line, but it is a broad profile something similar to dop Gaussian distribution, but slightly different which is known as Voigt profile.

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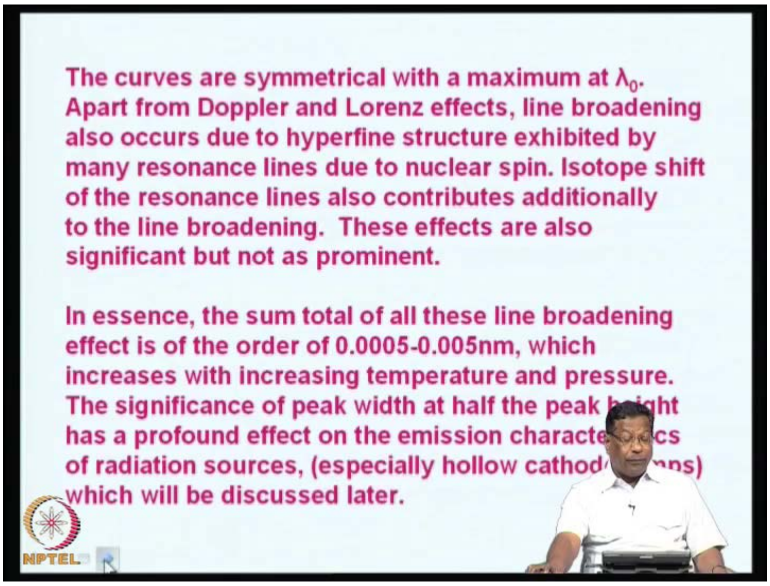

The curves are symmetrical with a maximum at λ_0. Apart from Doppler and Lorenz effects, line broadening also occurs due to hyperfine structure exhibited by many resonance lines due to nuclear spin. Isotope shift of the resonance lines also contributes additionally to the line broadening. These effects 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 h ght has a profound effect on the emission characte cs of radiation sources, (especially hollow cathod ns) which will be discussed later.

Now, the curves are actually symmetrical with a maximum at lambda 0. Apart from Doppler and Lorentz effects, line broadening also occurs due to nuclear spin we have not considered nuclear spin so far, because mostly the movement of the electrons is much more compare to nuclear movement. So, because the nucleus also is spinning, many resonance lines occur due to nuclear spin and this nuclear spin results in what is known as very fine splitting of the lines known as hyperfine splitting.

So suppose, there are atoms of the same element, but different atomic weight, but same atomic number then we have what is known as isotopes. And these isotopes also shift the resonance lines contributing additionally to the line broadening. So, these effects are also significant, but not so prominent as Doppler broadening, natural broadening and collisional broadening etcetera.

So, in essence what we are trying to say is that, the sum total of all these broadening effects is of the order of about 0.0005 to 0.005 nanometer; that means, it is a very small one, but still significant enough, which increases the broadening the range increase this with increasing temperature and pressure. So, if the atom population is subjected to very high temperature, the broadening increases more; that means, you will your chances of getting a monochromatic line are so much less.

And then, if the atomic population is also under pressure then also, this broadening increases because of the increase in the number of collisions taking place. So, the significance of the peak width at half the peak height as a profound effect on the emission characteristics of radiation sources, especially hollow cathode lamps, which will be will be discussing later.

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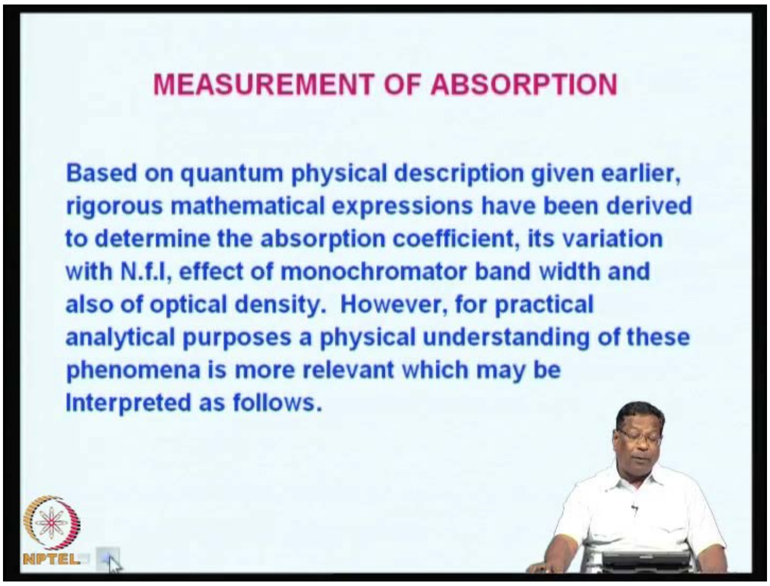

MEASUREMENT OF ABSORPTION

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.

Now, you can imagine how do we go about effecting atomic absorption? So, what do you need is, based on the quantum mechanical physical description given earlier, rigorous mathematical expressions have been derived to determine the absorption coefficients, its variation with N f and l, effect of monochromator bandwidth and also of optical density we can derive all these equations.

However, for practical purposes, it is not necessary to quantitatively define each and every term, what we have discussed earlier, because for practical purposes only a physical understanding of these phenomena is more relevant which maybe we can interpret as follows.

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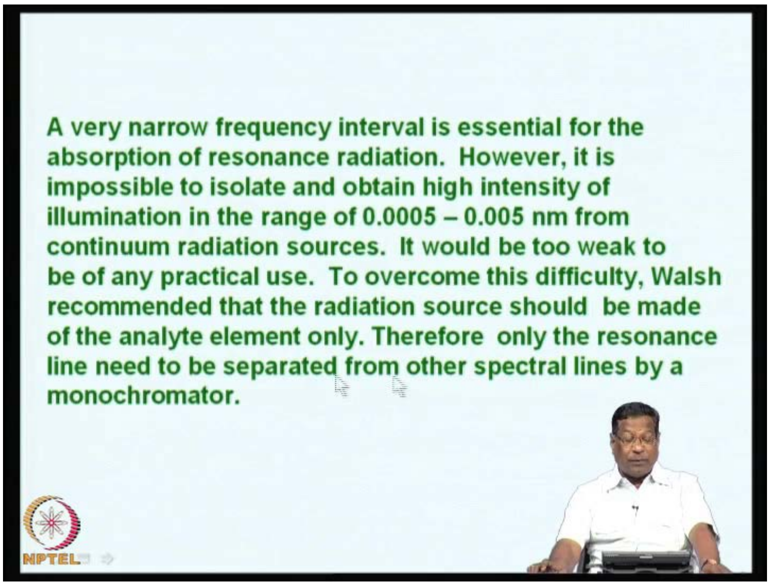

A very narrow frequency interval is essential for the absorption of resonance radiation. However, it is impossible to isolate and obtain high intensity of illumination in the range of 0.0005 – 0.005 nm from continuum radiation sources. It would be too weak to be of any practical use. To overcome this 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.

Now, the discussion what we had earlier about natural broadening and all these things can be summarized like this, what we need is, a very narrow frequency interval is essential for the atomic absorption of the resonance radiation. However, it is impossible to isolate and obtain high intensity of illumination especially corresponding to 0.0005 to 0.005 nanometer single wavelength essentially, it is almost impossible.

If the source of radiation emits all kinds of radiation, starting from X rays, ultraviolet, visible, I R etcetera. So, it would be even if you are successfully in obtaining a single wavelength, it would be too weak to be of any practical use, because the intensity would be low, strength would be low and detector would be difficult and isolation would be difficult and absorption will be difficult, so that it is of practical practically it is of no use.

So, how to overcome this difficulty? For this, Walsh has recommended that, suppose you use the radiation source, made of the same element that you want to analyze, then it is necessary because, if you are able to excite a radiation from a given atom which you want to analyze, only the elements specific emission lines would be obtained from the element; and you have to just filter the resonance line and use it for atomic absorption. So, the whole process has become very simple, if I can make an element source as a source; that means, if you want to determine copper you must have a copper filament as a source and a bulb made of copper.

If you want to determine iron, you need to have a filament made of the iron as a cathode and it will emit only the iron lines and they because they contain emission lines as well as, a continuum, what you need is? Only an emission line, not the continuum. So, it is very simple to filter out, all other radiations and permit only the resonance line to be taken out of the source and make it fall on the sample, containing the number of atoms you want to analyze.

So, if you are able to do this, prepare a lamp radiation source of each element then, we should be able to analyze all the elements that we can make the radiation sources off. Therefore, only the resonance line needs to be separated from other sources by using a filter, and these spectral lines can be separated we have discussed earlier, we can use a filter, we can use a monochromator, and we can use grating and all those things are possible. And it is required only to separate the resonance line and that will lead to this thing separation.

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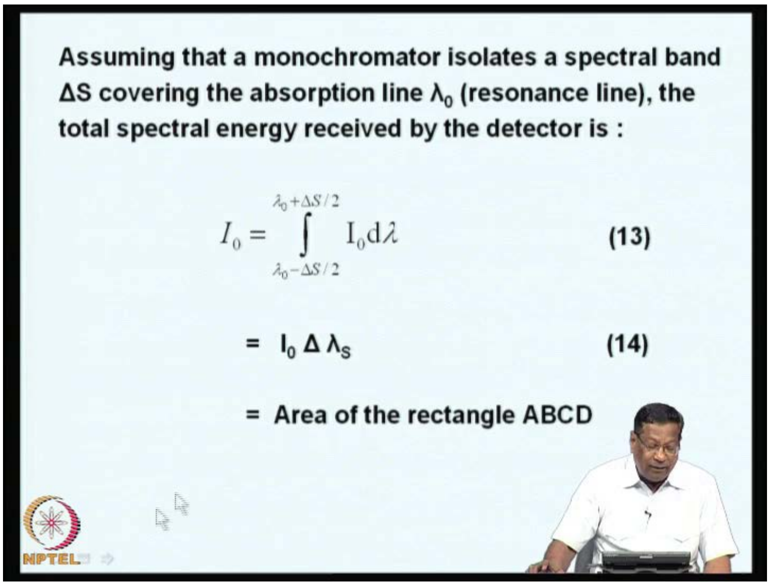

Assuming that a monochromator isolates a spectral band ΔS covering the absorption line λ_0 (resonance line), the total spectral energy received by the detector is :

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

$$= I_0 \, \Delta \lambda_S \qquad (14)$$

= Area of the rectangle ABCD

Now, assuming that a monochromator isolates a spectral band delta S covering the absorption line lambda 0 that is your resonance line, the total spectral energy received by the detector also should be much more, should be significant. So, you can evaluate that by determining the intensity over a lambda over a range of wavelengths, where delta S represents the negative and positive side of the of the Gaussian distribution that is lambda 0 minus delta S by 2 to lambda 0 plus delta S by 2; and intensity is integrated with respect to lambda. Now, if you evaluate this expression, you would end up with an expression like this (Refer Slide Time: 27:06), I 0 into delta lambda S, which is essentially a area of the rectangle A B C D.

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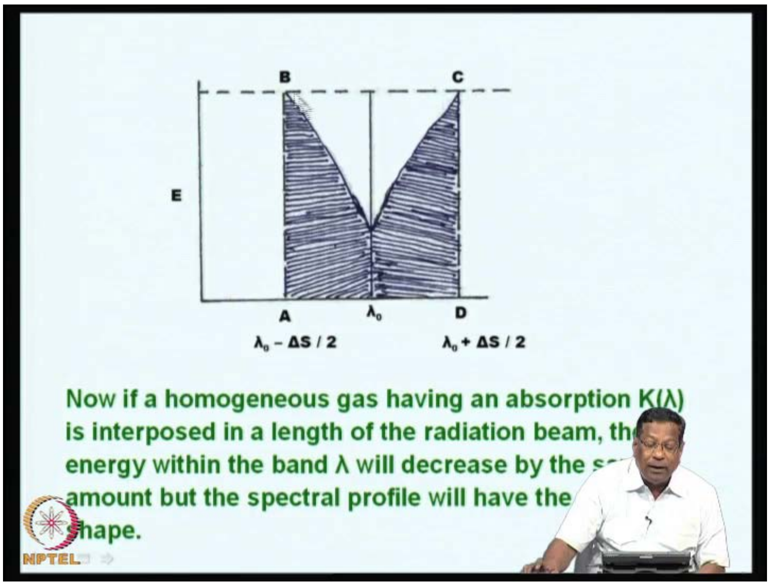

Now if a homogeneous gas having an absorption K(λ) is interposed in a length of the radiation beam, th energy within the band λ will decrease by the s amount but the spectral profile will have the hape.

This is the area (Refer Slide Time: 27:21), where we can where intensity can be integrated here is lambda 0 and here is lambda 0 minus delta S by 2 this side and then, the right side we have lambda 0 plus delta S by 2. Now, if a homogenous gas having an absorption K lambda, that is you have the atom source which can absorb this radiation monochromatic radiation is interposed I am going to interpose it here (Refer Slide Time: 27:59), if the in the absence of this I have the intensity represented by A B C D, this is A B C D this rectangle.

Now, if I am introducing certain amount of atoms in the light path, it is going to absorb the radiation and the profile of the radiation would be reduced by the amount of radiation that is absorbed by the number of atoms. So, you would see a profile like this, that the energy within this band will decrease by the same amount of the spectral profile, but same amount of the number of atoms that absorb the radiation. And the spectral profile will have the same shape that is like this (Refer Slide Time: 28:55), this is atomic absorption, this is total emission from the source A B C D and the distribution represents the atomic absorption.

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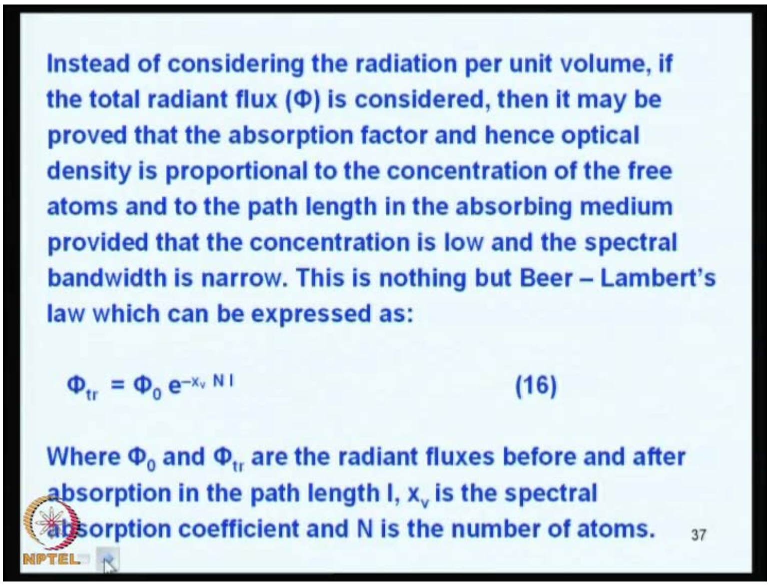

Instead of considering the radiation per unit volume, if the total radiant flux (Φ) is considered, then it may be proved that the absorption factor and hence optical density is proportional to the concentration of the free atoms and to the path length in the absorbing medium provided that the concentration 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 Φ_0 and Φ_{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.

So, instead of considering the radiation flux per unit volume, if the total radiant flux is considered like that, triangle in that A B C D. Triangle in the A B C D, if we consider that, the total radiant flux then, it may be proved that, the absorption factor and hence optical density is proportional to the concentration of the free atoms present in the path length. And the path length also is important because, if the path length is more, the number of atoms present in the radiation optical path would be more; and provided that, the concentration is low and the spectral bandwidth is narrow.

Then, we can have an expression something like this, phi transmitted is equal to radiation original radiation intensity multiplied by e to the power of x v N into l. So here, phi 0 is the original intensity, phi transmitted is the radiation transmitted; and e to the power of minus (( )) is the spectral absorption coefficient, l is the absorption in the path length, x v is the spectral absorption coefficient and N is the total number of atoms, this is essentially a essentially nothing but, Beer-Lambert's law.

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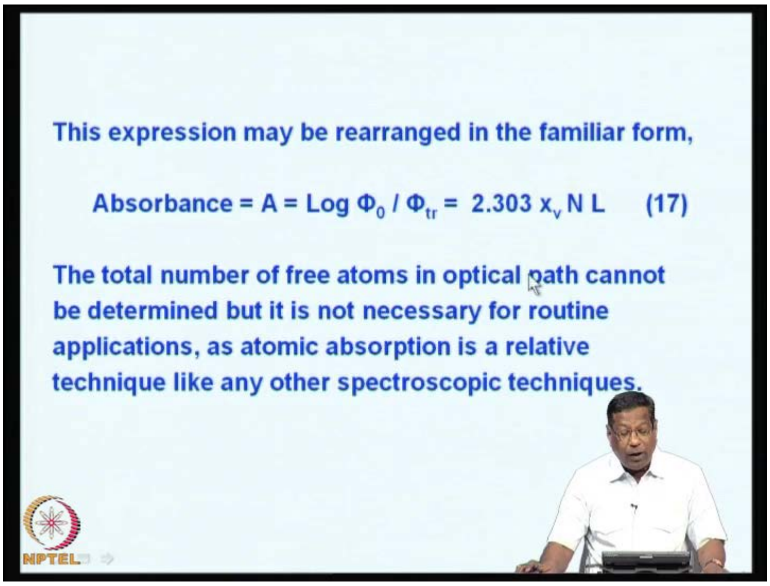

This expression may be rearranged in the familiar form,

Absorbance = A = Log Φ_0 / Φ_{tr} = 2.303 x_v N L (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.

Because, you can exchange this expression, rearrange in the familiar form instead of transmitted radiation I am going to put absorbance here, and I get log of transmitted radiation phi 0 divided by phi trans incident radiation divided by transmitted radiation, which should be a product of 2.303 into x v into N into l; that means, number of atoms cross-section absorption coefficient, l is the number of path length centimeters.

So, the total number of free atoms in the optical path cannot be determined, because I prefer that or rather, not to determine the total number of atoms because, it leads to lot of confusion, and it requires different kind of technology to calculate and also lot of calculations are involved, but it is not necessary for routine applications. So, what do we do is, just like in any other spectroscopic technique, we measure the atomic absorption as a relative technique; that means, I make my standard find out what is the absorbance I and then, I put my sample, find out what is the absorbance and if the system follows Beer Lambert’s law over a particular absorbance range, then I can simply say the sample contain so much of the analyte in the in the atomic form.

So, the physical conditions for the highest sensitivity we can summarize now. Now, what happens? We need an absorption line and the resonance line should have the lowest energy state and highest population of the atoms in the ground state, because absorption can occur from the ground state to excited state therefore, highest number of atom should be in the ground state, rather than the excited state; that means, I must be able to produce atoms in the ground state.

If several resonance lines are there, the one with the highest oscillator strength has to be chosen; that means, most intense atom absorption line we need to choose then, I can employ a source of radiation that emits a line of the same wavelength, but lower half width. Now, path length I can increase I can have 2 mm, 2 centimeters, 3 centimeters, 5 centimeters upto 10 centimeters, I can take a tube introduce the atoms in the tube. So, make the optical path to go through, then I should be able to obtain Beer Lambert's law, that is linearity of the absorbance with respect to the concentration, and the absorption also can be used for determining the unknown same entity.

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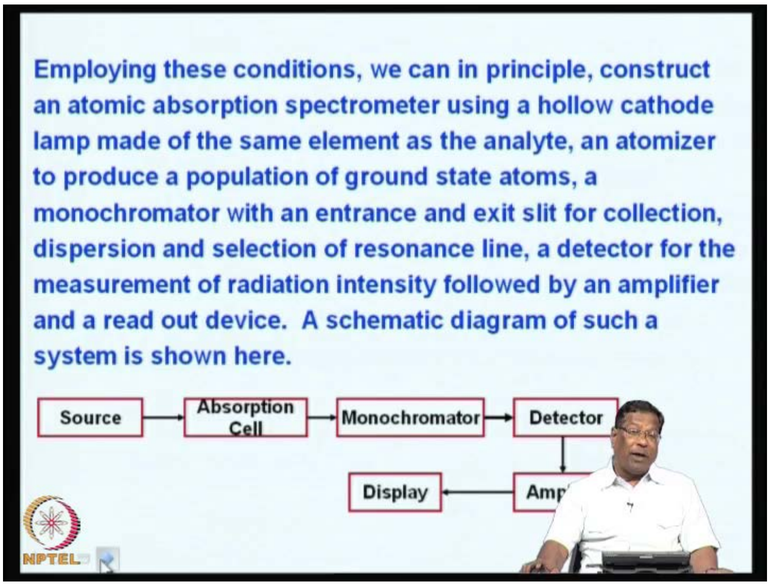

Employing these conditions, we can in principle, construct an atomic absorption spectrometer using a hollow cathode lamp made of the same element as the analyte, an atomizer to produce a population of ground state atoms, a monochromator with an entrance and exit slit for collection, dispersion and selection 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.

Now, employing these conditions we can construct an atomic absorption spectrometer. How do we do that? We employ these conditions, what do we need, we need to construct an atomic absorption spectrometer using a hollow cathode lamp made of the same element as the analyte. We have to construct one lamp of the element, what you want to analyze? Then, you have to have an atomizer; that means, the sample must be broken down into small particles, which can produce atoms.

So, the sample has to be broken down into produce a population of the ground state atoms and then, we need a monochromator with an entrance slit and an exit slit, you do not need a monochromator initially, because basically you are taking the hollow hollow cathode lamp output, which corresponds to only one wavelength. And the detector, subsequently you are going to put your sample in the path of the monochromator radiation and then, you need a monochromator to remove all other radiations, except the hollow cathode lamp resonance line output. And then, once you have that, you can have a detector for the measurement of radiation intensity followed by an amplifier and read out device etcetera.

So, the schematic diagram of a system atomic absorbance spectrometer is shown here, what you need is, a source then you need your sample in the form of atoms, which we call auto absorption cell and the radiation must pass through that and here, the atomic absorption will occur and the radi intensity of the radiation will decrease, but there will be other radiations coming from the absorption cell, which need to be filtered out. Therefore, you need a monochromator again to remove the unwanted radiation, except the source hollow cathode lamp resonance line; and then detector you need, amplifier and display, so this is how the architecture of an atomic absorption should be defined.

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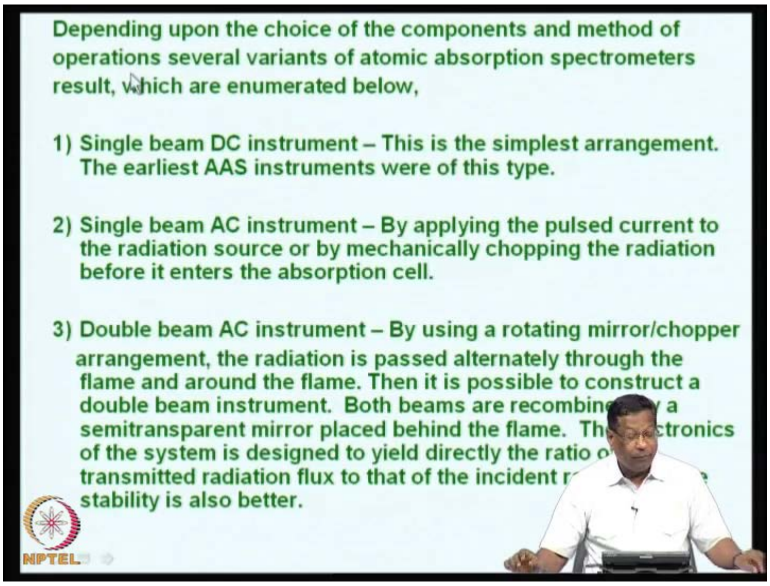

Depending upon the choice of the components and method of operations several variants of atomic absorption spectrometers result, which are enumerated below,

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 recombin y a semitransparent mirror placed behind the flame. Th ctronics of the system is designed to yield directly the ratio o transmitted radiation flux to that of the incident r stability is also better.

Now, depending upon the choice of the components and method of operations you can have a you can have a variety of atomic absorption spectrometers and these are all systems what you know already, we can have a single beam D C instrument, that is simplest arrangement. The earliest A A S instruments were of this type; that means, you take a single beam and put your (( )) put your sample and measure the put your standards measure the absorbance, constructed calibration curve and then, determine the unknown by putting it in the same cell. Then you can have a single beam A C instrument by applying the pulsed current to the radiation source are by mechanically chopping by putting a fan and then, radiation passes through etcetera, before it enters the absorption cell you can have a single beam A C instrument atomic absorption.

Then you can have double beam atomic absorption A C instrument, here what we do is, we use a rotating mirror or a chopper and then, the radiation is passed alternately between the sample and non sample, that is flame and non flame. Because in general, an atomic absorption we use flames to produce the atoms. So then, it is possible to construct a double beam instrument. So here, what do we do? We take 50 percent of the beam, away from the optical path and allow only 50 percent of the radiation to pass through the sample; collect the unabsorbed beam back through another optical circuit and then, combined both and then, the differences would be simple double beam atomic absorption just like a spectrophotometer; then both beams are to be recombined by using a semitransparent mirror placed behind the flame.

The electronics of the system can be designed to yield directly the ratio of the transmitted radiation flux to that of the incident radiation flux, and the stability is also better because, whatever changes occur during the operation will be reflected in the double beam all the time. So, any changes, change in the intensity would always be compensated by the (( )) reference beam.

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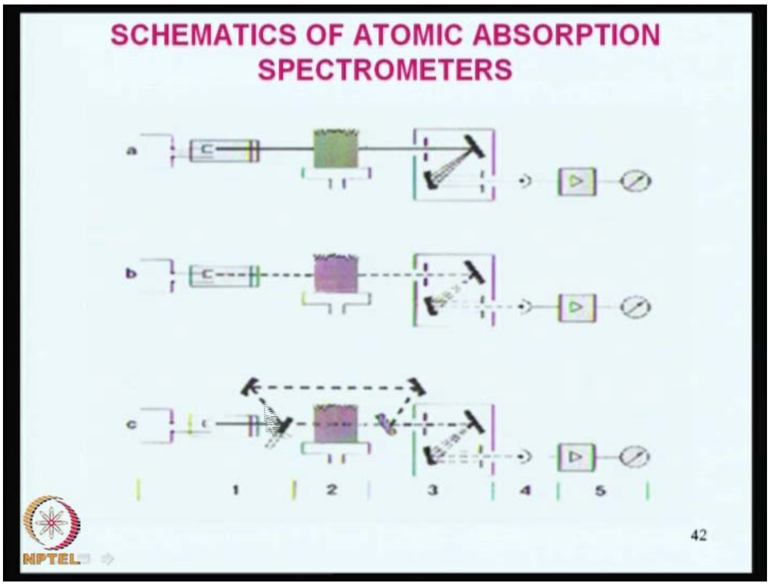

SCHEMATICS OF ATOMIC ABSORPTION SPECTROMETERS

So here, I am showing you this is the radiations electronic part a, is the electronics part and this is known as number 1, it is common in all the three that is hollow cathode lamp. First one is, single beam a c sorry single beam d c, second is single beam a c, third is double beam a c atomic absorptions spectrometer designs schematics. So here, I have a hollow cathode lamp, supported by the electronics here and then, it is I have a flame here, the green part represents a flame and here, I am introducing my sample to produce a population of the atoms in the optical path. And then, I have a slit and monochromator and then, wavelength that is to be taken to the detector d I have a detector here and associated electronics here.

Essentially, same thing here happens here in single beam a c we need a chopper here and then, the same thing that is hollow cathode lamp and then, sample introducer absorption cell and then, slit monochromator grating and the detector. And in the third case, what we have is double beam a c, the incoming radiation is split into 50 50, before it reaches the absorption cell. It is recombined after the absorption cell and then, again the radiation can be separated from other unwanted wavelengths and then, it has to be collected through the monochromator and onto the detector. So, these are the three variants of atomic absorption in general, we can construct.

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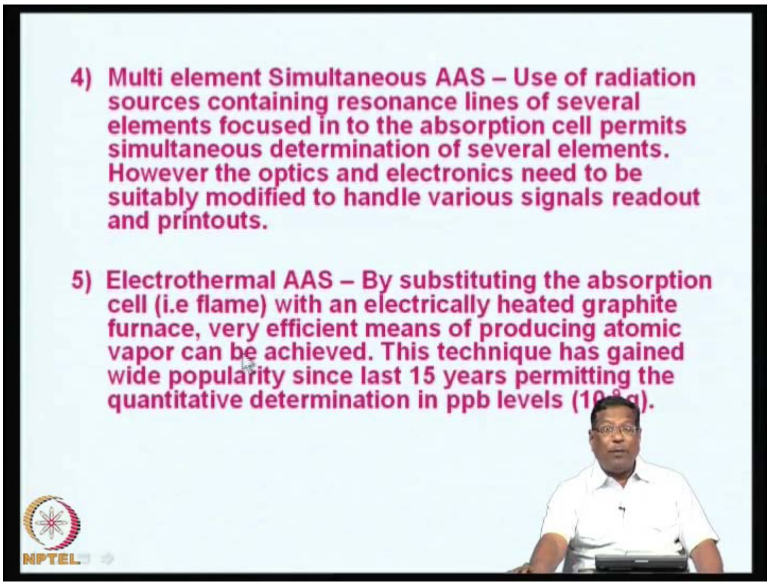

4) Multi element Simultaneous AAS – Use of radiation sources containing resonance lines of several elements focused in to the absorption cell permits simultaneous determination of several elements. However the optics and electronics need to be suitably modified to handle various signals readout and printouts.

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^{-8} g).

Now, we can also have instead of instead of one element, made of the same material as the analyte I can use an alloy as a source of source of radiation. Alloy will have number of metals and these metals when excited through a filament as a radiation source, can give multiple lines, resonance line corresponding to each element present in the alloy. Now, if I can have a collection mechanism for each wavelength, then I can do the multiple analysis simultaneously.

So, it is something something like multi element analysis using a radiation sources containing number of resonance lines. And how do we generate that? I make a filament out of an alloy and all the composition, all the elemental elements in the alloy would be emitting resonance line. Only thing is electronics gets complicated because, simultaneously you should be able to analyze the radiation flux corresponding to each wavelength and analysis can be done or you need to have separate electronics for each element.

Now, such instruments are available in the market now, radiation has to be separated using number of filters and funny thing is, we can do the we can use multi multi element lamp and analyze any element you want present in present in the sample sequentially also not simultaneously, but sequentially, so that, we will discuss in the, when we are discussing these sources.

So, the multi element simultaneous analysis, it requires the use of radiation sources containing resonance lines of several elements focused in to the absorption cell, which permits simultaneous determination of several elements. The optics and electronics need to be suitably modified to handle various signals and readouts and printouts.

Then, I can substitute the absorption cell that is, instead of the flame I can use a heated graphite furnace tubes and generate the same subject graphite is a conducting material, I can subject it to very high temperature, if I put my sample in the graphite tube I can generate the atoms electrically by heating heating with the current and that, would produce number of atoms in a very efficient manner, compare to flame because as we all know, flame is a a transient phenomena. It is not always reproducible to the same extend and electrically heated graphite tube can be heated to the same temperature by good electrical electrical control and it is a very efficient means of producing a atomic vapour.

So, this technique has gained wide popularities since last 15 years permitting the quantitative determination in p p b levels, parts per billion levels, this is known as electrothermal atomic absorption spectroscopy.

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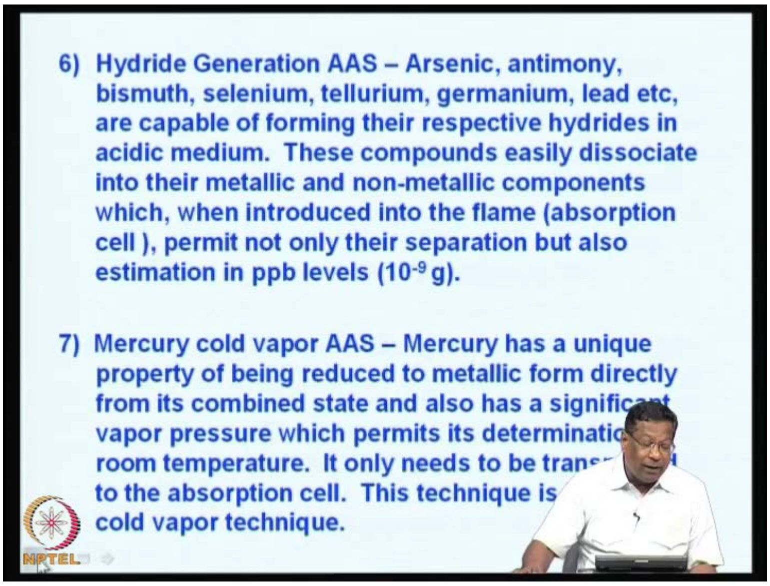

6) **Hydride Generation AAS – Arsenic, antimony, bismuth, selenium, tellurium, germanium, lead etc, are capable of forming their respective hydrides in acidic medium. These compounds easily dissociate into their metallic and non-metallic components which, when introduced into the flame (absorption cell), 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 determinatio room temperature. It only needs to be trans to the absorption cell. This technique is cold vapor technique.**

So, the other possibilities are, hydride generation atomic absorption. What happens is, I have a sample containing arsenic, antimony, bismuth, selenium, tellurium, germanium and lead, all these elements if I reduce if I introduce hydrogen, they all form hydrides; and these hydrides can be taken to the flame absorbance cell, where they decompose giving the element vapour directly. So, this is known as hydride generation atomic absorption; and the hydrides of these respective elements combined easily and then, the dissociate also very easily into that metallic and nonmetallic components which, when introduced into the flame, permit not only their separation from the matrix, but also estimation in parts per billion levels, p p b that is 10 rise to minus 9 grams.

Then another variant is mercury cold vapour atomic absorption here what happens is, mercury has a unique property of being present in the vapour form even at room temperature. So, it can form amalgams with number of elements. So, it is from the combined state, it is possible to determine the mercury just by subject to slightly high temperature or even, if mercury is present in the ambient air, the vapour pressure is enough to permit determination of mercury in the sample.

So, this permits its determination at room temperature, only requirement is it must be transported into the absorption cell; that means, you must have an arrangement to introduce air itself into the absorption cell. And if there is mercury in the air, it can be determined using atomic absorption, because we are not using any flame or any high temperature. Therefore, it is known as mercury cold vapour atomic absorption spectrometry.

So in general, the variants of atomic absorption are single beam D C, single beam A C, double beam A C and then, multi element multi element analysis, simultaneous atomic absorption and then, electro thermal atomic absorption and hydride generation and mercury vapour cold vapour atomic absorption. Among these, the hydride generation atomic absorption spectrometry is possible to use it only as an accessory to existing flame as well as, mercury cold vapour A A S can also be either a dedicated instrument or as an you can buy an accessory for the determination of mercury, that is mercury cold vapour attachment.

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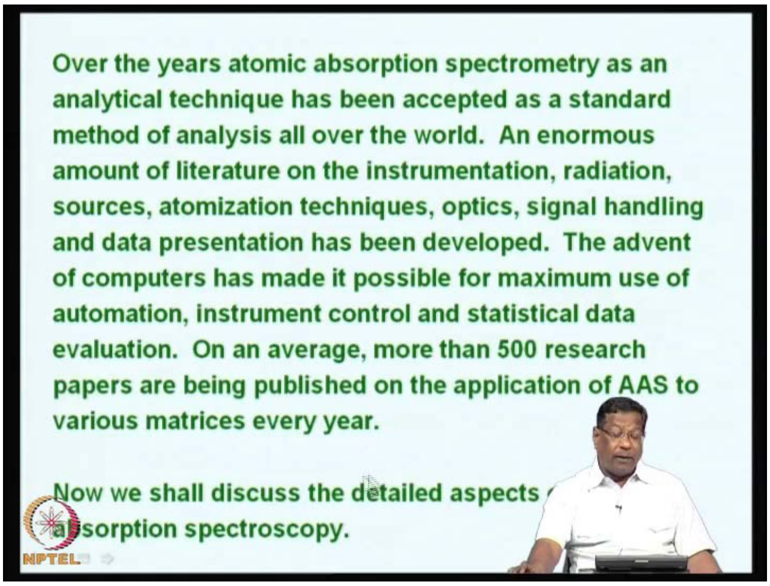

Over the years atomic absorption spectrometry as an analytical technique has been accepted as a standard method of analysis all over the world. An enormous amount of literature on the instrumentation, radiation, sources, atomization techniques, optics, signal handling and data presentation has been developed. 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

absorption spectroscopy.

So, over the years the atomic absorption spectrometry as an analytical tactic has been accepted as a standard method of analysis all over the world. And an enormous amount of literature exists on the instrumentation, radiation, sources, atomization, optics, signal handling and data presentation is there and combining the advances in electronics and computer, beautiful instruments are available for atomic absorption for the determination of p p m levels.

The advent of computers of course, has made it possible for maximum use of automation and then, instrument control and statistical data evaluation. On an average, more than 500 research papers are being published every year on the application of atomic absorption spectrometry to various matrix matrices every year. So, you can appreciate that, the atomic absorptions spectrometry is a very very versatile technique. Now, we shall discuss the details of the detailed aspects of atomic absorption spectrometry.

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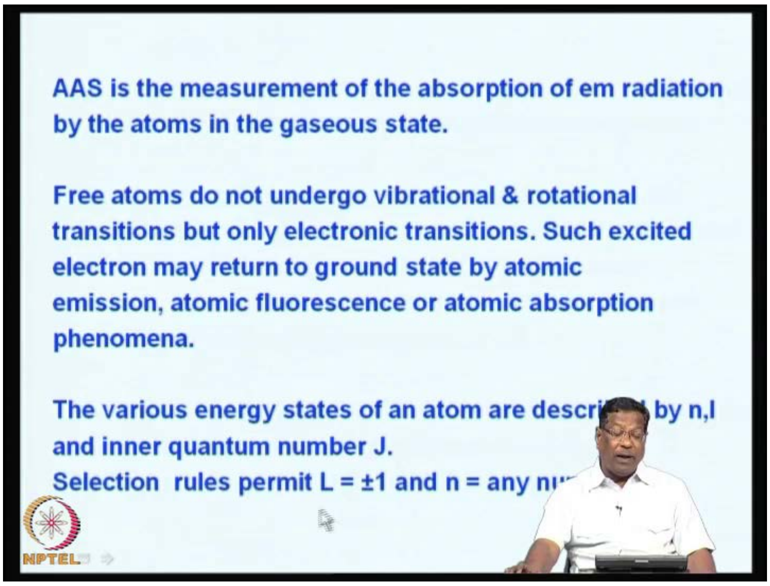

AAS is the measurement of the absorption of em radiation by the atoms in the gaseous state.

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 descri by n,l and inner quantum number J.

Selection rules permit L = ±1 and n = any nu

So, let us try to understand what we have discussed so far? Atomic absorption spectrometer is the measurement of the absorption of electromagnetic radiation by the atoms in the gaseous state. Free atoms if they are there, they do not undergo vibrational and rotational transitions, but they undergo only the electronic transitions. And such excited electron may return to the ground state by atomic emission, atomic fluorescence or atomic absorption, we are discussing only the atomic absorption for the time being.

So, the various energy states of the atom are described by n, l and inner quantum number J and magnetic quantum number m and spin quantum number are also there. So, selection rules usually permit the orbital angular momentum to vary by plus or minus 1. If it varies by plus or minus 2, atomic absorption does not occur and n can be any number, that is principle quantum number n can be any number.

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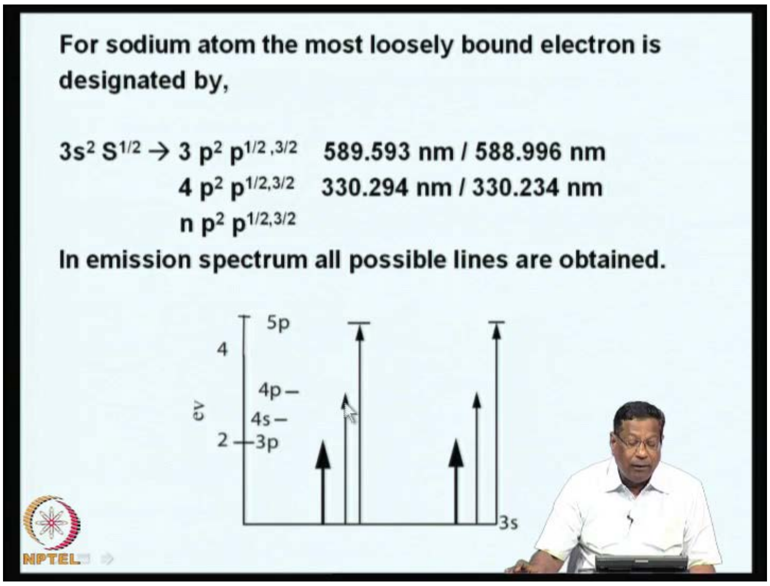

For sodium atom the most loosely bound electron is designated by,

$3s^2\ S^{1/2} \rightarrow 3\ p^2\ p^{1/2,3/2}$ 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.

So, for sodium atom the most loosely bound electron is designated by, 3 S 2 and S half and this can go over to 3 P 2 P half and 3 by 2, 4 P 2 P half P 3 by 2 or it can go to any of the P orbitals represented by other quantum numbers as 5, 6 etcetera. Here, I have tried to represent some of these transitions, this is the ground state 3 S and here, it is 3 P, 4 P, 5 P etcetera. So, all these transitions are possible permit and permitted also.

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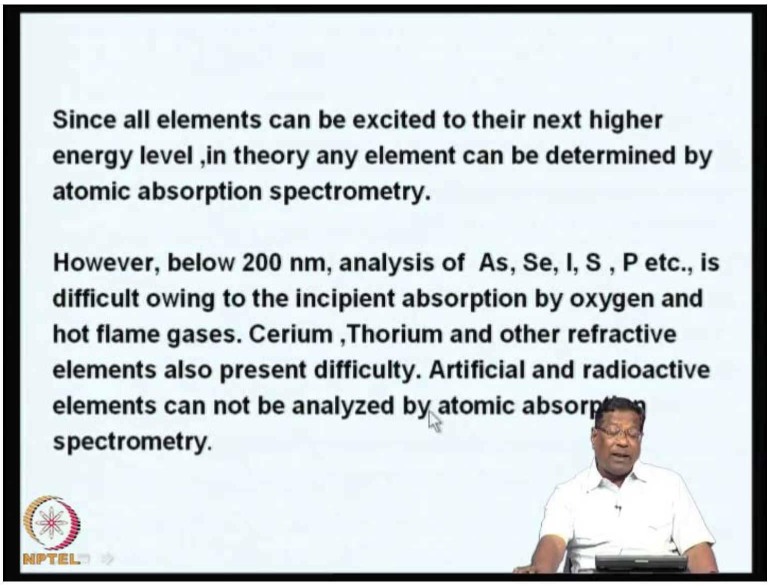

Since all elements can be excited to their next higher energy level ,in theory any element can be determined by atomic absorption spectrometry.

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.

Since, all elements can be excited to their next higher energy level, in theory any element can be determined by atomic absorption spectrometry, any element in theory. But, there is a small rider below 200 nanometers, analysis that is in the vacuum ultraviolet region, arsenic, selenium, iodine, sulfur, phosphorus etcetera present difficulties, because their resonance lines are in the vacuum ultraviolet region, somewhere between 190 and 200.

So, these things do not even though they are being determined, but they present difficulties, because of the optics (( )). And cerium, thorium and many other refractive elements, it is very difficult to produce atoms using the flame. So, these elements present difficulty in atomic absorption using flames. And then obviously, artificial and radioactive elements we cannot analyze, because of the obvious reasons, because radioactive elements are difficult to handle and there are other ways of determining the such elements.

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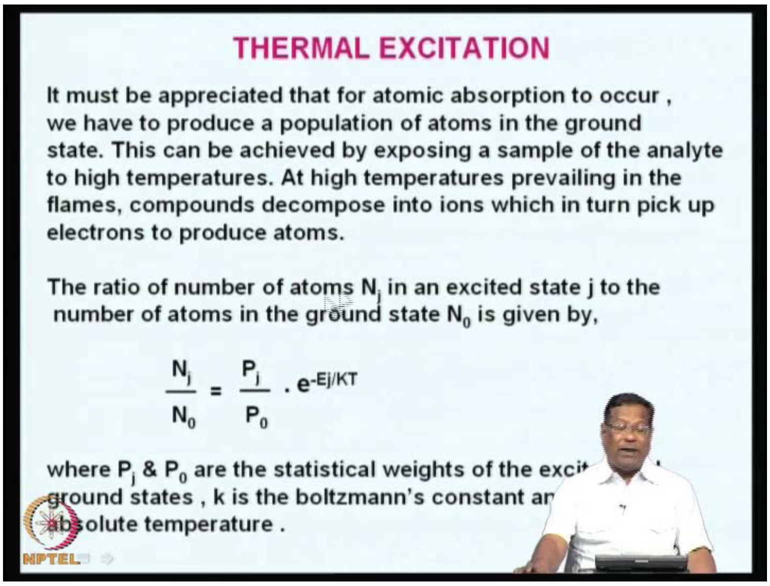

THERMAL EXCITATION

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 exci ground states , k is the boltzmann's constant ar absolute temperature .

So, we need to find the way to produce number of atoms in the ground state and this we will be doing using a flame, and to produce high temperature and into the flame, if we are able to introduce the sample the water the (( )) content or water content will evaporate and then, it will produce the compounds; and these compounds may decompose and produce atoms. And once these atoms are produced, they can be taken for atomic absorption. How we can do that, we will discuss in the next class.