Atomic and Molecular Absorption Spectrometry for Pollution Monitoring

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Lecture – 13
Deviations from Beer-Lamberts law, relative concentration error, instrumentation-I

Greetings to you, today we are going to continue our discussion on the deviation from Beer-Lamberts law. Last in the last class we I had indicated to you that Beer-Lamberts law deviations or do occur in real life and they are due to three reasons basically, and these three reasons include real deviations and an instrumental deviations.

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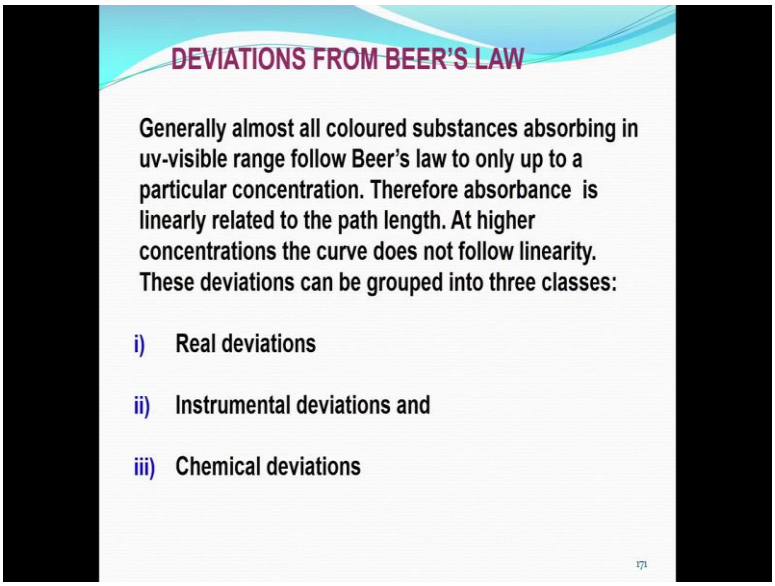

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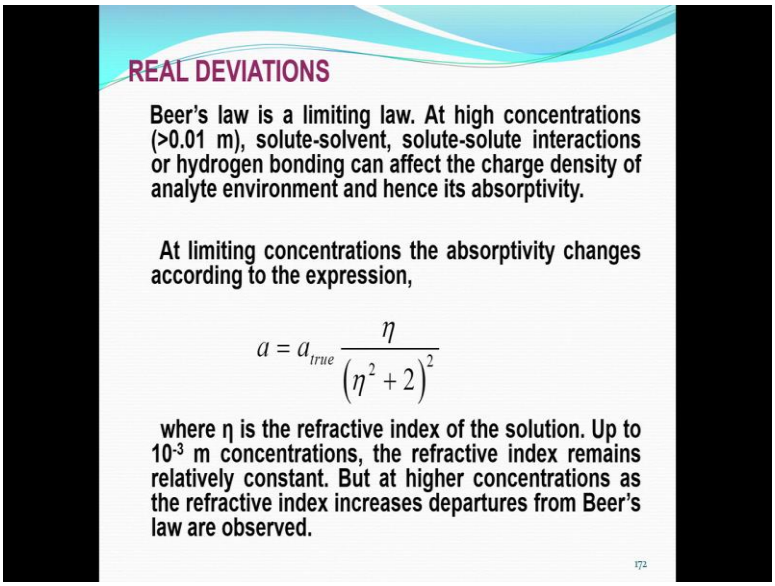

And chemical deviation this all this we have discussed except chemical deviations. So, in the real deviations we have the problem with refractive index which is a fact.

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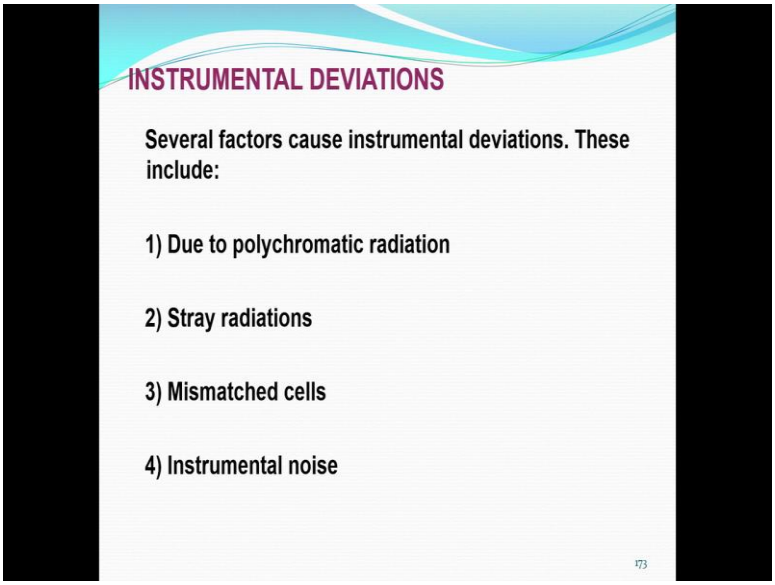

And then in instrumental deviations we have polychromatic radiation problem, stray radiation, mismatch cells and instrumental noise etcetera, and then we had also discussed the deviations for effect of bandwidth and slit width.

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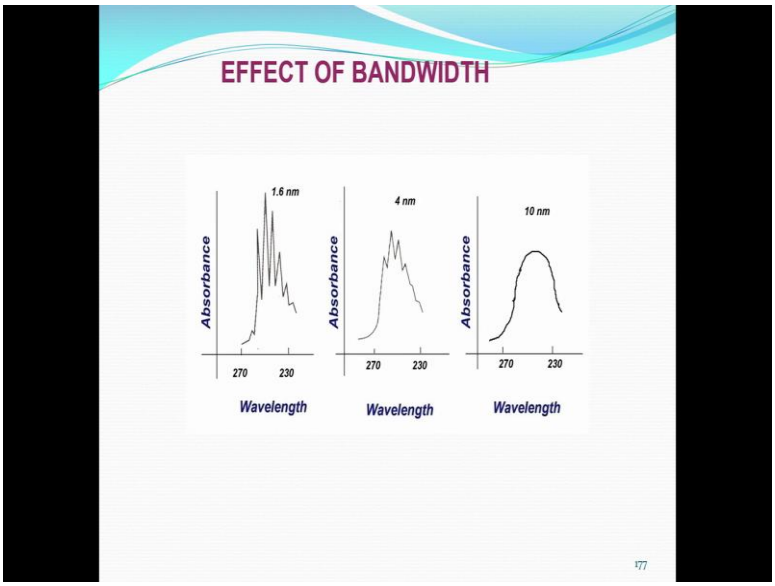

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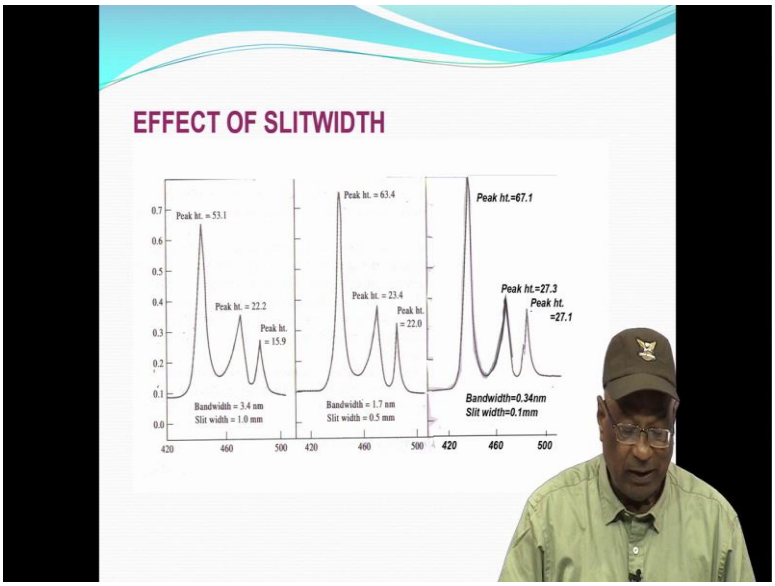

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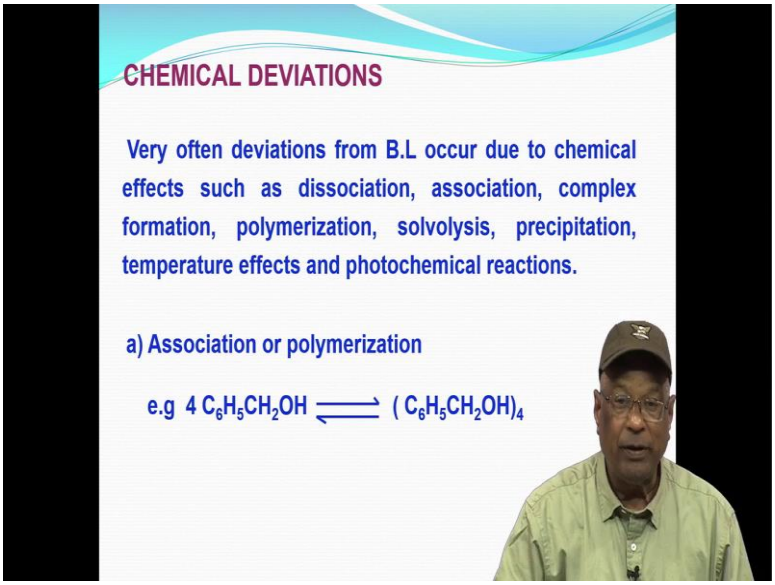

So, effect of slit width you can see that in all these cases how the peaks are looking at different slit widths. So, we will continue our discussion with the chemical deviations. So, normally this is the most difficult part of practice of spectrophotometry. You should understand what are the basically deviations occur due to chemical reactions, and this is the part where your knowledge of chemistry is very important. So, we have classified several types of deviations because basically it in Beer-Lamberts law what you measure is either transmittance or the absorbance. So, all they both these transmittance and absorbance are based on colour.

So, anything that affects the colour of the solution complex, which is going to affect the Beer-Lamberts law, that is the basic logic. So, very often deviations from Beer-Lamberts law occur due to chemical effect such as dissociation association, complex formation, polymerization, solvolysis, precipitation and temperature and photochemical reactions. All these things are real deviations only, but basically the requirement is the in all these cases the lambda max where you are measuring the absorbance or transmittance is going to change; that means, Beer-Lamberts law the first basic assumption of monochromatic radiation is violated. So, once it is violated means there will be definitely deviations and among this I have I am giving you below an example of benzyl alcohol, in solution if the concentration of this reagent is very high we have a polymerization.

So, four molecules of benzyl alcohol is going to give you one molecule of tetra polymerized benzyl alcohol so; obviously, the lambda max will change.

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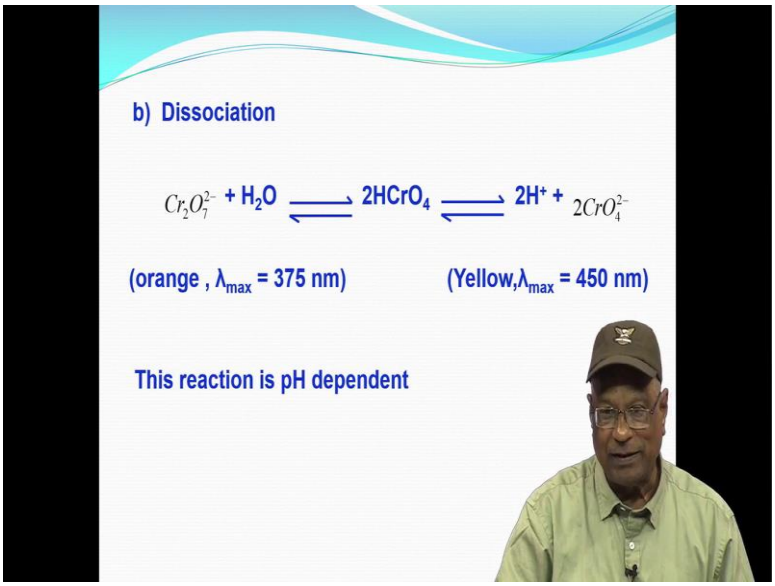

So, Beer-Lamberts law is going to be affected. Now sometimes we had dissociation, this dissociation is also very simple to understand if I have given an example of chromium a dipotassium dichromate, hexavalent chromium; it is if it is in very dilute acid dilute water it will be in equilibrium with potassium chromate, and chromic acid. And the as you can see from this slide we have the orange, and chrome potassium dichromate has got a lambda max of 375, and if the solution is very dilute you are going to get a yellow colour which is having a lambda max of 450; obviously, the absorbance or transmittance is not going to be the same whether you measure it 375 or 47 450 nanometers.

This reaction is of course, you have to understand that it is a p H dependent reaction because there is a hydrogen here, this hydrogen ion is going to affect the equilibrium and therefore, the species of chromium and dichromate and chromic chromate are going to the concentrations of these things are going to change.

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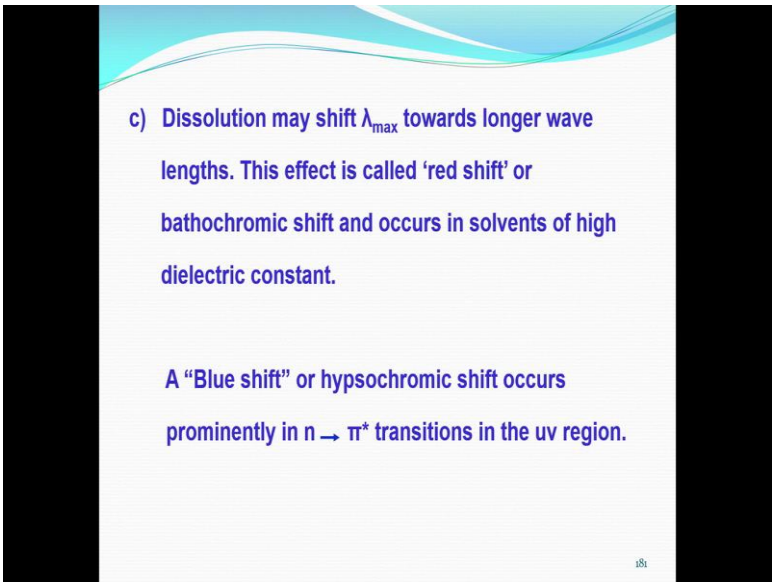

Now, look at one more this thing that is a dissociation dissolution; the dissolution normally effects shifts towards lambda max, shift the lambda max towards longer wavelengths this effect is called as red shift some or bathochromic shift; this bathochromic shift is very important especially in ternary complexes and this occurs in solvents of high dielectric constant.

Normally another effect that is shifting of the lambda max towards lower wavelengths occurs and that is all that is known as "Blue shift" or hypsochromic shift. So, this occurs mainly due to n to pi star transitions in the u v reason; that means, we are whenever we are going to use any oxygen containing solvents in spectrophotometry, we are going to end up with hypsochromic shifts and that is a real deviation.

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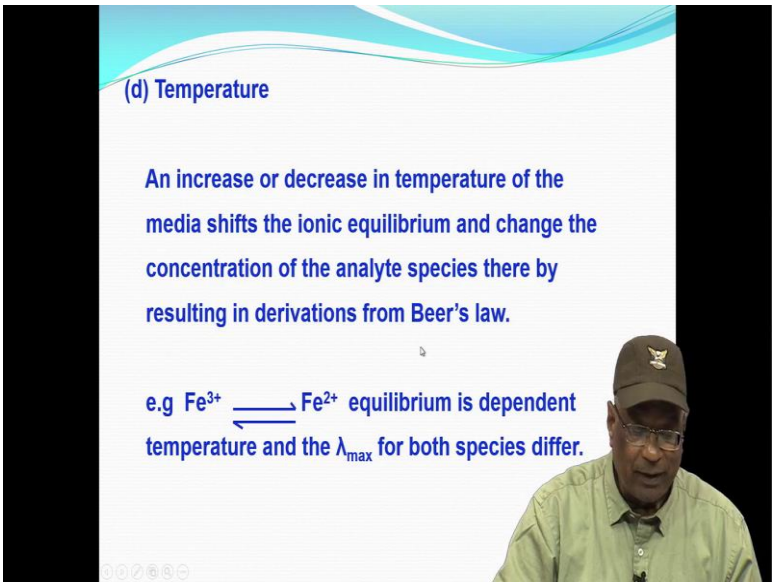

Now, temperature; temperature is another effect where the ionic equilibrium changes and the concentration changes, and the example what I have give what I am giving is ferric to ferrous this equilibrium is definitely dependent upon the temperature, and lambda max for both these species differ; because ferric is red colour and ferrous is green in colour in solutions.

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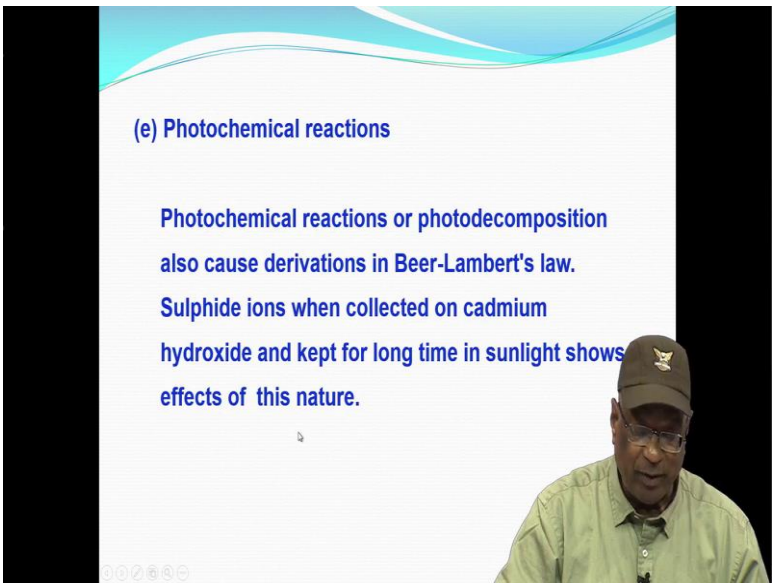

So; obviously, the lambda max is going to be different. Now another aspect is photochemical reaction; here you will have to understand that we are going to take some

amount of sample going to eradicate with the radiation. So, whenever radiation strikes a molecule and if it is photo chemically active, it may undergo a chemical reaction breaking into smaller molecules or association dissociation and many other complications which we are not go into detail, suffice it to say that photochemical reactions or photo decomposition also cause deviations from Beer-Lamberts law.

Usually, Sulphide ions when collected on cadmium hydroxide and we keep it for long time in sunlight, it turns into yellow even though initially it is white it turns into yellow and; obviously, there lambda max for white and yellow are going to be different; this is very simple example you should remember, the part there in actual practice you will come across number of situations like this it depends upon your knowledge of chemistry, and chemical ingenuity of your to device methods for proper estimation from spectrophotometry.

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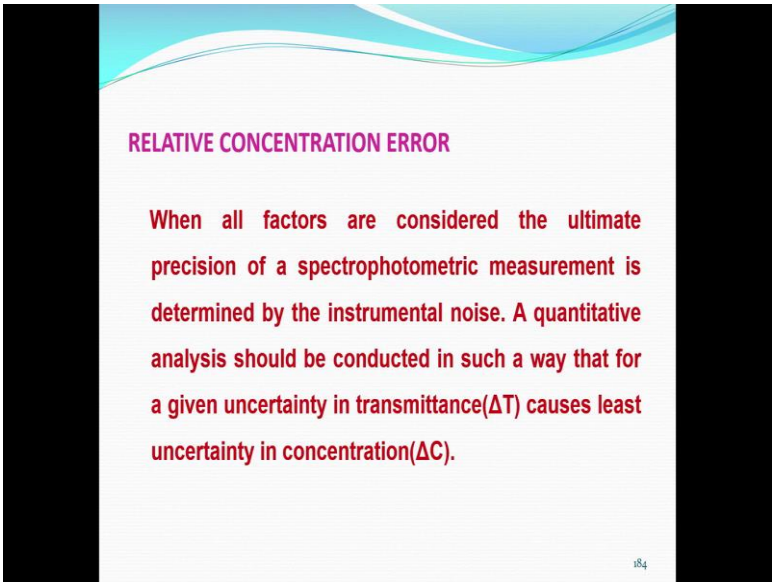

Now, this is so far we have considered; what are the different types of Beer-Lamberts law deviations. Now whenever we want to make a measurement in practice what we want basically is within a straight line. So, if it is not a straight line then we have to assume that it is the error should be minimized, there are methods of minimizing the error because as I have said real deviations, instrumental deviations, chemical deviations always occur and do occur and as a result there will be a measurement of error; there will

be some amount of error introduced in all these cases. So, the aim of a good chemist these two reduce the error measurement errors due to all these factors.

So, we what you want to do is we want to reduce the relative error to minimum, so that the accuracy of analysis would be optimum maximum. So, when all these factors are considered the ultimate procession of a spectrophotometric measurement is determined by the instrumental noise. Now a qualitative analysis should be conducted in such a way that for a given uncertainty transmittance should be minimum and for minimum change in the concentration. So, the uncertainty in transmittance must match the uncertainty in concentration then only the error will be minimum. Now this is known as relative concentration error there is a very simple quantitative relationship we can draw from this.

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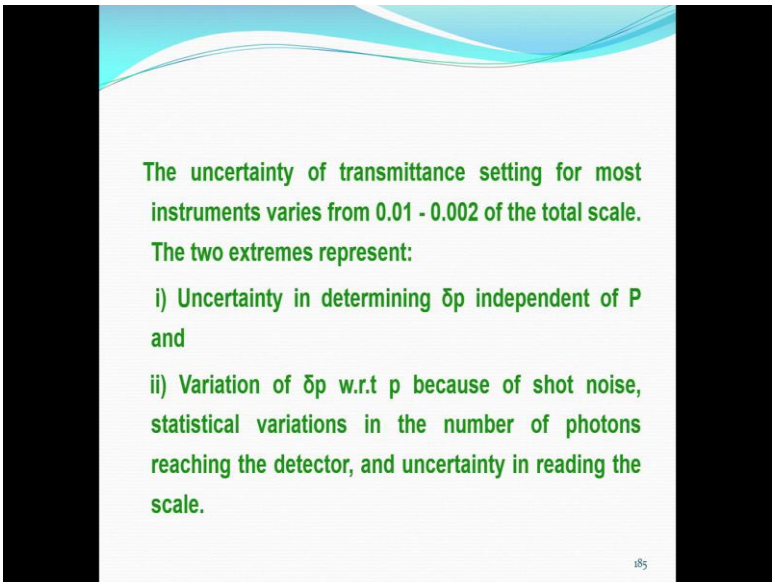

The basically the uncertainty of transmittance setting for most instruments varies from 0.01 to 0.002 percent of the total scale.

So, we have two extremes: one is uncertainty in determining the change in the initial power, and variation of initial power with respect to the power because of the shot noise, statistical variations and uncertainty in reading this scale. Earlier there use to be lot of analogue scales and it is to be difficult to read, nowadays there are lots of digital scales which will tell you in numbers, but still the basic principle of uncertainty remains the same whether it is analogue or digital it does not matter one way or another.

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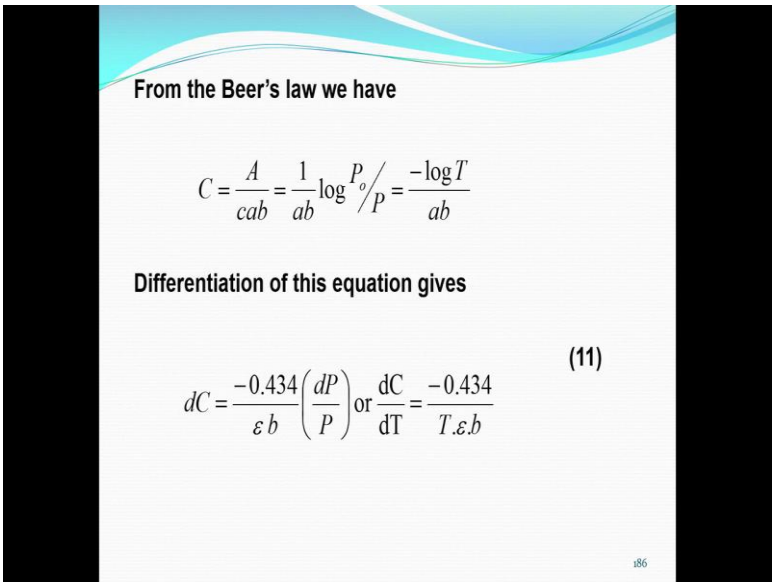

So, we have a small derivation coming up now, and what we do is we take from the Beer-Lamberts law the concentration a is equal to epsilon b c.

So, I have put here C is equal to A upon epsilon b. So, this is 1 over a b log of P naught by P, this is basic definition of absorbance and that is also equal to transmit negative log of transmittance and divided by a b. This is the basic equation what we are going to deal with. So, we differentiate this and we get a minimum. So, if I differentiate with respect to concentration I get dC is equal to log this log comes when I do this, I have this figure automatically coming 0.434 divided by epsilon b and d P by P. So, log of P naught by P I have when I differentiate I get d P by P or dC by d T is equal to minus 0.434 trans divided by transmittance into molar extension coefficient multiplied by the path length; so T into epsilon in to b.

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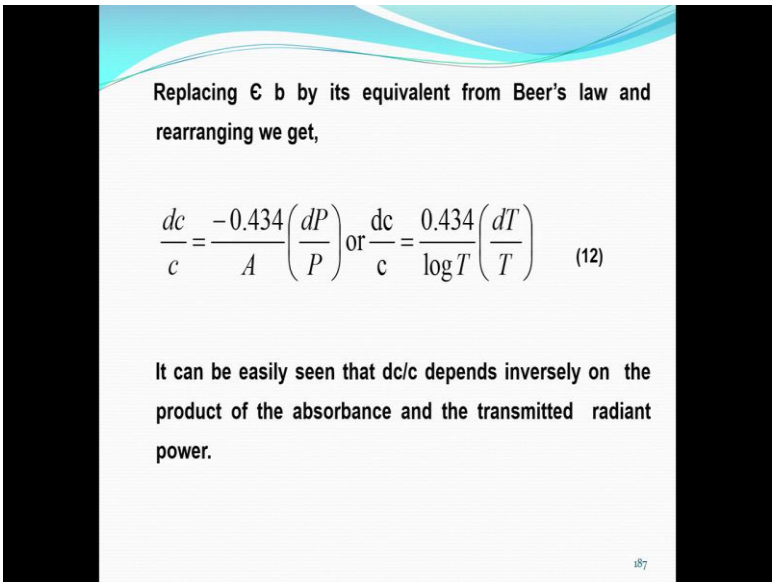

Now replacing epsilon b by its equivalent from Beer-Lamberts law, what I get is dc by c is equal to 0.434 divided by A of d P b y P or dc by c is equal to 0.434 d T by T this is in terms of transmittance the first part is in terms of power. So, we can see that dc by c depends inversely on the product of the absorbance and the transmitted radiant power.

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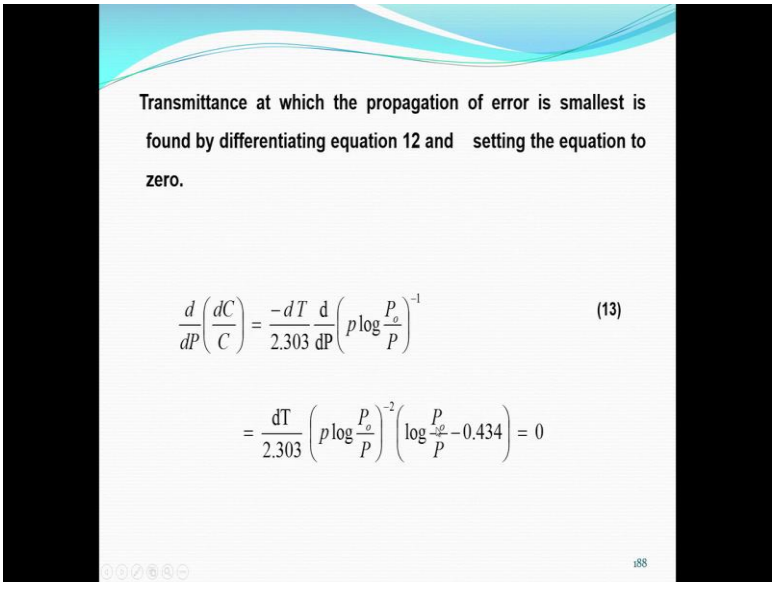

Now, to get minimum, what we do is we differentiate it second time and equate it to zero.

So, when I do this transmittance the at which the propagation of error is smallest respond by differentiating that equation, and setting the equation to zero, so what I get here d by d P of dC by C is equal to minus d T. All these things if you look at the equation they all look very simple when I am reading it for you it looks a little complicated, but if you refer any text books or something use your general knowledge in mathematics differentiation etcetera it is very simple. So, d by d P is of P into log of P naught by P raise to minus 1. So, this is should be equivalent this and if this is going to be 0 d T by 2.303 this expression I have to said it to 0 to get the minimum.

So; obviously, this is a first d T by 2.303 is a multiplication term it is a positive number, this P into log of P naught by P is a a positive number there is raise to minus 2, and the only thing that can become 0 is log of P naught by P is minus 0.434 should be equal to 0. So, only in this whole expression d by d P of dC by C can be equal to 0 only this expression log of P naught by P minus 0.434 is 0. So, if I said use this log of P naught by P would be equal to 0.434.

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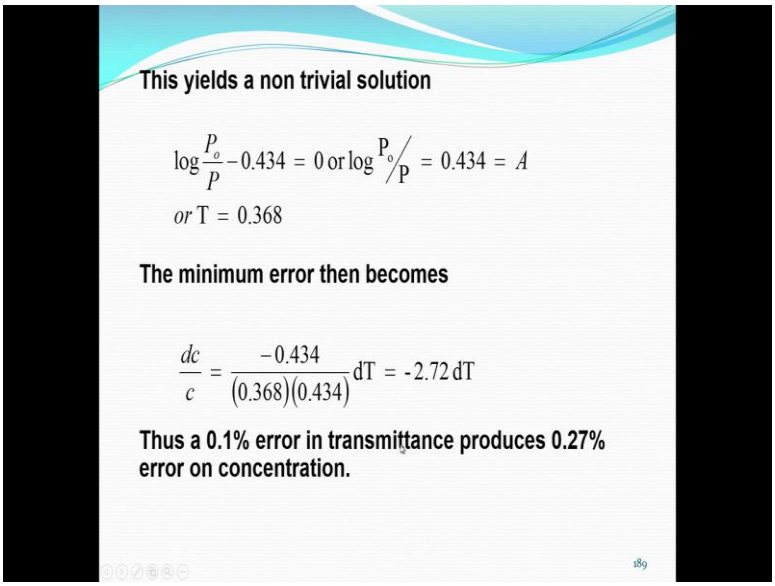

So, log of P naught by P is equal to 0.434 that should be equal to 0 or log of P naught by P is equal 0.434 which corresponds to a transmittance of 0.368.

So, the minimum error then it becomes dC by C is equal to by put all these numbers and then what I get is 2.72 into d T. So, a 0.1 percent error in transmittance produces 0.27 percent error in concentration this is the bottom line.

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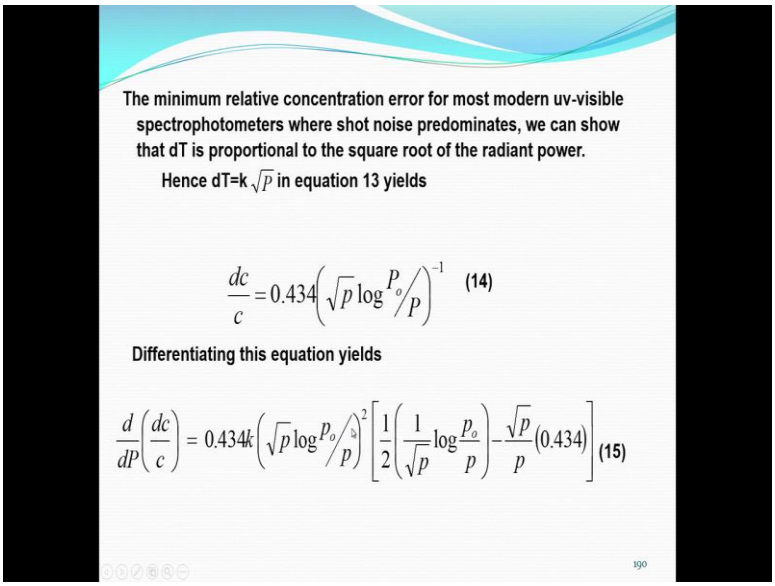

So, the minimum relative concentration error for most modern uv-visible spectrophotometers, where shot noise predominates we can show that d T is proportional to the square root of the radiant power. So, I put these numbers and then differentiating this equation again I get a multiplication term another multiplication term and then 1 over 2 this should be 0.

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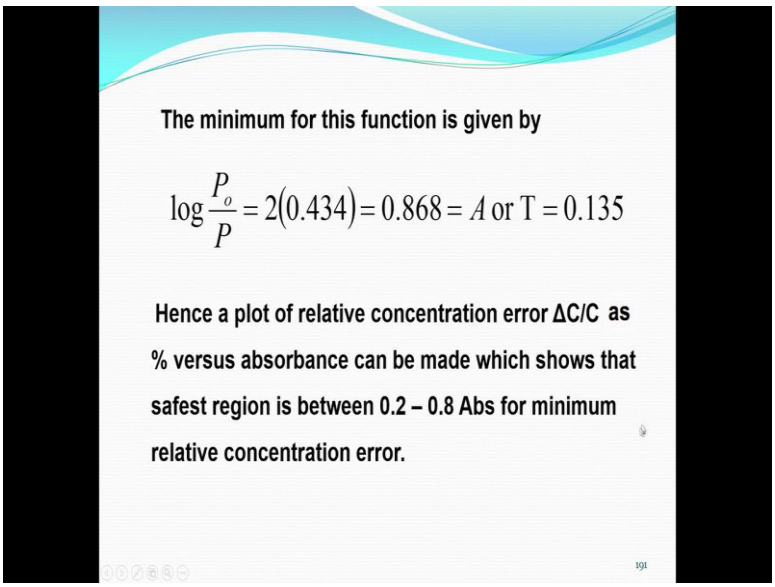

So, what is in square bracket becomes 0 again, if I had to get 0. So, for this the minimum for this function is given by log of P naught by P is equal 0.868, and that should be in

terms of absorbance or in terms of transmittance it is 0.135 therefore, what we normally do is whenever I make a measurement in spectrophotometry, I must always stick to absorbance of there in the range of 0.2 to 0.8 absorbance that is the bottom line. So, whenever if the consent, suppose the conse the absorbance reading is more than 0.8 then what do you do? If it is more than 0.8 we should dilute the sample. So, that it comes within the range of 0.2 to 0.8.

Suppose it is 1.25 we know that the relative concentration error around 1.25 is much higher similarly, if the absorbance is only 0.04 or 0.03 02 or 07 or something like that we know that the absorbance is always error is more in the dilute portion also. So, I had to bring it within the range of above 0.2. So, Beer-Lamberts law if it is straight line within between 0.2 and 0.8 absorbance, we get a straight line the concentration error will be minimum. So, this is the significance of relative concentration error.

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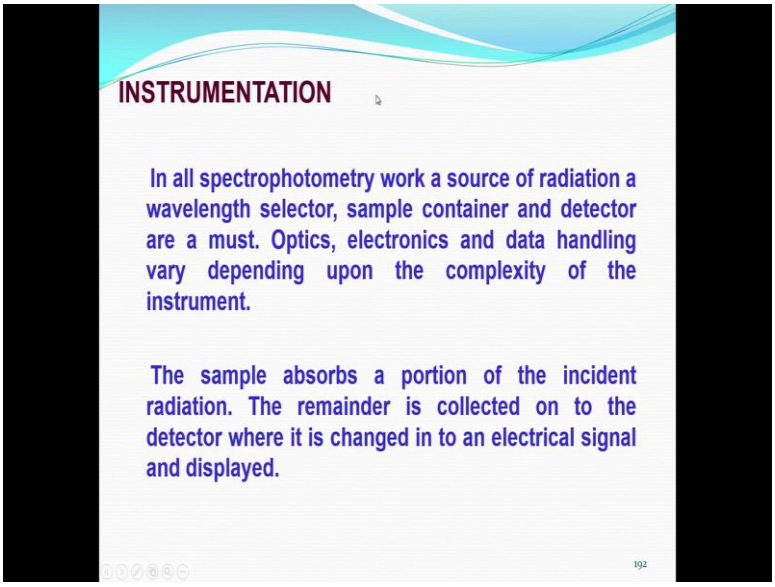

So, now we will go to instrumentation. So, that is the theory so far we had discussed the theory of spectrophotometry now we will concentrate a little on the instrumentation part. So, in all spectrophotometry suppose you want to buy a spectrophotometer or construct a spectrophotometer for your own purpose, what are the components that go into making a spectrophotometer, what are the desired qualities of the components like that we are going to spend some time on the instrumentation. So, it is very important for all scientists to know about the instrumentation, and the typical properties of the components. So, in

all spectrophotometric work, the component parts of a spectrophotometer are a wavelength selector, a sample container and a detector these are the must.

I must have a source of light and then where will I need to select the typical and desired wavelengths, because we know that all absorbance lead to a maxima and where maximize is there I have to make the measurement. So, I need a wavelength selector and then I had to place my sample in the path of the radiation that is a sample container, and then I must have a means of detecting the radiation that is coming out before and after the sample. So, the sample absorbs a small portion of the incident radiation, the remainder is collected on to the detector where it is changed into an electrical signal and that is displayed. So, once the electrical signal is collected, it can be converted into in terms of concentration or absorbance or transmittance or whatever typical measurement units we normally employee.

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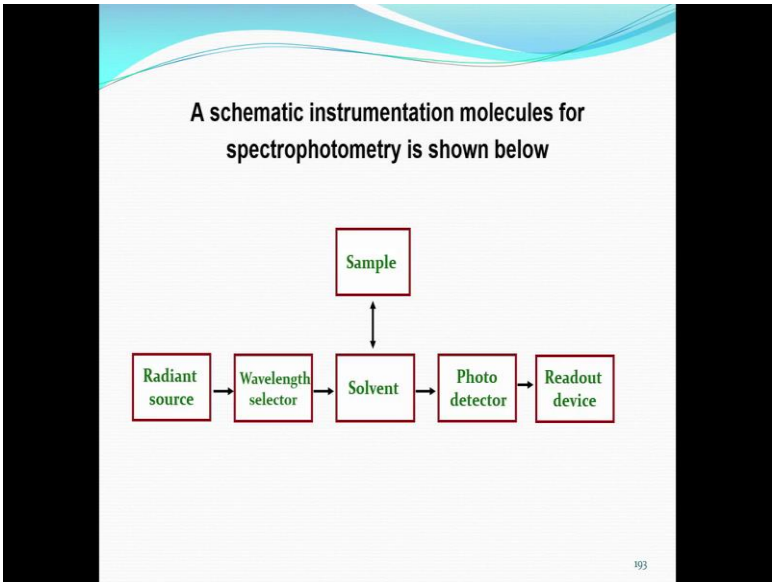

So, a schematic representation of the molecules for spectrophotometry is like this, I need a radiant source that is here and then I need a wavelength selector, I need a sample solvent; solvent is for reference, sample is for measurement. So, these two are interchangeable and then I need a photodetector and I read out device these are the basic components.

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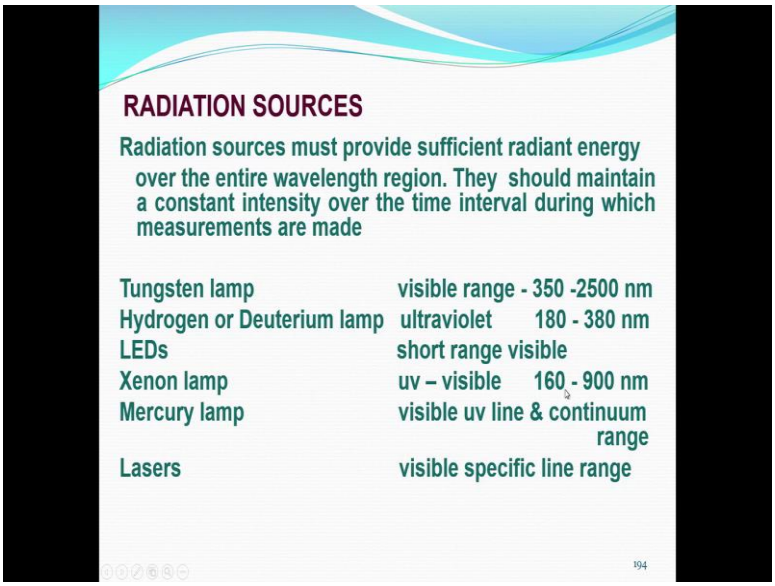

So, what are the radiation sources? So, I have a number of choices, depending upon the concentration, depending upon the cost and depending upon the sophistication I want. Normally radiation sources provide sufficient radiant energy over the entire wavelength region; that means; in spectrophotometry what I need is a lamp which gives light in all wavelengths.

So, then I can choose the wavelength whatever I need by using a prism or something like that or a lens. So, they should maintain a constant intensity over the time interval also, during which the measurements are made; that means, the power of the light source should be stable during that. I have a typical choices one is a tungsten lamp; nowadays people are not using tungsten lamp in a even in day to day life, but all of you would have seen it by tungsten lamp, bulbs in your houses earlier and legally it has been stopped, but in instrument we do use tungsten lamps. So, tungsten lamps normally give a wavelength range of 350 to 2500 nanometers and, but this is not enough for spectrophotometry why because, we also want to make measurements using between 180 to 300 or 350.

So, to cover the ultraviolet range I need a hydrogen lamp or a deuterium lamp, these are all available in the market you can just go there and purchase and make a construct on your own. So, now, a day's people use LEDs and a very small LED s for portable equipments. So, these are very short range, visible range and a Xenon lamp is again useful for instrumentation, but Xenon lamp automatically one single lamp will cover 160

to 900 nanometers this is; that means, it will cover both u v and visible; mercury lamp it gives you a visible u v line and a continuum range. So, lasers are very high intense radiations, but very specific line range all these things have been used in the spectrophotometers.

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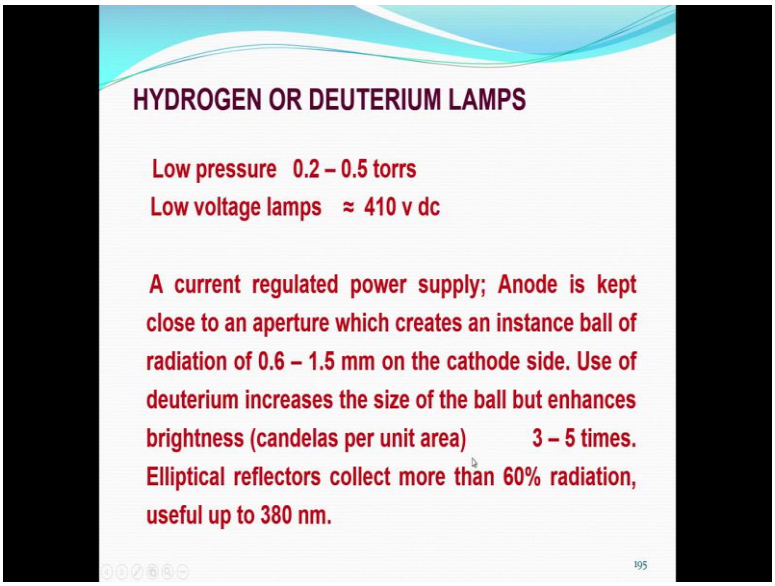

So, containing our discussion hydrogen lamp or deuterium lamp, so it is a low pressure lamp; that means, drival pressure in the lamp is only 0.2 to 0.5 torrs, it is a low voltage lamp also 410 volts and a current regulated power supply is required to generate; why because what we normally get is 220 volts dc.

So, anode is kept close to an aperture which creates an in instant ball of radiation of 0.6 to 1.5 mm on the cathode side, it is a what you need is basically a lamp with 2 filaments. So, one is cathode another is anode. So, in between hydrogen is filled and the when we apply the current and voltage the radiation is collected through a elliptical reflectors and that is useful up to 380 nanometers.

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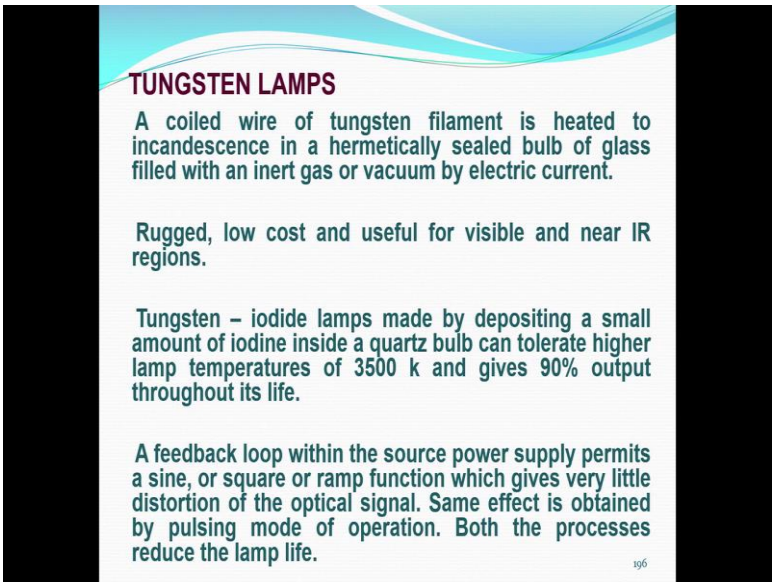

So, tungsten lamps again as I was telling you a coiled it is just a small bulb which you would have a seen in your day today life, it contains a coiled wire of tungsten or nickel or something like that, and then it is heated to incandescence in a hermetically sealed bulb; that means, no not high pressure lamp and then it is filled with in either inert gas or a vacuum or by vacuum and it is heated by electric current.

Tungsten lamps are normally very rugged, low cost and useful for visible and near IR region. Nowadays what people do is the use tungsten iodide lamps, which gives a higher intensity of the radiation compared to tungsten alone. So, what do we do, we deposit a small amount of iodine inside a quartz bulb which can tolerate higher lamp temperatures of up to 3,500 degree kelvin and it gives you a 90 percent output throughout its life. So, what we need is essentially a feedback loop within this power supply source and sine wave or it is a cosine or square or ramp function, which gives very list little distortion of the optical signal that is due to their requirement.

So, same effect is obtained by pulsing mode of operation both processes if we apply this kind of additional filters, they reduce the lamp life; if you use it as such there is not much problem, but the quality will always be different.

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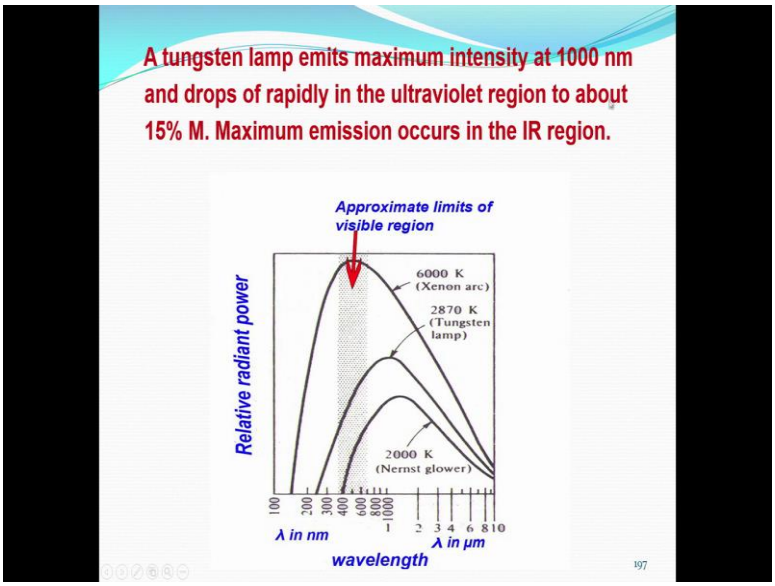

Now, tungsten lamp the problem with tungsten lamp is it emits maximum intensity not in the range of to 350 to 700, but it emits maximum radiation around 1000 nanometer which is not visible range. So, the intensity ultra in the ultraviolet range between 180 to 250 again the intensity drops quite a lot. So, the tungsten lamp is not an ideal source for spectrophotometry, but it is very cheap hardly 10 rupees, 15 rupees you will get a tungsten bulb and you can use it for all practical purposes it can be done, but for very high precision work not required. So, the thing is it gives 15 percent light in the visible range that is the bottom line.

So, maximum emission occurs only in the IR region, here in this figure I have shown you relative radiant power versus wavelength you can see that between are the maximum are this is around 6000 kelvin, the range 400 maximum is reached starts from 400 to 650 or something like that for Xenon lamp. For tungsten lamp below that you see second figure middle finger middle figure and here you see that only a very small portion the maximum power is not reached here in the visible range, up to 650, 700 range maximum power is not reach and up to 400 also it is not a, but there maximum lies somewhere around 1000. Now there is another source that is known as nernst glower which we use normally in infrared and, but that is a not very useful for spectrophotometry either and it is not convenient.

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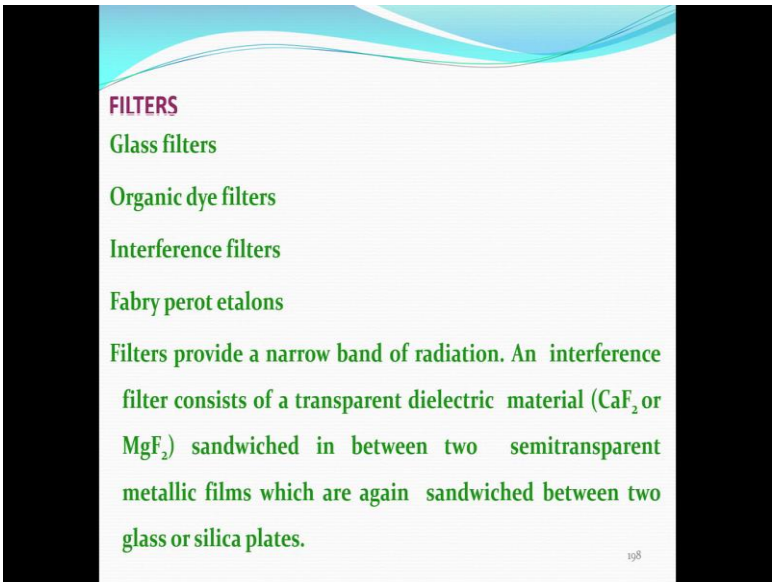

So, one can use any of the sources and constructor's spectrophotometry, all will work because what we need is a relative measurement. So, in relative measurement whether I use LED or tungsten lamp or Xenon lamp or lasers either way it is same, because the error introduced in measuring the wavelength gets carried in both the blank and the sample. So, the error percent error remains the same, so they get cancelled. So, we can construct a spectrophotometer using any of these only thing is you may not get the desired sensitivity, we will talk about sensitivity little later when we go into the practice of spectrophotometry.

So, now we move on to filters. So, what is a filter? Filter is a device which gives you a narrow band of radiation. So, an interfere we have different kinds of filters one is known as glass filter, which is nothing, but a coloured glass; you would have seen coloured bottles green, red, brown, yellow coloured bottles; blue bottles and these are all glass filters. So, if I make a small disk round disk of a colour glass it is known as glass filter. And then what I can do is I can also use an organic dye take two glass plates, I can choose an organic dye which we will give me about 20 to 30 nanometers and I can choose a different ranges from yellow to red, orange etcetera to cover the whole wavelength range of the visible range.

So, these are organic dye filters; and then interference filters are basically a transparent dye material dielectric material containing calcium fluoride or magnesium fluoride

sandwiched in between two semi transparent metallic films, which are again sandwiched between two glass or silica plates, we will see more of these things in the near future for example, this is a glass filter.

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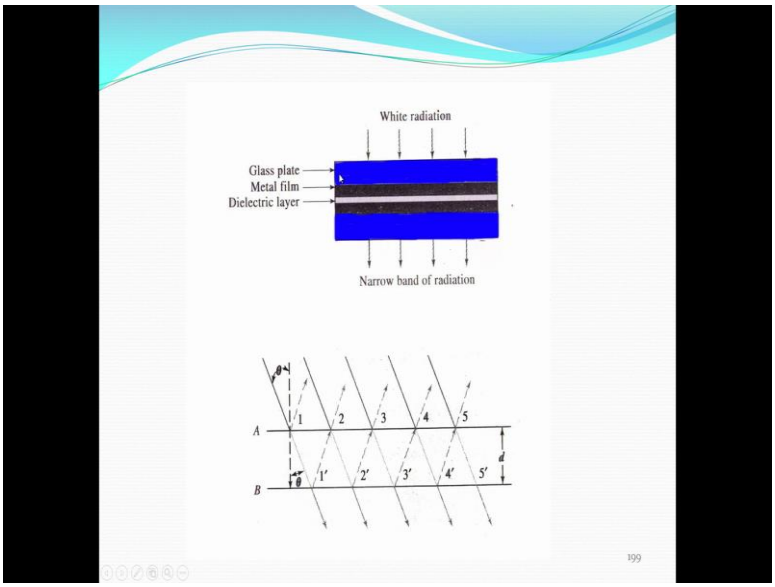

On the top there is a glass on the bottom there is glass and then there is a dielectric layer and this is the metal film and this is also a metal film. So, white radiation comes here, what comes out is a small narrow band of radiation. So, this is one type of the radiation or filters, and if there are different rays coming parallely from this, I had to I get a very narrow band of radiation because the things which are not in sync with the wavelength they will all cancel out in due to interference.

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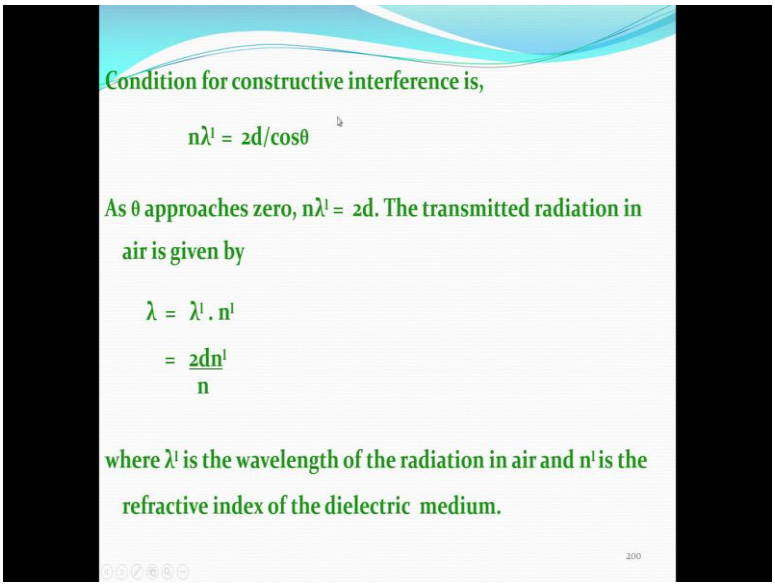

So, this is what I have shown here in the bottom figure. So, condition for constructive interference is given by n lambda is equal to 2 d cosine theta, and as theta approach is 0 cosine theta becomes 1. So, n lambda becomes 2 d. So, the transmitted radiation in the air is given by 2 d n by n dash by n, where n is the n dash and n are the refractive index of the dielectric medium. So, different compounds if you use magnesium fluoride, titanium fluoride and then any other chemical material in way to sandwich between the two plates, I am going to get different wavelengths.

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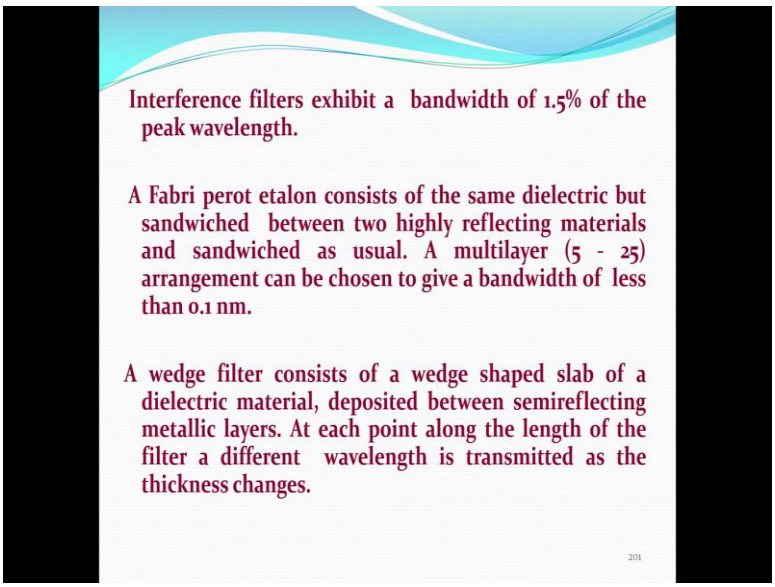

So, interference filters normally we have been we have talking about interference filters so far, but in normally interference filters exhibit a bandwidth of 1.5 percent of the peak wavelength. A arrangement known as Fabri perot etalon consists of the same dielectric material sandwiched between two highly reflecting materials and sandwiched as usual. So, multilayer arrangement can be chosen to give bandwidth of less than 0.1 nanometer. That is the accuracy you get in spectrophotometers in nowadays. A wedge filter means another type of arrangement and here the material is deposited between semi reflecting material metallic layers at each point again we have the constructive and destructive interference, and wavelength is transmitted as the thickness changes

So, that brings us to monochromators. So, filters are one thing which give you wavelength group; a group of wavelengths so, but monochromators give you a particular wavelength for example, if the glass filter what comes out is so let us say 410 to 430 nanometers all of it comes out, and that can be used, but it is not a monochromatic light anyway is not it. So, if I am the next improvement in the filters is monochromators.

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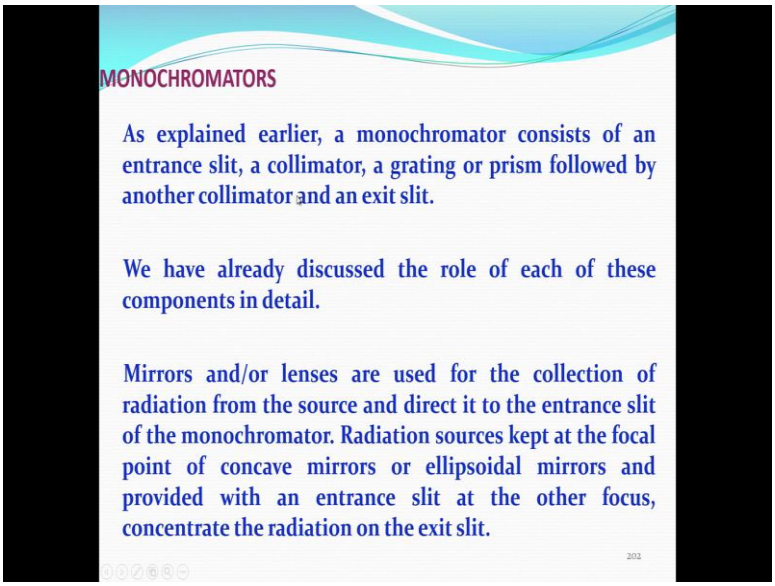

So, monochromators it consists of an entrance slit, a collimator, a grating or prism followed by another collimator and exit slit. We have already discussed the role of each of these components in detail during the general discussion.

So, basically mirrors and lenses are used for the collection of radiation from the source, and direct it to the entrance slit of the monochromator. So, normally radiation sources are

kept at the focal point of the monochromator, so that the radiation that comes out will be only in parallel bunch, from there which go choosing for the exact wavelength.

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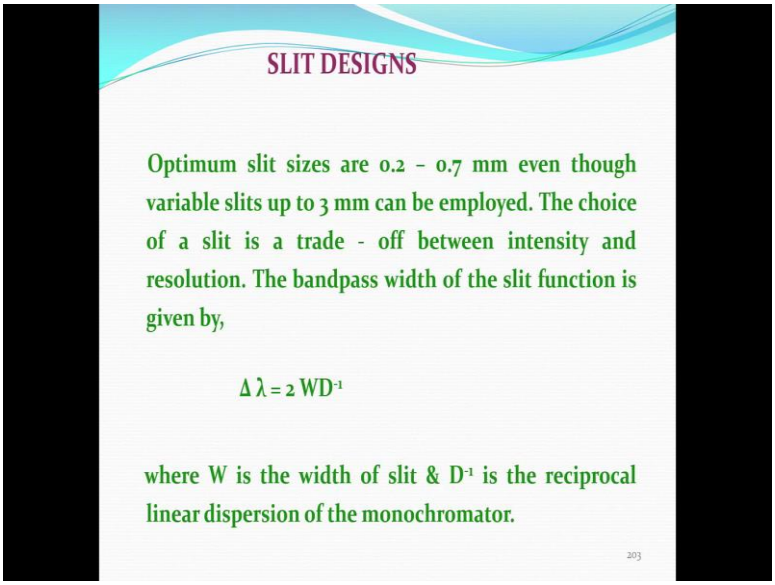

So, slit designs we will discuss next.