Course on Analytical Chemistry
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Lecture No 21
Module 5
Spectrochemical Methods - 2

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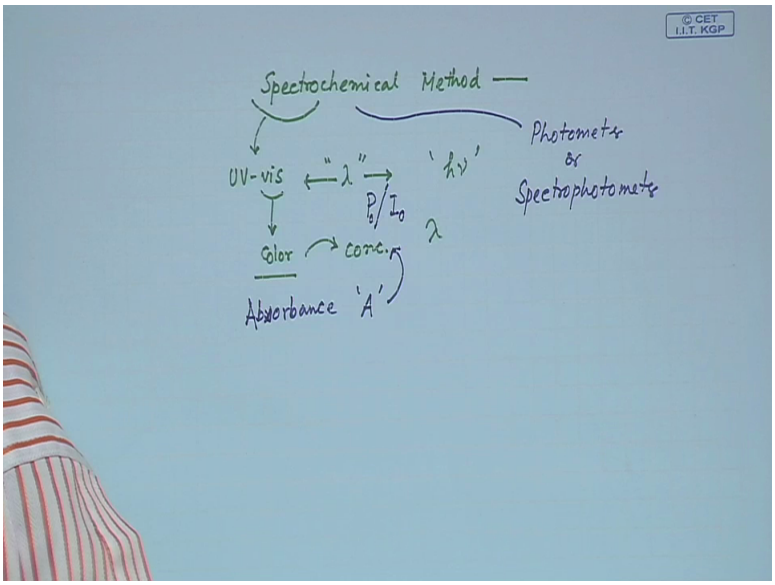

Good evening and welcome to this part of this course where we are still continuing with spectrochemical methods of analysis so the typical analytical chemistry is benefited from the use of the light spectrum. So when we use UV visible spectrum of the light of some range of wavelength as we all know that the visible part is directly related to the color where a particular solution color can be identified and can also be quantified for its corresponding concentrations.

So these are the things how we can correlate this nicely for a particular type of spectrochemical methods, how we judiciously the particular wavelength value and if we allow to apply that particular wavelength such as the visible light what we see the sunlight the h nu of sunlight or the visible light when it is falling on a solution or a colored solution we see a corresponding color and by knowing the corresponding color how we can identify the corresponding lambda for the absorption.

So that particular solution which is colored in nature it can be a corresponding metal ion solution or it can be any other analyte. So all these analytes can be analyzed or can also be

estimated by means of a typical spectrochemical method where we basically use a photometer or a spectrometer or a spectrophotometer. So we can have a photometer or a spectrophotometer.

And what it can happen there that we can find out something which we will call as absorbance A, so the amount of absorption earlier we used to say it as absorptivity that amount of absorption will be then correlated directly to the concentration following some law or following some rule.

So now we will see how all these things that means the absorbance of a particular solution is related to this particular wavelength which is following on the solution that means the power or the intensity P or I and when it is falling on the solution we consider it as P0 or I0. The intensity of the light which is falling on the solution causing some amount of that particular light to be absorbed and we get some information that means the amount of absorption which will be directly related to the corresponding concentration of the species to be analyzed present in the solution and also the color intensity that means the species which is responsible to give you the color is also give you the corresponding color intensity where from we are trying to get some amount of absorption of the light which is falling on the solution.

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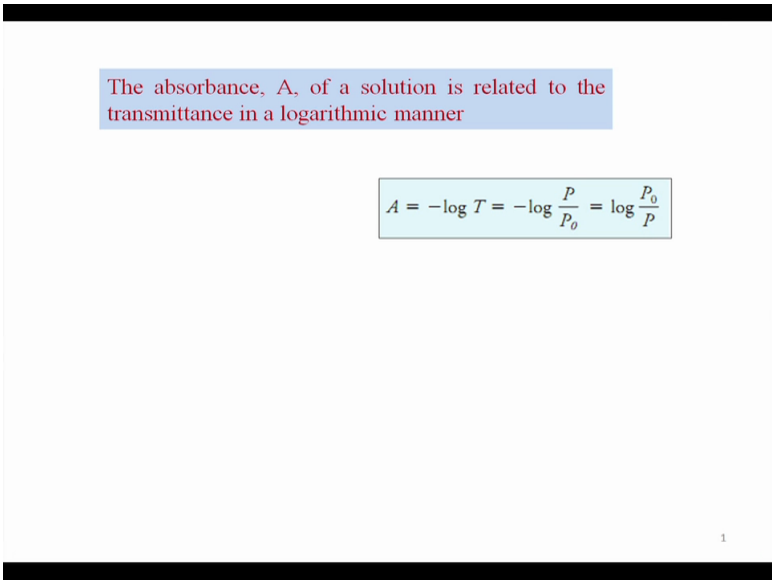

So let us see how we can quantify all these things, so if we have some quantity we consider it as A of a particular solution. So if we have a solution where we A is the corresponding absorbance is related to the transmittance in a logarithmic manner. So the scale like that of your pH scale is also a logarithmic scale and we can use that particular logarithmic scale for

the determination or the measurement of A but this A is directly related to the transmittance of that particular solution.

That means some amount of light is falling on the colored solution and a portion of that particular light will be absorbed and how we can measure the amount of absorption as well as at what particular wavelength this absorption is taking place.

So what we see that if we consider that this A that means the absorbance so that is the quantity we will be using that is the analytical term basically is a very useful term for UV visible spectrophotometry and all spectrochemical methods and where absorption can take place so A is equal to minus log of T T is the transmittance where T is nothing but the power of the light that means I0 I by I0 or P by P0 or log or P0 by P.

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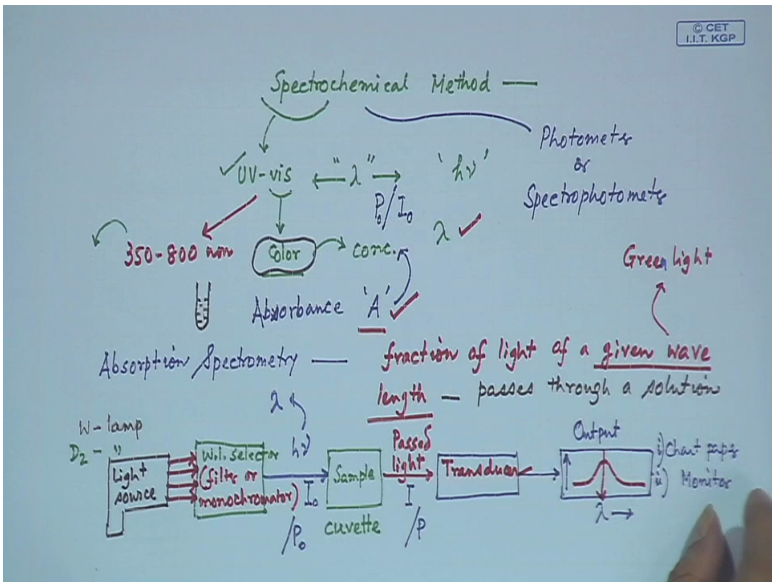

So these things are very useful for our absorption and when we apply these spectrochemical methods for this absorption we also call it as absorption spectrometry. So another name basically for this particular technique will be absorption spectrometry and thus we call it as we are using spectrochemical methods for the typical analysis.

So it basically involves the measurement of the fraction of light which is important to us so fraction of light of a given wavelength which is important is not that all the whole range of the visible spectrum that means as we know that is typically from 350 to 800 nanometer so the range the whole range 350 to 800 nanometer the photometer or the spectrophotometer can scan this particular range.

But we will be looking for something where we can have a particular wavelength and which can pass through the solution. So which is passes so that particular wavelength of light and we will be interested to know the fraction of that particular light which is being absorbed when it passes through a solution through a solution what is that solution that solution is nothing but our solution which is colored you can have that particular solution what we will generate in test tube we all know that the solution itself can be colored but also sometime we can add something some reagent we can add on a colorless solution such that we get a colored product due to the reaction of that particular analyst with the reagent.

So that analyst reagent combination giving you a colored product but we are only interested to know about the corresponding color intensity of that particular product. So the basic block diagram for a photometer how we can use that particular photometer and what type of photometer we can use this nothing but a light source. So in a figure of different blocks that means square boxes we basically call it, so it can be your light source there are different sources depending upon its nature when you talk in terms of the corresponding visible light we can have a typical tungsten lamp when we go down that this below this particular wavelength.

So below this particular wavelength is nothing but your UV range. So in that UV range we have to have some lamp which is based on the hydrogen or the deuterium so it will be a D2 lamp. So depending on the different light sources and all these so the light what is getting generated from there is basically next pass through the corresponding wavelength selector which we will consider as wavelength selector and that wavelength selector is nothing but a filter or a monochromator what is its function.

So as I told you that a given wave length will be interested to know that a particular wave length suppose this particular wave length is for your green light. So if your white light is passing or coming out of a range of wave length we should use some filter or monochromator for that such that we can get a corresponding filtered light that means one particular wave length will come out from there and if we can have a particular this green light that means if we use the green filter the corresponding wave length of light corresponding to the green color of the radiation will pass out from the solution.

So we should be able to know also the corresponding energy in terms of h nu or the lambda value for that particular wave length. So this is basically the selection of a particular wave length which can fall on a particular solution. So remember here that a particular wave length

suppose we are scanning from 350 to 800 nanometer using a spectrophotometer which can scan so the automated process is available such that we can scan the entire range such that from 350 to 800 nanometer of wave length can fall one wave length after another.

So suppose 350, 351, 352, 353 all these thing, so at different wave length how we can measure the corresponding absorption that is the basic alpha fundamental idea behind this particular technique. So what will happen then then we can have the solution that means this colored solution, so we can have the corresponding colored solution in our hand which will be in the sample tube or cuvette we call. So we have the sample here which is in the sample tube or we call it as a cuvette. So this cuvette is there and that particular cuvette is responsible for giving you a corresponding light of P0 or I0, P for power and I for the corresponding intensity.

So after passing through this sample so this wave length of radiation will pass through this solution and after passing through this solution we get the corresponding light of which can pass that means the passed light which can pass through the solution. So we have the passed light and now we have to analyze this particular passed light and this passed light is nothing but your this can be your I0 and this is your I. So these are the two things what we will be talking about or this can be your P0 or this can be your P.

So the magnitude of absorption by the colored solution is thus known when we will be able to measure the corresponding power or intensity of the light which is coming out from the solution. So what we can do next is a very simple process that some electronics will be available and that particular thing such that we get a corresponding output for that so the basic idea is that how we get the corresponding output so your output is nothing but how we get the corresponding plot that means with respect to the different wave lengths that means 350 to 800 nanometer the hole range you can have.

So if we consider that this is the lambda axis for this output so it can be a chart paper. So on a chart paper we can record or simple computer monitor is fine so the screen of the computer monitor is therefore utilized plotting of this thing. So lambda will be plotted against the corresponding thing that means these two quantities the ratio of these two quantities P and P0 will be plotted other axis, X axis will be the lambda what we are scanning one after another one will blend to the other starting from say 350 to 800 nanometer for the whole visible range.

So this is the corresponding electronics how this power the ratio of the power or in sometime its corresponding logarithmic fraction can be utilized for the direct plot of this thing if we want to plot A, so that is why we are talking about this A, that if we try to plot A in one axis. So these are the two things the lambda in one axis and A in another axis. So this particular electronics what is available there is known as transducer, so it is the transducer and in the output whatever it is the chart paper or the monitor we get a typical absorption plot and we can measure this particular wave length at a value which is known from the corresponding axis in the x direction. So this particular one is thus useful to find out the corresponding t value that means the transmittance value.

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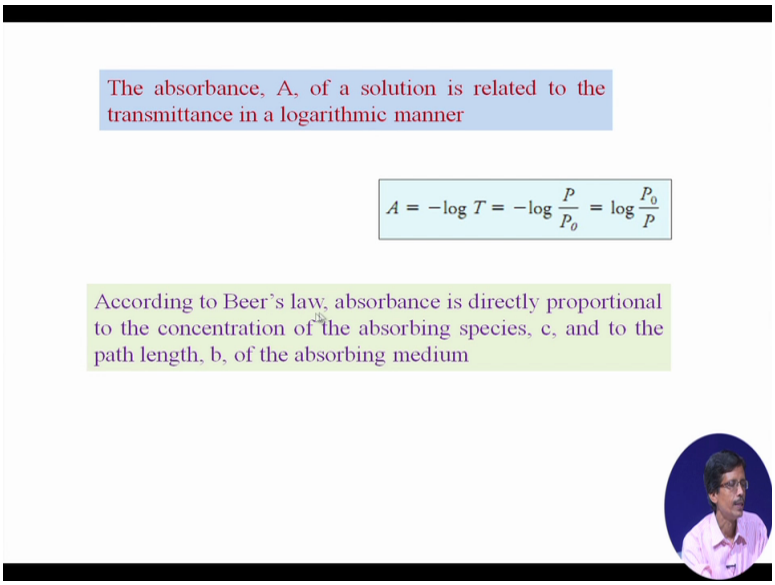

So this we get thus that the T so T is nothing but your P by P0, so we are simply correlating your A which is defined as absorbance so absorbance so the (())(15:50) the (transmuder) the transducer and the corresponding the chart or the output device will give us the corresponding direct recording of this A value against the lambda value.

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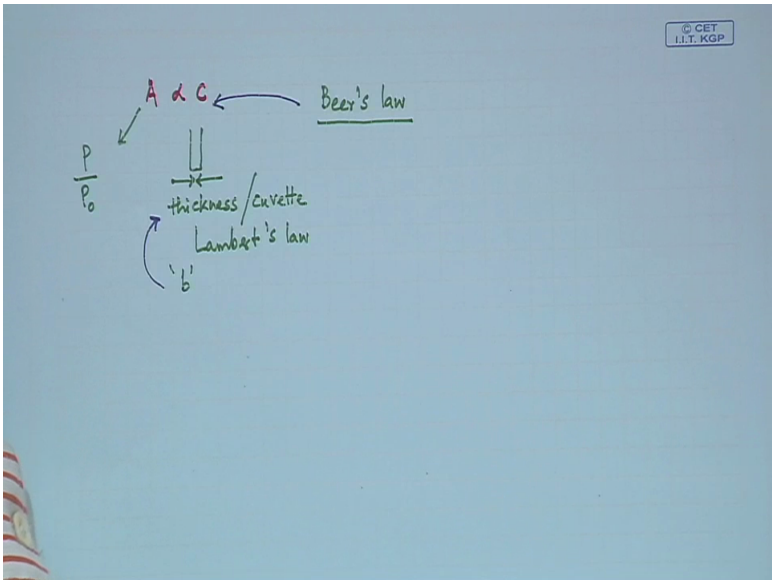

Then we will apply something we will consider it as the dependence that means how we know that that this particular A value will be proportional to the concentration of the solution that is very important how would I know that. So we have to take something where we directly apply this because we are talking about the relationship of this A with say P by P0, now we are bringing another parameter which is directly related to the concentration of the solution which is responsible for giving you the color.

So we will take the help of Beers law, that means the concentration of the solution which is being utilized for measuring this particular absorption and sometimes we also use Lamberts law Lamberts law is nothing but the corresponding sale or the cuvette thickness because this particular proportionality the P by P0, that means the reduction in the light intensity or light power will be directly related to this particular thickness of the cell or thickness of the cuvette cuvette thickness which is known as the corresponding Lamberts law and both these together we can combine such that we can have a relationship where we can consider this particular thickness that means if the thickness is b.

So this thickness so if the thickness is b so we get some relationship where A is directly related to C and also the corresponding contribution from the b because sometimes we find that the corresponding absorption is very less we have to go for a cell where the b value is high instead of the normal or the routine practice of using the cell of 1 centimeter thickness or 1 centimeter path length.

That means that particular path length the light will traverse and sometime we can have 2 centimeter, 5 centimeter or 10 centimeter of thickness depending upon the concentration which is available for that absorption. So sometime we combine these two we call it as Lamberts Beers Law or only the application of the Beers Law which is for the corresponding concentration.

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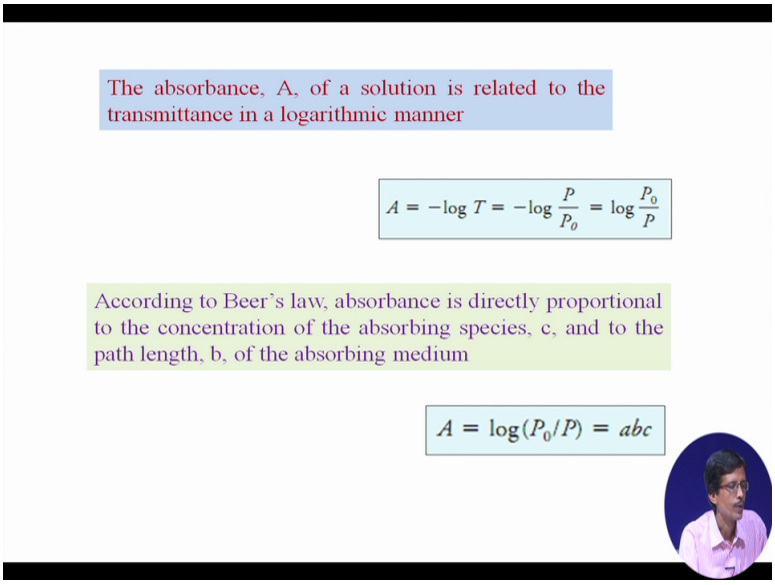

So as per this particular law the corresponding language wise its definition is that the absorbance the A value the absorbance will be directly proportional to the concentration, so that brings the corresponding relationship between A and C. And this particular c who is c it is nothing but the c of the absorbing species which is responsible for your color and to the path length b so you see that though we are calling it as a Beers Law but this particular path length definition of the incorporation of path length in the relationship is the corresponding b value of the absorbing medium.

That means the corresponding thickness of the cell or the cuvette is coming from the corresponding Lamberts law. So what we get we get something is A is equal to log P0 by P is correspondingly abc, if we consider that is the directly writing in terms of the corresponding English alphabets is very easy to remember is very easy to recall back also abc. So we all know we already define b and c so now we know A. So A is nothing but the corresponding proportionally constant because so far whatever we are talking about in terms of the A as it is proportional to b and is also proportional to c, so it will be proportional to the product of b and c and we are now bringing a corresponding proportionally constant as A.

So A will have something to say with the relationship with absorbance you see, A is very easy to remember also, A is therefore the absorbance, b is the thickness and c is also the corresponding abbreviated form of the concentration. So it is very easy to remember this small equation but it will be very much useful for our further studies and further identification of so many other things, ok.

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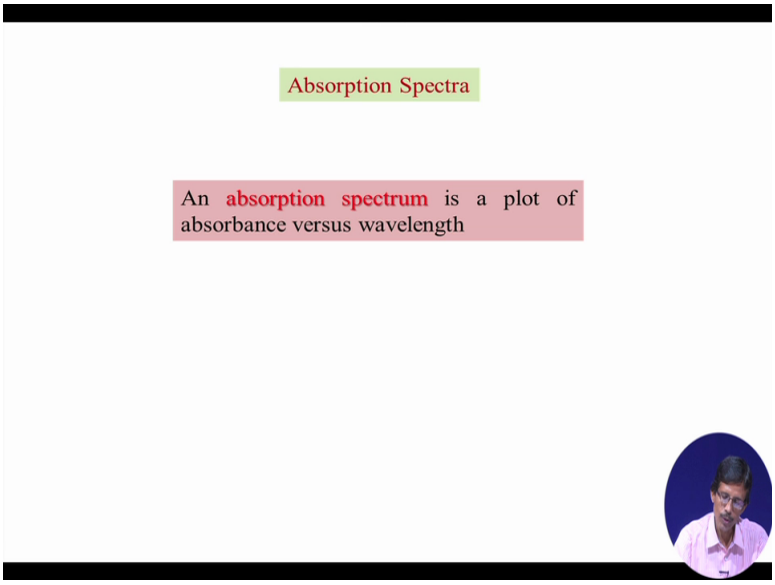

So what we get there that we will have the corresponding spectra we call it as a corresponding absorption spectra. So it is nothing but how we define an absorption spectrum absorption spectrum is nothing but a plot of absorbance versus wavelength.

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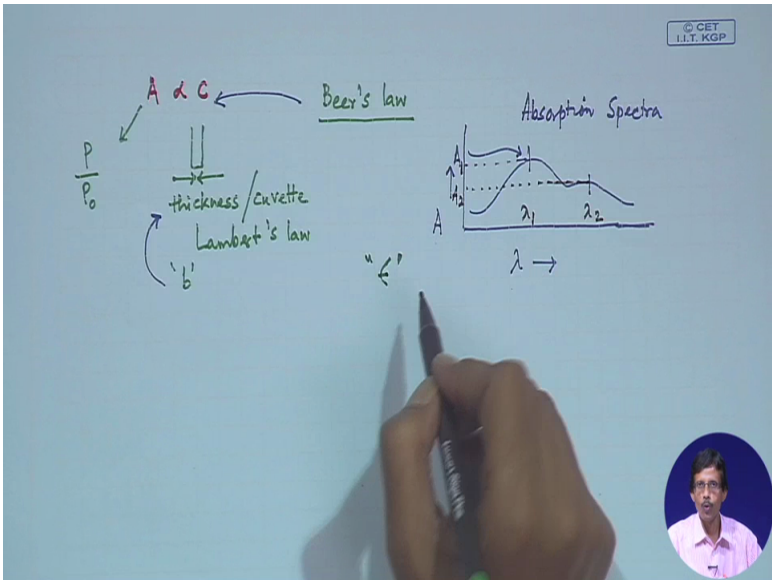

So as we have seen in our previous page that you have a corresponding plot what output device is taking care of from a chart paper or the monitor computer monitor where in one axis we have x lambdas and another axis y having the corresponding absorbance value, so this will be nothing but your absorption spectrum. So anything so is a very useful thing useful terminology in terms of analytical chemistry that any unknown compound or any known compound we can report what its absorption spectra like NMR spectra or any other spectroscopic technique.

So whatever we can have so you can have this sort of spectral plot, you can have multiple absorptions these are the two absorptions the two different lambda values lambda 1 and lambda 2, one is in the lower range and another is in the high range. So you can have a typical absorption spectra for any particular compound and we can recall that so it will be attached to any unknown compound or any known compound as it is corresponding absorption spectra.

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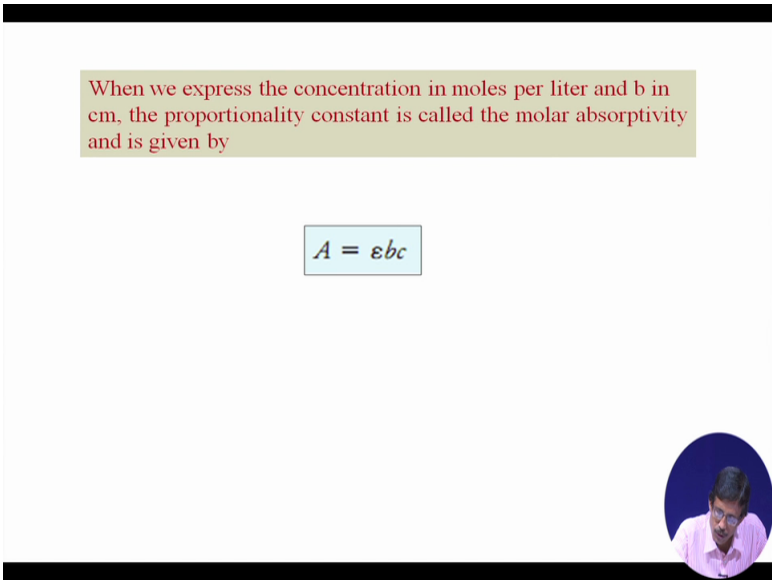

So by language also we should be able to define what is called absorption spectra. When we express the concentration we have to express the corresponding concentration that means the c in terms of moles per liter that is the (())(22:27) convention of reporting the concentration of any unknown solution and b in centimeter which is your path length and as I told you that the standard path length is 1 centimeter such that we do not bother about the corresponding magnitude of this b value and we have a proportionality constant earlier we just taken it as A but for a very standard practice you will be define it as something which is the small case epsilon value.

So which is known as the absorptivity so the absorptivity or the absorbance what is absorbance so A epsilon is the corresponding absorptivity and when the concentration is expressed in moles per liter we will call this as the molar absorptivity. So as a particular unknown compound or any other known compound or a molecule of interest what we want to analyze is that we have to have the corresponding compound and its absorption spectrum.

So next thing is what you can level it with this the corresponding different lambda values if you can have more than one lambda values that means you can have a lambda 1, lambda 2 and lambda 3 its corresponding absorption. So at that particular lambda value because at that point you have the maximum absorbance so if you take this as the corresponding value this is the A value.

So A corresponding to this lambda value so if it is lambda 1, if we consider this is as lambda 1 and this is as lambda 2, so this will be therefore A1 and when the second one we get it over

here in the A2. So we can have two different absorbances one is A1 at lambda 1, another is A2 at lambda 2. So when in writing we say that we can have all these values the characteristic absorption spectra for a particular compound is that we have to report the corresponding maximum absorption at a particular wavelength.

So if it is more than 1 we say that you can have the absorption at lambda 1 and lambda 2 and its corresponding absorbance values. So these will all be very much characteristic and sometime we see that not that A values are very important because it can vary from solution to solution and all other thing. But if we fix the corresponding concentration in moles per liter we will find that the most important quantity will be your epsilon value that means the molar absorptivity.

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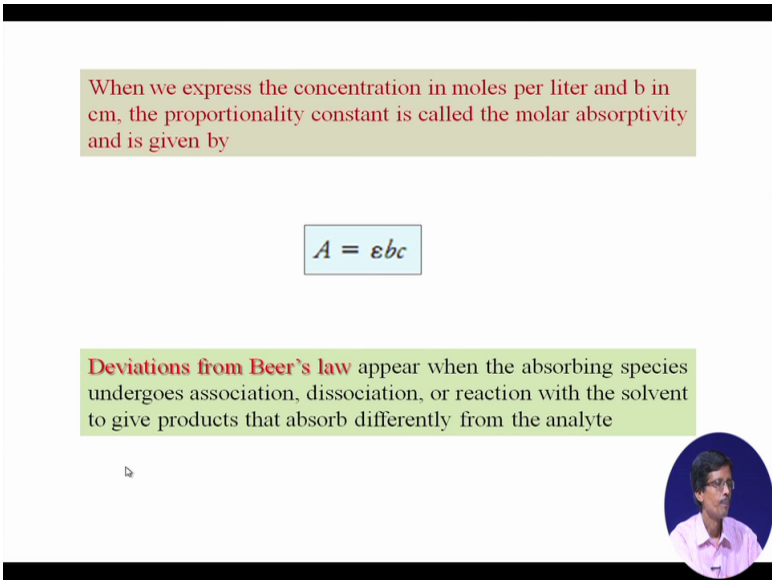

So from this relationship of Lamberts Beers Law we get A is equal to epsilon bc and now what we see that how much this proportionality can go that means if you can have a deviation from Beers Law how it happen because when the absorption (())(25:37) so if we are talking about some absorbing species x but we see that it can go for association that means your x is converting to x2 or x3.

So the species which is responsible for the direct color absorption or the radiation absorption will vary. Similarly that particular species can go for dissociation and it can react with the solvent the solvent can give you the corresponding solvolytic product or solvent can give you some coordination if it is a typical metal ion.

So all these three things so these are the corresponding difficulties that means we should avoid to apply Beers Law for this particular measurement such that we do not have association, we do not have dissociation, or we do not have any reaction with the solvent what we use.

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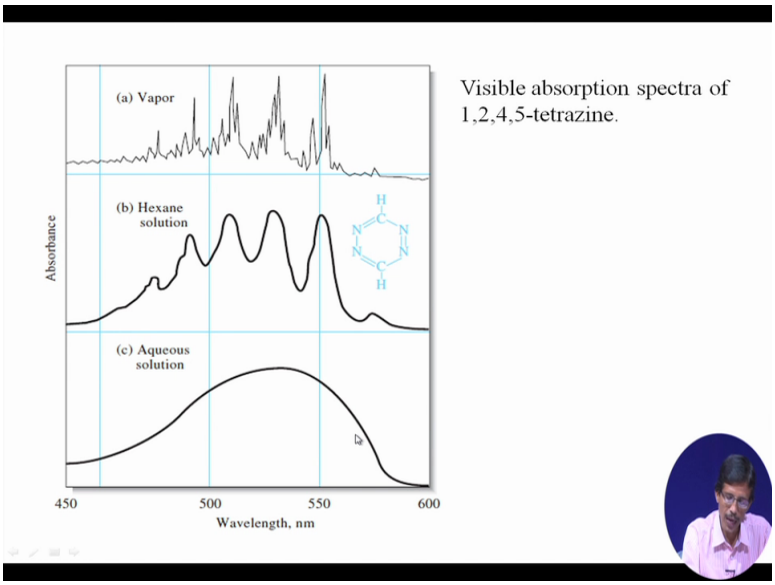

So what we get that a particular example of a visible absorption spectra of a particular compound or how it looks like, it is 1, 2, 4, 5-tetrazine compound. So that particular compound we can analyze by using this particular spectroscopic technique you see this is the corresponding tetrazine compound which is very much similar to that of your benzene ring benzene ring we all know that is C6H6 but instead of these four carbon centers we have two nitrogen on the left hand side and two on the right hand side.

So this particular tetrazine molecule can be very interestingly analyzed and this also gives us some opportunity because this is again a text book material it has been taken again from Skoogs book. So it is given in that particular Skoogs book and how it goes like this that if we can have what we are talking about the Aqueous solution how we get that so this tetrazine therefore definitely to a certain extent that means to give you a corresponding molar solution or a mini molar solution it is soluble in Aqueous solution.

And when we plot so this is its corresponding absorbance spectrum of this particular thing that means that means that absorbance spectrum of the tetrazine and we get a corresponding broad lambda max values. So if we can get that this is correspondingly the maximum one which is in the range of 525 midway is 525 to 530 nanometer.

So these tetrazine molecule dissolve in water solution can give rise to a very broad absorption spectrum in the visible region which is being recorded from 450 nanometer to 600 nanometer giving rise to a corresponding absorption at 525 to 530 nanometer. So which is definitely a characteristic signature for the molecule itself when it is measured in Aqueous solution.

So what about if you go for some other solvent, so you see the spectral feature that means the center of the spectrum that means this particular range of 525 nanometer is detaining not only in Hexane solution but also in the vapor of that particular molecule. So what we see that we can consider that what is there that means in the vapor state we have several of these lines instead of that we can have four prominent and one very small line or the absorption or absorption peak we consider we call it as absorption peak so 4 plus 1 very small absorption peak in Hexane solution.

So in organic solvent which is different from water medium is giving rise or just now we have discussed that the solvent should not interact with the corresponding molecule such that your corresponding pattern is changing but this particular thing is different kind of interaction we may not consider or we should not consider or we cannot call it as the typical interaction of these two solvents with the tetrazine molecule because your tetrazine molecule is not undergoing any kind of association or dissociation or direct interaction with the solvent molecule only thing is that your feature of the spectrum which we have recorded in Aqueous medium has been changed from Aqueous to Hexane solution.

And the Hexane solution spectrum is giving rise to some feature which is there already present in the broad absorption spectrum what is that this broad absorption spectrum we are not able to separate out all the four plus this small peak in this particular spectrum. So what we see that this is not giving you the final details.

So the Hexane solution is giving us a final detail for this particular measurement which is absent in case of the Aqueous solution, so that is why if we want to get something related to the molecule how we get all these features we will see because we are talking about something where this particular absorption is due to electronic absorption. So this absorption spectrometry we consider it as also electronic spectrometry.

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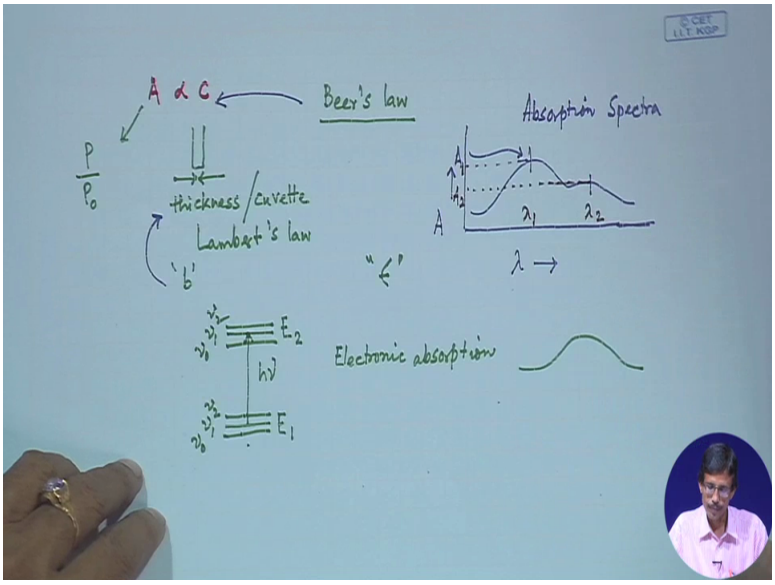

So if we have two electronic states one is the ground state which we consider as E1 and the second one is E2 and if there is due to that particular absorption of that visible UV light we have electronic orientation or electronic distribution is getting changed such that you can promote the electron from this level to that level or any other electron which is involved in bonding can be promoted from one level to the other such that the corresponding orientation in the molecule is getting changed and in a transient period because it is a very transient one for few seconds only it basically goes for this particular excitation from one level to the other level due to this absorption because we are not going to get this molecule in this only E2 level because it will again relax to this particular E1 level.

So due to this electronic absorption so we consider it as electronic absorption so this electronic absorption we are looking at for the typical transition what we get for this aqueous solution but if this underlying electronic state can have some other levels which are the vibronic levels or the vibrational states. So this vibrational levels you can have small vibration levels you can have in the lower electronic state as well as in the upper electronic state.

And how these particular transitions we can see that how these different transitions can change that means these vibrational levels which can be v0, v1 and v2. Similarly the different vibration levels associated with the energy level E2 is also v0, v1, and v2 so if these levels are involved which we do not get in case of the aqueous solution in case of aqueous solution we get the average electronic transitions. So it is getting averaged out we cannot separate out the different vibrational levels such that we get a very broad absorption spectrum like this, ok.

So next in the next class we will see that how the different vibrational levels will be interfering. So we will again start from here to discuss this thing to see the final detail of the corresponding electronic spectrum of tetrazine, ok thank you very much.