Course on Analytical Chemistry
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Lecture No 23
Module 5
Spectrochemical Methods – 2 (Continued)

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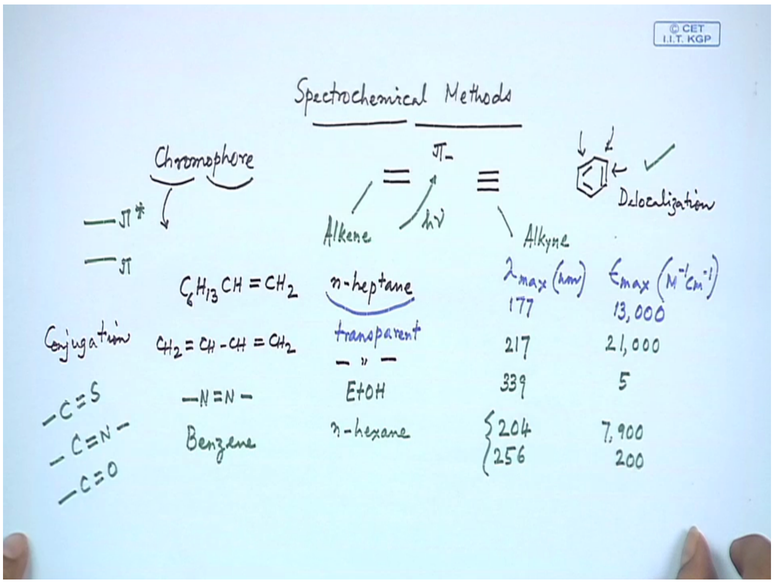

		λ_{max} (nm)	ϵ_{max} ($M^{-1}cm^{-1}$)
$C_6H_{13}CH=CH_2$	n-heptane	177	13,000
$CH_2=CH-CH=CH_2$	— " —	217	21,000
$-N=N-$	EtOH	339	5
Benzene	n-hexane	204 256	7,900 200

Good morning everybody so we are still continuing the spectrochemical methods where we now wants to see the species which are responsible for some amount of absorption that means they are responsible for electromagnetic radiation absorption giving rise to a colored solution and in that way we have defined some species which is known as chromophore which is related to the chrome we all know the chrome is the color and phore is the color absorbing species.

And we have just also seen in our previous class that if a particular bond is made up of a double or a triple bond and we are just simply looking for the pi electron density or pi electron cloud even it is present in your simple benzene ring, as all we know in a particular benzene ring we have that delocalization of the pi electron above this plane and below this plane.

So whether we can excite these pi electrons the pi electrons are confined between these two centers that means it is confined to some carbon center to another carbon center or some other hetero atom and during this process whether that particular radiation can be absorbed by all these species and we can get some information about the corresponding binding that means the bond nature of the bond, how many of those types of bonds are present and whether they are in the conjugated form or non-conjugated form.

So once such thing that we know all that this is the thing that where we have the double bond we consider there these are the alkene species and these are your alkyne species. So how do they absorb and how do they respond to electronic transitions and how the electronic absorption spectroscopic and help us to characterize the alkene species or the alkyne species.

So one such alkene species of interest can be taken as an example where we can have several of these carbon center which is C6H13 then CH double bond CH2 who with we consider as a terminal alkene function. So if all other part is saturated only this part will be responsible so this part bearing the chromophoric group is responsible for the corresponding color absorption.

So what we find that these particular species if we take in in a particular solvent that means it is if it is a liquid one. So we take n-heptane and this is a typical solvent where the solvent should not show any kind of electronic absorption that means solvent should be transparent in that particular medium of study or the particular wavelength of study for this particular range.

So what we get we get basically from the absorption which is a corresponding lambda max value and corresponding epsilon max values. So what we see that these are the two characteristic species for this particular one and if we know critically that this is the corresponding lambda max for this compound and epsilon max is also known to us for this compound then we can say or we can characterize electronic spectroscopically this particular compound in solution by knowing its corresponding absorption as 177 nanometer.

So this is a nanometer and this is a mole inverse centimeter inverse. So 177 and the corresponding magnitude of this epsilon you see is very high is 13000. So this 13000 epsilon max value and the corresponding magnitude for this this absorption is characteristic one for this particular alkene compound.

So now the contribution for the conjugation if we see that will be this particular double bond, so pi pi conjugation like this thing we see that there we have the one then the single bond and then again double bond (())(5:24) consider for the benzene (())(5:27) structure but later on we know that this is the thing that where the entire pi electron the six pi electrons are delocalized over all the six carbon centers of the benzene ring so these are not confined. So a sort of delocalization is there and what is that particular effect of the delocalization on electronic spectroscopy that we will see.

So if we take this and is a conjugated one so which can be CH2 double bond CH-CH double bond CH2 again if we measure it in heptane solvent. Now how we can guess, so there is typical rule for that (())(6:14) rule but we will not going to discuss all this in detail for this calculations the theoretical estimation we are very much interested to know the experimental findings how much we can get for this particular one since these two are there and they are having some conjugation like that of your benzene ring that means double bond single bond double bond.

So this particular pi electron cloud for these two particular double bonds will be delocalized. So the corresponding energy for this separation if we are looking for this pi to pi star transition say what we are looking for this pi to pi star transition this gap we all know this is the delta e values and due to this conjugation or the delocalization of pi electron what we will see that the energy of this particular separation will decrease.

So this corresponding absorption will go to a longer wavelength of 217 nanometer and the epsilon is also increasing so that means the probability of the corresponding electronic transition will also change or will also increase and that give rise to the corresponding value for this epsilon max due to this particular conjugations.

So secondly we can see that how if we go from C-C double bond to N-N double bond N-N double bond the (())(7:42) the most common and experimentally determine solvent medium is the ethanol and in the ethanol medium this goes to further longer wavelength of 339 nanometer with a very low epsilon value of 5.

Then if we can go for this characterization that means the benzene characterization whether we have a benzene in the solution or some other compound. So the aromatic compound like that of our benzene can also be characterized when it is studied in hexane it has two characteristic bands at 204 and 256 nanometer.

So you see this particular two absorptions are sometimes characteristic which you can find only for benzene and these two values as well as their corresponding epsilon values of 7900 in one case and in another case it is less which is 200 only. So these two values are also very much characteristic for the corresponding electronic absorption of the benzene molecule.

So what we see now that for these organic molecule bearing double bond this N-N double bond so similarly we can have the (())(9:06) function what we most of the time we encounter in different (())(9:10) condensation or the (())(9:11) molecules. So see double bond N can also be characterized in that particular way.

Similarly you can have C double bond O, then we can have C double bond S, all these things so we are just simply looking at the corresponding presence of the double bond for all these. So this is all about your corresponding thing for your organic molecules.

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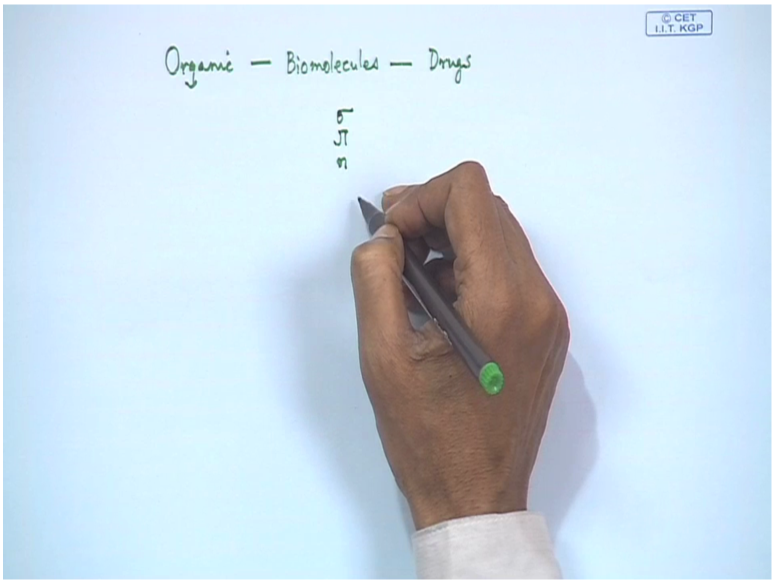

So we can characterize some organic molecules, then some biomolecules also we can characterize which are very interest though so some biomolecules are also and some drugs also drugs and medicines also. So if we have some organic backbone and all these having some pi electron density or not only pi we all know that we can have the sigma electron density then pi electron density and n the nonbonding electron density.

So if those all can be excited and we can find some absorption so we see the characteristic absorption spectra for all these molecules.

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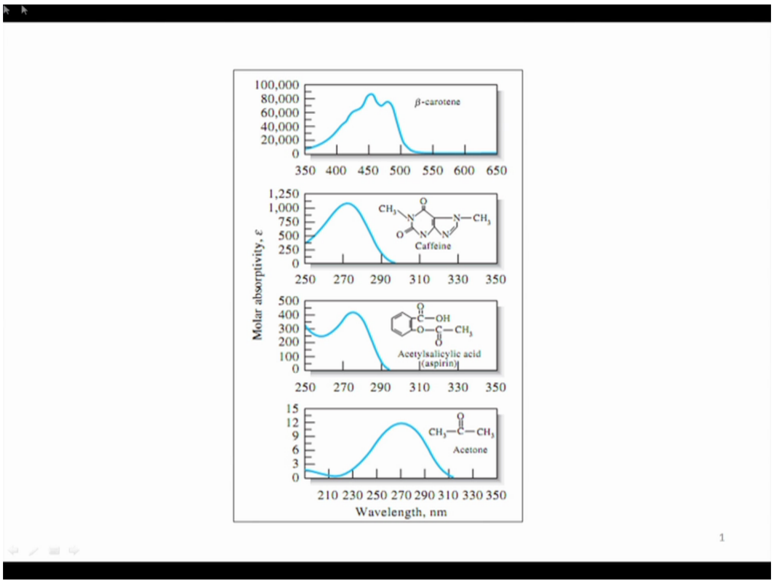

So some example for this is is taken from that Skoogs book again that how the corresponding absorption spectra looks like for beta carotene we know it is present in the carrot and the color the corresponding color of the carrots the orange to red color of the carrots are responsible for this sort of absorption.

So this particular color as you know that beta carotene is present in carrot so immediately you can say that ok I know that is the thing that you have the corresponding absorption close to 500 nanometer in one case and another one is at 450 nanometer due to that particular color. And this is therefore what we measure that how we measure and what we measure in a particular spectrophotometer is a simple one that we scan it in the axis where we have the wavelength in nanometer.

So this is the lambda lambda wavelength value for 350 to 650 nanometer and in most of these cases we find that depending upon its (())(11:28) position. So this is in the visible region that is why we are talking about the yellow and orange color of carrot and you see the corresponding epsilon values because absorbance can be converted because in terms of the corresponding Beers law we have seen A is equal to epsilon BC.

So A what is measured by the machine the spectrophotometer can be recalculated for its corresponding epsilon values ones we know the corresponding solution concentration of the species or the analyte responsible for your absorption. So you see that these values are pretty high closed to 80000 or something like that, so 70000 to 80000 of these epsilon values.

Now another active ingredient is the caffeine which is present in coffee and tea, we all know this is a typical heterocyclic. So by cyclic molecule so structure is pretty complicated though and you have four nitrogen atoms along with carbon hydrogen and oxygen. So this particular structure can also have a very characteristic absorption spectra close to 280 nanometer, so this 280 nanometer can be a complex thing where we can have these C double bond N, these C is double bond C, these C double bond O and C double bond O.

So overall the ground state energy value that means the E1 can be defined by the combination of all these molecular orbitals for this particular molecule which is responsible for the corresponding absorption at say 280 nanometer giving rise to a corresponding epsilon value of above 1000 then we know that the drug molecule we all know that the pain killer we always consume the aspirin the acetylsalicylic acid molecule.

So this acetylsalicylic acid molecule can also have some characteristic absorption spectrum close to 285 or 280 to 285 is a typically broad absorption spectrum for that and a epsilon value is not very high it is around of 400 but these two are very much characteristic for the analysis.

So if your analyte is a drug molecule if you want to analyze the acetylsalicylic acid or the aspirin molecule we can go for this for direct acid based titration as we all know because this is simply this part is simply the corresponding aromatic benzoic acid part and this is also the phenol part which has been acetylated because the salicylic acetylsalicylic acid what is being derived from your salicylic acid through acetylation.

So salicylic acid is nothing but is ortho hydroxybenzoic acid which has been acetylated. So this will be very much characteristic and the electronic spectrum for that is different from that of you salicylic acid. So this value can be characterized and compared if you also want to monitor the purity of the drug molecule.

So in that way also the pharmaceutical industry always rely on this sort of spectroscopic measurements to analyze this particular molecule first and then its corresponding amount present in the tablet, in the syrup and all these thing because this particular one is directly related to your concentration of the aspirin molecule present in the analyte then if we want to see something for a typical and a simple molecule which is acetone which can also be utilized for a solvent and as a solvent because several organic molecules, organic complexes and other materials can be soluble in acetone.

So if your acetone has a corresponding band at 270 nanometer we should be very much careful about using this as the solvent for measuring other analyte because these absorptions is starting from 310 nanometer with giving a very broad spectrum upto 250 nanometer. So within this range we should not use any other analyte to be characterized in terms of its unknown concentration in this medium. Because acetone itself will have a very broad absorption spectrum centered at 270 nanometer due to the presence of this C double bond, O bond having some pi electron density between this carbon and oxygen double bond.

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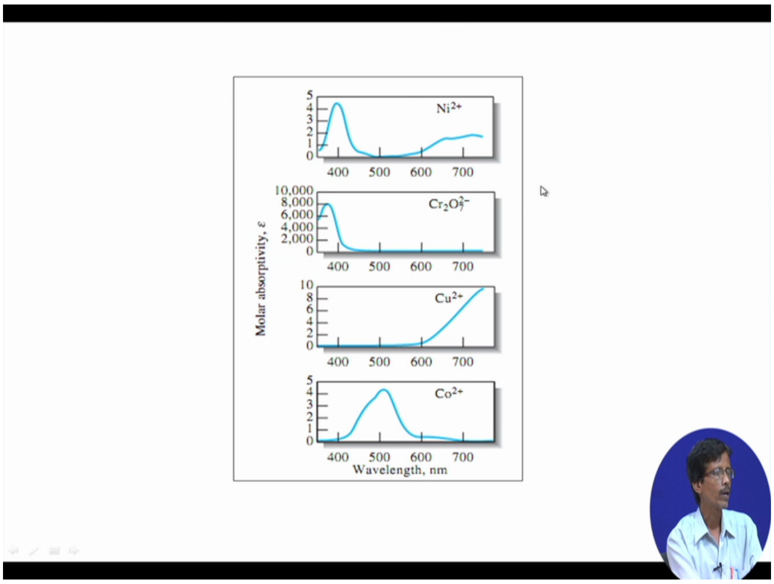

So this has also be there in the Skoogs book so this is some parts for this molecules in the organic compounds but what about the metal ions because we are talking so much about the corresponding manual titration, the acid based titration then some amount of gravimetric estimation and all this thing.

So this basically this particular power point slight is giving you some example again in from that particular book and because always I am referring you for that particular book because you should follow that particular book and it is the particular information what you gather from here can be applied to anyone else. So these metal ions say metal ions and nickel, chromium, copper and cobalt.

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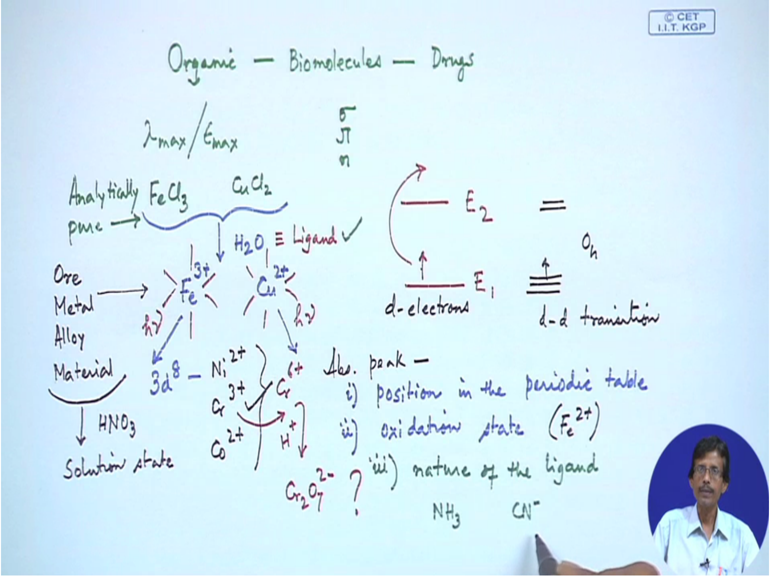

So we all know a simple standard transition metal ion like that of our ferric chloride, or copper chloride when these metal ions are available from these sorts by the resolution of these in water medium we all know from our school days knowledge that they give rise to Fe3 plus and Cu2 plus and now we want to see whether these two metal ions will be responsible for absorption of electromagnetic radiation h nu in the UV visible range.

So when water is present we all know that water is a very good ligand. So this particular one will be surrounded by several water molecules and in most of the cases that in these two examples it is the six number which will be bound to this particular central metal ion centers which are hexacoordinated so if these two are colored because sometimes they are very friendly colored.

So we will be talking something related to the transition of those electrons from the level of E1 to a level of E2, we want to promote that particular electron from this lower level to the upper level by the absorption in the UV visible region but these are present. So what we are looking for these are transition metal ions iron 3 plus and copper 2 plus are transition metal ions.

So these transition metal ions will have the d-electrons, so these d-electrons are there so like that of your sigma pi and n electrons in the organic molecules, d-electrons if they are promoted so one d level to the other d level as we all know octahedral geometry most simplified approach for the corresponding d orbitals we all know that we have 5 d orbitals and this 5 d orbitals in octahedral crystal field can be splitted.

So if some electron like this is present in the lower level this can be considered as the lower energy level after crystal fields splitting this can be promoted. So what we get here that is known as your d-d transition which will be different from that of your transition corresponding to n to pi star, or pi to pi star, or sigma to sigma star transitions.

So these species along with the metal ions like nickel 2 plus, than chromium 3 plus, or cobalt 2 plus how we can characterize this. So do they have a very good characteristic absorption spectrum due to this d-electron transitions because these corresponding separation this gap compare to this other previous one is energy difference is there but the difference in magnitude so you have a corresponding absorptions peak what we are looking for.

So we are looking for the corresponding absorption peak in this particular electronic transition will therefore depend on what are the factors on which this particular electronic absorption which is centered on the metal ions. So the metal ions are containing some d-electrons and those d-electrons are responsible for these transitions will be depending on the position that means how many electrons are present in a particular oxidation state and what are the total number of electrons present in it that we all know that the Ni 2 plus we conventionally we tell that is a 3d8 system.

So in the periodic table position in the periodic table is important that tells you that this particular will have in the bivalent state 8 d-electrons. So how this 8 d-electrons will be arranged in all these available levels and which particular electrons will be responsible for your d-d transition will be dependent on the periodic table because the number of unpaired electrons will be varying from chromium to nickel to cobalt to copper to iron.

Then one more important thing is its oxidation state which is very important as well as crucial because whatever we are talking we have taken this particular ferric chloride solution we dissolve this ferric chloride solution directly from a salt. So this is say analytically pure salt analytically pure salt which is a very standard one and its purity is also telling you that whatever measurement you do and the corresponding electronic absorption spectra what we can get from these is the best one for its corresponding lambda max as well as its epsilon max value.

But if we want to analyze something related to some say iron metal or iron containing alloy or some material containing iron what we can do because all these things has to be moved to a solution state and if we use some acids such as dilute or 1 is to 1 nitric acid which is a very good oxidizing agent as well.

So in presence of that nitric acid if we treat this particular one for its dissolution from the metal itself the iron metal or some ore if you go back ore or mineral. So starting from ore to any good material sophisticated material what is utilized for all different good purposes can be analyzed for their iron content.

So nitric acid is given, so solution state what you will be getting in the getting this ferric ion. So nature of this ferric ion in this water medium and its corresponding electronic transition will be completely different compared to that of your ferrous ion. So we are not getting ferrous ion, so this particular absorption peak its position and its corresponding epsilon value will be dependent on this oxidation state.

So take this example of the presence of chromium 3 plus that will be showing in the in the corresponding power point slide is that if you have chromium 3 plus and we have to use some other one because chromium we all know is a good component for your stainless steel and any other material so it is alloying material or alloying metal. So this initially we know that the chromic chloride if you have you can dissolve that chromic chloride to get the corresponding chromium in the 3 plus oxidation state but you can oxidize it initially to chromium 6 plus by some fusion technique.

So any other oxidizing agent or some oxidizing flux can oxidize this chromium 3 plus to chromium 6 plus and this chromium 6 plus which can be present as chromate now they are not present as the beer chromium 6 plus. So they will be present in the chromate form, so this chromate form is stabilized in the alkaline medium if you acidify it by H plus it will be converted to Cr2O72 minus that means it will be directly converted to the dichromate species.

So how to analyze this dichromate species present in the medium, so that will directly tell you that your original material have this particular chromium 3 plus which has been oxidized to chromium 6 plus and then is dimerize to dichromate. So if we know that the dichromate has the characteristic absorption spectrum so that we can nicely identify by knowing its corresponding absorption is corresponding molar absorptivity, we can find out very nicely that the presence of dichromate in the medium which is deriving we are deriving it from a chromium containing metal ion, chromium containing ore, or a chromium containing other material.

So you see all these things that the oxidation states 3 plus, 6 plus and this is also 6 plus but in the dimerized form so these two are slightly different. So the absorption peaks the presence of absorption peaks and positions will be dependent on oxidation states then its corresponding nature of the ligand. So the corresponding nature of the ligand is also important because this we have considered that these are your ligand.

So if we move from there that means if your solution is present and if you add some amount of simple ammonia aqueous ammonia if we add or if we add some other solution containing cyanide ions. So these will directly go and bind to the metal ion center but your electronic spectra will change due to the binding of this ammonia, due to the binding of this cyanide these are the very characteristic examples for the changing the corresponding electronic spectroscopy but changing the corresponding nature of these ligands because these water molecules which are very loosely bound to this iron center will be replaced by ammonia then by the cyanide (())(27:31).

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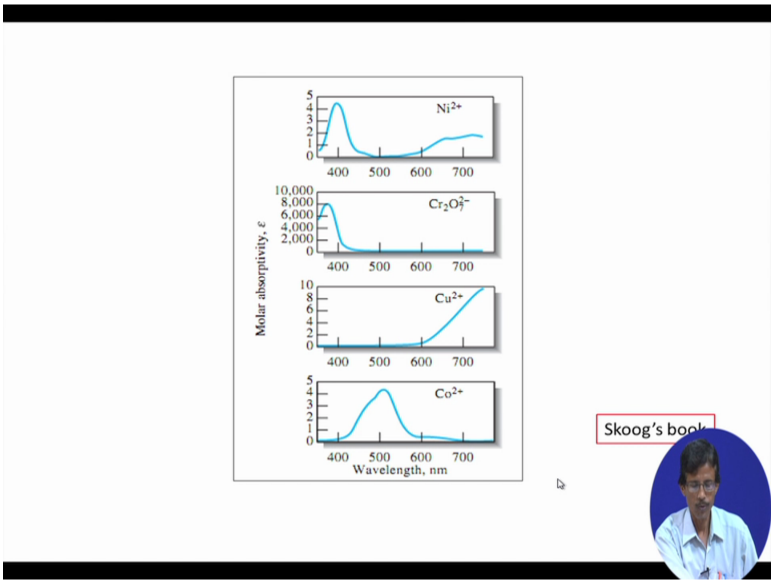

So what we see that in this particular case you have this dichromate you have the characteristic spectrum at say it is in the range of say 350 or 360 nanometer having a characteristic epsilon value also. So this dichromate characteristic peak in solution state analysis can give rise to the presence of the corresponding chromium in any unknown solution.

Similarly the nickel will have a different absorption it can have some broadband in this particular range also in the low energy range but this can also have a characteristic one at 400 nanometer but the epsilon value is not very high. Similarly the copper gives a very broad one because if we go beyond 7 or 800 it gives a very good characteristic one or a very broad absorption spectra in this particular range.

Similarly cobalt 2 plus is also giving at a 500 nanometer absorption. So looking at all these this is a typical example again taken from that book that this particular absorption the nature of these absorptions is characteristic for these species also if we do not see the spectrum only the values are reported the electronic spectral data we analysis report. So the lambda max values and the epsilon max values for nickel, for chromium, for copper and cobalt all will be different.

So this is one point by looking at the corresponding data for all these absorptions which can characteristic that the corresponding presence of these metal ions and also the unknown concentration at the same time but if we directly look at the corresponding spectrum which gives us it gives us a very other pleasure for knowing the thing very nicely for their identification.

So all these spectra so starting from your organic molecule to inorganic ions we find that these are very much characteristic in terms of their electronic spectra for their identification and analysis when these metal ions are present as some unknown analyte in your unknown solution, thank you very much.