Course on Analytical Chemistry
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Lecture No 24
Module 5
Spectrochemical Methods – 2 (Continued)

Hello welcome back to this class again.

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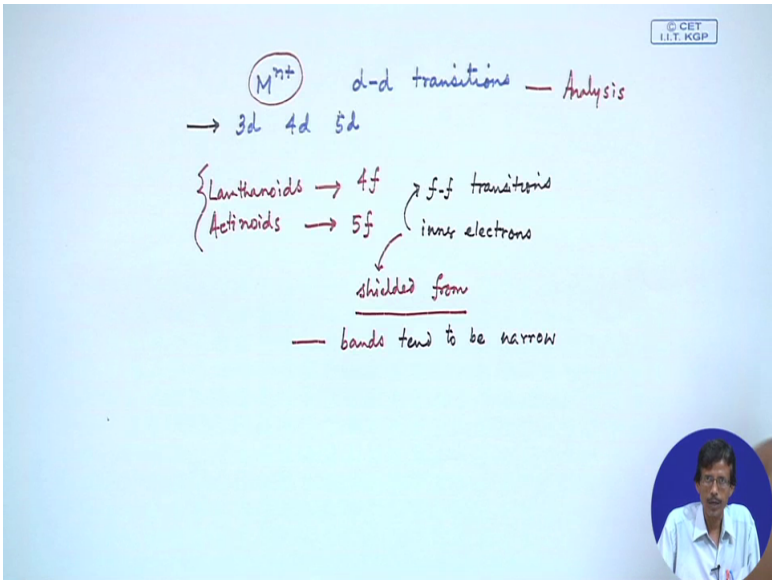

So where we are talking about some d-d transitions centered on some metal ions say Mn plus and we have seen that how d-d transitions are helpful in identifying the presence of these metal ions as well as their unknown concentration.

So these are for the transition metal ions say for 3d, for 4d, as well as 5d metal ions but their nature will be different as we move from 3d metal ion to 4d metal ion to 5d metal ion. So the same Mn plus if we can have for the other metal ions say Lanthanoids and Actinoids we call them earlier, these are Lanthanoids and Actinoids.

So whenever we see these the analytical chemistry in that particular form whether we will be able to apply this particular thing because some information we gathered we are experienced now that how we can use this d-d transitions for analysis. So it is very simple that how we can utilize for analysis the d-d transitions but as per definition these metal ions in the periodic table they belongs to the category where we have f electrons. So 4f electrons we all know that these are the Lanthanoids and containing 5f electrons they are Actinoids.

So the presence of these electrons because the nature and the type of these electrons are completely different so we will try to apply our knowledge whatever we have gathered for the d-d transitions for the transitions for the different metal ions which are also colored. So here also we ask the same question whether we can have some colored solutions and also if the solution is colored, whether we can have the corresponding one that means whether we can have these f-f transitions or not, so f-f transitions.

So these f basically when we go for so when we after this particular one so this thing that means 3d, 4d and all these things we get. So these are basically the inner transition elements we call so these are the corresponding transition elements when we have delectrons and when we every electron we call it inner transition elements. So inner transition elements are nothing but we are having some inner electrons where those electrons are so inner electrons are present in all these f levels.

So these inner electrons will be responsible if we at all see any effect transition but these inner electrons are nicely shielded so they are shielded from any external influence of orbitals coming from the ligands. So these external influences what can have so shielded from these corresponding orbitals having larger principle quantum number.

So this shielding is there so shielded from all these things. So are inner electrons which are shielded by the outer electrons say that of delectrons and then the corresponding reagents or the species surrounding these things. So that basically gives rise to some good information by seeing the nature of that particular transition. So these bands for this f-f transition the bands will be narrower, so they are tend to narrow in this particular case.

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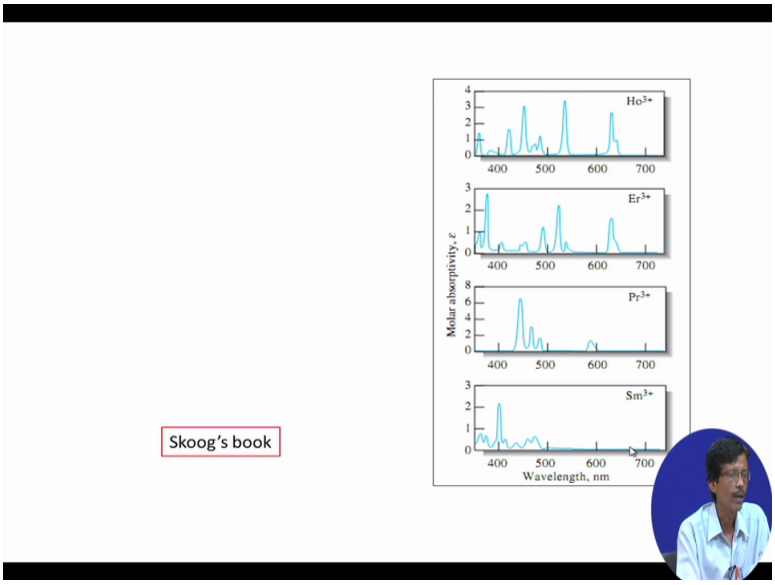

So if we see for some metal ion centers like this so these are the corresponding absorption spectrum, see you can characteristically distinguish them from the d-d transitions what we can have that if you get that this is for holmium, this is for erbium, this is for promethium and this is for samarium and all them are in trivalent state but you see the number of bands present in this particular case this is 5, this is also 5, 6, this is also 4, 5.

So the number of these peaks and their corresponding positions so they are very lightly colored or the friendly color because the epsilon values are very less it is only ranging upto 4, upto 3, upto 8 and upto 3 but these narrow bands for all these things are very characteristic for their absorption in this particular case. So here also like that of our transition metal ions we can change by those the presence of those ligand that means from aqueous solution to ammonia solution to cyano complexes.

But the external influence because we are talking about something where the inner electrons are involved for electronic transitions. So the perturbation from those ligands will so be less. Therefore again these inner electrons are shielded so we do not find any such effect in a bigger way for the presence of those ligands and when those ligands are bound to these metal ions centers, ok.

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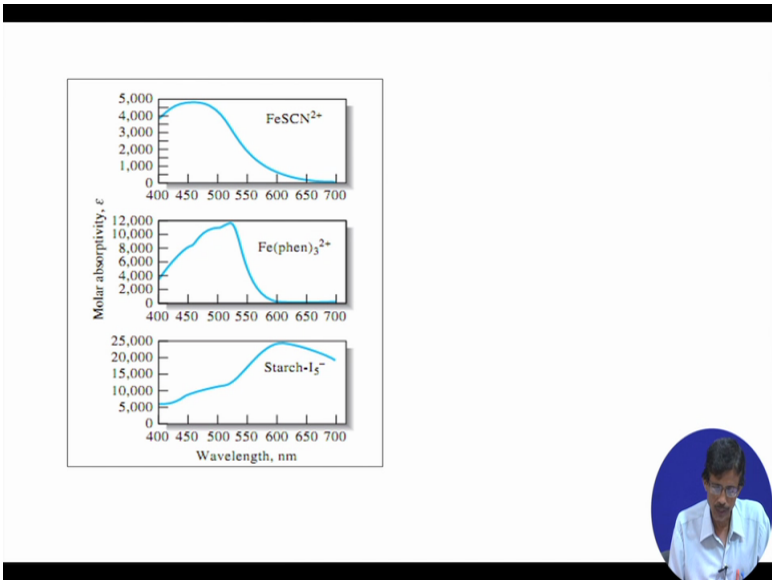

So these are the things what we are talking about so far about the organic molecules and all these things then the metal ions and metal ions of two different categories the transition metal ions and the inner transition metal ions. Then we will see something where we can find the application of something which we can consider as some metal complex or some assembly type of thing.

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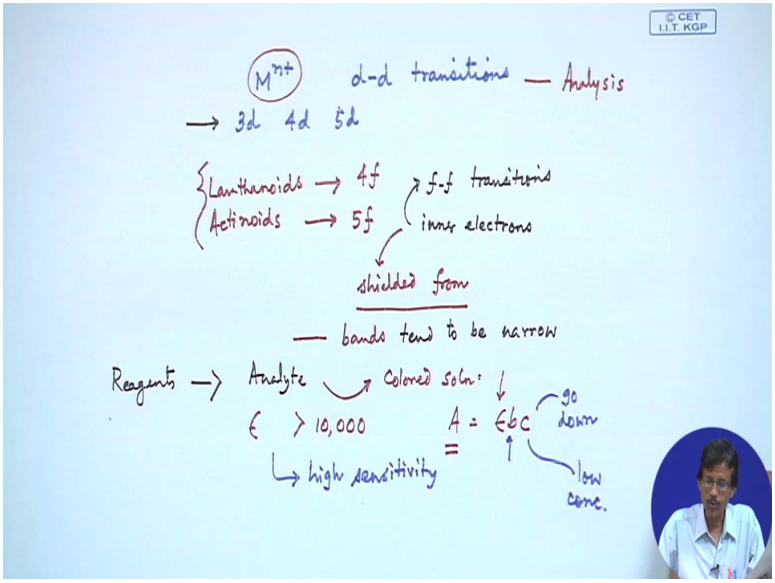

So this we can have some reagents so what we are talking from the very beginning of this particular class. So these reagents and if we now add these reagents such that the analyte plus reagent is added to the analyte so this analyte plus reagent combination can give rise to a colored solution and that colored solution if that is highly intense one and we can get a very

low concentration range also which can be detected because if your epsilon value is pretty high several thousands, so if your epsilon value is greater than say 10000 or so and applying the A value epsilon bc.

So if this magnitude is pretty high and we have a fixed epsilon value and to that fix epsilon value b is also fixed. So we can go down with that concentration. So that means a very lower limit of concentration can be detected by this particular analysis.

So electronic spectral analysis will be helpful for this case where reagent can give rise to a very colored solution and where the epsilon value is greater than 10000 and we consider that particular process we will have a very high sensitivity, so highly sensitive procedure so it can have high sensitivity. So we can go to find or figure out a very low concentration regime.

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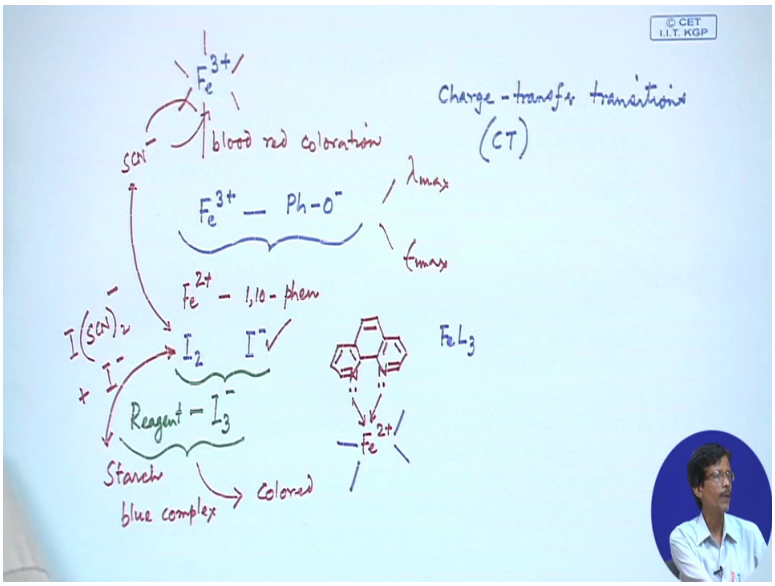

So a low concentration regime can be found out by this particular approach. So what will be that approach say approach is very simple as we all know if you have a Fe3 plus earlier I gave you that particular example the very well-known example well established example of detection of Fe3 plus by addition of thiocyanate ion giving a blood red coloration.

So how that blood red coloration is forming that we can find it out and due to this combination this can be considered as the ligand because it is substituting the 6 water molecules surrounding the ferric ion in the hexaaqua Fe3 ion, so hexaaqua ferric ion can give rise to one by one replacement of this thiocyanate ion but only one replacement that means one single replacement of that particular ligand can give rise to a corresponding blood red coloration and a very high epsilon value.

And we consider those as a charge transfer complex where some amount of charge we are talking about the electronic charged transition from the orbitals involving pi, sigma, n, d and f orbitals. But now we consider something if this particular reagent or any other group which is bound directly to the metal ion center which have some acceptor level now the metal ion centers are acceptor level and these are the donor levels. In terms of the acid base concept we all know the metal ions are acidic the ligands are basis.

So that is also a typical acid based combination. Now in terms of this charge transfer transitions so for this charge transfer transitions which can also be abbreviated as CT transitions so charge transfer transitions can give rise to something where the electronic charge can be accepted from the ligand to the metal ions center.

So this basically gives us something where we can detect the ferric ion by thiocyanate, it is also possible to detect this ferric ion by phenolate group that means Ph-O minus the phenol can also give rise to a coloration rate coloration to the ferric ion and that can also be estimated for the unknown amount of ferric ion.

So this is the advantage of doing this analytical chemistry that anything you can identify if you know the product of that particular reaction. So the phenolate ferric ion can give rise to a colored product that can be estimated because you know the corresponding lambda max and the epsilon max values. And in the same way also because this is a very good constituent for anything starting from your organic compound any organic compound in any organic reaction, any biological system, any drug molecule, or even in the biological field also.

So the detection of phenol can also be done indirectly in a opposite way by addition of ferric ion or a standard solution of ferric solution to that phenol solution giving rise to that particular colored medium.

Then Fe2 plus if Fe3 plus can be detected by presence of this thiocyanate and phenolate ion, Fe2 plus can be detected by orthophenanthroline or 1, 10 phenanthroline as the ligand. So which is a very simple ligand N N so these are the (())(12:28) so when these two (())(12:29) are attached basically so we get this is known as bipyridine but again a third ring is there if it is there we get a orthophenanthroline or 1, 10 phenanthroline group and through these two nitrogen you have the loan pair electron, one of the binding of this Orthophenanthroline to Fe2 plus center is like this.

Similarly to other Phenanthroline unit can be attached over here and here giving rise to a corresponding compound which is a FeL3. So this can also be detected due to the formation of this corresponding color then if we try to identify the concentration of I2 or I minus separately or sometimes some typical reaction also because these two are if these two are allowed to react is a very simple reaction can take place which is I(SCN)2 minus plus I minus. So this I is positively charged, ok.

So the formation of these species can also be identified if the reaction between these two can give you some colored species which is strongly absorbing. So the strong absorption concept can be very nicely utilized for the identification of this ferrous ion also and these two. So these two so anyone again this can be your analyte, this can be your reagent but these two if they do not give any color reaction due to the formation of (())(14:17) formation I3 because we all know that the KI the potassium iodide solution aqua solution of potassium iodide if it is added to iodine we get a potassium triiodide formation.

So this particular species can be identified but if it is not strongly colored we add some reagent to that to this analyte and these two combination can give a color, so you have all sorts of options. So if you do not know anything related to the analyte you try for all these reagent like the choosing acid base reaction by identifying what indicator will be useful to detect the N point of a particular acid base titration.

So this reagent can give rise to this particular one, so it should be colored and we all know that this particular Triiodide formation or the addition of this free iodine also it is the Starch Starch can react with iodine free iodine also giving a blue complex. Similarly it can also react with this Triiodide containing this iodide I2 minus.

So this particular species which is quantitatively formed because if you add access of iodide ion all the iodine present over there is formed this I3 minus which is reacting with the Starch particular one starch one and giving you the corresponding blue complex. So how we can analyze that particular blue complex so this we can see.

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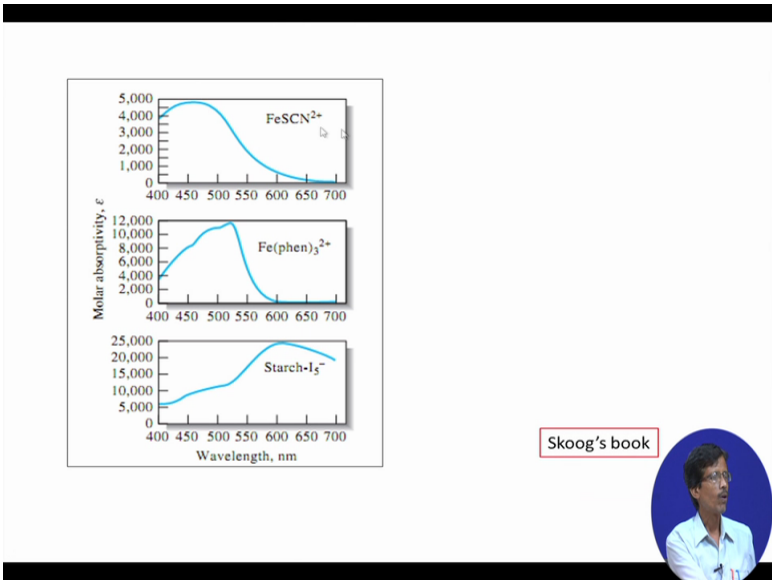

So this is the corresponding blood red coloration what we are talking about for this FeSCN2 plus, so with the simplistic manner of writing is that simple Fe3 plus is attaching with one SCN minus because this is the aggregation or this is the assembly which is very much applicable for identification as well as quantitative identification of either iron or Thiocyanate, so this is been written as this but this iron can have also the five other positions occupied by water molecules.

So it will have due to this color the blood red color you have the corresponding absorption at 460 or 480 nanometer. So you have a characteristic wavelength in that way you get you can identify you figure out a particular wavelength where you can analyze this thing when we utilize the quantitative estimation of all this thing. So we can utilize that particular wavelength for quantitative analysis as well.

When we go back from ferric to ferrous ion, so in this particular case in case of ferrous ion a band is also available but the position is different which is in the range of say 540 nanometer. So this is 480, this is 540 nanometer so definitely the color the red color is a different one corresponding to your Thiocyanate one. By looking at the color of all these species your naked eye can also figure out whether your test tube contains a solution of iron Thiocyanate complex or a ferrous Phenanthroline complex.

So this will have a different one, so we will choose this particular wavelength so the maximum wavelength it is corresponding epsilon value which is pretty high which is 12000. So this 12000 thing is also interesting to know that this is also charge transfer but this charge

transfer transition is of different type because we are talking about the ferric which is the acceptor and the Thiocyanate is the donor.

So when this Thiocyanate is donating the electron density of the charge density to the ferric center we get a ligand to metal charge transfer.

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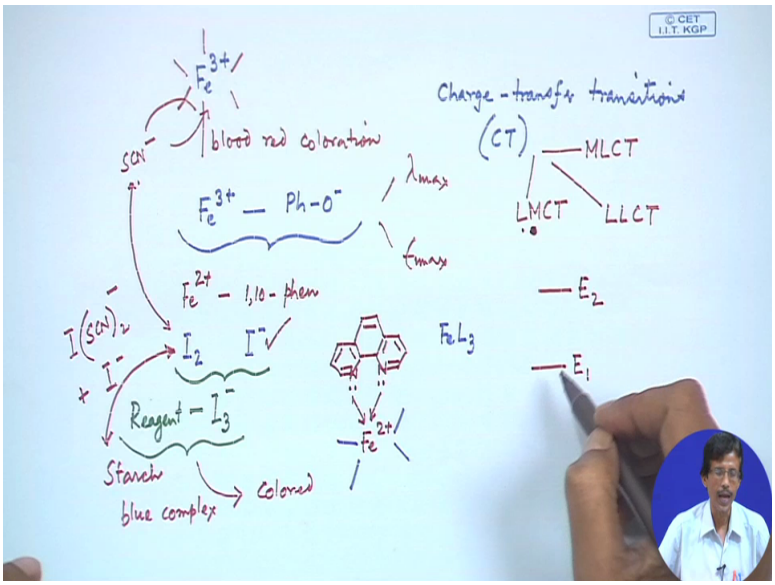

So now we can differentiate these two transfers that means we can have a metal to ligand charge transfer or a ligand to metal charge transfer. So if your Thiocyanate is your ligand and if a ferric ion is your acceptor level that means it can accept the electron density from the corresponding one, we can have this transition from L to M and is the charge transfer transition. Then the third category also is available or is known to us is ligand to ligand charge transfer transition.

So these two levels so assigning these two levels is always very important that whether you have a corresponding one in terms of this corresponding pi electron or any other electron and whether you can have a charge transfer transition involving both metal as well as the ligand.

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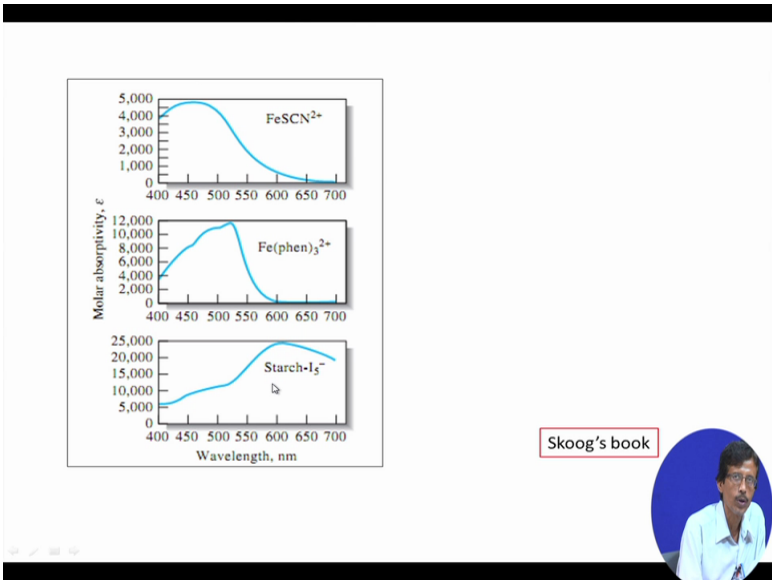

So this particular one which is divide of any metal ion presence but it giving rise to a corresponding charge which can be transferred from this particular iodide ion to starch which is their present for this, so it is I3 minus or I5 minus if two of the iodine molecules are attached to this particular framework of this absorption.

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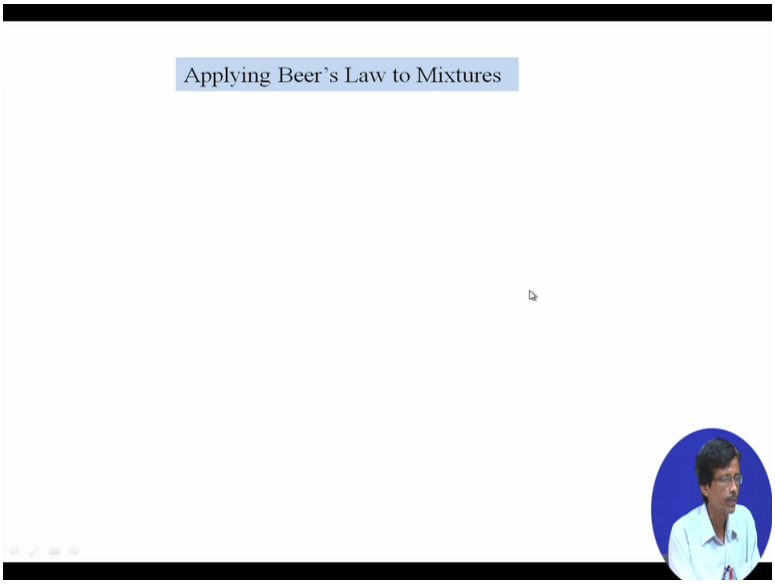

So how we can now quantitatively apply the Beers law to the mixtures that we will see, so once we try to understand, or try to figure out, or try to estimate the unknown concentration.

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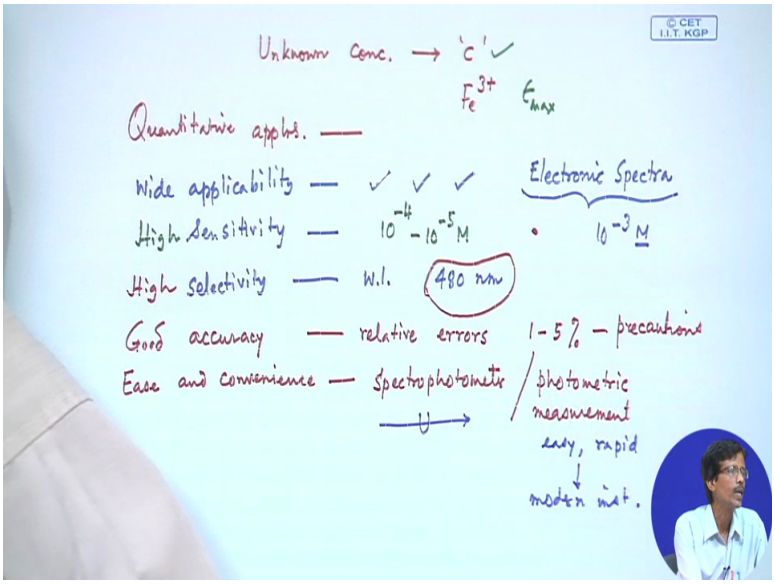

So if we try to determine the unknown concentration C for a solution it can be your simple ferric solution Fe3 plus and all. So we can have a typical Quantitative applications Quantitative applications.

So these quantitative applications will tell us that this particular methodology the absorption spectrometry is useful for its wide applicability. So it has wide applicability because we can apply it to organic molecules, we can apply it to inorganic metal ions, we can apply it to biochemical species. So is a tremendous range of applicability for a species like that of your beta-carotene to hemoglobin we can analyze any materials like this very sophisticated metal containing species as a compete or components to alloys and ores we can analyze.

And when the epsilon values are very high we can talk about their corresponding sensitivity how sensitive the method is, so in terms of that the sensitivity is also very high because the detection limit that means what low concentration this concentration you can handle if your epsilon max value is very high as I told you that if it is above 10000 what we can get that we can detect a very low concentration in the range of say 10 to the power minus 4 to 10 to the power minus 5 molar solution, ok.

So it is not so easy only if you have a charge transfer transition then only you can go down to 10 to the power minus 4 to 10 to the power minus 5 molar solution otherwise in most of the time or most of the cases we prepare a solution for electronic spectra we want to measure the electronic spectra. So the solution what we can prepare is in the range of 10 to the power minus 3 molar.

Then after sensitivity we can talk about the corresponding selectivity because we are going for molecular characterization. So the choice of the particular wavelength of the analyte is very important because we have seen a particular wavelength say 480 nanometer is fine for its characteristic wavelength for the iron Thiocyanate complex. So if you want to measure its concentration at this particular wavelength so it is this particular wavelength which is useful.

So no other species if the background is also contaminated with some other species if the matrix or the environment is contaminated with some other species but those species will not be able to absorb at this particular wavelength. So it will also have very high selectivity then how good it is in terms of the accuracy, so in terms of your accuracy that means how far we can measure in terms of its corresponding relative errors for multiple numbers of measurements.

So in all these cases the relative errors can only range from 1 to 5 percent, if we just only keep it towards 1 percent or less than 1 percent what we can find that we can push it for that particular lower range by taking some special precautions, ok that means contamination or the errors which are being kept in for this particular solution depression and the measurement should be avoided.

So we have good accuracy for this particular purpose and is very easy to make this measurement so ease and is convenience also because what we can use and what we can measure is a spectrophotometer. So spectrophotometer is being used or we can use a simple calorie meter or a photometer. So we have a corresponding photometric measurement, how good this photometric measurement if we have a spectrophotometer and if we have a solution in the cuvette is a very fast process.

So it is very easy to measure and is a rapid process also once you insert the cuvette in the light beam of the spectrophotometer you can measure the corresponding absorbance and many sophisticated and modern instruments are available. So these modern instruments are very useful to measure all these things even it can measure a multiple number of all these measurements and we can also go for the corresponding kinetic measurements also if we are able to measure it in different times also.

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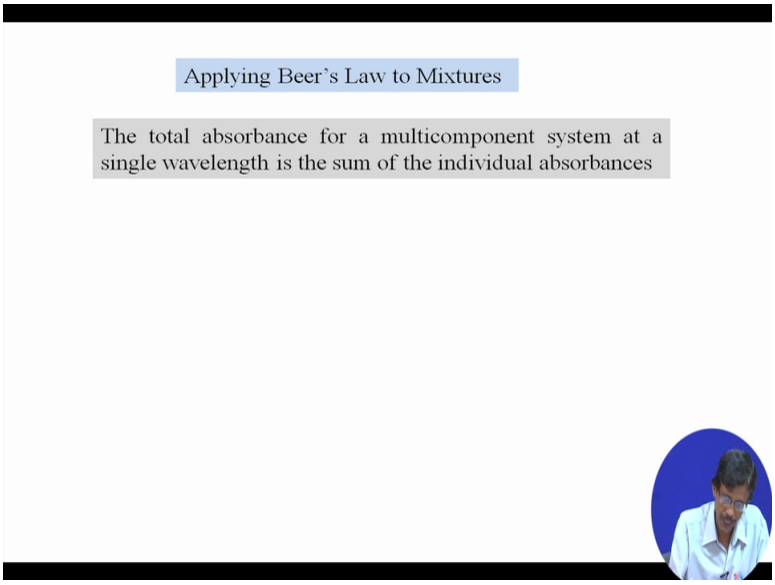

So to measure this particular C what we can use we can use the corresponding Beers law for the different mixtures also now we are bringing a complicated factor that if we have mixtures because right now we are talking about the estimation of the iron putting Thiocyanate in that particular mixture but if we can have this particular one that means when you have more than one component for this particular species suppose we are having some mixture what we have just now seen in this particular class that we can determine dichromate solution.

So similarly if we can have a mixture of dichromate and potassium permanganate.

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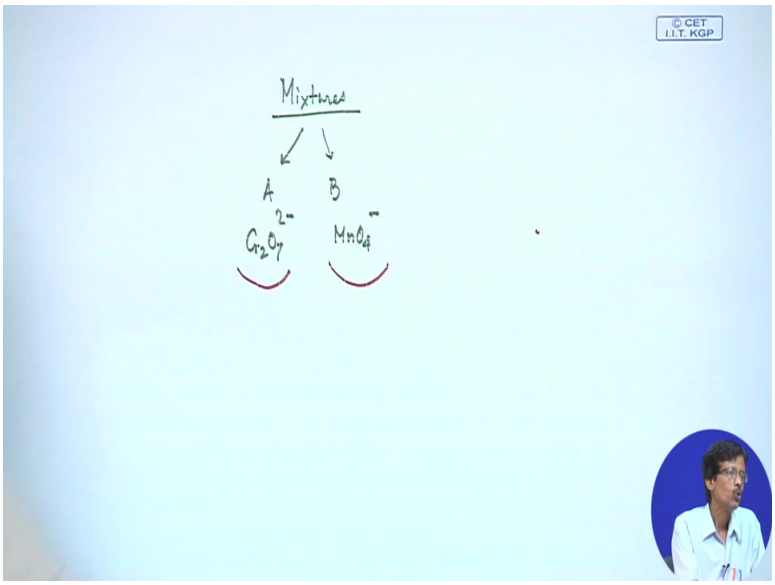

So what we will be talking about in a mixture whether this mixture is also give rise to a good measurement. So these mixtures how we can use for two components component A and component B where A can be your CrO72 minus and B can be MnO42 minus and both of them we are relying on charge transfer (())(26:37) because this particular manganese we know, this manganese having no delectron is acceptor level and oxygen is a donor.

So giving rise to the corresponding charge transfer transition intense charge transfer transitions. So these two mixtures so these two mixtures so we want to determine the unknown concentration of dichromate and unknown concentration of potassium permanganate but whether we will be able to apply Beers law for these mixtures or not.

So the measurement at that particular wavelength that means the measurement where the potassium dichromate absorbing is not absorbing the (())(27:14) potassium permanganate.

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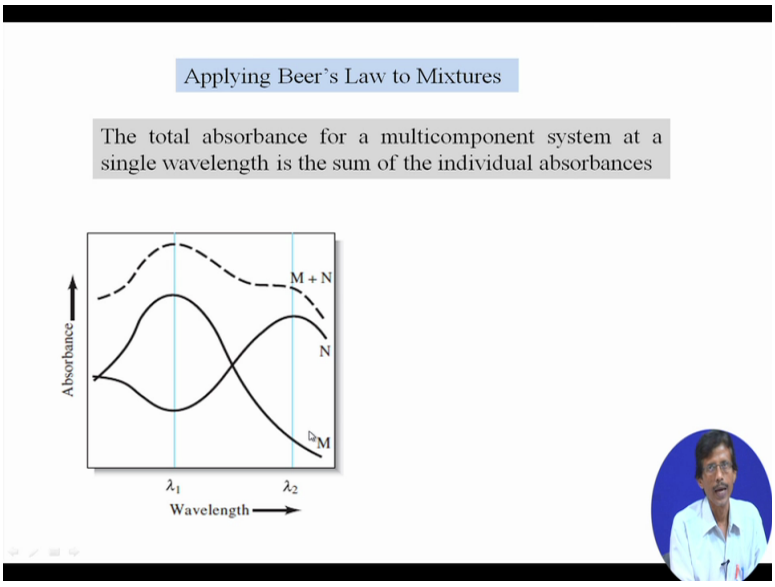

So the total absorbance what we will get from there for a multiple component system at a single wavelength is the sum of the individual absorbances so how we can use this sum of this individual absorbances that is very important.

So if your lambda 1 is utilized if we use lambda 1 for one component and lambda 2 for the second component. So what we get that particular one that M is absorbing it has a maximum absorbance that means the it has the M has the lambda max at lambda 1, whereas N has the lambda max at lambda 2.

So if your M is your potassium dichromate and N is your potassium permanganate, so it is very easy to apply for that also because the individual absorbances we should know and applying the typical Beers law formula for individual concentration of M and N in separate solutions and which can be applied to the corresponding final mixtures where both the species are present that means both M and N has been added N is added up you see this particular value that means the absorbance.

Now we are talking in terms of the corresponding epsilon value of the absorptivity, so this axis is now absorbance axis, so this absorbance axis will tell us that why this has been gone up to this particular value because you have this particular base absorption for this N species. So for M plus N this has been added up, so this particular magnitude has been added up.

Similarly this magnitude at this point has been added up to give you this one because when we are recording M absorbance for M and absorbance for N, this was the base line but when the instrument is recording the M plus N for this measurement it is the value which we can get it due to the corresponding value of this particular absorbance. So the base line has been moved from here to here.

Similarly for the wavelength lambda 2 the base line has been moved from here to here. So that is why it has been added up so we get the corresponding absorbance for the mixture but clearly it shows that you have an absorbance at the lambda 1 value and also another absorbance at the lambda 2 value.

So next day we will see that how we can utilize this particular thing that means this measurement as well as the individual measurements can be useful to identify the corresponding concentrations of M and N, ok thank you very much.