Course on Analytical chemistry
By Professor Debashis Ray
Department of Chemistry
Indian Institute of Technology, Kharagpur
Lecture 26
Module 6
Spectrochemical Methods - 3

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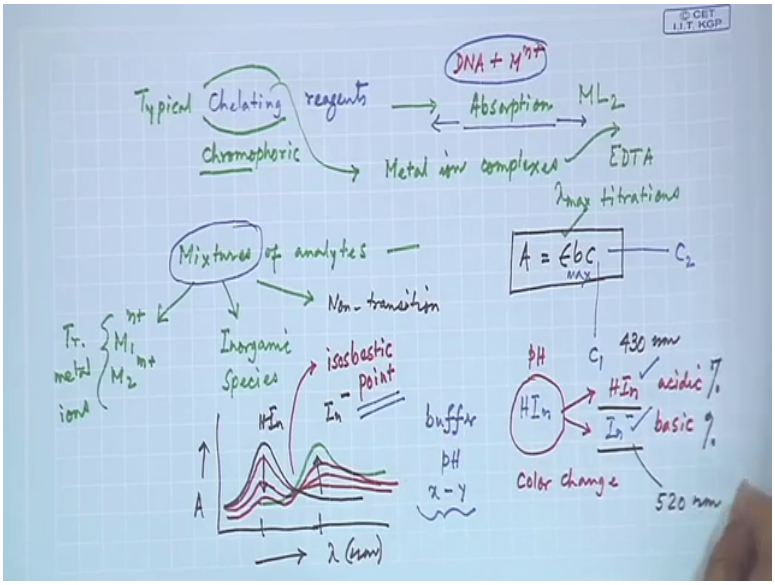

Ok welcome back to this class again were will be continuing the corresponding chromophoric reagents for your analysis so we are taking the help of chelating reagents so this is interesting to note over here because we are talking about something were we are just looking for the chromophoric reagent. So once we alter this stall the chromophoric reagent that means it should have something well the chromophore can take part in this particular reaction so this chelating reagents can also be useful for your typical absorption of colour.

So several typical chelating reagents starting from your diethyl carbonzone, diethyl carbonmate and dimethylglyoxime, all these are typical chelating reagents, they are very much useful for absorption so so absorption spectrometry can be very much useful for doing all these things using a chelating reagent when we talk this chelating agent definitely we can have the concept of metal iron complexes so we should not forget the particular part that how metal irons are forming complexes because this is also the corresponding backbone for your titrations like that of your EDTA titrations also.

So now we will take the advantage of this particular use of this chelating reagent for mixtures of analytes, how we can use a mixture of analytes it can be a mixture of metal irons say M1 or M2 M plus or M plus it can be mixtures of some inorganic species or it can be any other thing that means it can be this, these two can be your transition metal iron and also these two can be your non transition.

So we can have these two components of these things that means you can analyse and again the very simple thing is that we will be applying that formulae to find out this unknown concentration and now what is the difference of this is that applying Lambert Beer's law to absorbance and the molar absorptivity all everything is known for this particular reaction because once we have this we know that this is absorbing that means this particular species which is your ML or ML2 species which is forming over there, we should know it's the corresponding Lambda max and the epsilon max.

So once we know the lambda max of that particular species which is responsible for your absorption of colour we have to know the corresponding epsilon max. Now when we talk about this mixtures so these two things we will now be handling, one will be C1 another will be C2 which will be concentration for these species and C2 will be the concentration of the other species and this can also be very much useful because this can be there and this absorbance how it looks like will also be there.

If the species that means two of the species such as your indicator or methyl red or methyl orange indicators so this is once species we know that where its absorbing where it is it has the corresponding lambda max value and the epsilon max value and this particular indicator by now as we have that particular knowledge we have knowledgeable now that with the change in pH it will change its colour that means the species which is responsible for your colour absorption is different. Why it is changing so with the change in pH if we consider that this is a weak acid organic acid we all we know for methyl orange and methyl red this is a weak organic acid, so this particular is present as its impact form in acidic form. So at low acid value or acidic value it is present in each iron but in the basic form what it will give it will go for deprotonation and give you Hn minus. So these are our mixtures of analytes if we do not control the pH or the medium is not buffer.

So you must have a buffer medium such that we know a pH at a particular range say x to y within this particular pH range which is buffer you have either the species present in that purely acidic form or in the purely basic form, but we know that this will have a different

lambda max value this will also have a different lambda max values. So to detect all these thing we should know all the corresponding concentration that means the percentage of this species and the percentage of the other species.

So what will you get will you get something where we can have the corresponding change in the corresponding absorbances so if one of these species say this particular HIn say we consider that it is absorbing at say 430 nanometre and the other one is anionic form is absorbing at say 520 nanometre. So it how it will look like so if we have this so it is 0 we mark it as 430 and this mark is that 520 so this is our lambda in nanometre scale and this is our absorbance access.

So what do we get we get basically a corresponding absorbance like this for this particular species that means HIn and we will get for In also all the nature will be definitely different so what we get that if you if make a solution of this particular indicator the methyl red or methyl orange at several pH value say 5 or 10 pH values we make all our buffered medium and we keep on measuring these things from the acidic medium to the basic medium what will you find that this particular one because if this is for HIn and this is for In minus what you will get that this particular thing is decreasing and this particular thing is developing.

So as a results what happens basically because this is the intersection so with the change in these values will get something where we get this particular one changing so we get this and we get like this, we get like this so it is developing so this will decreasing and this will increasing and we get some point some crossing point which is known as isosbastic point which is very much characteristics for all these things and for anything any problematic method because this iodometric method are also very much useful for analysing biological samples, analysing DNA molecules also, deoxyribonucleic acid also.

When DNA is binding with some metal irons say M M plus that can also be very nicely studied by this particular method. So DNA if we consider the DNA itself is the corresponding chromophoric reagent is not necessarily that it only gives you colour but it should only give you some absorption, absorption in the other range also that means the visible range at the lower side or the near infrared region on the other side. So if it is responsible for your absorption what we can do we can measure the corresponding concentration of the DNA and the concentration of the metal iron also and also sometime this binding product that whether the metal iron is binding the DNA molecule or not.

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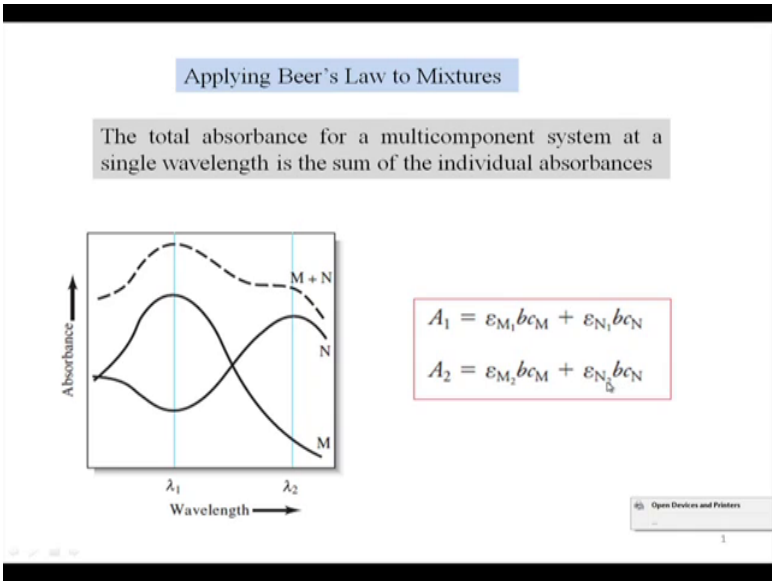

So this isosbestic point will be very much characteristic for all these things, so now we will see how this corresponding application of Beer's law last time in one of our previous class we have started that discussing this as the total absorbance if we consider that if we have a mixture of two M values or M plus N also because M is one metal iron and N can also be another metal iron or M can be inorganic species and N can also be another inorganic species or it is the metal iron chelate and this is also another metal iron chelate.

So directly or in a straight way manner we apply the corresponding Beer's law for that and the formula for that will be this that as we all know that is this all these two absorbances that means A1 and A2 these two absorbances are nothing but A1 is for the corresponding absorbance, the total absorbance if M and N plus present so this magnitude is the total absorbance of M plus N at lambda 1, A2 is the total absorbance at this particular wave length for M and N, so how do we know? We know that the corresponding A1 is nothing but since these two are additive so it is the corresponding individual absorbances of M1 species and individual absorbances of N1 species.

What is this M1? M1 is the absorbance of M as we all know that this has maximum at lambda 1 but minimum at lambda 2, so this is the corresponding absorbance of M at lambda1 and this is the corresponding absorbance of N1 this magnitude this N1 at lambda1 such that we get the overall absorbance over here with added up with this magnitude of this. Similarly for absorbance two also we get is epsilon M2bcm so this is the absorbance for this particular one where this particular one we get this absorbance of the individual component that means it is a absorbance of M2 species M species at lambda 2 and N species at lambda 2 also.

So these are the two absorbances at this particular point so absorbance at lambda 2 but these are the corresponding sum.

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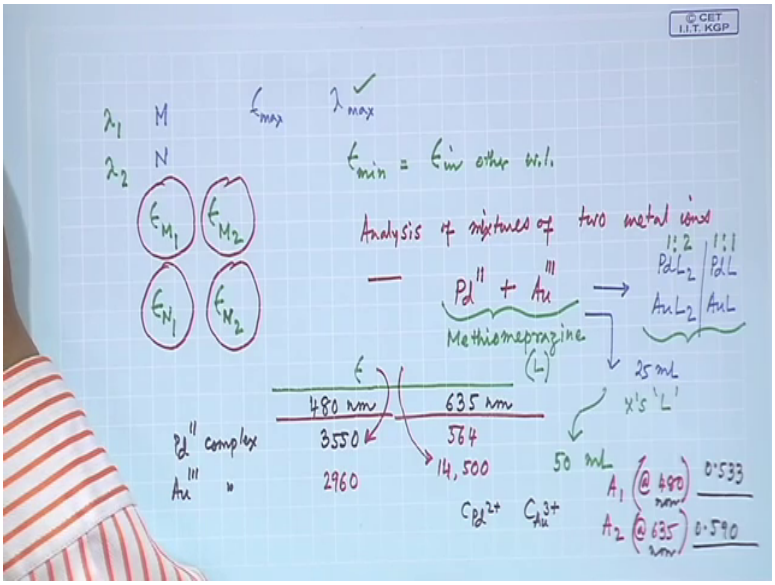

So what we should now because earlier we are taking about the corresponding lambda max values related to your epsilon max values and if your species is M is there and if your species N is there and if your M has a corresponding lambda max at lambda1 and N has a corresponding lambda max as lambda 2 only.

Now we should know the other absorbances also which we can consider as the corresponding epsilon not as maximum but we can consider as epsilon min or the epsilon in other wave length, okay. So that is why we get this particular species for this epsilon of M and epsilon of N which we are talking about the corresponding epsilon values at the max but we are nowhere we are writing is that the max but we are taking this as the max, but when it is there so it is at lambda1 so we will have another one also which will be at lambda2 it will be epsilon M2.

Similarly this one will be lambda 1 and this will be epsilon N at lambda 2, so will be handling or will be using not only one epsilon match values but two components we will be handling four epsilon values so these are the four epsilon values we should know the precise magnitude of these things. So if we know separately because one such example we can use or we can handle like this that analysis of mixtures of two metal irons analysis of mixtures of two metal irons.

Such that these are quite known a very normal not very normal metal irons, one is palladium 2 another is gold 3 so we have to choose some reagent for that so the name of this organic molecule is methiomeprazine, so when methiomeprazine binds separately to this palladium 2 and gold 3 they can have their individual lambda max and epsilon max values so for these two that means what the palladium 2 and the gold 3 so they have two maxima values like that of the indicators what we have seen just now in that particular way that you have this one one will be at 480 nanometre and other will be at 635 nanometre.

So this palladium 2 complex which has a corresponding epsilon max value at the lambda max at 480 nanometre well epsilon value is 3550. Similarly this gold 3 complex will have a corresponding lambda max value at 635 nanometre having an epsilon value of 14500 so these are your epsilon values so this is also epsilon, so this is one epsilon, this is another epsilon. So we should know to other also that means the corresponding absorbance of the palladium complex at the wave length of absorption of gold 3 as well as the corresponding absorbance of gold 3 at the lambda max value of the corresponding palladium complexes, but these are very small values so it is 564 nanometres and this is 2960 sorry epsilon values mole inverse centimetre inverse ok.

So these four quantities are very much essential then we can have the mixture of these two and these two mixtures are basically reacting with this reagent give rise to the complexes of PdL2 and your gold L2 say it can be PdL or gold L also if it is (())(17:06) one so it can be PdL or gold L also. So you have the corresponding mixture and this mixture is taken and we can have this corresponding one that means the total observances what we see over here we will be able to measure this two observances A1 and A2.

So we can have the total observances so in a mixture of these two what we do we take, give a 25 millilitre solution of this reagent. So 25 millilitre of this reagent when it is added that means this 25 millilitre of this reagent is an excess quantity it is not that we are following a ratio of 1 is to 2 for this type of complexation or 1 is to 1 for this type of complexation, but we are putting this particular reagent is in excess, so excess of this L we are adding L is your this L they are ligand so L is in excess so that means the magnitude of this that means whatever maximum amount of this ligand attaching to the metal iron centre is forming is formed and some free ligand will be there, but the free ligand is not giving us any trouble because your colour absorbing species is the corresponding metal iron complexes.

So next we get this one and we dilute it to say 50 millilitres for our convenience so a final 50 millilitre volume and we can have this corresponding one and we measure this observances that mean A1 we measure and A2 we measure so A1 and A2 we have to measure, so where it is A1? A1 is at 480 nanometre so this is the wave length so this is at 480 nanometre and where we will measure A2, A2 will be at 635 nanometre so we will be at 635 nanometre, so this will be definitely nanometre and this will be definitely nanometre.

So the total absorbances we have to measure and the reading of these will be say in one case 0 point 533 in another case it is 0.590. So what I see now that the absorbance values A1 and A2 if we can measure out of these so these two things that means these two are in data in our hand along with these things by applying the equation for our this mixtures we should be able to that means we can have two equations out of that forming these two what we have seen just now that A1 and A2, A1 and A2 is known we can put these and also we just know these values that means epsilon value b is known only thing we can have two unknown concentration one is the cpd2 plus that means is a small case c concentration of palladium 2 plus and another is cau small case statement concentration is always small case au 23 plus. So these are the two unknown quantities what we can have that one can be cN another can be cM, okay.

So this we have seen in these two these consecutive equations what we see over here is that for your corresponding one that means your this c that means if c that cM is here cN is also here cN and cN so you have two unknown quantities so these are your two unknown quantities we can solve these two equations to get your corresponding concentrations of these unknown palladium and unknown platinum.

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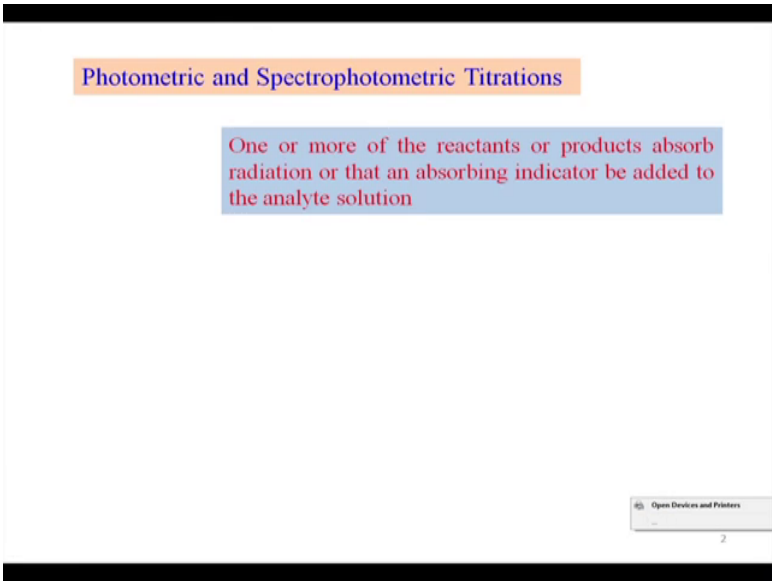

So this is a typical methodology what we can follow for all these things for your identifications and what we can do for now a continuous process because these are the two individuals things what we have monitored that means individually your palladium 2 plus and gold 3 plus you can you can measure, but if we can go like this a titrimetric method like your simple acid based titration but we will take the spectrophotometer itself for blood titration that means the (())(21:45) covaid of the spectrophotometer or the covaid of the photometer is utilised for your reagent that means your conical flask, reagent flask or the conical flask where we can go for the typical titrations by simple burette or a micro burette also.

So what we do there that one or more of the reactants or products if they absorb nicely what we have seen just now it is the corresponding product which is absorbing the corresponding radiation so if the reactant or the product absorbs radiations so far whatever we are discussing here is the products, the metal iron is reacting with your ligand and that metal iron complex is your product and product is responsible for your colour.

If can be your nickel dmg complex it can be your corresponding lade carbozone complex thio carbazone, diphenyl thio carbazone complex all will be the corresponding products similarly whatever examples we have seen just now for your that palladium and gold case that means one reagent can give you two products and those two products can absorb radiation and that and other case also the reactant can be coloured so three things can be there in your hand that means either your reactant can be coloured that means your (())(23:14) or your metal iron indicator or your product can be coloured in that case your chromopholic reagent is not

coloured, your product is coloured that means the chromophoric product is your chromophore and sometime than absorbing indicator be added to the analyte solution.

Or we can add some analyte indicator such that there will be a change in the colour for that particular reaction.

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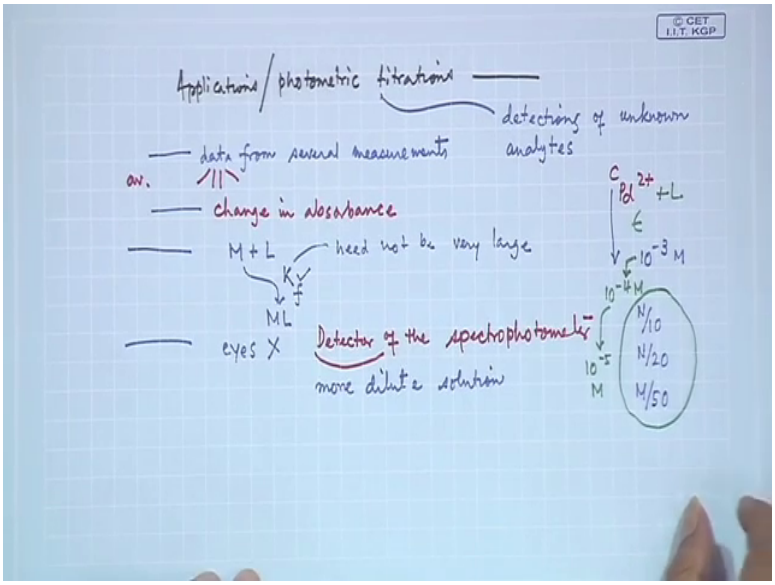

So that we can have the typical applications of these photometric titrations, okay so what we can apply we can apply this particular one for the different photometric titrations so these are very much useful for your photometric detection so what we do these titrations because we can go for the photometric detections of unknown analytes, okay.

So these unknown so why these are very convenient very useful these things are therefore that we can have several measurements not that only one measurement because we can have two three measurements or two, three, four titrations and we can take out the average of these, so several measurements can be used so we can take the data from several measurements so those are very much useful because we can have the data and we can have three or four data in our hand, we can take the average of that such that we can get more reliable data for this particular measurement such that we can go for any unknown concentration of say caladium 2 plus because this is our ultimate goal how we can get more precisely the unknown concentration of your palladium.

So the change of absorbance is being measured so because what we can measure we are just monitoring the corresponding change in absorbances so change in absorbance we measured and that is why we are going for this with the wave length scan that absorbances we are

getting. So for this particular reaction of this M plus L giving rise to corresponding ML definitely some K is involved the formation constant is involved for metal iron complex formation.

So in this particular case because most other cases for the precipitation reaction or the gravimetric estimation we require a very large value of this Kf or the K formation but in this particular case the equilibrium constant for the reaction that means the K need not be very large, it can be 10 to power 5, 10 to power 3 to determine any unknown quantity of this palladium by some analyte giving a coloured reaction.

So what we can find that if this is not there that means if the case value is not required to be much also and since the detection is not by manual that means not by visual not by our eyes so eyes are not utilised to detect the colour change or the intensity of the colour it is the detected of the spectrophotometer, detector of the which is being utilised so detector the eyes are replaced by detector so we can use more dilute solution that means we can go down to a low concentration of say 10 to power minus 3 molar which we cannot do for usual manual titrimetric methods.

Because in titrimetric method most of the time we know from our school days that we are making some solutions which can be N by 10, which can be N by 20 or sometime it can be up to N by 50. So these are the most conventional and most useful concentration being what we do by simple titrimetric methods but in this particular case if your case is not required to be very large also so these particular one with reaction with this reagent and depending upon this absorbance values which are several thousands.

So we can go down to even 10 to the minus 3 molar but we can go down to 10 to power minus 4 molar or even 10 to the power minus 5 molar which is the most conventional working range of concentration for fluorometric methods of analysis that means by using molecular fluorescence we can go down to 10 to power minus 5, 10 to power minus 6 or 10 to power minus 7 concentration that we will see when we talk about the molecular absorbances.

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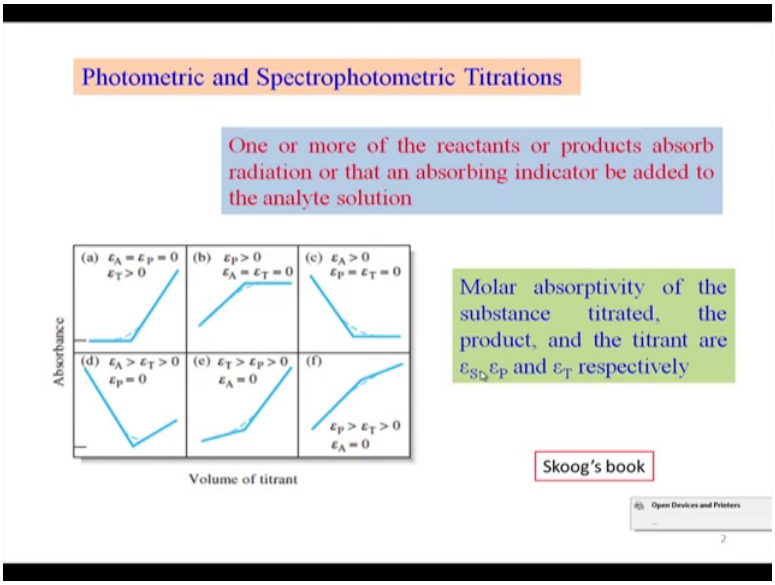

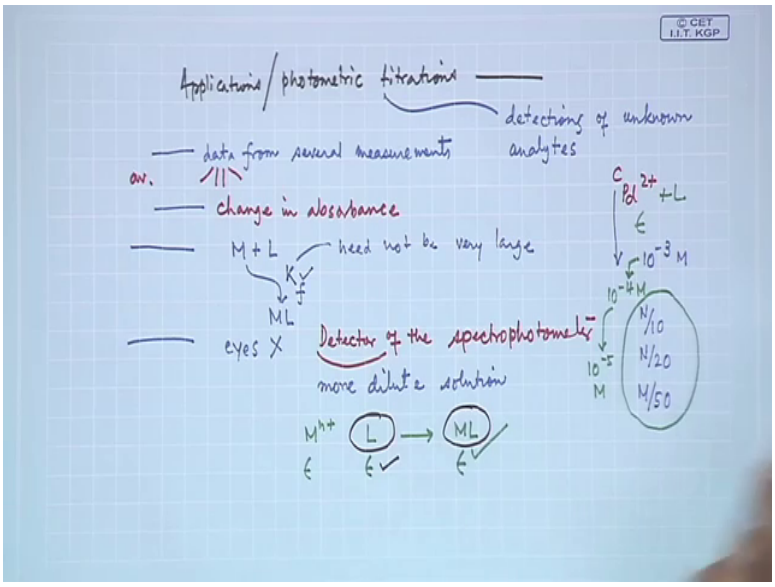

So this photometric titrations are very much useful in that way if we one of this species can be coloured. So like our conductometric titrations what we see again from your the Skoog's book that you can have all these different plots, so nicely you see that all these plots and whatever we are talking about here is some epsilon values only. And always we think we do something where that the you have the corresponding analyte and all these so we consider the corresponding epsilon values only for your corresponding species that means the molar absorptivity of the substance titrated that means your analyte then the corresponding product or the titrant. So the substance being titrated the titrant and the product if these are the corresponding epsilon values so any of them can give rise to your colour, what do you see that just if you have the metal iron MN plus which reacting with the reagent giving rise to the corresponding concentration ML.

So we can talk about in terms of the E epsilon of this, epsilon of this and epsilon of this, so this this are very simple strategy for that that you have the corresponding one that means the absorbances that means the corresponding absorbance what absorbance we can talk about this particular species and the corresponding theme that you can have the correspond one that means you can have the different absorbances for epsilon, for the metal iron, for the ligand and for the so any one can be very high.

So any one can be very high means that we can monitor this as the product that means the product epsilon will be useful but in some case your this reagent the chromophoric reagent or the ligand can be useful that means this value is high or sometimes this can be very high such that it can give rise to the decrease in the corresponding absorbance values. So when the corresponding titrants that means the titrants is only that epsilon value for the titrant is only greater than 0 and two other cases it is equal to 0 what we get that after the end point your absorbance will increase and in this case also if your product is only increasing greater than 0 but if your other two are 0.

So at the after the M point you have so what we basically get like your conductometric a metric titrations we basically get we should be able to detect this particular cross over so this cross over, this cross over, this cross over, this cross over and the other cross over so these are the most reasonable possibilities for all these titrations what we can see for these things so any one of these that means any one can be useful for your colour absorption.

So we get this as your M point so when we go for this typical titration this is your M point, this can be your M point, this can be your M point so like your conductometric titration when you see the corresponding ionic conductance in the solution the electrical conductance of the ionic solutions are changing and there is a soft change what we call all these cases that these are very soft changes so sudden change.

So this part is horizontal then sudden increase is there so this is monotonically increasing but after sometime it is tipping horizontal, this is decreasing then it is keeping horizontal it is decreasing then after the M point it is also increasing again then this particular thing that means both the two parts that means this two things are positive magnitude of your molar absorptivity is increasing chain part the magnitudes are different because these two magnitudes are definitely different.

They are greater than 0 but one will be very high so that means the positive slope in one case is less in other case the slope is completely different, so all these things will be very much useful for detecting that particular components so in this way also the photometric or spectrophotometric titrations in our next class we will see that how we can handle this for a mixture of the metal iron, just now we have taken one example of this palladium 2 plus and gold case for reacting with some reagent but we should know or solving this particular simultaneous equations of that Lambert Beer's law but in our next class what we will see that a metal iron indicators that means the EDTA titrations we can do for a mixture of metal iron and how the corresponding photometric plots will look like okay.

Thank you very much.