Course on Analytical Chemistry
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Module 4
Lecture No 18
Spectrochemical Methods - I

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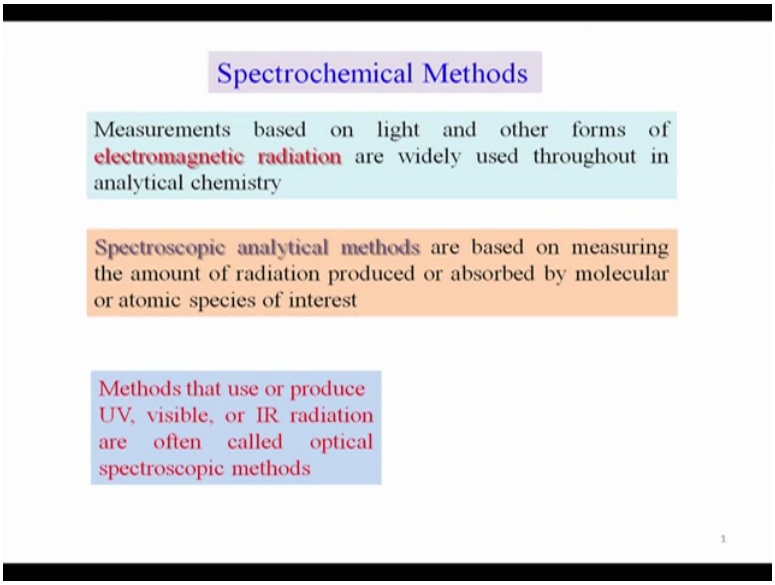

Hello and welcome to this class of spectrochemical methods where we are trying to see that how a spectrometer can be utilised for the measurement of a titration reaction or how we can follow a titration or titration chemistry. So since we are utilising a spectrometer or a spectrophotometer, we should be able to talk in terms of corresponding coloured solution so it is basically the utilisation of certain amount of this particular light.

So measurement techniques which is based on the light and other forms of electromagnetic radiation, so here basically all we see the for this spectrochemical method that the electromagnetic radiation will be utilised for this particular analysis or the analytical measurement, so this spectroscopic analytical method are based on measuring the amount of radiation produced or absorbed by molecular or atomic species of interest. So what we are looking for is the corresponding colouration reaction.

So that colouration reaction we are talking about is this particular visible range, so if we have other methods also that the other methods starting from the UV to IR radiation x-ray and the corresponding gamma rays also can be utilised for this analytical purpose. So right now we will focus our attention on the visible range that means what we see by our naked eyes.

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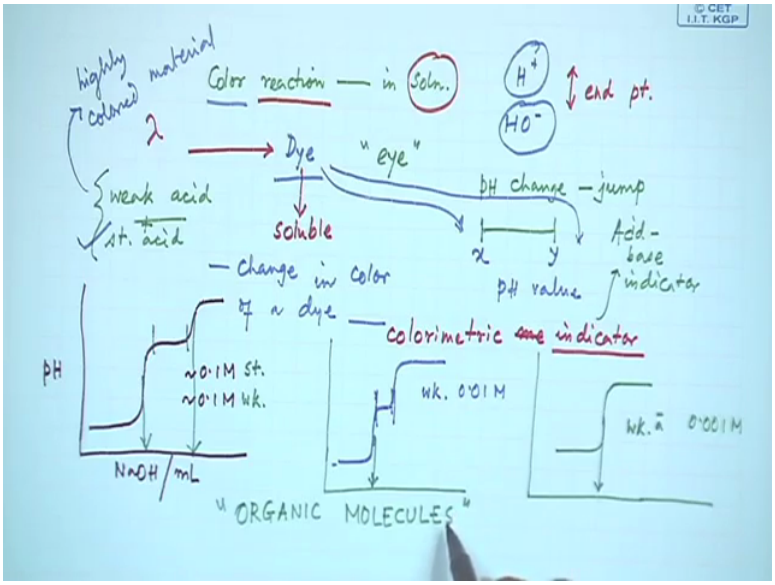

So we have to go for a color reaction that means we have to who produce some colouration in solution, so in solution how we can produce a color? And what we can monitor, we have to monitor the corresponding titration reaction or the neutralisation reaction between these 2 that you have acid and you have base, they are reacting together but thing is that we want to use it by a color reaction.

How we can do that is a very simple thing that externally if we can use something as a dye, so what is dye, which can give rise to a color reaction to the solution. Why it is a dye? Because we are talking about the corresponding electromagnetic radiation so electromagnetic radiation of certain wavelength or say frequency is passing through this particular dye so this thing whatever we are doing this colouration action or the color reaction in solution which is very much important.

So this dye what we are thinking of, of introducing for this particular titration reaction, it should also be soluble give rise to a solution. Suppose we have either acid solution or a basic solution you add this particular coloring matter which can produce color to the solution which is soluble over there. So the use of this dye which is a very important thing, that use of this dye we can utilise for the detection of this end point between the titration of some acid or base we can have an endpoint and that endpoint can be detected, how we can detect? Initially we think of the non-use of (())(4:21) spectrometer so how we can use this particular change by our naked eyes.

So our eyes can be utilised to detect a corresponding color change, so since this is there we know that there is a pH change or rather we can call it as pH jump. We have seen that there is a sudden pH jump basically, so this particular pH jump that means we have a particular window of that pH, so one particular pH to another particular pH. So from X to Y pH value, so this dye basically at this point giving one particular type of color if it is available or it can be colourless also and the same dye and above this so at a particular pH value less than this and a particular pH value above this you can have 2 forms of these dyes.

So these dyes if it is soluble in that fashion and if it can be utilised to see the jump of this pH value, so what can happen there can be a change in the color of the dye. So the change in color of a dye is utilised and when the guy is utilised to detect or to see or to identify the corresponding pH jump we see that this dye can be considered as a colorimetric indicator which can be considered as a colorimetric indicator. So we are introducing some term, how we can see an indicator that means this indicator will be utilised to detect the endpoint of some acid base neutralisation reaction.

So we can consider them as some indicator which can detect that endpoint of the reaction and we can label them as acid base neutralisation indicator. So what should be its actual property for this particular dye? So if this dye is there so we know that this can be an acid also and if it is a weak acid the dye itself can be a weak acid and this particular dye which can give you corresponding titration reaction will see, if we mix this particular weak acid to a strong acid, so weak acid this weak acid a strong acid like the way we are talking about the corresponding carbonic acid or salicylic acid where you can have 2 protons available from 2 parts of the molecule or the same molecule for the titration reaction.

So if we have a mixture of these two and they are of different strength such as we are mixing strong acid with that of a week acid, if we consider the strong acid is a typical inorganic acid and weak acid is a organic acid like acetic acid, so acetic acid and sulphuric acid and if we titrate it with that of some amount of NaOH and the volume of that NaOH we can monitor for certain volume of those 2 acids or the mixtures of these acids and we keep on titrating at thing and your pH changes will take place in this particular case like this.

When this concentration of this week acid and strong acid are same which are close to 0.1 molar for the weak one and 0.1 molar for the strong one, so we should be able to detect of these 2 acids and we can have a 1 endpoint for one acid and another endpoint for the second acid. Now what we can see that we can have this particular type of plot only by varying the

related concentration of the week acid with respect to the strong acid, so when keeping the strong acid concentration same that means this is your say strong one and this is your weak one.

So keeping the strong acid concentration same what we can do, we can reduce the weak acid concentration to that weak acid concentration to 0.01 molar and if you do the same titration everything remains the same only the nature of the plot is changing. So what we see? This particular horizontal position horizontal area horizontal line basically. So this horizontal ports of this corresponding pH plot is getting reduced as we go for a lower concentration, a lower concentration of the weak acid so slowly what we are seeing that if you go for a lower concentration or the lower range of that particular concentration, here this horizontal range is the horizontal range is decreasing.

So this particular one is basically if you go for the other concentration where we see that we are unable to detect the corresponding break for the weak acid concentration, when the weak acid concentration is reduced to 0.001 molar strength. So this particular concentration from . 01 to .001 molar consultations we are not in a position to detect is horizontal position but in all these cases this position the first position remains the same in all these cases.

This position is basically same so when we go for this particular titration and we see that this particular titration can be utilised for the determination of this corresponding strength of this strong acid. Forget about this nature of this weak acid what is available over there, we should be able to detect this particular thing, if we have a corresponding highly color material of this week acid.

So if you are this weak acid is a highly coloured material which is a highly coloured material and that particular material we basically get as the indicator so this particular coloured material is nothing but your indicator for the titration as we all know how we can use this amount of indicators, so only few drops of indicator are required for this particular acid-base titration as we all know that a strong acid strong base titration.

A good indicator is your either the corresponding methyl red or methyl orange or phenolphthalein we all know. So there will be a color change from one particular stage to the other that means the typical acidic condition to the basic condition and this particular indicator what we can use, they are all organic molecules. So the very basic information what we get is that we are handling something which are nothing but organic molecules and these

organic molecules can function as a good indicator and those indicators are nothing but they are simple weak acid is because we have checked this with that of your titration.

We have to (())(13:45) this horizontal line with the previous one such that in this particular is when the concentration is less that means the weak acid in a very low concentration we all know that it is very difficult to detect that particular endpoint so in presence of this strong acid is typically merging with this and this week acid in a very low concentration if there is a change in the color the organic molecule can function as a very good indicator for this titration.

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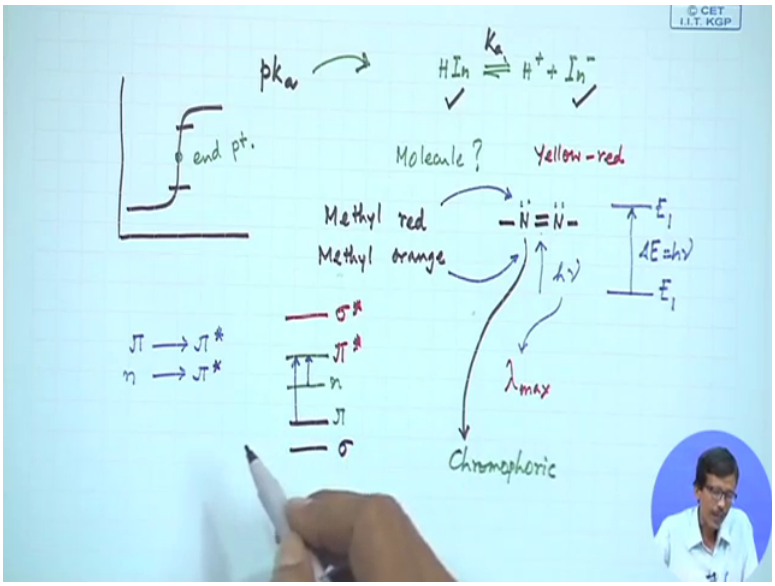

So what we see is that have a weak organic acid and that weak organic acid can have a pka value and this pka value using that particular Henderson Hasselbalch equation, we see that the corresponding pH of the medium is related to the pka and the 2 other form the salt and the acid concentration. So this pka which can be labeled nicely that means you can tag a particular organic molecule with this pka value because this we all know because if you have HIn, In stands for indicator, if it is a weak acid you can have a responding indicator which have a dissociable proton and the equilibrium the chemical equilibrium we can think of or can talk about that is H plus and In minus and these 2 things you can have a particular color of this acidic form and the corresponding color for the basic form.

So since this is their so you can have a ka value and you can have corresponding pka value and this pka value if it is such that at the point of at the time of your titration where we see that there is a jump in this particular pH value and your pka value of that neutralisation

titration indicator, this pka value of this neutralisation titration indicator will be close or clear to the pH value of the solution at the endpoint of the titration, so this is the range where you see that during the addition of some drop of this alkali solution or the basic solution the jump in the pH value is there and this jump in the corresponding pH value we see that if it falls within the range of the corresponding pka value of the indicator.

We see that at the time of your neutralisation reaction the pka value will fall within the range of the pH value of the solution at the endpoints. So if this is your endpoint we should be able to detect the corresponding endpoint by the use of this indicator. So how we can use this particular indicator that we will see with the use of certain organic molecules, so what is that molecules? Which can be used as a good indicator and we only know some names like that of our methyl orange, methyl red, phenolphthalein, et cetera.

So methyl red is one name then methyl orange, so thing is that they are organic molecules they can have 2 different forms one is the acidic form and other is the basic form and they should be coloured such that during this particular change in the pH value it can go from typical acidic color to the basic color and indicating the endpoint of the titration reaction.

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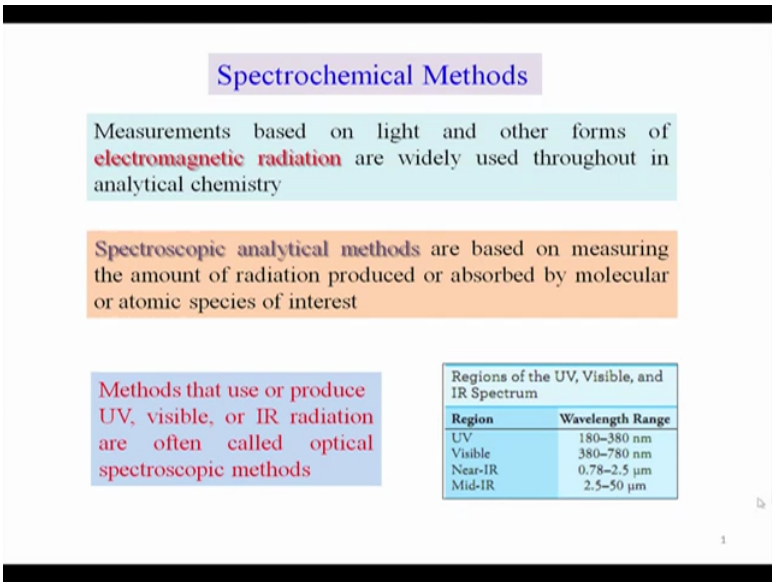

So we will be utilising the simple visible light for this spectrochemical method of this measurement so we can also call them as optical spectroscopic method and when we talk in terms of the corresponding regions basically because it should be very much familiar with the range what we are covering.

So for ultraviolet, for visible and the IR spectrum what we are using, so for the visible range that means particular indicator or a particular thing what can be coloured is that it can absorb the corresponding electromagnetic radiation in the range of the corresponding wavelength starting from 380 nanometer 780 nanometer as we all know that this is the only visible range but we can see our eyes also and all the colors in the responding color (())(18:56) from violet to the whole range of the light the corresponding (())(19:04) we all know.

So that will basically fall under this particular range but how we can use because sometimes we may not so lucky that we get the color reaction but sometimes we see that a colorless solution but it still it can show the corresponding electronic transition and it can absorb in the UV range particularly some organic molecules will see that the electronic transition can take place within this particular range that means the UV range from 180 to 380 nanometer because when we talk little bit about the spectrophotometers will see all these individual range of this electromagnetic radiation we can have certain amount of the corresponding sources, so what are the sources what are the lands we can use for this spectrometric determinations.

Similarly for near infrared region we can have in the micro-meter range of radiation and in the mid infrared also we can have corresponding micro-meter range 2.5 to 50 micro-meter. So these are some longer wavelength region so nowadays our spectrophotometers are available where we can scan basically a UV range to near IR or mid IR range altogether in a single instrument.

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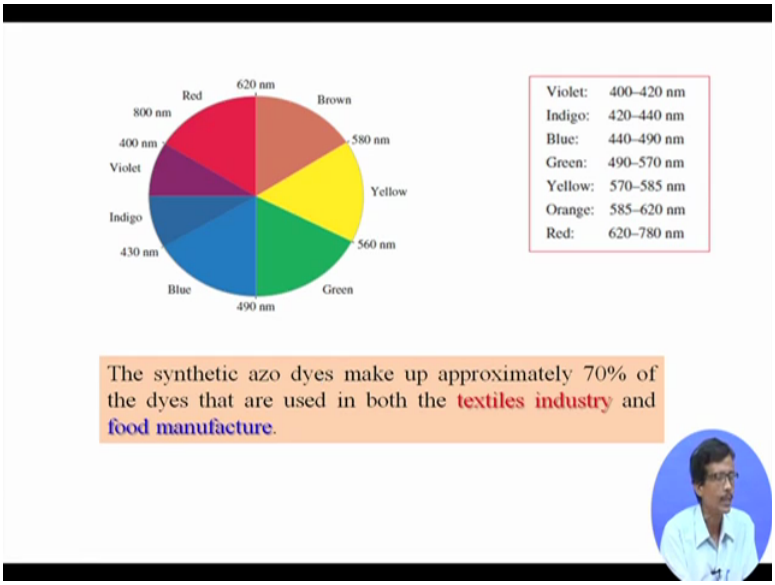

So if we see that corresponding range for this colouration reaction where we see that a particular color reaction what we can see the solution is colored with violet or the solution is coloured with red but if we know that these are the typical range for the wavelength of the colored radiation that means the corresponding lights what we can have for violet, indigo, blue, green, yellow to up to red.

So this is the typical coloured wheel we all know and the breakup for all these ranges is starting from your violet range, violet range is nothing but 400 to 420 range then indigo is 420 to 430 or 440 then blue, green and all these things so these are the corresponding colouration of the corresponding lights or the electromagnetic radiation. What we can utilise which can fall on the solution and we have to see something that means whether the solution can absorb that particular energy of the radiation.

So we are talking about the dyes so what are those dyes, so one particular organic molecule what we can think of which can be prepared synthetically like that of the 2 examples what we are talking just now about the methyl orange or methyl red that these synthetic azo dyes, the synthetic azo dyes means we can synthetically prepare in the laboratory and these basically makes approximately 70% of the dyes industrially used in the industry like textile industry or in the food manufacture industry because most of the food materials what we consume they are safe to our health and they can be utilised for the different types of dyes, we will take 1 or 2 such examples where we can see that these azo dyes are very much helpful to give a corresponding color reaction.

So these 2 dyes also when we can see the detailed structure of the methyl red molecule or the methyl orange molecule what we can see one particular function what we can tag on it is the azo function. As we all know from your knowledge of organic chemistry little bit of organic chemistry knowledge will tell us that how we can get the corresponding azo compound starting from a some nitrogen based compound or amine compound or aromatic amine compound which can be diazotized than can be coupled up with beta naphthol or any other phynoil to give you azo phynoil type of compound. So similar type of functionality we can generate with respect to your methyl orange or the methyl red.

So what we can see that this particular part of the molecule which can absorb the corresponding electromagnetic radiation in the visible range, such that this molecule and show the corresponding electronic absorption that means you can go for electronic absorption from the ground state to the excited state that means E1 to E2 and the corresponding gap between these 2 energy state is delta E which is equal to your H new value so how this H new value can be co-related or can be made equivalent to the corresponding lambda max that we will see that due to the presence of this azo function because most of this compounds which are solid in nature is basically yellow to red in color.

In solid powder from there also yellow to red in color and in also the solution there are also yellow to red in color and this particular thing when we change the corresponding pH value so there will be a change in this color also from yellow to red. So in one form it is yellow in another form it is red so that is why all these things are very much helpful in understanding our idea of introducing corresponding indicator for this acid-base titration or his neutralisation titration.

So these simplistic approach or a very simple way of telling that what should be the separation or these 2 things when an electronic transition can take place and when we go for this we know that these are some covalent bond are there. If on the left-hand side you have a carbon and on the right-hand side so you have a carbon, so what we get this particular double bond so double bond is forming we all know that pi bond is forming over there so if we can have a Sigma bond that means electrons present in the Sigma level then we can introduce a double bond character in this azo function, why azo is becoming a chromophore?

What question we are asking now is that how a azo function which is a responsible part or this whole organic molecule for a coloured solution or a coloured solid sample because the chromophoric part attached to this molecule this organic molecule is the azo function. So you

have the Sigma bond on the second one is your pi bond and sometimes you see that you can have also lone pair of electrons because this nitrogen and have lone pair of electrons on it.

So you have the non-bonding electrons so these are the electrons available which are in the field level that means all these levels are field that the Sigma bonding level, the pi bonding level and the non-bonding level all will have the electrons in it so once we know that during the formation of the covalent bond, all these things can also give rise to the corresponding anti-bonding level which is the pi star level and the Sigma will have the corresponding level as the Sigma star.

So what are the transitions available for this is very simple, thing that when you have the lone pair of electrons on this azo function what we get? We get a transition from n to pi star or it can go to n to Sigma star also and another transition is also very much visible is your pi to pi star transition. So mostly for all these molecules where you have a n and double bond or sometimes you can have a amine function what is originating from a seed base condensation where one of the nitrogen can be replaced by carbon where you get a carbon, nitrogen, double bond and that will also have the distribution of all these electronic levels like these and you can have the most dominating transition over here is the corresponding pi to pi star transition where the energy gap is more and where the energy gap is less is your n pi star transition.

So this n pi star transition is gap is low that means it is in the higher wavelength region, so at higher wavelength region we find some transitions what we can monitor by a spectrophotometer is the corresponding n pi star transition otherwise we can have in all these cases the corresponding pi pi star transition and other things will also consider is corresponding intensity of these transitions not only the wavelength of transition but intensity of those transitions are also useful, so we have leveled this thing as your corresponding azo function, so wherever we get the corresponding azo function (())(29:23) or the corresponding nitrogen nitrogen double bond we consider that these are the typical dyes.

Why they are dyes? Because they are coloured they can impaired color in the textile matter or some food materials and this azo function will be very much useful because we are still of that particular molecule where we are considering that azo function we present in the well-known acid-base indicators then neutralisation indicators like your methyl orange and the methyl red.

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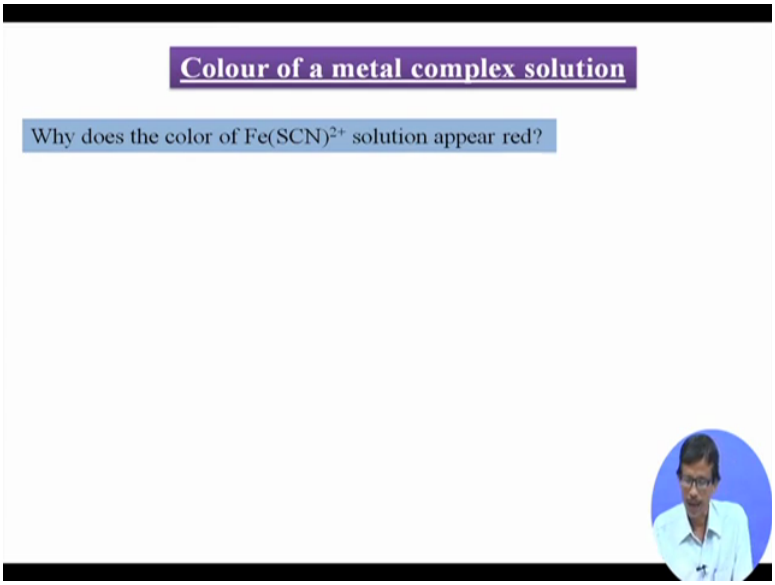

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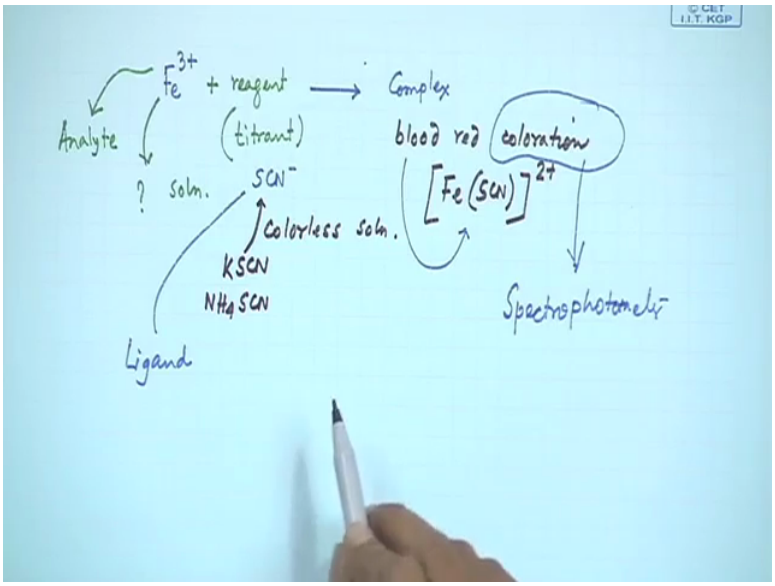

So for these 2 things what we see that this can be extended, this color reaction will extend it for a particular type of mental complex solution also. So one more question will be asking that is during this particular acid-base titration what we see that a typical indicator is coloured. Now we will see that anything coloured for you whether you have a ferric iron solution which is an unknown solution to you and we want to determine that unknown concentration of that ferric iron solution. So we will add some reagent and this reagent can also be titrant for your analyte Fe3 plus. So when these 2 are reacting to each other what we see now is that ferric iron is reacting with some reagent giving rise to a complex.

We all know that the complex species, the coordination compounds we are talking about now since we all know that this is a 3-D metal iron and 3-D metal ions are very easy or very nicely can react with some reagent or the ligand. So in this particular case if is a thiocyanate ion or the thiocyanate anion which we can derive it, where from we get it? We get it from a corresponding salt of potassium thiocyanate or ammonium thiocyanate.

So this potassium thiocyanate ammonium thiocyanate which is giving rise to a colourless solution to you and when it is added to any light yellow solution of ferric iron we get a blood red colouration so you have a blood red coloration and that color reaction is due to the formation of Fe3 plus and thiocyanate complex, so what we can consider is that a very first one will discuss it in detail in our next class that how this particular species that means Fe SCN 2 plus species because one of the trivalent charge will be neutralised by SCN minus. So giving rise to this species and we will see whether this particular one is your end product or not.

Whether more thiocyanate ion can be attached to this particular iron because that will be related to the corresponding tacheometry of this reaction because for any search acid-base type of reaction as we discussed earlier also at your metal ion can be acid and this SCN minus that the SCN minus for the complex species it has also another name we call it as a ligand. So metal ion ligand reaction is also an acid based reaction but here our basic idea is that how you generate a color reaction so that color reaction will tell us that once it is coloured we can detect the presence of iron by using some titrant or reagent and this colored can be monitored by a spectrophotometer.

So that is our basic idea that how we can utilise a spectrophotometer, not that we are going for a regular titration using burette and pipette but spectrophotometer will be utilised to detect the corresponding coloration and where the we will be able to detect unknown concentration of Fe3 plus the use of some standard solution because there will be a known there will be no need to use a standard solution of this type because we are doing some corresponding reaction, the complexation reaction will follow we will study for its production of this particular species and one is to one reaction is fine to detect or consume all the Fe3 plus ion for this blood red coloration in this particular case so spectrophotometer can detect the color we can identify the unknown concentration nicely by using this first example of your spectrochemical method for metal iron analysis, okay. Thank you very much.