Course on Analytical Chemistry
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Lecture No 25
Module 5
Spectrochemical Methods – 2 (Continued)

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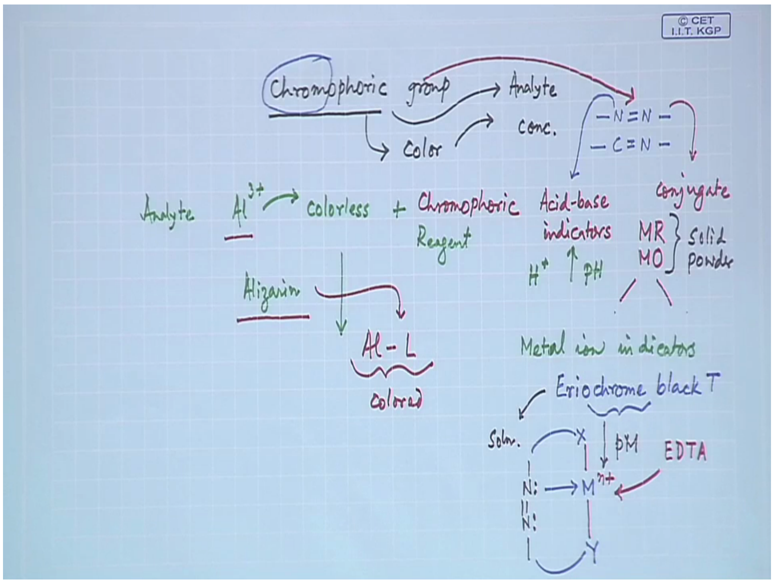

Hello and welcome to this class of the continuation for the spectrochemical methods where we will just looking at some chromophoric groups because that is very much essential to generate color to the solution. So how we can generate that particular solution color so that we can estimate the unknown amount of analyte in a solution by looking at the color intensity which will be directly proportional to the concentration as per Beers law.

So we have also seen that when this particular chromophoric part it can also present to the analyte itself and at the same time if we consider that as we discussed as it can have a very good azo function in it the organic molecule containing azo function or the MN function and this particular group we have discussed in detail in terms of the acid base titration reactions that these are the typical backbone for different acid base indicators.

So what we see here that this particular azo function along with some kind of conjugation in the corresponding benzenoid part or the corresponding (())(2:02) part as we know in case of methyl red and methyl orange only variation is there substitutions, ok. So a long range of color variation starting from red to yellow or orange to yellow for this one is in the acid form and another is in the basic form what we find.

So if this particular species is present so if the analyte itself contains this particular chromophoric group that means this chromophoric group is present in the analyte itself. So we can measure the unknown concentration of these two as well. So the corresponding presence of these groups which will be responsible for absorption of electromagnetic radiation in a particular range in particular the visible and the UV range.

So these particular molecules can be identified very nicely by looking at the corresponding absorption of radiation but in some other case what we find that there will be some chromophores or the metal ions like say aluminum 3 plus in solution we know this is not a de metal ion or the transition metal ion having unpaired electrons in the d levels. So in solution color it is colorless.

So how do we measure the corresponding concentration of this Al3 plus when Al3 plus is your analyte. So our unknown analyte is aluminum trivalent aluminum ion so it is colorless. So as I told you in our previous class that if we add something that means this chromophoric group that means some reagent and that particular reagent will give this example more in detail when we see for the other technique that means the fluorescence technique in our future classes.

So if this particular reagent can bind to this particular species so some molecule is known as Alizarin say alizarin is the class of organic molecules. So alizarin itself can give rise to some color like that of our metal ion indicators we all know what are metal ion indicators like these acid-base indicators the clear definition for this acid-base indicators is that with the change in PH values that means the hydrogen ion concentration in one form to the other it can change its corresponding color.

Similarly this particular metal ion indicators such as we know one name particular you should remember Eriochrome black T sometime these are mostly name attached as a very commercial name but it has some origin definitely and you see this particular part is chrome is not due to chromium but is due to this particular chrome that means the color generating function.

So this Eriochrome black T what it does because it has again this particular and important azo function. So this Eriochrome black T can change its color that means in one form when the metal ion is not present that means in terms of the PM the negative logarithm of the metal ion concentration it can vary its different colors. So in absence of this metal ion this Eriochrome black T definitely it is in the solution because the compound which we get like your methyl orange and methyl red they are solid powder compounds they are solid powder which are soluble in ethanol.

So in a mixed solvent medium ethanol water medium we make the typical solution for solution measurements. Similarly Eriochrome black T can also be dissolved in alcohol to get the corresponding solution and in absence of that metal ion that means in a when the metal ion is not binding to your this indicator it has one particular color and when it is bound it has a different color.

So what this azo function can do over there so we just simply know this in this particular form that azo function can have the loan pair of electrons. So when these loan pair of electrons are donated to the metal ions center so only one of them can form a coordinate bond to this particular metal ion and it has some other groups attached to it this azo function can have the groups like this X and Y.

So it can form a good (())(7:19) to the metal ion this metal ion is nothing but your MN plus, so it can form three bonds together to this particular metal ion and we all know that this is a very useful technique when we go for EDTA titration because EDTA can compete with these particular species where the metal ion is bound to the ligand and when it EDTA can take up the metal ion or can make the metal ion free from in the bound form of this particular ligand we get the corresponding species as the free form of the ligand and the metal EDTA complex.

So what we see now is that the incorporation of this azo function that means the binding of the metal ion, this is also your metal ion. So your reagent if it is Alizarin so we get some reagent we name this it is Eriochrome, this chromophoric group so this can be our chromophoric reagent when we get this particular chromophoric reagent. So the species Al-L is your alizarin the ligand that is now colored.

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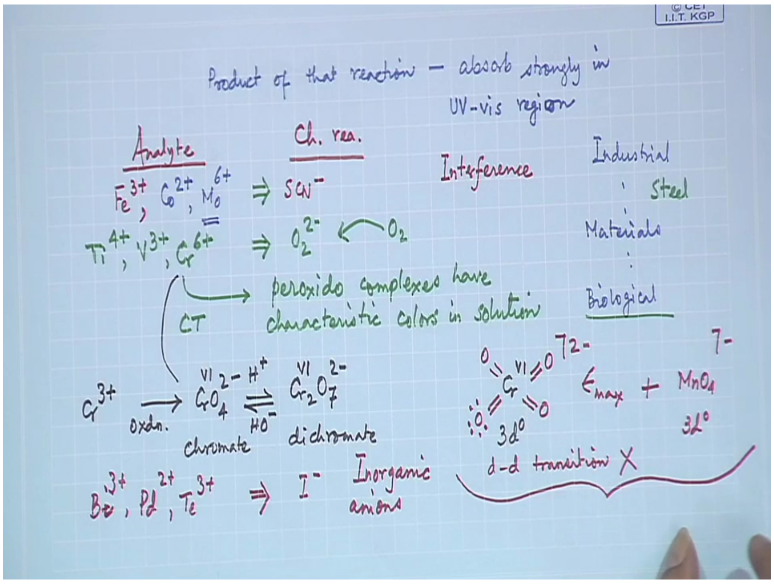

Product of that reaction – absorb strongly in UV-vis region

Analyte

Ch. rea.

Interference

Industrial

Steel

Materials

Biological

$Fe^{3+}, Co^{2+}, Mo^{6+} \Rightarrow SCN^-$

$Ti^{4+}, V^{3+}, Cr^{6+} \Rightarrow O_2^{2-} \leftarrow O_2$

CT → peroxido complexes have characteristic colors in solution

$Cr^{3+} \xrightarrow[\text{oxdn.}]{} \overset{VI}{Cr}O_4^{2-} \underset{HO^-}{\overset{H^+}{\rightleftharpoons}} \overset{VI}{Cr_2}O_7^{2-}$

chromate dichromate

ϵ_{max} + MnO_4^{7-}

3d° 3d°

d-d transition X

$Bi^{3+}, Pd^{2+}, Te^{3+} \Rightarrow I^-$ Inorganic anions

So there are large number of these species or these corresponding groups present which can be considered as the corresponding chromophoric reagent and this chromophoric reagent we can get in such a way that the product of this particular reaction product of that reaction can absorb strongly in again our most interesting region of understanding that means the UV region, ok.

So this particular case or this particular thing already we have learned so many things so if your analyte is here then chromophoric reagents these are chromophoric reagents so we can have the analyte as well as the chromophoric reagents so already we know that we can have Fe3 plus ion and due to the charge transfer transition we get a corresponding blood red coloration due to the addition of some reagent which can bind to the ferric ion which is nothing but our Thiocyanate ion.

So when this binds over there we should also be very much careful about one particular terminology is the interference due to the presence of other metal ions which can also bind to this particular anion inorganic anion which is your chromophoric reagent but gives a different type of color but it can hamper the absorption of the radiation in the UV region for due to only Fe3 plus.

So what we see that not only Fe3 plus but cobalt also in cobalt 2 plus it can also bind to Thiocyanate ion, it can also bind to Molybdenum hexavalent Mo6 plus. So whenever we use all these things for the analysis for this particular say ferric ion what we should know that when ferric ion is present and we want to use this particular method or the methodology for the determination of unknown ferric concentration the solution should not have cobalt 2 plus or Molybdenum 2 plus.

In other way what we can also state that this cobalt 2 plus if it is present alone can be determined in presence of this Thiocyanate. In similar fashion if Molybdenum 6 plus the hexavalent Molybdenum we know Molybdenum is present in all sorts of analytes that means it can be present in your steel sample to Molybdenum enzymes. So industrial sample starting from say industrial sample the steel to the biological sample which are Molybdenum enzymes.

So in between you can have different materials and all, so if all this can have your Molybdenum center and if we want to measure the corresponding unknown concentration of Molybdenum we can safely use Thiocyanate ion for that particular purpose. So this is useful for Thiocyanate.

So in a similar way we should know the responses what can be given by say peroxide ion we all know that this peroxide can be nicely converted even in your biological system by reduction of your O2 molecule otherwise this peroxide can be given to the solution as your chromophoric reagent from hydrogen peroxide or its corresponding salt or in presence of some week base.

So this can form correspondingly good peroxo compound, so you all know while we go for the detection of titanium 4 plus again it is a very good industrial sample in terms of steel sample then titanium can be there titanium as the titanium oxide. So large number of samples to be analyzed containing titanium can be handled by this particular technique then vanadium 3 plus can also be analyzed by this and hexavalent chromium 6 plus because side by side these are in the same group of the periodic table chromium and molybdenum and down you have tungsten.

So you see that when you determine molybdenum so what about chromium chromium can give you very characteristic peroxo complex so these all these three metal ions can give very useful peroxo compounds and these peroxo compounds have a characteristic color. So these peroxido complexes have characteristic colors in solution. So what we find that this particular one and if it is there that means if it is a titanium 4 plus having no unpaired electron in this T level but this is saturated with some electron it has extra electron in the anti-bonding level also it has electron compared to your O2 molecule orbitals.

So you have a typical charge transfer reaction so as we all know we have already seen that how the charge transfer complexes are useful for identification because it will have high value for your epsilon max. So we are able to produce some of these interactions for the peroxido complexes. So these chromium peroxido complexes we get a corresponding charge transfer species for this color absorption.

And one more interesting species what can be derived from chromium is your CrO42 minus and Cr2O72 minus that will see right now that if we go for this chromium because this chromium in hexavalent state, this is also in the hexavalent state it is chromate the chromate anion and this is dichromate anion which can be formed from chromium 3 plus through oxidation and it has also some equilibrium with regard to your acid, so if you have acid it will go from left to right and if you put base it will go back to your chromate form.

So this chromate what we can have you see that this chromium is in hexavalent state which is a 3d0 system that means no unpaired electrons is present over there for its corresponding d-d transition. So we will not have any d-d transition for it but instead of that this chromate ion which is bound to for convention we can write double bounded one or arrow it, for this which is 2 minus.

So if there is any charge transfer transitions because these will have filled electron pairs in their P levels, so if the charge electronic charge can be transferred from O to chromium we get a good charge transfer transitions such that we can have an appreciable magnitude several thousands of this epsilon max value which will be useful for determine the unknown chromate concentration as well as the dichromate concentration.

Because very soon we will see also when we have the other component like your MnO4 minus the permanganate (())(17:09) this is also a case of 3d0 system and again a charge transfer transition will prevail over there but we will see how we can handle if both of them are present as a mixture, ok.

So we are talking about these chromophoric reagents and all these so these are typical assembly because all these things these peroxide things and also we can have this reagent as Iodide ion, so all are starting from your Thiocyanate ion to peroxide ion to iodide ion, all are inorganic anions. So these inorganic anions can be very much useful to detect some of these metal ions.

So it can react with bismuth 3 plus, then palladium 2 plus, then tellurium 3 plus so in solution mostly in aqueous solution all of them can give rise to very good coloration with these iodide ions. So what we take the example just now I told just now I told some higher that aluminum can be detected by a species which is alizarin and in all these cases what we see that your Thiocyanate, your peroxide and your iodide all are inorganic anions.

Now we will move to some reagents which are very much useful which is a typical organic molecule that is very much useful for some other type of analysis we have seen earlier.

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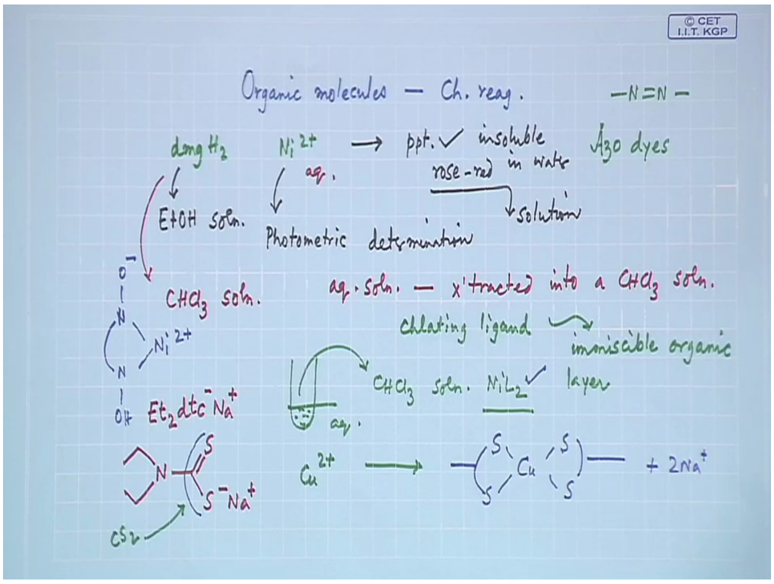

So organic molecules we can have and these organic molecules will be your chromophoric reagents. So how these organic molecules can be chromophoric reagent, one example we have seen just now that it can have a azo function and if these azo groups the azo molecules because there are large number of groups of molecules are known which are azo dyes because these azo dyes are very much useful for dying febrics, for dying different materials because these are in the category of paints and pigments because of these azo function.

So if a typical organic molecule can give rise to this particular information. So we get something where we get some colored reagent, so one such example we already discussed it will be very easy to understand by you that your dmg molecule which is useful for detection of Ni2 plus so nickel 2 plus and we all know that the combination of this dmg in with Ni2 plus in ammonia calmedium can be a precipitate.

So is rose red precipitate so calmetic estimation can be also useful but that color now we will can utilize that coloration that means in very dilute solution if we try to avoid this particular precipitation we can have this rose red coloration in solution. So once we can develop some coloration or color in solution we can measure that unknown intensity of that color related to the concentration of either Ni2 plus or dmg for its corresponding detection as a corresponding spectrometric method for identification of unknown analyte.

So when we get this particular nickel (1) 2 plus for this titration we usually get this as your photometric determination, ok so this is a photometric determination where this dmg H2 you have 2 dissociable protons you make the solution because in the laboratory we get this as available solution in a dilute ethanolic solution because initially we dissolve the solid powder is a white powder compound.

We dissolve in ethanol and then dilute with some amount of water sometimes it can be 1 is to 4 or 1 is to 5 or 1 is to 10 even that means 10 milliliter of alcohol is fine to dissolve that corresponding amount of dmg and which is diluted to 100 milliliter.

Now if you see this particular color and if some small particle because we have seen that this particular product is insoluble in water so it is insoluble in water so what precaution we should take for avoiding this precipitation of this one if we try to do this is in aqueous solution and this is in alcoholic aqueous medium.

So we should avoid that thing in such a way that we can take something where you have this aqueous Ni2 plus and we will take this is in some other solvent one such good example of that solvent is your chloroform because this is also soluble in chloroform. So if nickel 2 plus is present and we can go for as we all know as aqueous medium that means the water medium and this particular CHCl3 medium this can form two separate layers.

So that means this aqueous layer of this nickel 2 plus can be extracted into an corresponding chloroform solution of dmgH which having some chelating reagent. So aqueous solution can be extracted into a CHCl3 solution of this dmg that means this CHCl3 solution of your chelating ligand because this chelating ligand is present in your this particular chloroform and forming some immiscible organic layer organic layer that means whatever nickel you have you can use the separating fennel also or you can use something in a test tube also.

So you have this as the aqueous layer of it, if we can extract it with the corresponding CHCl3, so what you get you get a CHCL3 solution of your Nil2 that means the nickel dmg complex soluble in chloroform. So the color intensity of that so the same rose red coloration can be there in this particular organic layer and that organic layer we can put in the spectrophotometer to determine the unknown concentration of nickel in that particular species.

So what we do we do the corresponding use of this organic molecule as again some chromophoric reagent to develop some coloration? So quickly we will see two more examples of those groups which can be very much useful for our analysis one is it is the ethyl function attached to your nitrogen so it is the diethyl function so if we take diethylamine we can use that particular one in basic medium and react it with carbon disulfide to get something chelating ligand where the sulfur sulfur atoms can bind to a particular metal ion center.

So this sodium salt if we use sodium hydroxide for this preparation it is known as diethyl Et2 because these Et2 functions are present attached to this nitrogen of ethyl amine. So it is Et2 dithiocarbamate anion so if it is there this dtc minus and it is sodium. So once you name this in this fashion you should also be able to write down the name of this particular precise it is the sodium salt of diethyl dithiocarbamate dithio means you have you have two sulfur groups which has been coming from your carbon disulfide liquid which is organic liquid unlike your CO2 which is a gas.

So this particular one so what we find that this is again a chromophoric reagent which can import some color for photometric determination of other metal ion. So it can be your copper 2 plus what it can do with your copper 2 plus because this particular species this one is your SS function like that of your dmg function the dmg function we all know that it is your NN function NOH this is O minus and this is OH, this NN function is bound to Ni 2 plus, two of them are present to give you NiL2 form.

So this is there so when we have this so what we get over there is that this NN bond here you have the SS bond in same way. So this copper 2 plus forming the corresponding (())(27:02) with that with 2Na plus.

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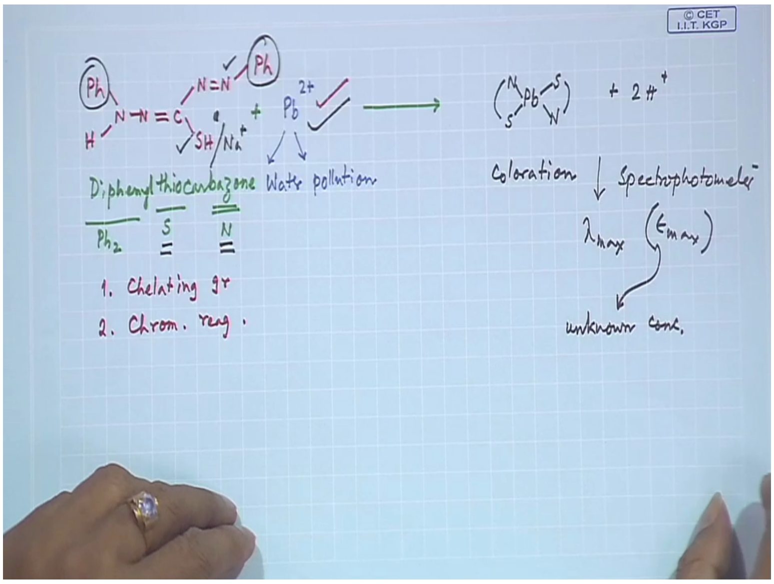

So more and more of these organic molecules can be useful for us for the determination of this and sometime we find that is not the transition metal ion but also the corresponding main group ions also the main group metal ions like (())(27:32) because we all know that (()) (27:34) is a industrial pollutant also, it can contaminate the corresponding water. So in terms of this particular technique the spectrochemical methods for analyzing the water sample for water pollution because pollution it is polluting the air so water pollution so how to determine this (())(27:56) like that of your aluminum.

So we have to choose some specific reagent which can react with (())(28:04) giving you a corresponding complex. So we take something that just now we learned something that how we can see the corresponding molecular structure or the molecule itself and then how we can name it.

Now we will do in the reverse way that we name it first that if the chromophoric reagent is your diphenyl that means two phenyl groups are present thio that means sulfur function is also present diphenyl thio and the carbazone it is a carbazone function that means you have azone function that means nitrogen is there, thio means sulfur is there and diphenyl definitely your Ph2 is there.

So we get some idea though you are not getting the information that what should be the structure that means the chelating function. So it is basically the chelating group, as well as it is a chromophoric reagent to determine the unknown concentration of (())(29:20) 2 plus, ok.

So it will be Ph then like that of our dithiocarbamate but it has H, so it is NN because this particular part we all know it is coming from phenyl hydrazine type of things.

So PhNNH2 type of thing and then when it is tautomerizing and in presence of some azo function as well as carbon and sulfur bond it is double bond C and SH and N double bond N and Ph, so these are the two phenyl functions so that is why the name is your corresponding diphenyl, so this is one phenyl function and this is one phenyl function and what we see there that it can be H plus or it can be its corresponding sodium salt.

So that immediately tells us it is a different type of corresponding (())(30:17) agent where you have this sulfur will be utilized for your bonding to that (())(30:24) center and your nitrogen that is why we have taken this the name you will not forget the name of these as sulfur and nitrogen. So if this particular one because we have to count the corresponding size of the rings so NNCS and then the metal ion center so metal ion center can be put over here, so this is the group which will be attaching to the center of the metal ion and this is another group so it will be a NS type of bidentate ligand, then another will be in the opposite direction giving rise to your Pb forming a base (())(31:00) of like this plus if this protons are available we will get 2H plus.

So our basic idea is to develop some coloration by using chromophoric reagent is that you develop some color out of this and then we use your spectrophotometer to estimate the corresponding color intensity that means we measure the corresponding lambda max and we will take the help of epsilon max such that we can determine the unknown concentration, ok whose concentration is this this is the concentration of this (())(31:46) 2 plus.

So we have to correlate everything and all this thing we will see in our next class that how we can have more than one metal ions also taking the example of the mixtures how we can handle, ok thank you very much.