Course on Analytical Chemistry
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Module 4
Lecture No 19
Spectrochemical Methods - I

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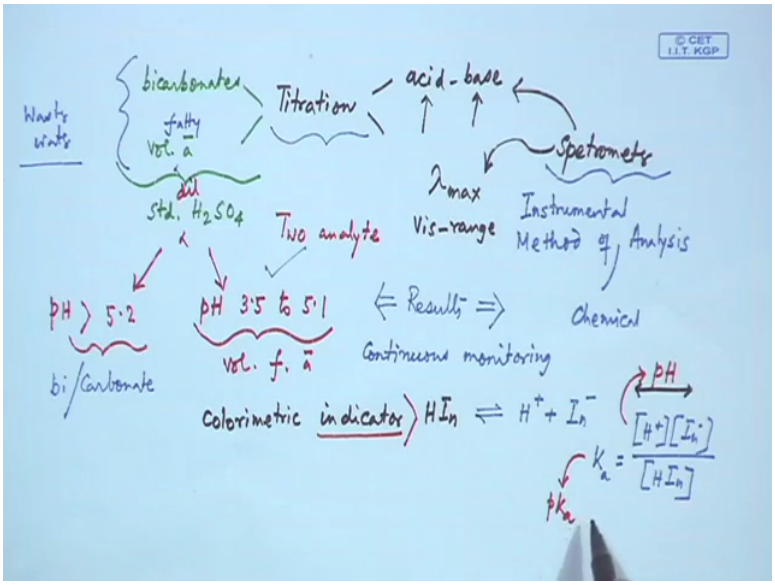

Welcome, good afternoon to everybody we are still continuing the spectrochemical methods of analysis where we are talking about something which we can consider as a titration and we want to detect that particular titration when we introduce a spectrometer or a spectrophotometer to identify where the titration gives us the corresponding endpoint, so in case of a typical acid-base titration where we know visually we can do by corresponding manual titration that both the acid as well as the base they are colourless so we cannot use for this particular titration to detect its endpoint by a spectrometer or a spectrophotometer.

So what should be the solution that particular purpose and also sometimes we can see that a complex situation may arise as we are talking about the corresponding titration of a sewage water where the titration you can perform of where we can have both the bicarbonates as well as the corresponding acids. So volume of the acids or the amount of the bicarbonates we can go for titration so these we can analyse by using a standard sulphuric acid solution that means a known solution of sulphuric acid can give rise to that particular acid so the corresponding volume of the fatty acid, see this is fatty acid so the mixture of the fatty acid so this is after degradation of waste water.

So at some point we are talking about these things but right now what I want to tell you is that how we can move or how we can design how we can think of a particular titrimetric method with the help of an instrument because when we introduced a spectrometer we can call it as a method involving the instrument so instrumental method of analysis or chemical analysis so that is a huge area of interest and that can itself be a separate course where you can talk about the corresponding instruments but in this particular course I will try to introduce some basic aspects of all those instruments and how can design.

If you know what is your problem because the problem is the how you treat the waste water and how you decompose the waste water to get 2 components and you want to analyse the corresponding concentration of those analyte in terms of the corresponding fatty acid concentration and the bicarbonate concentration. So when you go for this particular titration using a standard sulphuric acid solution obviously it is a dilutes sulphuric acid solution so standard and dilutes, dilutes solution. So for these 2 components basically we can have 2 analyte so is a situation where we can consider it as a 2 analyte situation where we can go for a titration where the final pH that means the pH at the neutralisation point can range from 3.5 to 5.1 that means in the typical acidic region you can recall back the amount what we have utilise or acetic acid pka value which is 4.75.

So this particular case so this one if you can go for the titration this will definitely determine the volume of the fatty acids so this fatty acid neutralisation can give rise to the corresponding n point at a pH value of this 3.5 to 5.1. In another case if we go this particular one where the pH of the neutralisation point can be above 5.2 which can be for your corresponding amount of carbonate present in it.

Carbonate as well as the bicarbonate, so this particular one so whether we can go for a instrumental methods of analysis or a simple manual volumetric acid-base analysis but we can compare is their results so if we compared the results using a spectrophotometer will just discuss today only in that how we can introduce an instrument how he visually detect corresponding endpoint for this titration of this 2 mixture of the analyte or the components.

So the results if the results are comparable we will find at this manual titration is very good and we can go for analyzing these things but a continuous analysis or continuous analytical process for this would not be that much feasible for us because in industry when you have the reactor and the reactor is responsible for your wastewater treatment with in an anaerobic condition so bacteria degradation is producing bicarbonate and fatty acids, so if we go for a

continuous monitoring so in that particular case it is the instrumental method which will be beneficial and that instrumental method can give rise some important information. So what we can do now is that because this spectrometer can detect the lambda max value if it is coloured in the visible range Vis range okay in the visible range.

So to how to get that particular thing is that we will introduce something which we call as a color changing indicator or a colorimetric indicator so that particular indicator which is again a weak organic acid and that week organic acid as we all know now that it can also remain as the chemical equilibrium what we are talking so far if it gives rise to the liberation of the corresponding protons and the and ironic form of that indicator as In minus and if both of them are in equilibrium that means since the corresponding Ka value for these would also be the corresponding concentration that means H plus and In minus and undisassociated weak acid which is HIn.

So in a similar fashion or in a similar way we will introduce something as a colorimetric indicator which can be a very weak acid and which can go for this disassociation. So this we all know that this particular one will be related to that particular compound in a medium say it is aqueous or non-aqueous medium and have a very characteristic pka value for that molecule and which will be related to that particular pH value as we all know like your acetic acids the corresponding relationship between the corresponding conjugate base and the free acid. So in this particular one if we choose something as the indicator having a characteristic pka value and that indicator can change its color in a particular pH range so this pH range is of interest to us which will be directly related to the pka value of that basic indicator.

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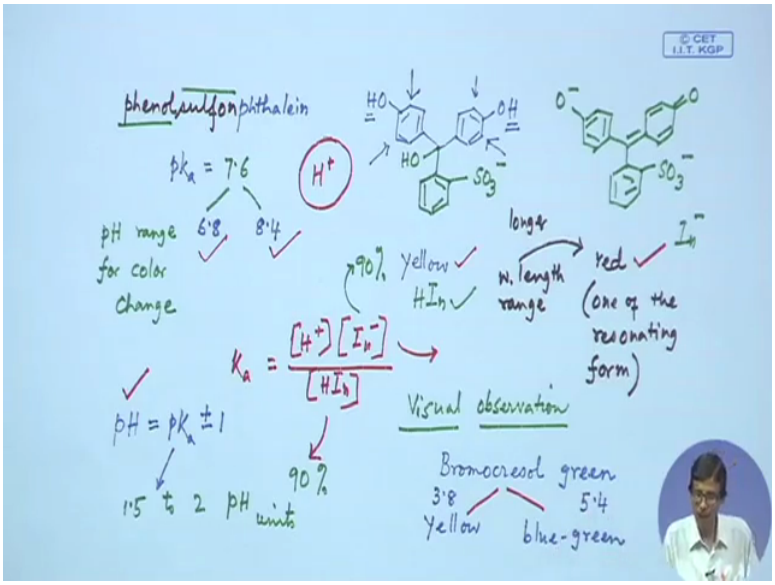

And if we see that in one case we get that a particular example of that (())(9:19) weak acid we will take something we all know about the phenolphthalein and we all using that particular phenolphthalein but here we will talk about something very much related to that which is name is phenol then we will talk as sulfon so just remember the name very well so because the name will tell you something that phenol then sulfon and phthalein.

So this is one such indicator which is related that of your phenolphthalein and this particular one the molecule is nothing but again related to your phenolphthalein molecule. What you have you can remember it nicely, this is your phenol part so we have the phenol and something which is coming from the phthalic acid or the phthalein part is your this part and we have this (())(10:44) part over here and this group when it is SO3 minus it is the sulfonephthalein and when it is carboxylic acid this your phenolphthalein, okay so by the introduction, why I am talking about this?

This that means sulfonic acid group what says the carboxylic acid group is the fundamental difference is that its corresponding pka value for this acid disassociation constant these are all weak acid like your acetic acid so these are phenol based molecules, so this phenol based molecules can undergo dissociation and it can have the corresponding color change range so the pH range for the color change related to the corresponding pka value so if we take because this can also be experimentally determine quantity we can determining his pka value of this molecule I knowingly corresponding concentration at different buffered pH values of the medium. So this pka value is 7.6 and what we get in all these cases so whenever we get

the pka value should be some rule at how we can tell about the corresponding color change range.

So the pH range for color change that means the color for the HIn and In minus, these 2 colours will be different. So in this particular case this is 6.8 to 8.4 so when the pH is less than 6.8 the molecule in solution can show its corresponding color in acidic form that means this form this is the corresponding phenol form so this is the acidic form and this acidic form has a yellow color. Then this yellow color is for corresponding HIn, if you are HIn is present over there and through deprotonation what happens it can go to other form which is colored.

So the colored form again SO3 minus unit is there and this remain as O minus but this particular one with the removal of this hydroxide group as well as the corresponding phenol is going to a quinone form this quinone from you see that more number of this double bonds the CO double bond and CC double bond are there so there is a conjugation so the corresponding absorption in electronic energy can be in the longer wavelength region that means the low energy region so as a result we get this particular compound showing a red color we call sometimes we call something as something is red (())(14:03) that means it is going to a longer wavelength range. Since it is going to longer wavelength range and it is in the red so this is can be a one of the quinonoid form.

So another resonating from is that this can also be a quinonoid form so the (())(14:24) is more between these 2 ring so this red is one of the resonating from. So one of the resonating forms, what we get for this? So we get one is yellow so yellow is this one at a pH value of 7. and another is red is 8.4. So we can define in that way was that particular corresponding indicator for any acid-base titration because we are talking about something where the change in is in your H plus concentration, when we talk about the corresponding redox titration we will see that the E0 value can also do something related to the oxidized form and the reduced form.

Here is the corresponding protonated form that means the acid version and the anionic form that means the corresponding conjugate base giving rise to a different color. So what we have seen that here if you have a Ka value which was your H plus and your In minus, so this will give rise to your HIn and that basically give rise to the corresponding concentration of these and corresponding concentration of that. So what we get over there is your HIn, this is your HIn that is written over there and this is your In.

So when you do the titration visually so you have the visual observation for the manual titration so visual observation, so visual observation what we get for this is that, what is the color of this species and what is the color of that species. So when they are present mostly at a concentration of 90% this particular color of this species that means the yellow color will be dominating over there and when this is present at 90% of that anionic form so red color will be dominating so that corresponding ratio that means 10 is to 90% or one is to 9%.

So we get that the ratio this is corresponding the pH value is in the logarithm function so we get one unit change so there will be that corresponding pka value for this can give rise to the corresponding color change range which will be plus minus 1 so that is why we get a value one unit less than the corresponding pka value and one unit more in that of your corresponding pka value will be your range for the color change. So whenever you have a particular compound we immediately know its corresponding Ka value as well as the pka value and indicator range will be there it can vary not is going to up to 2 units it can vary from 1.5 to 2 pH units.

So the color formation what is happening over there we can detect nicely and all other indicators which are related to this molecule also because phenolphthalein is related to this particular one similarly another one molecule which is bromocresol, so this bromocresol green where we have the substitutions suppose you can have substitutions the bromine substitutions at all those positions in this particular ring, what happens then?

So if we have the beer corresponding beer groups over here your Ka value will be changing so your pka value will be changing and since the pka values changing your pH will also be a different one so that is why is bromocresol green like that of your phenol sulfamethazine can change its color into to the green itself tells us that you can have a color which is blue green and another one which is similar to that of the previous molecule which is yellow.

So HIn color for bromocresol green will also be yellow but the corresponding anionic form that means the form which is giving you the extended conjugation that means your energy values are changing in that particular way which is blue green in color, so that is why this color change for this particular range is different and the corresponding PK value is giving something and its color change pH is from 3.8 to 5.4. You see the change what we can introduce so there are several molecules like these and people are trying for that also that how you can change the corresponding range from 6.8 to 8.4 to 3.8 to 5.4 because our neutralisation point where we have the endpoint.

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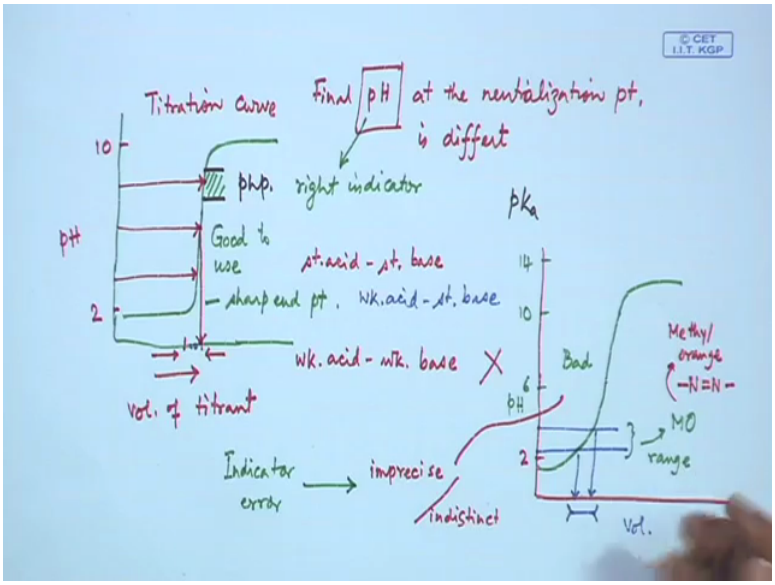

So at this particular endpoint we have the corresponding difference in all these values where the final pH at the neutralisation point, neutralisation point is different. So since this particular pH value is different for different acid-base combination for this titration so we have to use different indicators and that how you know that we can have a corresponding indicator and how you choose the right indicator. So we must have some good knowledge about the final pH for the endpoint of a particular titration.

So this pH basically is changing for a considerable range, what we know that the titration curve if we follow to a low value of pH to a high value crossing the particular endpoint, so what we get this corresponding thing for this particular plot against pH and pH is starting from say 2 to say this is 10 then 12 and 14. So this particular case when we have a corresponding change in this color so when we have this steep rise is particular titration curve so in this titration curve when there is a steep rise in this change so what is the particular pH we should look at these pH values, so these pH values are characteristics for this particular titration which can be a strong acid strong base combination like hydrochloric acid and sodium hydroxide.

So any of those discussed indicators can be used over this to indicate the corresponding sharp endpoint but as we all know that if it is not a strong acid strong base combination what happens that we just go for the rising of this particular part and is basically not so sharp that in this particular range is less, if you go for a weak acid strong base combination and finally the weak acid or weak based combination. For a weak acid weak based combination weak base combination this vertical lines the size of this vertical lines is very less so we cannot use

a good indicator that is why all these no indicator or available indicator is there which can be used for this titration where we do not have the steeply rising part of a titration curve.

So what we will do that the pH change over a minimum volume of the titrant because this is the volume of titrant we are adding so volume of titrant. So if this is very sharp you see this much change in volume, so this is the changing volume of this only small volume, so this much small volume change of the added titrant. Since we are talking terms of a low pH range then in the acid in the conical flask and in the burette you have the base so when we are adding so due to the small addition of that particular base your steep rise in the pH value take place and it is crossing the corresponding PK value of that particular indicator.

So we know that this particular value which will be the close to that 6 to 8 value, 6 to 8 if there is there in the 6 to 8 range, so your phenolphthalein can be a good one so you have the indicator range so this is the corresponding indicator range for the phenolphthalein and therefore phenolphthalein is a good indicator to use for this particular type of titration where we get a sharp endpoint, okay.

So this is therefore a very interesting thing to know that how good the plot is but if we move to a different titration and we know the example for that also is your corresponding value for this one where it is changing from less than 2 it is the pH value of 2 to say 14 so in between you have 6 and 10 okay so 6 and 10 but this plot is something broadened and like this and if we go for this sort of titration if it is not like this one this is not sharp and even it is for this particular one and if we use another indicator which is methyl orange we abbreviate as MO, so is methyl orange if we take orange is related to again its corresponding color and it has a good azo function which we all discuss once again which is the chromophore responsible for its color absorption.

So most of this azo compounds or azo molecules are coloured so this is giving rise to that particular color so what we see that in this particular case even for the strong acid strong base condition or any other one that means the weak acid strong base combination, weak acid strong base titration and if you are this range is coming over here only you see this is very much vertical and horizontal one is very sharp and is not much volume change so one drop of this change. So this change is coming from 1 or 2 drops of this addition for this particular sharp change but here you see the volume required for this is more.

So this volume this much volume for the volume of the titrant is much more so use of this particular range which is the corresponding MO range that means the range for the indicator methyl orange is not good therefore we label it as a bad to use because what it can give you that the detection is not very much distinct therefor we can have imprecise or indistinct determination or indication that means which is indicated. Indicator is indicating your endpoint so if it is not very much perfect or not very much right one we can label it as imprecise or indistinct change in the corresponding pH for its color change.

So this corresponding equivalent point will not be detected nicely because as per this curve what we get, we get this responding actual equivalent point so this is actual equivalent point we are trying to detect by the use of an indicator where it is changing its color but you see the difference this point to that point is only within the range of 1 drop of that particular titrant what is being added but in this case is it is in this particular case it is not it can be millilitre so this particular millilitre range of error will be (())(28:51) if we use methyl orange as the indicator so that will not give rise to or we cannot afford of this particular type of titration and who will consider this particular one for a indicator error.

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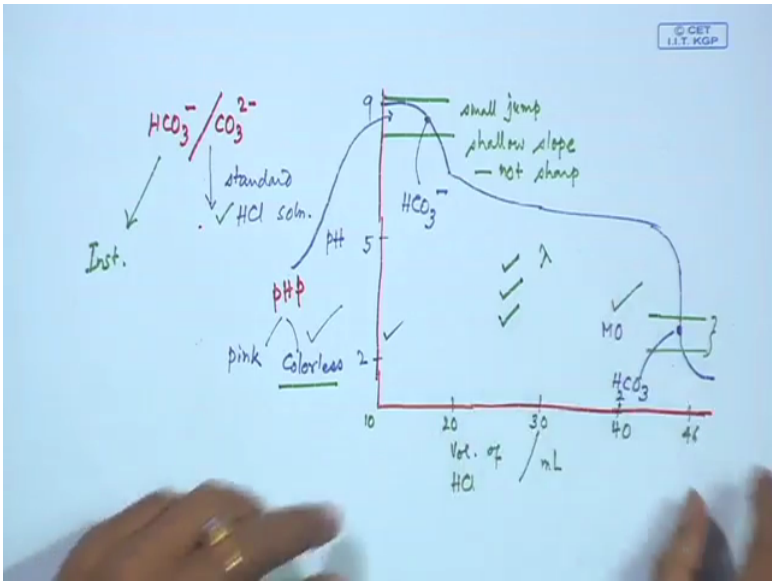

So the right choice of that particular indicator is important and how do we lose that particular indicator of this titration is also important and when we have this like the previous examples what we are talking earlier is your the mixture that means if you have a carbonate mixture and we are trying to determining both carbonate ions and the bicarbonate ions into the mixture and in that particular case what sort of plot we basically get because always we should keep in our mind the corresponding titration curve. So this particular titration curve as

we move so this will be titrated by standard hydrochloric acid solution, so that particular one when we titrate and if we see by looking at corresponding change in the pH values.

This is 2 and this is say 5 so if we get that and this particular one is not a very sharp one but is going like which is a broad one and when it is going and moving and moving and up to this particular point is giving a very good change. So what we get there is that corresponding volume of this acid what you are adding in millilitre so volume of HCL what we are adding in millilitre, so it is 10 it is not showing 0 to 10 so from 10 how it is changing and this is basically 20 then 30 then 40 and between 40 and 46 actual value for that this is 30, this is 20 and this is 40. So what we see that this particular point what we get over there is your corresponding indicator what we can use so this is one indicator range and this is at the lower pH values.

This is another indicator range what we get, so for all these cases what we can use is your phenolphthalein so if you use first phenolphthalein what will happen so phenolphthalein we all know the color change range is close to that of 8 7 – 8 in this particular range so this is the corresponding range for using pHp which is your phenolphthalein and this phenolphthalein can give rise to a corresponding change at this change in pH the jump is very small.

So you have a small jump for this pH change and so you have a slope which is a shallow one we call it as a shallow slope therefore the detection of that particular point is not sharp what we can detect anyhow in this particular range if no other indicator is available we can use this particular phenolphthalein indicator to detect this particular endpoint but the most useful one we will discuss afterwards is the corresponding use of the instrument or a potentiometer for the potentiometric titration but this one is very sharp and this range as I discussed just now is your range what we all know this particular range, this particular range is useful your methyl orange.

So if you add the methyl orange you get and for this combination at this point this is the midpoint we get the for the corresponding formation of carbonic acid H_2CO_3 and that can be detected for very small addition of hydrochloric acid a sharp change for this and the color changes also very much sharp using methyl orange and here also the corresponding 1 the corresponding color that means pink to colorless situation for the addition of phenolphthalein is in this particular midpoint is basically we are getting for the formation of HCO_3^- minus.

So thus we get that this you have the corresponding change so phenolphthalein originally when it is in the basic condition so when we add phenolphthalein the color will be pink and when it is changing to this particular range is going to more acidic condition have the colourless. So you do not have to bother about the use of multiple indicators so this is one such example or a good example for the titration of carbonates or a mixture of carbonate and bicarbonate by hydrochloric acid such that at one point if you start from higher pH value you can add or you can use indicators like phenolphthalein to detect this particular endpoint when it is going you keep on adding this particular one and when you reach about 30 and 35 millilitre of this addition of this acid you add methyl orange.

Since the medium is colourless there is no harm in adding the second indicator to the solution and we can detect nicely also the corresponding second indicator so that is why it is a good example of knowing the use of the indicator and use of the color. Here we have the pink and here we have the corresponding yellow to red color for this indicator also (())(35:21) color change so if we have 3 color one is pink another is the corresponding orange red and another is yellow so we will see that how different lambda values will be helpful if we consider if we try to detect the same titration using any instrumental method for this particular analysis, okay. Thank you very much.