Natural Dyes

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Lecture No. # 36

We have been studying so much about dyeing, dyeing machines, and various different types of dyes. Now, let us take a different route completely, and try to understand the role of a dyes in you know in non textile use. And one such use is finding a dye for acid base indicators. And we in the laboratory have been able to find that since the anthocyanins had pH variation, and color change from red to blue and blue to red, as the pH was altered with art of using this dye rose anthocyanin dye as an acid base indicator. So, this particular lecture is a completely non textile use of dye extract from natural source, and the rose anthocyanin extract which we discussed in great detail the structure and the dyeing properties and so on and so forth has a new role to play in this particular lecture.

So, you will appreciate that dyes are not just meant for textiles or for coloring leather of or you know making inks and prints, but they also have a different kind of role, and that role is directly related to the structure of the dye. So, let us take a look at rose anthocyanins as acid base indicator, where the rose anthocyanin dye is the one which plays the main role.

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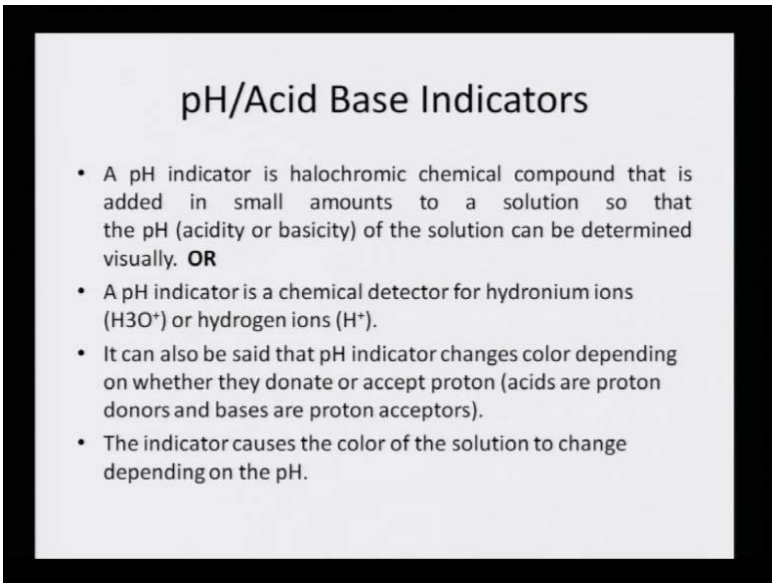

pH and acid base indicators: Let us try to understand a pH indicator is halochromic chemical compound, that is added in small amounts to a solution. So, that the pH; that is the acidity or basicity of the solution can be determined visually or a pH indicator is a chemical detector for hydronium ion; that is H3O plus or hydrogen ion - that is H plus. Now, you must have seen lot of litmus papers which change color in the pH, similarly we have different kind of halochromic chemicals, which alter with acidic or basic solution conditions.

So, we are trying to see whether rose anthocyanin can rarely fall into this category, because this reaction has to be or any dye that we are now looking are envisaging for making a pH indicator must have a reversible nature; that means, the protonation and the deprotonation must occur at the required acidic or basic condition, it can also be said that pH indicator changes color depending on whether they donate or accept proton.

Acids are proton donors, and bases are proton acceptors; the indicator causes the color of the solution to change depending on the pH. So, that is the main crux of the whole story of using a dye for being into or to be able to be valid for this kind of pH indicator work or business must have one very crucial property, and that is the indicator or the dye extract causing the colors the color of the solution to change must be affected by change in pH. And as the pH is increased it should have one color, and as the pH is decreased it

should have another color, and this can go on as many times you want to do. Only then this dye will be considered as a good model for being a candidate for pH indicator.

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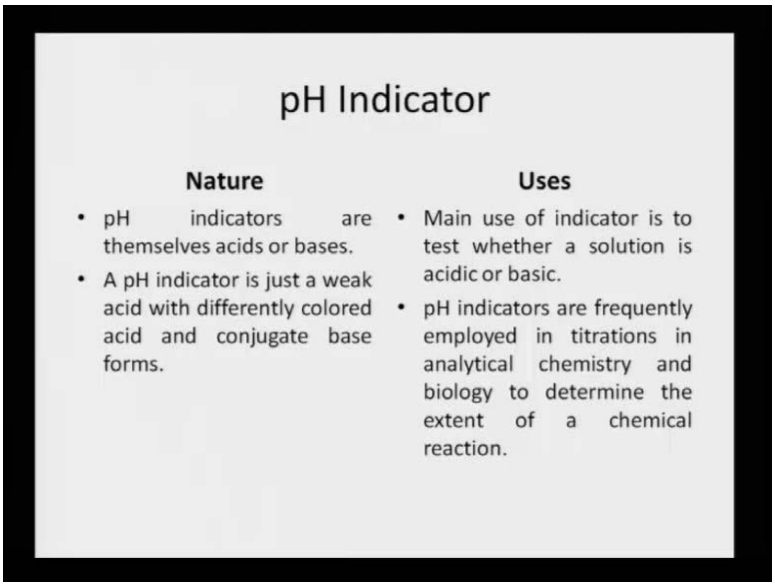

Now, pH indicator - the nature of pH indicators are themselves acids or bases, a pH indicator is just a weak acid with differently colored acid and conjugate base form when we have any acid there is a reversible reaction, and H plus goes away and whatever remains is the conjugate base. So, that is what is meant by if any molecule is protonated, at one point of time the loss of proton will leave behind the un protonated part is the conjugate base. Uses - many use of indicator is to test, the main use of indicator is to test, whether a solution is acidic or the basic.

Because we are trying to either we have a pH meter or if we have no access of pH meter, we just make use of a simple way to find whether the solution is acidic by with dipping the litmus paper; now the litmus paper has been coated by a dye which shows change in coloration. So, that is the kind of you know exercise that we wanted to do with rose anthocyanin, and we unless and until we understand what is the requirement for a pH indicator. We will not be able to see whether this rose anthocyanin actually fits into the requirement of its salient features and its salient requirement. So, the main use of indicator is to test a solution whether it is acidic or basic. pH indicators are frequently employed in titrations in analytical chemistry and biology to determine the extent of chemical reaction. So, when we see that you know we have this pH, and there is a

different color that is given on the box and we try to match the color, all of you must have at least come across some time or the other with this litmus papers or pH papers.

Now, how are they made? It is basically a filter paper, over which some dye mostly synthetic dyes are coated, and these dyes are pH sensitive under wet condition. So, once the you know you dip this pH paper into the solution it shows from the color whether it is acidic neutral or basic.

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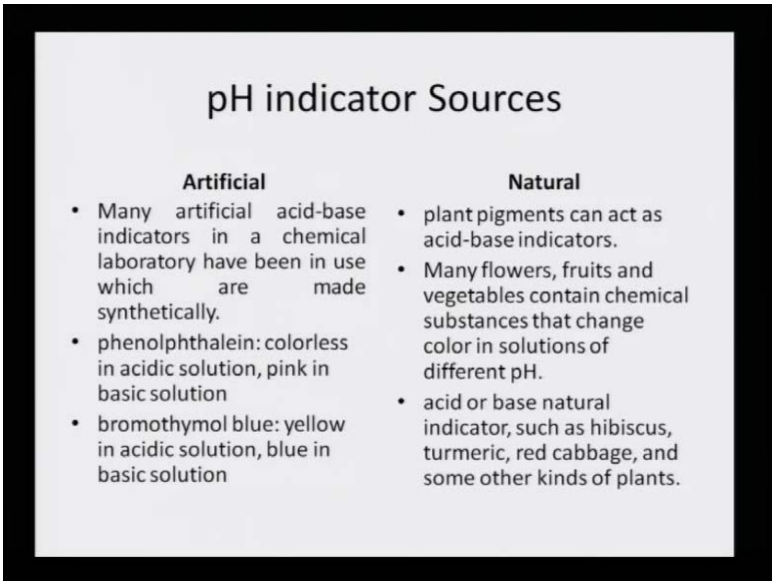

pH indicator sources: There are many, many sources; that is the dyes that have been used for coating the filter paper to make the pH paper. Many artificial acid base indicators in the chemical laboratory have been in use which are made synthetically phenolphthalein is colorless in acidic solution, but turns into pink color in basic solution, I think all of you must have done this titration using phenolphthalein as an indicator. And it when it is added under acidic condition, it is absolutely colorless as though nothing has been added, but at the point end point, where it is turn from acidic to basic it turns pink, and the intensity of pink colors intensify as the basicity increases. Bromothymol blue yellow in the acidic solution, and blue in basic solution.

So, another indicator that one uses very popularly in titrations in analytical chemistry, if the bromothymol blue which is yellow in color when it is under acidic conditions and it turns blue in the basic condition. But there have been some natural sources also from the plant pigments that can act as acid base indicators.

So, this prompted us to you know take a very serious look as as to find out which are the natural dyes that have been use for acid base indicator work. Many flowers, fruits, and vegetables contain chemical substances that change color in solution of different P H, acid or base natural indicators, such as the one from hibiscus, turmeric, red cabbage and some some other kinds of plants. So, people have explode from hibiscus flower which is an anthocyanin, a turmeric which is has a lot of conjugated system; red cabbage again is a source of anthocyanin and many other such sources had been explode as natural sources for indicators for pH.

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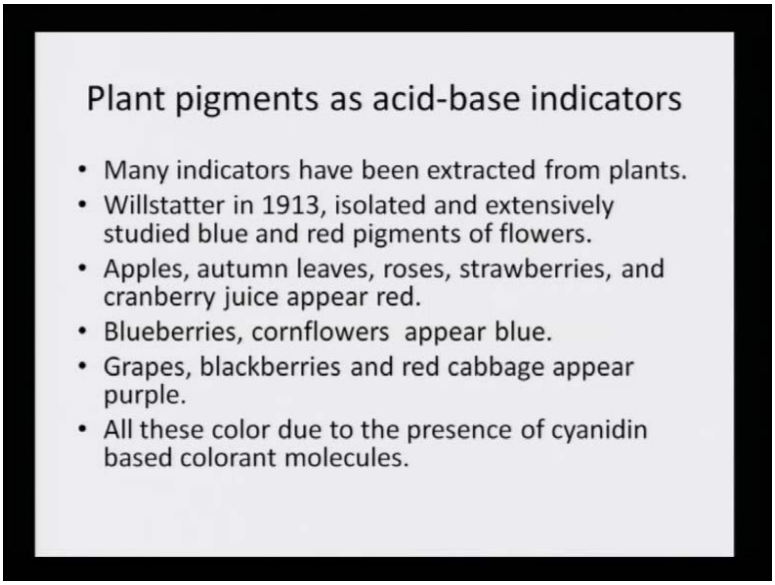

Plant pigment as acid base indicator; many indicators have been extracted from plants. Willstatter in 1913, isolated and extensively studied blue and red pigments of flowers. Apples, autumn leaves, roses, strawberries and cranberry juice appear red. Blueberries, cornflowers appear blue. Grapes, blackberries and red cabbage appear purple. All these colors due to the presence of cyaniding based colorant molecules I mean they he also found out that there is one common anthocyanin, and that is cyaniding; and that is what is responsible for this bright coloration of the red color and the blue colors. So, way back in 1913 it was possible for Willstatter to find out that you know these colorants have this kind of anthocyanin structures. And therefore, this can be good you know items or good material for pH indicator work. Some other natural indicators from other plant source, many naturally colored compounds can behave as acid base indicator, alizarin is one of the them.

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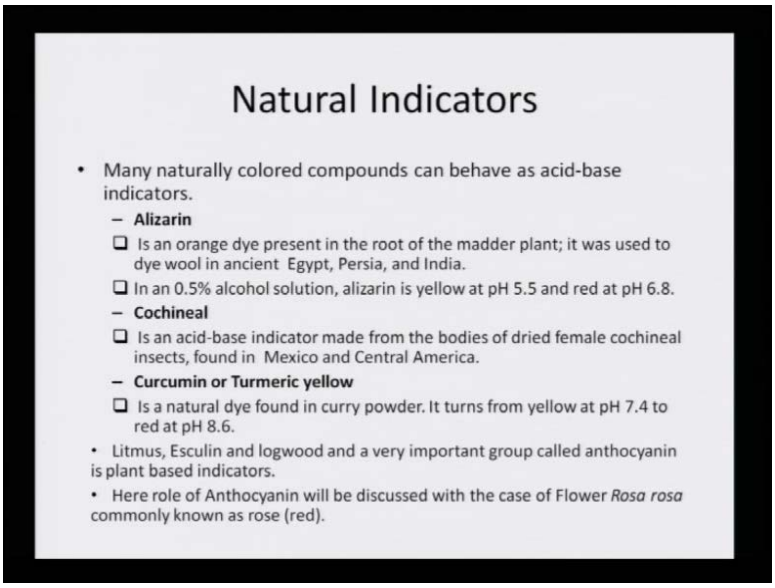

Yesterday we were talking about the anthocyanin anthoquinoid dyes, alizarin is one of the members of anthoquinoid dyes is an orange dye present in the root of madder plant, it was used to dye wool in ancient Egypt Persia and India. And in about 0.5 percent alcoholic solution, alizarin is yellow at pH 5.5 and red at pH 6.8. So, this is where alizarin has a small range it can be yellow from 5.5 and it can become red to 6.8.

Similarly, cochineal is an acid base indicator made from the bodies of the female cochineal ex insect found in Mexico and central America. So, even that was found to be a good acid base indicator. Curcumin or turmeric yellow is a natural dye found in curry powders it turns yellow at pH 7.4, but it turns red at pH 8.6, and rightly so if you recall, if there is a turmeric mark on your wrist, and if you try to wash it with the soap which is alkaline; it makes the yellow mark turn into reddish orange shade, and that is what is the this acid base indictor is all about.

Because if it shows change in color at different pH, that then it kind of falls into the category of being material which can be used as an acid base indicator. Litmus, Esculin, and logwood are very important group called anthocyanin in plant base indicators. Here role of anthocyanin will be discussed with the ease with the case of the rose of the I mean of the flower which is called rose, commonly it is called rose, but it is about botanical name is Rosa Rosa. Now the anthocyanin from this rose plant has been shown how it can be used as an acid base indicator.

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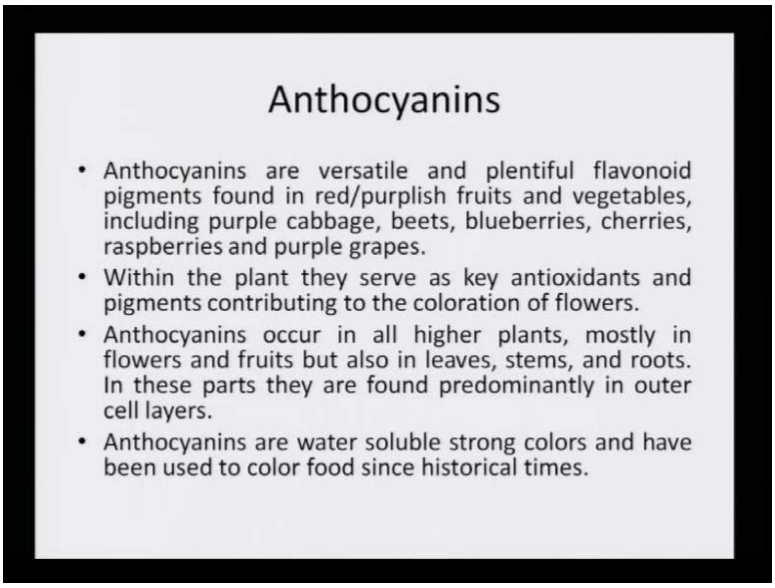

Anthocyanins are versatile and plentiful flavonoid pigments found in red purplish fruits and vegetables including purple cabbage, beets, blue berries, cherries, rose berries and purple grapes. Within the plant they serve as key anti oxidants, and pigments contributing to the coloration of the flowers. Anthocyanins occur in all higher plants mostly in flowers and fruits, but also in leaves stems and roots in these flowers they are found pre dominantly in outer cell layer, so they are in the cytoplasm. The the anthocyanins are water soluble strong colors, and have been used to color food since historical times. So, they are in the edible category of the natural dyes, and they are water soluble, so that makes it more easy for it to be used in acidic solution and in basic solution, because solubility is no issue with anthocyanin.

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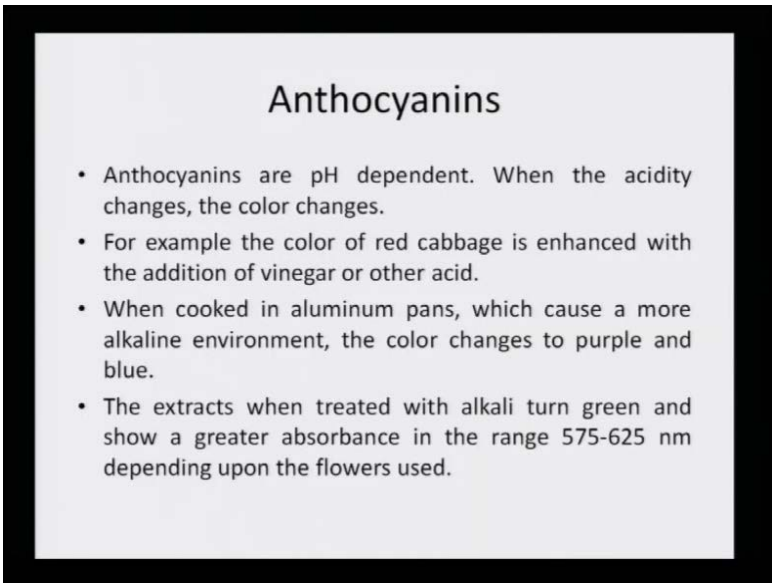

Anthocyanins are pH dependent, when we were doing this chapter on dyeing even then we had discussed about the pH dependency of anthocyanin. When the acidity changes the color changes; obviously, if it is a pH dependent dye, the acidity or the basicity when it is changing the color of that particular dye at that point of time will definitely change if a change in the pH is brought about. For example, the color of red cabbage is enhanced with the addition of vinegar or other acid; vinegar is nothing but the dilute form of acetic acid. When cooked in Aluminum pans which cause a more alkaline environment the color changes to purple and blue. So, these were indications that anthocyanins are really pH dependent, and any kind of alteration in the acidity or the basicity of the solution will make a change in the extract.

The extracts when treated with alkali, turn green and show a greater absorbance in the range of 575 to 625 nanometer depending upon the flowers used in a u v visible spectrophotometer. So, that is an indication that anthocyanin is present.

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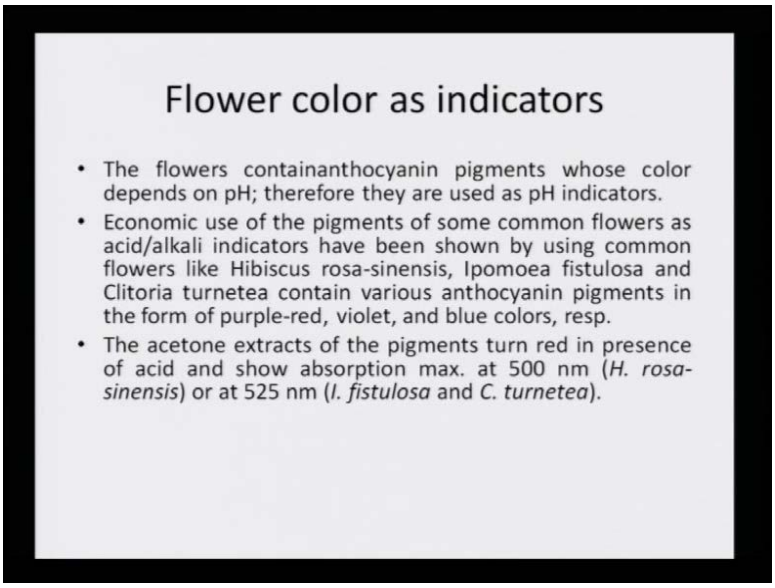

And therefore, flowers when they are used as indicators; the flowers containing anthocyanin pigments whose color depend on pH; therefore, they can be used as pH indicators easily, this we have understood.

Economic use of the pigment of some common flowers as acid alkali indicators has been shown by using common flowers like Hibiscus rosa sinensis, ipomea fistulosa fistula, clitoria turnetea and they can contain anthocyanin. So, all of them are actually anthocyanin based structures. So, what does it go to prove that anthocyanin by itself is a moiety which can have a reversible reaction when h plus is added or h plus is abstracted.

The acetone extract of the pigment turn red in presence of acid, and show absorbance as at five hundred nanometer for Hibiscus Rosa sinensis or at 525 for ipomea and clitoria. So, you see that all the blue ones are slightly shifted and show at 525, and more red one is the hibiscus one which shows at 500 nanometer; these are namdamaxes of the colorant anthocyanin which is present in the acidified or the basified structures.

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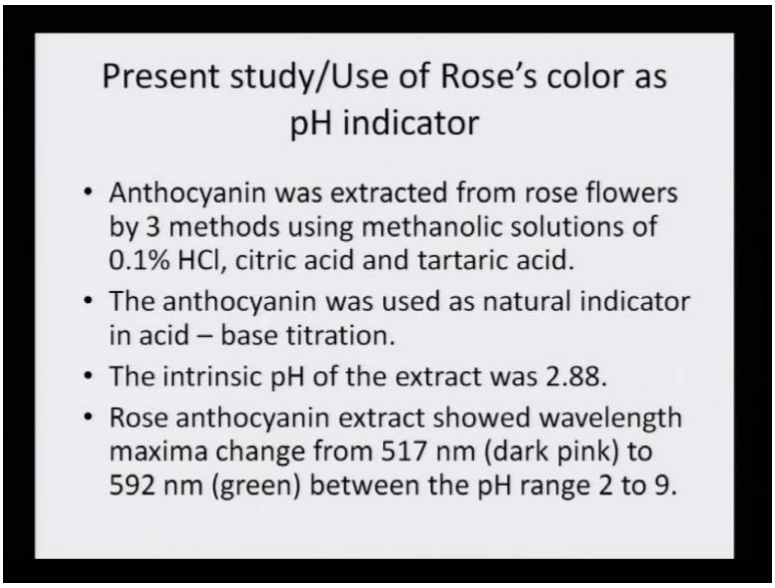

Present study where we use the rose color as pH indicator: The anthocyanin was extracted from rose flowers by three different methods using methanolic solutions of point one HCL citric acid and tartaric acid.

So, the whole idea was to show whether we can take out this colorant more effectively, if you recall we had shown that the rose anthocyanin and the Hibiscus anthocyanin extraction we had replaced the point HCL method by using citric acid. Why because we were trying to make the process of dyeing more eco friendly, here also we have tried to use three different methods for extraction of the dye anthocyanin from the rose flower. One is 0.1 HCL, second method is citric acid use, and the third method is the use of tartaric acid. The anthocyanin was used as natural indicator in acid base titration, the intrinsic pH of the extract was2.88. So, when the extract, because it is acidified extract; obviously, the pH will be fairly low, and it was found to be 2.88. Rose anthocyanin extract showed wavelength maxima change from 517 nanometer; that is dark pink to 592 nanometer which is green between the pH range of 2 to 9.

So, now you see that the range is so vast, it is going from 2 to 9; whereas, in the case of alizarin, if you recall it was only between 5.5 to 6.8; obviously, the range in this case is far beyond you know is far beneficiary as compared to the use of alizarin as a pH indicator. Though it was tried out, but wherever there is a marginal change one can use alizarin, but this really provides a big range from 2 to 9, and that we were able to analyze

on the UV visible spectrophotometer, because under the two conditions of pH. The the lambda max that was shown by the anthocyanin pigment was 517 nanometer which was dark pink in color while the basic solution at 9 pH showed a lambda max at 592. So that means, that the molecule has slightly changed, because of the protonation and that is what has created the situation to go from 517 to 592 nanometers

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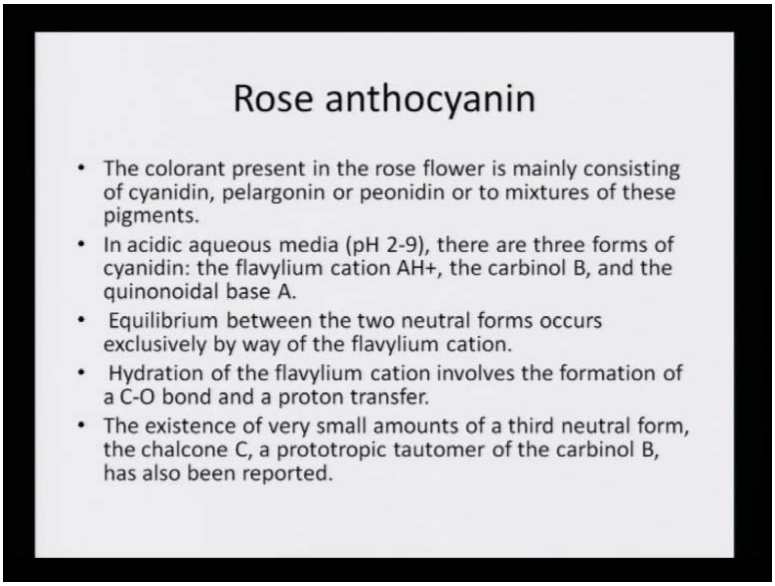

Rose anthocyanin, the colorant present in the rose flower is mainly consisting of cyaniding, pelargonin and peonidin or to mixtures of these pigments. So, you see there are three main pigments, which are participating in this acid base indicator work. And these are all anthocyanin and the anthocyanins are called cyaniding, pelargonin and peonidin.

In in acidic media that is the pH 2 to 9 which in acidic aqueous media pH ranging from 2 to 9, there are three forms of cyanidins the flavylium cation A H plus, the carbinol B and the quininoid base A. Equilibrium between the two neutral forms occur exclusively by the way of the flavylium cation. So, it is all related to structural details; flavylium cation is the main which is protonated anthocyanin pigment; then there is a carbinol and then there is a quininoid structure, which is the basic form. And there is an equilibrium between all these three structures.

Hydration of the flavylium cation involves the formation of ACO bond and proton transfer occurs. The existence of very small amount of a third neutral form that is the

chalcone C, a prototropic tautomer of the carbinol B has also been reported. So, it is very well understood chemistry, on the basis of the presence of various protonated and deprotonated structures and neutral structures that it is possible to understand, why this change in the lamdamax is occurring, because the lamdamax can only change, if the structure is changing.

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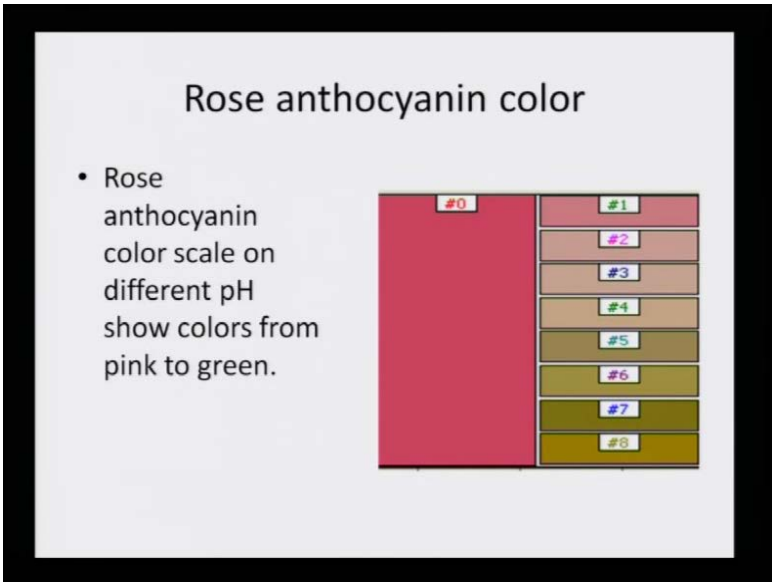

So, this is the various range of color that is possible with rose anthocyanin, if we want to took take a look at the color scale on different pH and it shows from pink to green. So, this is how we from on the colors can we tried to make this filter papers and take a scan to see the variation in pH. So, different pH will show different change and from pink it which is pH, lowest pH to it shows the it is sample number one, but the pH is 2 it is ranging to 8, which is the pH 9 and it is completely green. So, various shades of green and various shades of pink as the pH is altering.

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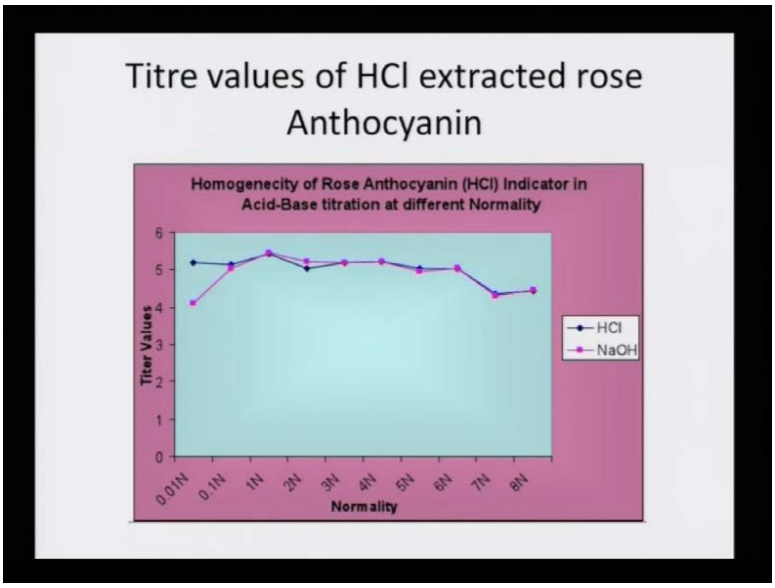

Now, when we try to take a look at the titre value of the HCL extracted from the rose anthocyanin; we see that as we go on there is a homogenecity of anthocyanin HCL indicator in the acid base titration at different normality, when one normal HCL and one normal NAO H is titrated the change and changing back of the color of the indicator.

Just the way, we were able to use anthocyanin, just the way we were able to use phenolphthalein, a synthetic source of indicator, it was possible to use a rose anthocyanin and the change occur from pink to green and green to pink whenever acid or base were altered. So, with 0.01 normal, 0.1 normal, 1, 2, 3, 4, 5, 6, 7, 8 normal it shows a consistency of result.

You see it is important to evaluate different types of normality for both these solutions of HCL and NaOH, then only we can say that the titre value should not alter. If the titer value is altering that means, the indicator is not working effectively. Now in order for the indicator to work effectively, the titer value should remain almost similar or almost constant; and if you see that you know below 0.01, they show a variation, but from 0.1 onwards you see up to 8 normal solutions, they have similar values of titre value.

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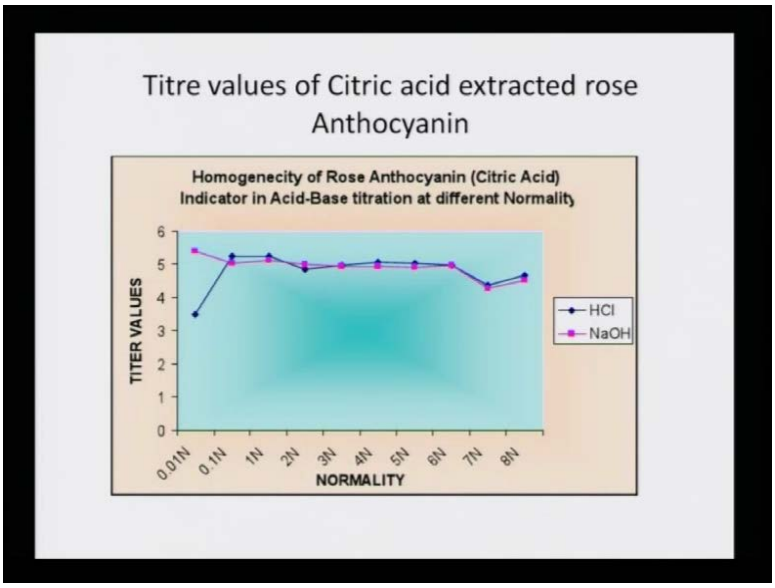

Even when you know the the extract was it was extracted with citric acid we wanted to see, whether this extract now has the same functionality as what was shown by the HCL extracted rose anthocyanin. And we found that the homogenecity of rose anthocyanin extracted by citric acid also can act as a good acid base titration indicator with different normalities of HCL and NaOH. In order to if we able to prove whether this is good extract, whether citric acid is creating any problem in in its acting as a pH indicator can only be proven, if we use these differently extracted. Remember we I we discussed the fact that three different types of extractions were carried out; one was with 0.1 HCL the second one was with citric acid and the third extract of the rose anthocyanin was done with tartaric acid.

So, do they give the same product, does the product have same functionality, when it comes to acid base titration, then only we can say that it is a versatile indicator in the range of two to nine pH, and it we have shown the color variation that from pink it will turn to green, and that will be the ultimate. And once it is acidified at the green stage, it should go back to the pink again, then it is considered as a good acid base indicator.

And the citric acid extracted anthocyanin also showed very similar and close results for from 0.01 to 0.1 to 1, 2, 3, 4, 5, 6, 7 normal solutions of HCL and NaOH. The third exercise that was done in order to show its versatility was to look at the tighter values for

the tartaric acid extracted rose anthocyanin and it was found that with different normalities it did not show similar results.

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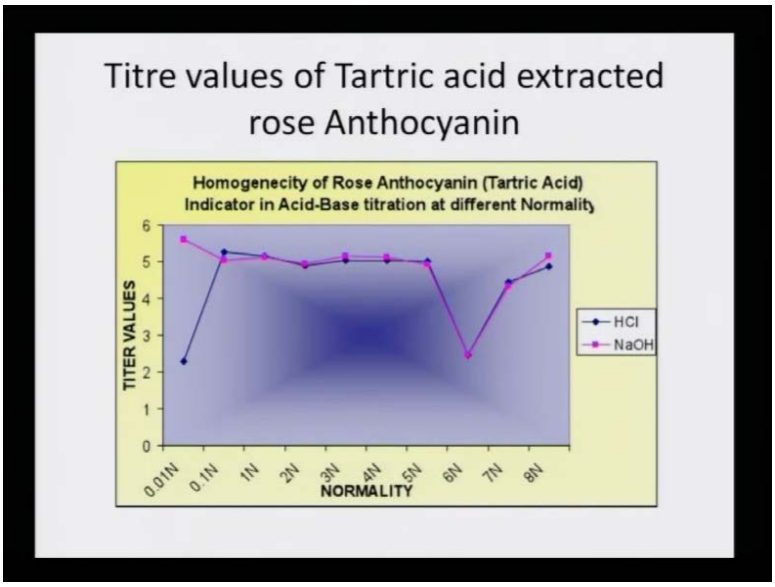

Now, you see that that means, the tartaric acid extract at you know, nine sorry six to seven normality solution is again although it is showing similar results, but there are mild variations, and these variations are not very desirable. So, that is why we came to a conclusion that extraction with citric acid is almost equivalent to at extraction with point h 0.1 normal Hcl, and these two extraction processes are very, very similar, are going to give us very similar type of rose anthocyanin, and this citric acid or Hcl is only keeping the acidic level of the extract as 2.88 and is not interfering with the chemistry of the cyanadines and the (( )) and so on and so forth.

So therefore, we come to one very major conclusion the tartric acid is not one of the desirable acids, but never the less it is also showing a lot of you know similarity in the values of the tighter values when Hcl normal 0.01 normal, 0.1 normal, 0, 1, 2, 3, 4, 5, 6 have been used.

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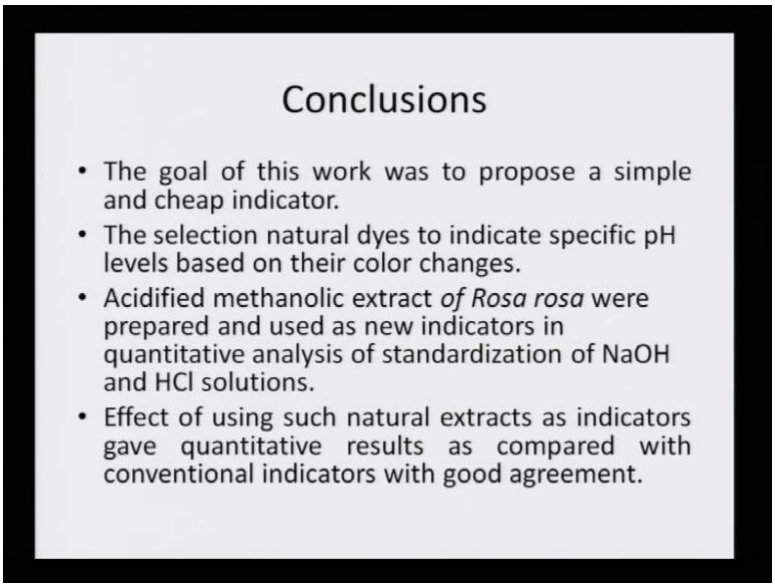

So, in conclusion, we can say that the goal of this work was to use have a have a non textile use of this rose anthocyanin; is it possible to make a use of this such a indicator and a simple and cheap indicator from the anthocyanin was proven and shown that it is possible to make pH indicator out of rose anthocyanin extracted by 0.1 Hcl or citric acid. The selection of natural dyes to indicate specific pH levels based on their color changes; and we found that it works under the pH range of 2 to 9, which is a fairly good range of pH.

Acidified methanolic extract of Rosa Rosa flower were prepared and used as new indicators in quantitative analysis of standardization of NaOH and Hcl solutions, because these are the standard titrations that a person needs to do in the laboratory in the analytical laboratory. So, can it replace phenolphthalein, because phenolphthalein is a synthetic pH indicator can a natural dye be used there, and the answer is yes. So, we have tried to show that effectively, it can be used such as natural extracts can be used as indicators, and they give quantitative results as compared with the conventional indicators, and the results are in good agreement. Because the final aim of the of finding another use for a dye is whether it is fulfilling all the criteria of a good indicator, if it is doing so it is a good candidate to be used for pH indicator work.

Second thing is what is the kind of pH range that it can cover? In case rose anthocyanin, the pH ranges from two to nine, which is a fairly good range if we try to make a

comparison with alizarin, where the pH range was only very small - 5.5 to 6.8 or for that matter even cochineal was given very slow small range; when the range is very small, the use becomes very limited, but if it has a good range, it can use for acid base titration very easily, because the color change also can be noticed. In this case the color change was so apparent from pink shade to green shade, it gave such a beautiful range of color that one could actually be able to make pH paper out of it, and that exercise is a worthwhile exercise, because there are pH papers available in the market and but those are made out of synthetic dyes.

So, now here is a candidate of the rose flower extract without any purification that is required to isolate these anthocyanins the three different types of anthocyanins. The main function is the structural flaminium cation, the carbinol and the quenonoid base, which are the conjugate base of the flaminium cation. So, you know every acid has a conjugate base and the equilibrium, as the acid is added to the quenonoid base it moves towards flaminium cations structure, as the you know, hydroxide is added to the flaminium cation, it moves towards the quenonoid base. And in the process there is a intermediate neutral molecule which is the carbinol molecule.

So, it is all dependent on the chemistry of these three structures, which are a part of the acid and base chemistry, and that makes it a good candidate for being a pH indicator or being an acid base indicator. So, with this, we have come to an end of this chapter, which was related to using dyes for a non textile purpose. And I am sure that this has given you an insight about the possibility of using a natural dye for this purpose, thank you.