Natural Dyes

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Lecture No. # 11

Till now, we have been learning about natural dyes or vegetable dyes; that how harmonious they are towards nature, and therefore they are very friendly to man. And in order to be able to use it more expensively and just keeping them at pair with the synthetic dye it is important to standardize these natural dyes or the vegetable dyes.

Now I gave you an example yesterday that if the same plant is grown by organized forming in north eastern India and say for example the indigo, and the same indigo plantation is carried out in somewhere in the Madhya Pradesh, and the same indigo if it is grown grown in the southern part of India, all the three indigos will have a different kind of indigo tin yield in their product. Now the plantation remains the same, but the content of indigo tin in all these three regions were found to be different, and the reason I gave you was that this is because of the climatic condition firstly; secondly, the soil and water condition, and third is the forming condition. So, because of this variation in three parameters the dye content in the plantation varies.

Now if a supplier if a manufacturer of natural dye is suppose to collecting material from different places then he needs to standardize them. So that it does not give any variation in color, because if the dye percentage is low or high, it would reflect on the dye.

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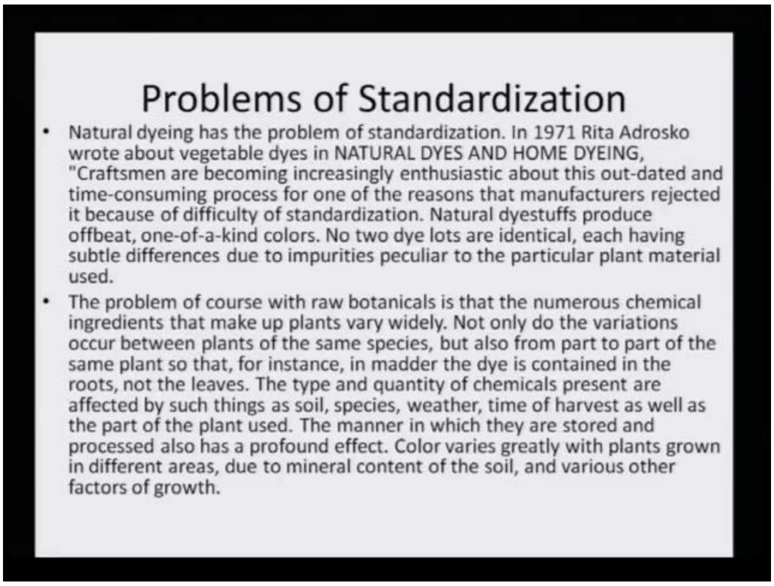


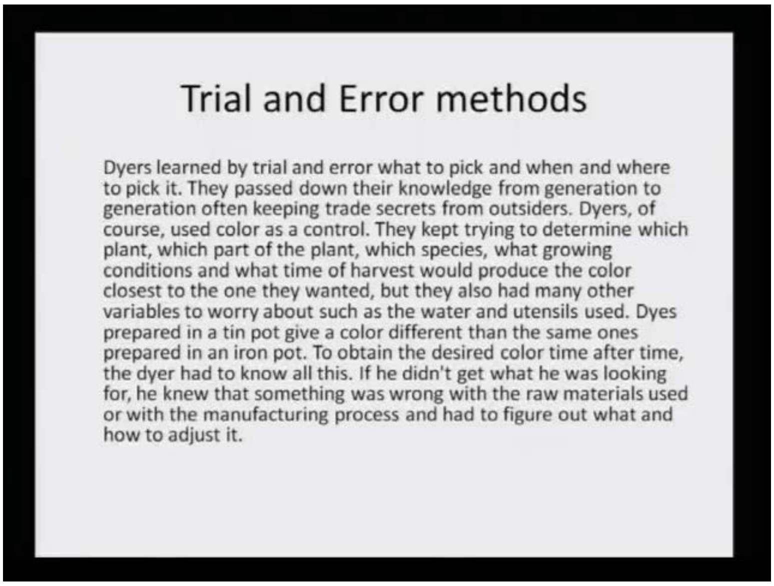
So, therefore, it is important that standardization of vegetable dyes is also understood very clearly. Now this chapter will be dedicated to the standardization of natural dyes. What are the problems that one encounters while doing the standardization?

Natural dyeing has the problem of standardization. In 1971 Rita Adrosko wrote about vegetable dyes in natural dyes and home dyeing book. Saying that craftsmen are becoming increasingly enthusiastic about this out-dated and time-consuming process for one of the reason that manufacturers reject it because of difficulty of standardization. Natural dyes stuff produce of the one-of-a-kind color. No two dye lots are identical and have very subtle differences due to impurities peculiar to the particular plant material used.

So, the craftsmen who were having this kind of difficulty first thing is that is it is a time consuming process; second thing is that there is no standardization available. Every time it is a new color or new hue or new stain, and therefore, no two dyes you know lot would give the same identification, because dye content were different, now that created a lot of difficulty for the craftsmen.

The problem of course with raw botanical is that the numerous chemical ingredients that make up plants vary widely. Not only do the variations occur between plants of the same species, but also from part to part of that of the same plant, so that, for instance, in madder the dye is contained in the roof and not so much in the leaves. The type and quantity of chemicals present are affected by such things as soil, species, weather, time of harvest as well as the part of the plant that is being used. The manner in which they are stored and processed also has a profound effect. Color varies greatly with plants grown in different areas, due to mineral content of the soil, and various other factors of the growth.

So, I gave you this many factors which actually affect. What are these factors? The soil factor which species is grown where, the weather, the time of plantation and so on and then also because you know the way it has been the part of the plant. They also which is being used for dye extraction is also very important. Now I will give you one example as what is given here madder rules have maximum dye content stem has a little less and leaves have the least of dye content, but at the same time the same manner if we try to use a rule then the plant will be gone. So, along I been emphasizing that one should look at the plant parts, which are renewable, which can grow again. If we destroy the root then the plant will be gone or will be died therefore, we have to concentrate on the plant parts which give optimal dye content, but are also equally renewable or can be regenerated. (Refer Slide Time: 06:43)



Trial and error methods were the once which was tried initially, although now there are standardized methods available, but initially there were lot of trials and error methods that were tried. Dyers learned by trial error what to pick and when and where too pick it. They passed down their knowledge from generation to generation often keeping trade secrets from outsiders. Dyers, of course, used color as a control. They kept trying to determine which plant, which part of plant, which species, what growing condition and what time of harvest would produce the color closest to the one they wanted, but they also had many other variables to worry about such as water utensils used and so on.

Dyes prepared in a tin pot give a color different than the same ones prepared in an iron pot. To obtain the desired color time after time, the dyer had to know all this. If he did not get what he want was looking for, he knew that something was wrong and the raw materials used or with the manufacturing process had to figure out what and how to adjust it.

So, you see that there were many, many parameters that the dyer had to keep in mind; it is not only the plants species; it is not only the plant part that should be you know specified, but a thorough study of the time of harvest, when is the best time, when is the plant having the maximum dye content, because plants also go through their biosynthetic path way. Dyes are not, it is not like a factory that it is synthesize just in a day; it has its own gradual bio synthetic process. So, if the harvesting is done at the initial stage of the bio synthetic path way of the dye a molecule - the dye content; obviously will be very low. Therefore, it is important for the dyer to know when to choose, what to choose, how to choose, and then the procedure that harvesting condition the soil conditions all put together, what is the optimal condition for farming was first established. Then after that was established then the second thing that came to their mind was when is the optimal conditions for harvesting.

How should these plant parts be stored, because even storage can cause deterioration in colors? So, the whole purpose of growing the plant would be lost, if the entire plant cannot provide the dye content. If suppose it is stored badly and there is a fungal growth on it; obviously, the color content will go down. And therefore, it was important to figure out all these important parameters and to optimize them.

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An effort to standardize natural colors: In an effort to standardize colors dye plants were often cultivated rather than gathered wild. Many were grown commercially. In order to get standard color from particular species of dye plant 400 years ago, the farmer would have had to have worked empirically by selecting and cultivating plants that produce a dye that got closer and closer to the color he wanted. He would also have had to have tried growing the plants under different conditions to see what type of soil etcetera is required gave the which would give him the best results. When he reached his goal, he would then have had to have maintained the results by always growing the same species under the same conditions using color as his control. By keeping good records and adjusting the variables, he learned by experience how to obtain the desired color, but it was not easy and exactly the same each time. Even today it is not possible to precisely match color from batch to batch, not even with synthetic dyes.

So, you see this task is very tedious, but with the hit and trail methods by error and trial methods these were tried to optimize to the best of the capability of the farmer or the dyer. To produce fully standardize eco-friendly vegetable dyes from potential herbal vegetables sources, evaluation of the color - natural color for eco-friendliness, standardization of processes for various textile, substrates large scale production and development of commercial natural dyes, there are certain specification that need to be followed. And they are we will see in the next slide that what are these specifications that needs to be kept in mind while standardizing any natural dye from any natural source, because this law holds good for all of them because none of these were initially standardize.

So therefore, if it has to be used in commercial processes one cannot do all these trials all along then what would happen from batch to batch the color will vary. And if the color varies from batch to batch that is not acceptable to the consumer.

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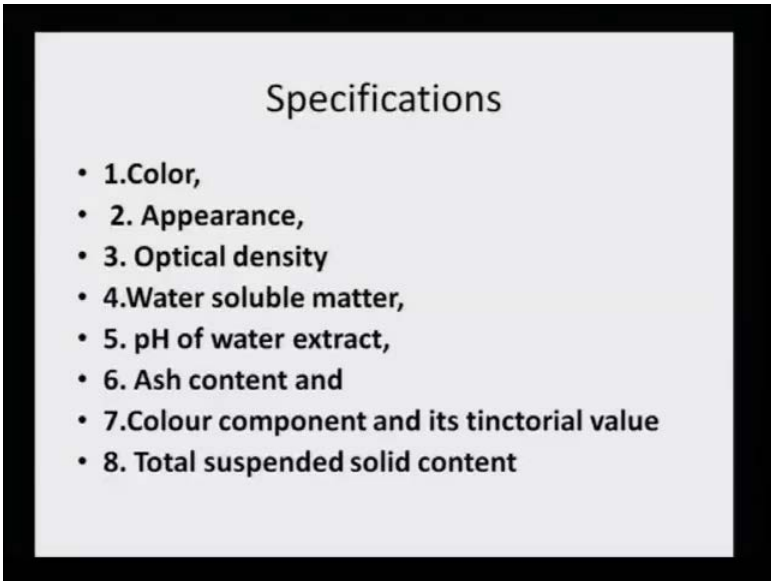

So, these specifications that need to be followed are color, appearance, optical density, water soluble matter, pH of the water extract, ash content, and color component and its tinctorial value, and the total suspended solid that are present when the dye is extracted and dried. So, mainly you will see that there are eight things that need to be kept in mind.

First is the color; that means, what is the color we are concentrating; suppose if we taken example of madder madder has a color between orangish red to orange. So, this color has to be fixed. Now appearance, whether it looks like dull color or bright color will also be kept in mind. Then the optical density, I told you in the last few lectures when we were doing the fundamental methods of evaluation of dye stuff, how UV visible spectrophotometer helps us to find out the dye content and the dye content is reflected by the optical density; that means, there is a direct relationship between the dye molecule concentration and the absorbents - it is directly proportional. So, it is easy to a certain the optical density.

Water soluble matter - now if a dye has to be used for dying and most of the dying processes 99.9 percent are carried out in water. The dye should bare minimum that should qualify to be a water soluble material; otherwise it does not fit in to the category of dyes. pH of water extract - if the pH is very high or if it is too low, it will become either very alkaline or very acidic respectively. And such adverse acidic or alkaline conditions are not good for the fabric. It will eat up the fabric. So, one has to keep a track of the pH of the water extract of the dye. Then the burning of that ash content gives an idea about what would be the kind of carbon, hydrogen, oxygen, nitrogen, sulphur content in that.

Color component and its tinctorial value: What is the colorant molecule? We just learnt about the structures of various types of colored molecule - indigoid dyes and anthroquinoid dyes and anthracynadine dyes, dihydropyrin dyes and so on and so forth, caratinoid dyes. So, these are basically the color varies because of the structure, and the structure has a auxochrome component and a chromophore component to be a responsible for the color content. So, that adds the tinctorial value to it and then when this dye is totally extracted in the water solution a lot of other plant material also get co extracted, and therefore they you know create a lot of total solid - suspended solid content, so all that would be also matter.

Now if the total suspended solids are higher than much, much, much higher than the dye content, the dye will get lost in that. If the if the dye is more and the suspended solids are lesser in ratio then it is considered to be a good dye. So, these are a few points which need to be understood very clearly and these are the specification color, appearance, optical density, water solubility, pH of the water extract, ash content, color component and its tinctorial value, and the suspended solid content - these are eight specifications which need to be taken into consideration while standardizing the natural dyes.

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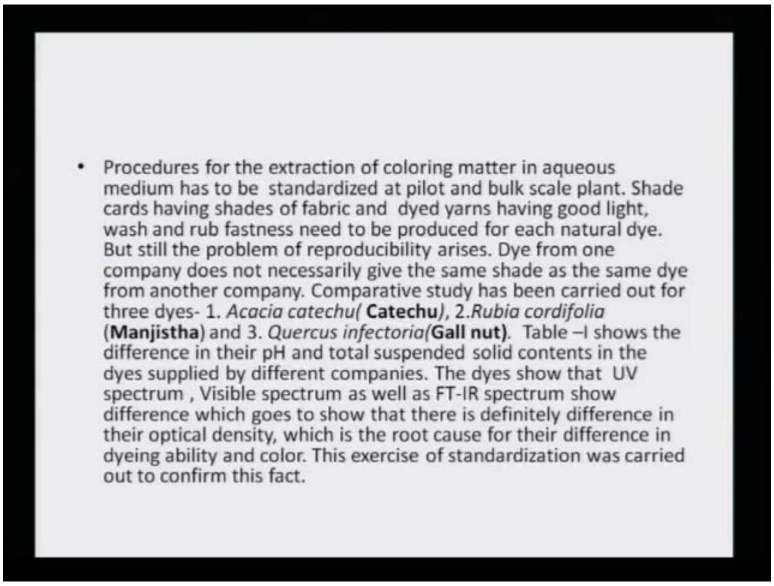

Procedure for the extraction of coloring matter in aqueous medium has to be standardized at pilot and bulk scale plant. Shade cards having shades of fabric and dyed yarns having good light, wash and rub fastness need to be produced for each natural dye. But still the problem of reproducibility arises. Dye from one company does not necessarily give the same shade as the dye from another company. Comparative study has been carried out for three dyes; that is Acacia catechu that is catechu cutch; the second one is Rubia cordifolia or Manjistha, and the third one is Quercus infectoria - a Gall nut. Table-1 in the next slide will show that the difference in the pH and total suspended solid contents in the dyes supplied by the different companies have been tabulated. The dye show that UV spectrum, visible spectrum as well as FT-IR spectrum show difference which goes to show that there is definitely difference in their optical density, which is the root cause for their difference in dye ability and color. This exercise of standardization was carried out to confirm this fact.

Now these particular works was extensively done in our laboratory, because we were trying to help two different companies to standardize. Now the way we started doing it was from these analytical machines which are ideally used for evaluation of the dye content. Now only when the dye content are the same, the color and the tinclorial value and other things will match, if there is an this difference in the UV visible spectrum, if there is a difference in the IR-spectrum there is bound to be difference. Secondly, we it was also observed that the pH and the total solid content also made difference that is why among these parameters or specifications for standardization pH of also plays a very vital role, because some of the dyes are very, very pH sensitive.

So, there is the color intensify at a particular pH, but it changes to another hue color particularly the anthocynadine dyes. What happens is that under acidic conditions, there are more towards the red and under alkaline condition they become blue or purple. So, this has to be kept in mind that if we are looking at anthocynadine dyes and the extraction must be done under acidic condition, but that acidic condition should not be very high. Otherwise, if it is very high acidified solution it may corrode the fabric. So, all these things have to be kept in mind three examples where taken from two different companies. In order to where a check, whether these dyes have the same value or they have different value, if they have this same value they will give same result, but if we have different values; obviously they will give results and that is what we observed.

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TABLE- I COMPARATIVE STUDY OF pH and TOTAL SUSPENDED SOLIDS

Dye	Sample code	pH	TSS
Manjistha	Man-1	7.28	787.6 gm/Kg
	Man-2	6.04	112.9 gm/Kg
Acacia catechu	AC-1	6.46	180.0 gm/Kg
	AC-2	6.99	178.7 gm/Kg
	AC-3	5.34	74.3 gm/Kg
	AC-4	5.33	
	AC-5	6.16	426.5 gm/Kg
	AC-6	6.05	244.9 gm/Kg
Quercus infectoria	QI-1	4.33	107.2 gm/Kg
	QI-2	4.32	179.5 gm/Kg

Now in this table, where a comparative study of the pH and the total suspended solids is shown. Manjistha - two samples from company-1 and company-2 are labeled as man-1, man-2 had different pH – now one had 7.28 and other one had 6.04 which is fairly different. The total suspended solids in Manjistha one sample was found to be 787.6 gram per kilo gram at the same time the other company sample showed a very low total suspended solid. So, now I was just telling you the example if the total suspended solid is higher than the dye or if the total suspended solid by itself is a very high value obviously the color content will get over shadowed.

Similar examples were seen in Acacia catechu. Here of course, there were samples drawn from other sources also and we tried to evaluate six different simples - AC-1, AC-2, AC-3, AC-4, AC-5, AC-6. AC-1 and AC-2 were from the two different companies in we were trying to help in standardization. The pH did not vary too much that only in the case of AC-3 and AC-4 and pH was 5.34 otherwise most of the pH(s) were in the region of 6 or 6.99 to 6.05.

Now when we started looking at the total suspended solid, we found that there was a fairly a big amount of the variation. There was very high TSS - total suspended solid, in the case of the sample number five and the lowest suspended solid was value was 74.3 for the case of the third sample. So, you see the variation itself goes to show that they are not similar; they have lot of major differences, and we will go and understand this as we go along.

The third example was the different Quercus infectoria or the gull nut which is used both as dye as well as natural modern. Now these were from two different companies - the same two companies and the pH was more or less similar. And it was found that was total suspended solid; however, varied in the first case it was 107, whereas in the second case it was about 179. So that was the differences that cause them to act or dye differently.

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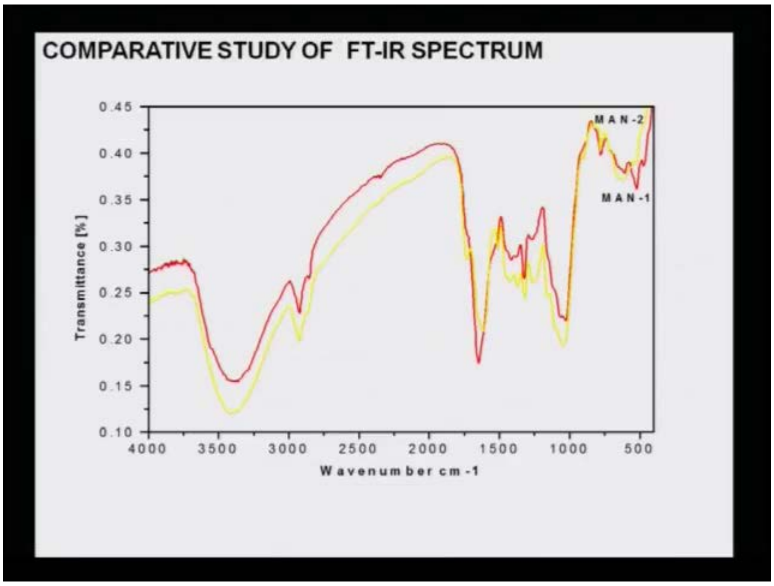

Now if we try to look at the comparative study of FT-IR of just the majesty's are simple that is really acquired Rubia-cordifolia sample you will see that the red spectrum is given by the first sample and the yellow sample is given by the second sample hence there are minor differences in the spectrum now as I told you that FT- IRs spectrum tells us about the functionality. So, therefore, in the majesty's dye.

There variations of some of the components being in a different proportion we had learnt when we were doing manjistha or rubies cord folia that it has anthraquinonoid dyes and among the anthaquinonoid dyes it has six different types of components which makes the anthaquinonone that this manjistha or dye as a dye now because of the variation in these six components that dye is showing different FT-IRs spectrum which differs only marginally now if we look at the samples of the catechu if even there all the six samples show minor minor differences which is an indication we saw that there were changes in the pH they were changes in the total suspended solid.

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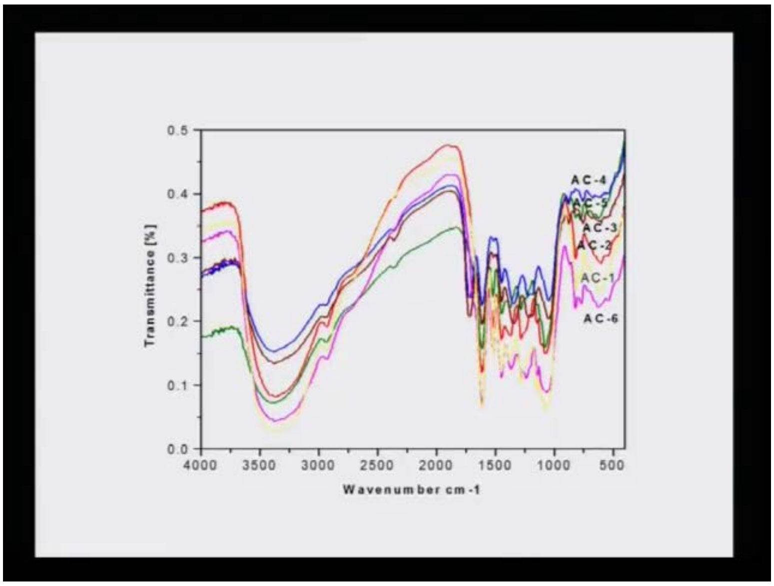

And now, there are changes also in the FT-IR spectrum. Now, this is the example for quarks inventorial in three different spectrum or the two different samples showed that there are differences where it is not totally super impossible. If suppose the quarks infector samples were identical the spectrum would have been totally super impossible and there would not have been any differences, but by enlarge they have similar groups.

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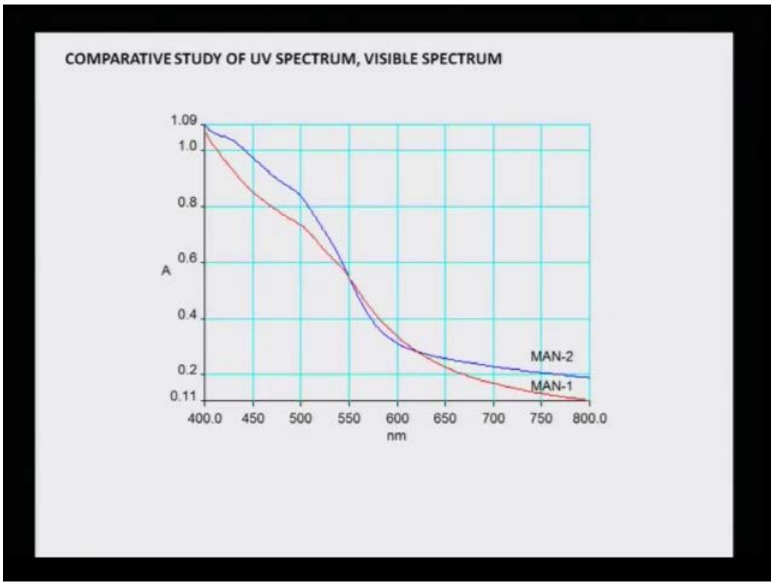

And, So that dye content may only be the variable in this case when they tried to look at the visible and u v spectrum of the same two dyes in the case of Manjistha-1 and in the case of Manjistha-2, the there are obvious differences in the UV in the visible spectrum because this is a spectrum, which is recorded between 400 to 800 nano meters and that is the region for visible light because we can only see or of all the dyes fall in that region

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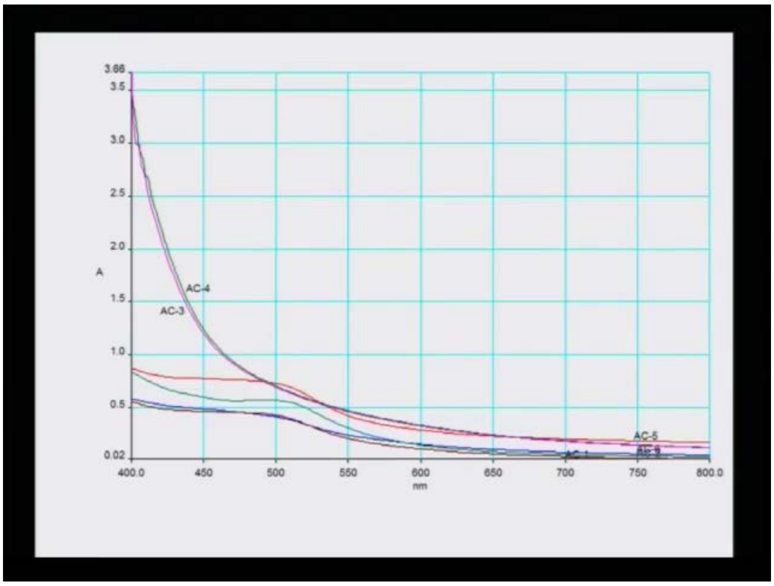

Now when we try to look at the six UV visible spectrum of the catechu samples you will see that there are very obvious differences in the case of the samples one to six. And these differences are reflected on the visible spectrum of these this dye also, and therefore, we know that there are very, very discrete differences in the samples.

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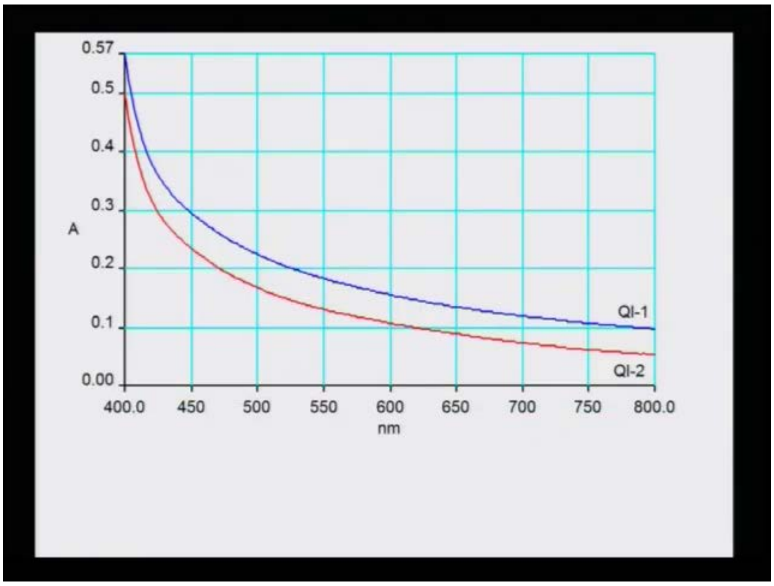

Similar examples where seen, but here the only difference that was we can see in the case of Quercus infectoria QI sample 1 and QI sample two that more or less the spectrum that is shown or the graph that is shown between 400 nano meters to 800 nano meter is showing a very similar pattern. There are no difference in the pattern, except the optical density is higher for the sample number 1, and the optical density that is the absorbance is slightly lower for the sample number two. And this is very, very obvious one this visible spectrum of Quercus infectoria.

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So, when we try to look at the quality standards of the vegetable dyes. Quality standards for vegetable dyes vary widely, so it is necessary to first contact an importer to find out what they are looking for. The problem arises with standardization of the colors as no two dye lots are identical, technicians in the pharmacology, food and textile industry loathe this lack of consistency. Now you see, if there is so much of variations then it is kind of hard too as you know we able to use it for a specific purpose, suppose if a consumer or if a dyer has to have a shade and he develops a procedure that I will take this much of dye power and this how the procedure will go on and with further for this much of fabric weight of this much dye should be optimum. All that will go heavier, because there is a no you know recipe that will fit it; today the recipe is fitting tomorrow is lot, when he gets the dye - it will not fit, he will again have to vary.

So, it was necessary that some kind of standardization must be done by the manufacturer and provides that standardize data giving mainly the optical density information - particularly and the pH and the total suspended content. So that when the dyer is developing the procedure he knows how much dye he should take for a particular weight of the fabric, because dye is always taken with effect to the weight of the fabric and that kind of relationship must be known to the dyer from the manufacturer then only the vegetable dyes can be called as standardize dye and then only they can be use as easily as what the synthetic dyes are used of the shell. So, it is important that there are some things that need to be carried out very carefully.

And those for attempting that the there is a repeatability of shade. The textile dyeing is recommended procedure as mentioned in the earlier chapters which I have motioned in earlier lecture, but strictly a few things must be followed in order to keep other parameters in time. Use of only stainless steel dye bath; second is water hardness should not be more than 300 ppm, and the third thing is that yarn water ratio should be 1 is to 20; these are basic fundamentals for the dyer to observe and then if we gets the manufacturer certified dyes from the manufacturer then that will be fit in to these system and still some repeatability can be obtained. Reproducibility of shade is a big, big criteria when we work with natural dyes or vegetables dyes.

We just saw one example, I had fleetingly mentioned that when the dyers were making observation they found that if the dye is extracted in tin part, it shows different hue color and if it is extracted in iron pot it gives different color. Now why is that happening? What causes the tin presence of tin and iron to make the same dye look so different in their extract? Now these are certain things which we will learn while we are doing mordanting. And that is why the there is an attempt for stainless steel dye bath uses. Because if we use stainless steel dye bath then there is no effect of this stainless steel on the dye extract, whatever metal participation we observed in the case of tin or iron pot was eliminated. So, at least one hurdle was taken care of.

Secondly, if the water is hard then the miscibility of the dye and its adherence to the fabric will be affected by the presence of this calcium-magnesium salts which are a part of hardness of water. So, it is important that when dyeing is carried out; it should be done with soft water. So, there should be a procedure by which the hardness should be reduced or at least kept under check and the hardness - water hardness should not be more than

300 ppm. And also the yarn to water ratio is a very important criteria. If I make a very concentrated solution even that is not very good because dye aggregates will form; if we make very dilute solution then no color will adhere to the fabric, it will be so light the several times that dye will have to be done. So, there was an optimization of the dye to yarn or dye to fabric ratio which was set it should be somewhere between 1 is to 20; sometimes for certain dyes which have good dye adherence, it can be reduce to 1 is to 15, but definitely not less than that. So, these are certain factors which need to be kept in mind.

And so, if I have to conclude this chapter, I would say that several things have to be kept in mind, but the main thing that needs to be kept in mind is the optical density. And that could be only obtained from the visible spectrum of the dye.

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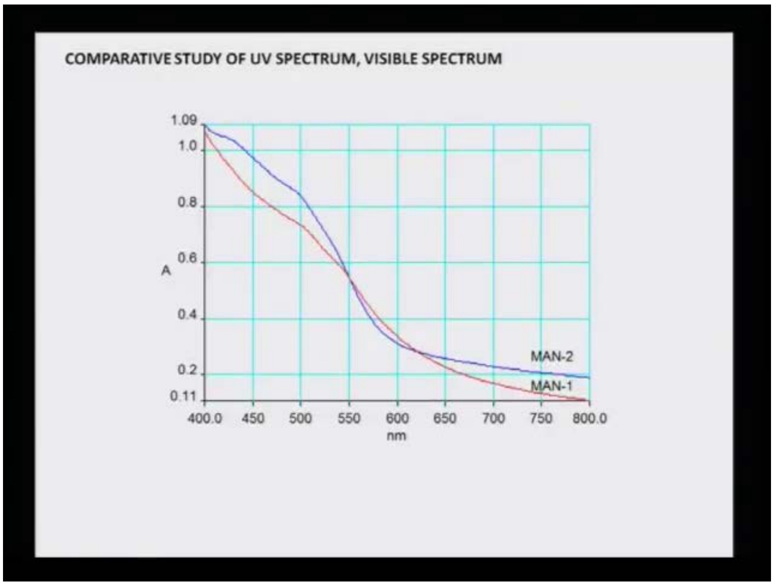

If we have example, I will go back again to Manjistha, see in this case the optical density is also were different not only did the spectrum show different you know line graph where there were ups and down at different positions that is the tuffs and the peaks were one different point showing that the chromophoric are slightly different in each case and that was only possible because of the difference in the six components of the Manjistha. Because they were not in equal distribution, suppose if we have in a class - six boys of the same height then we say that the average height is so much, and therefore the optical density becomes like an average; I am just giving an example for you to understand, but the same thing if there are boys of different heights then the average will show a different value it will not be the same as the average of the previous case. Similarly, when you know concentrations of these six components eluzarin, perfurin, pseudo perfurin and so on and so forth are different then they the the graph also looks different or the spectrum looks different and the spectrum looking different means its optical density is also different.

Also you will see that the absorbents value for the Manjistha sample 1 is slightly lower than the Manjistha sample two; that means the dye content in these two samples is also different. So, the pH was different, the total suspended solid were different and the visible spectrum was different the FT-IR spectrum was different - so that is how we try to do the standardization or vegetable dyes. All the instruments, the pH is evaluated with the help of a pH meter, total suspended solid is also evaluated by the method that you know the dye solution is evaporated and the weight before and after are taken and that is how one tries to evaluate the total suspended solids similarly UV visible photo spectrometer evaluates the UV visible spectrum, the FT-IR machine evaluates the FT-IR spectrum and all put together give us an idea that the dye is similar in its dye content or dissimilar. And if it is dissimilar, what is the kind of ratio that must be enhance for sample 1 to become like simple two. So, these are the optimization processes which need to be backed up by instrumentational methods.