Atomic and Molecular Absorption Spectrometry for Pollution Monitoring

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Lecture – 30
Boron, chloride

So far we have discussed different aspects of spectrophotometry, but never ventured into specifics. Now in the last slide I had shown you number of parameters that are prescribed for the determination of drinking water quality. So, it is obvious to us that the water should be as pure as possible, but in the given circumstances several water bodies in India are as of now stand pollutant therefore, it is important for us to determine the several metal ions especially non metals also including surfactants anions and cations.

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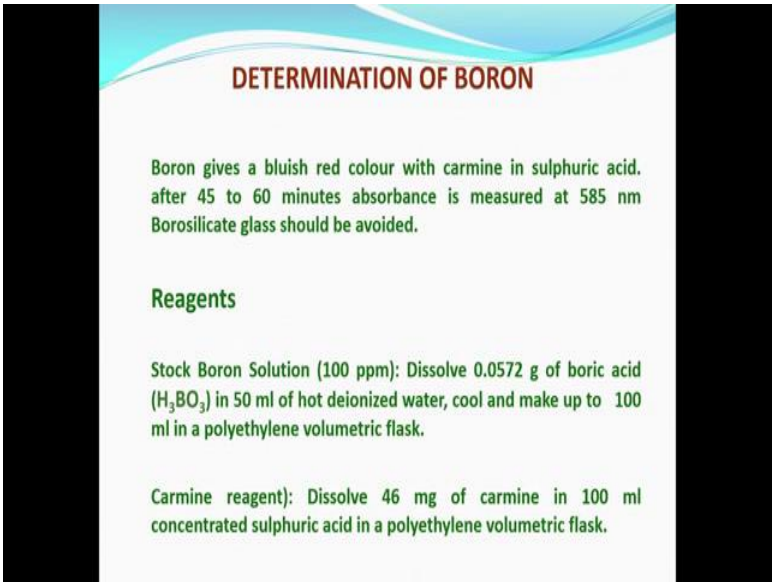

Sometimes we are expected to do the analysis of alkalinity and then hardness all these things, including the phenolics oils etcetera. But we have spent lot of time and efforts to make complete water analysis using spectrophotometry that is the beauty of this course. In this course what I am going to teach you is selected spectrophotometric procedures which will give you a procedure for the determination of these metals, and or non metals or surfactants as the case may be, but we also will tell you how to prepare the reagents, we will also tell you a little bit about the nature of the complex.

And then we will give you a cookbook value that if all the reagents what you use are good and accurate they do not contaminated, then what should be the standard value you should get. So, that is known as cookbook value; a cookbook value tells you the us tells you that when you do an experiment if you get the cookbook value what we have written in the book, if you do know if you get it; that means, all your reagents are pure, your laboratory is pure, your chemicals are pure and the method is reliable. And all these data that we have collected done in our laboratory several times repeated they are all standard sized averaged and within the acceptable limits. So, if you are able to determine the buy or collect the chemical reagents and water etcetera, then you do a standard sample and then with the standard sample if you get the correct value as reported in this course if you get it the analysis is within your control.

We also try to give you certain information about the interference of the other metals anions etcetera, I will emphasize as and when we come across these things, and another point I wanted to tell you is that if you refer to number of books you will come across same procedure and the problem is that sometimes you the procedure is tells you that you must add your reagents dilute it to 10 ml, dilute it to 100 ml, dilute it to 50 ml like that before you make your measurement and go for calibration curve and do the unknown as per our procedure so far we have discussed.

Now earlier about 20 years before to some extent even now spectrophotometry was not considered as a reliable method for the chemical analysis, there are two reason main reasons for this: one is the spectrophotometry as practiced since last 100 years has undergone a (Refer Time: 05:23) change. So, earlier people used to have very small instruments colorimetry colorimeter (Refer Time: 05:31) colorimeter and then eel colorimeter etcetera, where you could do in the laboratory, but none of them were standardized; because none of the methods were standardized with respect to the instrumentation.

Nowadays very good instruments with gratings, prisms etcetera and very accurate electronics has improved quite a lot stability of the noise, noise stability also has improved quite a lot. So, the reproducibility has improved therefore, given all these things we feel that spectrophotometric result should be accepted as a standard, this is our effort to make the spectrophotometry as a standard. So, what we have adopted in this procedure in this course is all the solutions are to be diluted to 10 ml final solution, I do

not want you to dilute to 25 ml, 50 ml, 100 ml several books write the different procedures, but the fact remains that for all spectrophotmetric procedures you require only 5 ml of the solution, only 5 ml that is 5 you can imagine one square centimeter cell can hold hardly 3 m l; 2.5 to 3 ml is more than enough for measurement.

So, the there is no point in preparing a solution for beer Lambert's law checking for 50 ml dilution, it does not serve any purpose. So, what we have decided is we will use only micro liters for the preparation of the samples, still it will give you a reliable value and the final volume of dilution should be 10 ml. So, with this introduction I would also like you to remember that most of the information has been collected from the standard methods of analysis, but all of them have been modified to make your reagents within the experimental errors and also to whenever you make a preparation of the method it should be reliable. So, with that in mind I would like to continue our discussion for different parameters in the next 4 or 5 classes ok.

So, coming back to the determination of boron; what is boron? Boron is a micronutrient, almost all plants what we mean by micronutrients is all the plants and animals human beings including human beings need boron, it is a part of our physiological system. So, the boron should be determined in all drinking water. Now I want to tell you a fundamental truth also that is any substance in excess is a toxic element; any substance including water, including salt what we eat daily for our daily survival. So, any substance that is part of our environment must be monitored, whether it is micronutrient whether it is an essential element or non essential element does not matter, because if the concentration exceeds the particular limit anything can become carcinotoxic or carcinogenic; for example, if God has made this oxygen pure then all of us would have been burnt or oxidized long back therefore, god has diluted oxygen with 80 percent nitrogen, otherwise oxygen is a very corrosive element.

Similarly salt which salt 5 milligram or 5 gram of salt or something like that per day we are all very comfortable, but the same thing if the concentration doubles in our daily up take, we are all in trouble. Same thing is true with respect to other salts for example, sodium chloride is a common salt what we eat daily we can feel their taste, but suppose it is lead chloride or lead acetate, then the it has no taste, but the concentration if it increases and goes in our body it will cause the damage to the same to the extent it is capable of. So, that is not desirable. So, what is important is irrespective of whether a

substance is carcinogenic or non carcinogenic, if it is part of our environment and part of physiology, we should determine that element in our drinking water and food and other things also, but here we are concentrating on the effluent drinking water etcetera.

So, if somebody is letting out these chemicals into the environment, it is essential that we monitor it right. So, coming back to boron; boron is an essential element, so we work for the determination of boron. Now boron gives a bluish red colour with carmine that is the reagent we are proposing in that carmine has to be dissolved in sulphuric acid. So, the next sentence here says after 45 to 60 minutes of a absorbance is measured; that means, the complexation of carmine with boron in sulphuric acid medium is maximum around 45 to 60 minutes, and the substance is absorbing at 585 nanometers that is within the visible range, and because boron is part of the glass borosilicate glass we should not determine boron in glass vessels you should use plastic vessels, very simple logical explanation and requirement of the procedure.

Now what are the requirements the here you can see that the reagent first we give a this is a the style of the cookbook also, that is first we give the reagents how to prepare the reagent; that means, you have to prepare standard boron solution and standard borons as I have told you yesterday that 1 to 5 ppm or very low ppm solutions are not stable therefore, we prepare what is known as a stock solution; a stock solution is about 100 ppm which is stable for long , for this what you have to do you have to calculate how much of boric acid corresponds to 100 ppm of boron. So, boric acid is H_3BO_3, and boron is only a simple element and if you calculate the molecular rate and simple chemistry, you will remember you will know that we have to dissolve 0.0572 gram of boric acid in 50 ml of hot deionized water you have to cool it make it up to 100 ml in a polythene volumetric flask.

So, carmine reagent how do you determine carmine reagent, how do you make it of course, you cannot synthesize all organic compounds in the laboratory that is understood therefore, what you should do is you should buy it these reagents are available across the shelf with chemical suppliers. So, if you take 46 milligrams that is 0.046 gram of carmine in 100 ml of concentrated sulphuric acid, that too again you should use a polyethylene volumetric flask and it will dissolve and give you a reagent.

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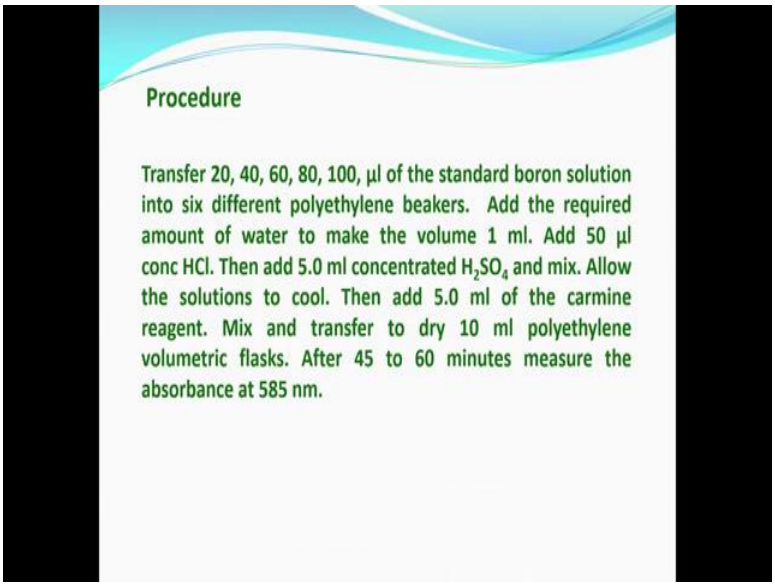

Now, what you should do; the because you are doing the experiment in you are doing the experiment in the laboratory, you have to prepare 20, 40, 60, 80 and 100 micro liter of the standard boron solution into 6 different polyethylene, because to make the beer lamberts of calibration. So, I have to tell you that one microgram per milliliter is 1 ppm. So, if I ask you to prepare one 100 ppm; that means, one ml one milliliter will correspond to ne 100 micrograms of boron, you can go show the slide please. So, 100 ppm will have 1 m l; that means, if I want you to take 20 microlitres here, I want you to take 20, 40, 60 100.

So, with if I take one ml I will get 100 microliter, if I take 0.8 that is 18 microlitres I get 80 micrograms like that we have to prepare 20, 40, 60, 100 liter of the standard boron solution, in 6 different polythene beakers add the required amount of water to make the volume almost up to 1 ml, then you add 50 microliter of concentrated HCL to keep the sample in acid medium, then add 5 microliter of the concentrated H2SO4 and mix and allow the solutions to cool; then you have to add the carmine reagent mix and transfer to dry 10 ml polyethylene after 45 to 60 minutes you will measure the absorbance at 585 nanometers.

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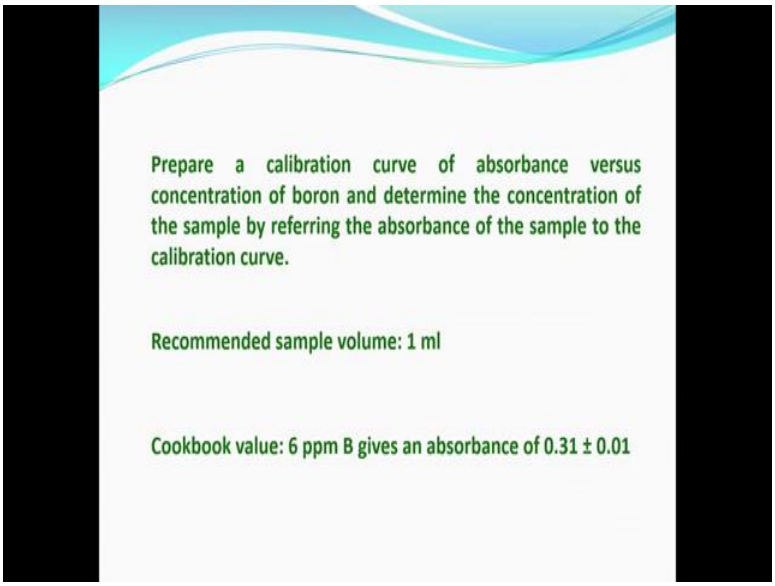

Now, once you make the measurement, once you make all the solutions and make the measurement etcetera you have to prepare a calibration curve. So, from 20, 40, 60, 80, 100 microliter what you have developed the colour you take it to the spectrophotometer make your measurement, and then you have to prepare a calibration curve by plotting absorbance versus concentration, and determine the concentration of the sample by referring the absorbance of the sample to calibration curve. So, how much sample you should take is the question; because quite often you do not know the how what is the contamination level. So, this is a sort of judgment you have to do as an analyst.

Normally we recommend using our experience that you must take one ml of the sample that will come within the experimental Beer Lambert's law range. So, the cookbook value is 6 ppm boron gives you an absorbance of about 0.31 plus or minus 0.01; that means, you go back you prepare all your calibration curve, and then 60 microgram that is in 10 ml would be 6 ppm; 60 by 10 is 6 ppm.

This 60 microgram will give you absorbance of 0.31 plus or minus 0.01, and for to do this you need to prepare you need to be prepare yourself for a high quality laboratory work using milliliters or microliter pipettes, and if you continue doing the experiment if you if you get 6 ppm 0.31 absorbance all is well, that is the speciality of the cookbook value. If you do not get it what you should be doing is go back to your reagent check your reagent, check your p H, check your chemicals, check your operator handwriting

check your puppets whether they are broken or something like that if you do not 0.31 plus or minus 0.01 something is wrong so, but if you get it. So, ahead with the remaining chemical analysis that is the beauty.

So, this is the characteristic absorption spectra for carminic acid, boron and boron carminic acid complex.

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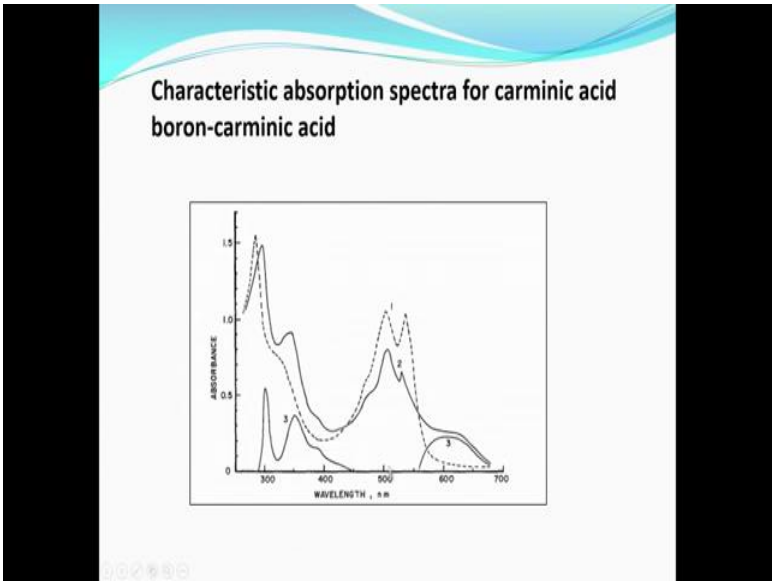

So, number one is the boron carminic acid, and number two is the sample. So, three is another sample. So, like that different 585 nanometer is somewhere here. So, this peak we are normally monitoring or somewhere here, the molecule you can see that molecular absorption peaks are somewhat complex, but you need not worry about it because the required the recommended range it should be possible for us to determine within reasonable limit the specifications of the water sample with respect to boron.

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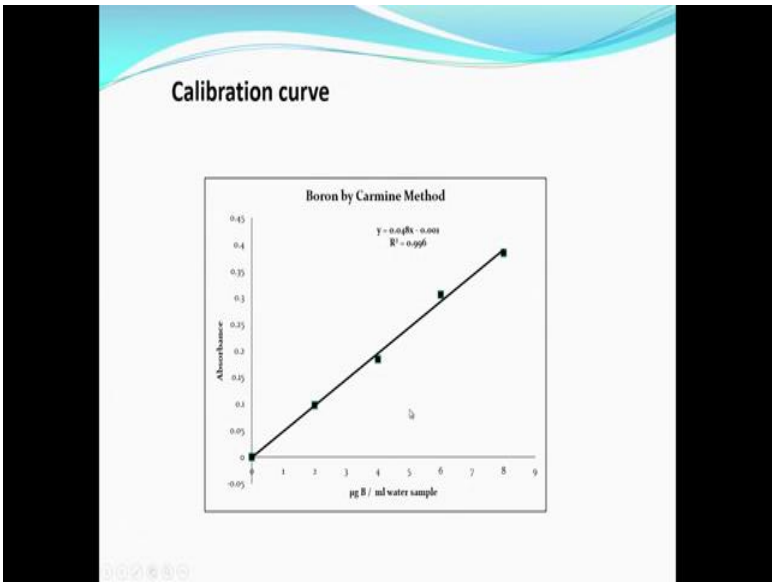

Now, this is the calibration curve, you can you need not check only 0.6 ppm we can check any of your absorbance values between 0, 2 ppm, 4 ppm, 6 ppm, 10 ppm etcetera you can see that it is a reasonable absorbance curve fairly a linear and the linearity does not change up to 8 ppm. 9 to 100 we have seen some absorbance variation from Beer Lambert's law, we where the sample will absorbance will be lower than this. So, this is I am giving you the cookbook value also as well as Beer Lambert's law.

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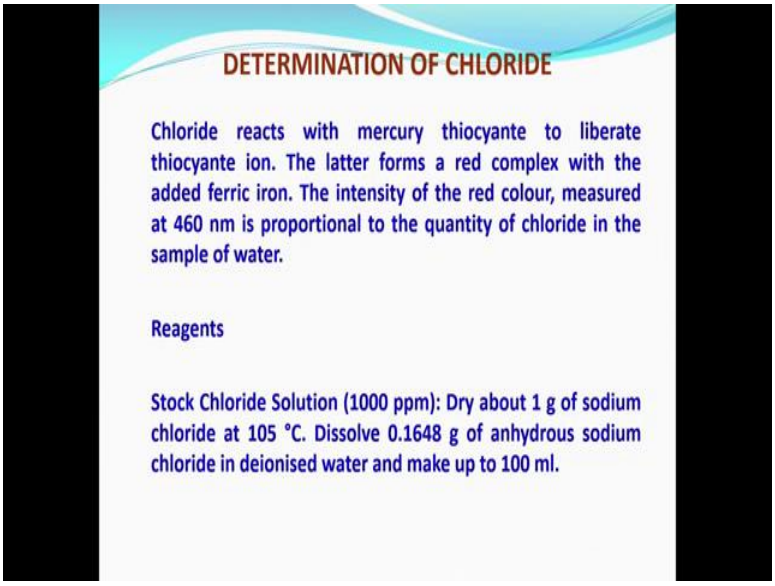

Now, we do have certain information about the pollution about the interferences of other metals, that we will take a look as and when we require, and for the time being what I would like you to do is if you are able to understand all the (Refer Time: 22:18) and if you have a spectrophotometry at your disposal at 585 nanometers you go ahead do this and you will be able to determine boron in from 1 to 8 ppm, and that is the range in which you will find most of the water bodies in India approximately showing you the concentrations in their matrix. So, that brings me to the next one determination of chloride.

So, in the chloride what I would like you to do is I have to inform you a little bit about the importance of chloride in the method in the environment. The chloride is a ubiquitous element it is not part of our nature, chloride comes to us from the soil and most of the soil is having chloride as a content and since the earth is having lot of chloride on the surface of the soil, and it has been raining since millions of years; what is happening is most of the chlorides soluble chlorides have dissolved and gone to the sea, that is why sea water is very salty. All the sodium salts and potassium salts are highly soluble in water and because of the rain all of them have taken out the chloride and sodium and potassium chlorides from the surface of the soil into the sea, that is why see lot of chloride. By the same analogy we do not get lot of bromides and iodides, fluoride also to that matter because fluoride is not part of the natural cycle in the of the element. Same thing is to bromide, you do not find bromide bromine as a natural element anywhere in the world, same thing is true with iodine you would not find, but sodium bromide sodium iodide etcetera they are all in the sea water.

So, chloride is important for us because whenever we take out water from the surface water or from the well water or from rain water or somewhere chloride is always associated with the water. And chloride imparts certain amount of dry taste to the water, chloride of course, is not desirable in industrial situations also because chloride normally will form scales, chlorides sulphates, all these thing will form scales in the pipelines etcetera not good for health. Normal river water contains about 130 to 150 ppm of chloride if you look at the slide what I have shown you earlier, the WHO standard prescribes about 100 to 500 milligram per liter that is ppm of chloride, and the chloride should be within that limit.

So, the chemistry of this refers to the reaction of mercury thiocyante to liberate the thiocyante ion. So, it is a very simple reaction whenever there is chloride in the water we had mercury thiocyante to liberate the thiocynate ion, and the liberated thiocyante ion forms a red complex with added ferric iron; that means, we add a little bit of ferric iron also, and it is very well known reaction that ferric thiocyante is a very dark red colour measured at 460 nanometer, that is proportional to the quantity of the chloride in the sample of water because thiocyante liberates the chloride reacts liberating thiocynate to the same amount of equimolar in the ratio.

So, what we need is stock chloride solution, that is about one gram of sodium chloride at 1 not 5 degree centigrade, and we have to dissolve to get the solution we have to dissolve 1.1648 gram of anhydrous sodium chloride in deionised water and make up to 100 ml.

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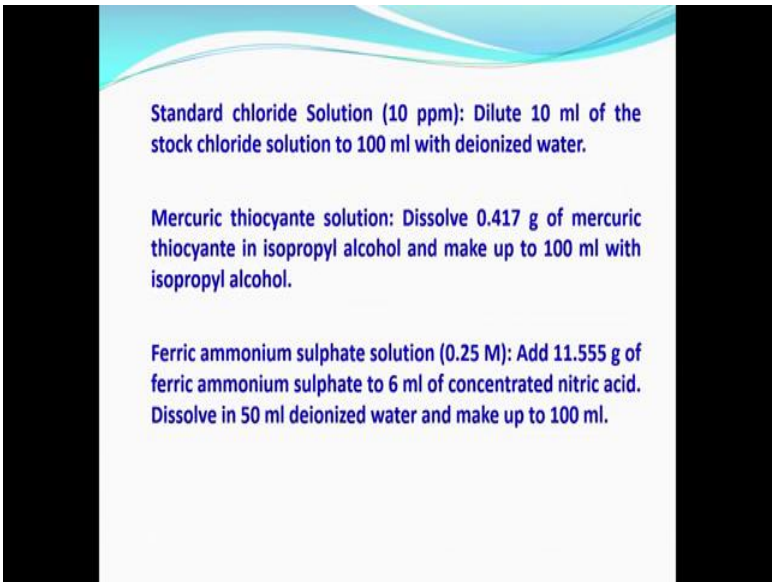

So, from this we prepare the working solution of 10 ppm that is dilute 10 times, how do we do that? We take 10 ml of the stock chloride solution to 100 ml with deionised water I get 10 ppm. Now I need to prepare mercury thiocynate these all these procedures are already available in the book, but here our aim is to make them work at very low concentrations and less chemicals in the environment. So, we dissolve 0.417 gram of mercuric thiocynate ion in isopropyl alcohol and make up to 100 ml with the same isopropyl alcohol.

So, we also need ferric salt. So, the best solve best salt to get ferric in reproducible form is ferric ammonium sulphate, and you should take 11.555 gram that is 0.25 molar you have to prepare, and 11.555 gram of ferric ammonium sulphate must be added to 6 ml of concentrated nitric acid so that can be dissolved. See generally what happens is if the concentration if the ferric ammonium sulphate does not contain so much of acid it will precipitate, that is why we say use concentrated nitric acid for ferric ammonium sulphate and you can dissolve it in 50 ml water and make it up to 100 ml.

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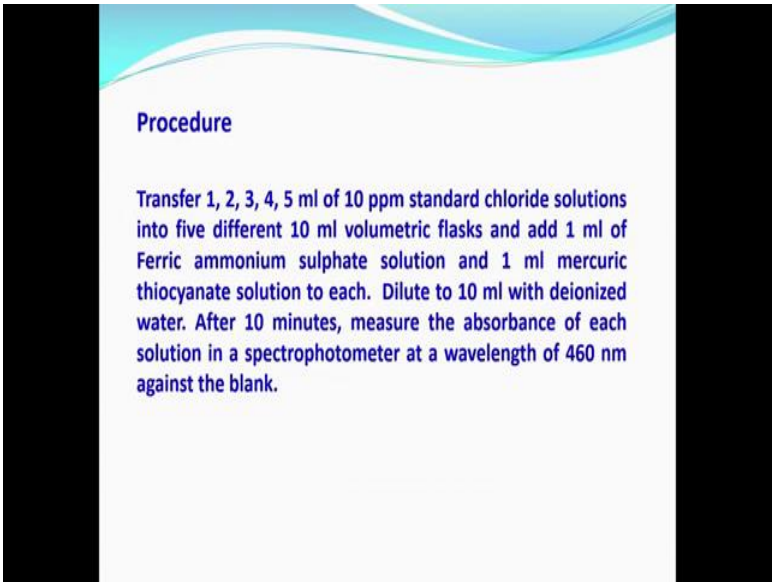

So, the procedure again as usual I have to take 1, 2, 3, 4, 5 ml of 10 ppm standard p pm solution in different 10 ml flask, add 1 ml of ferric ammonium sulphate, 1 ml of ferric thiocyante to each and then that will liberate equal quantities stoichiometric quantity of chloride, dilute to 10 ml with deionized water and after 10 minutes measure the absorbance of each solution in a spectrophotometer at a wavelength of 460 nanometer against the blank. Of course, I do not have to over emphasize that we have to carry out the blank, because every water you come across nowadays will have certain amount of iron that will turn red the moment it comes in contact with the thiocynate ion. So, taking it further we have to prepare a calibration curve and then use usual way we have to have a recommended sample volume is about 0.2 ml.

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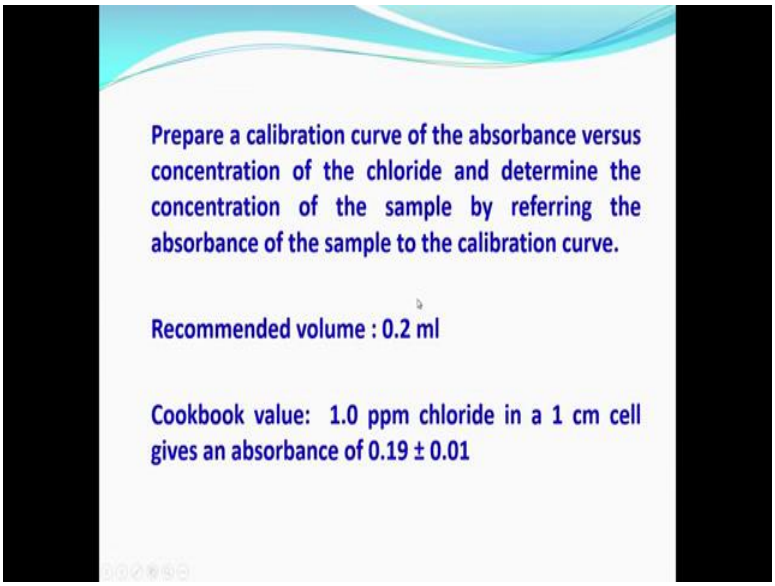

And cookbook value is 1 ppm of chloride that is a standard in 1 centimeter cell should give you an absorbance of about 0.19 plus or minus 0.01 ppm.

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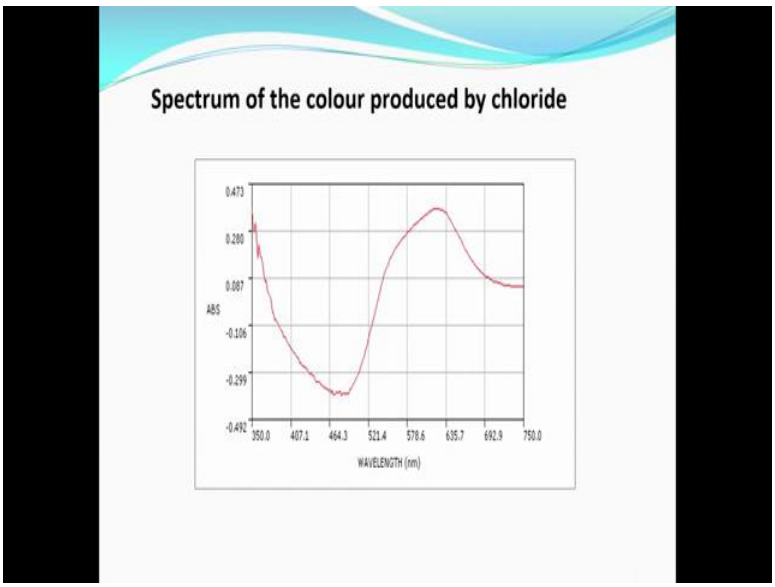

And this is the spectrum of the ferric thiocyante that is produced, you can see that the substance is having a lambda max somewhere around 630 or something like that, and earlier what we have said is 460 nanometer this is somewhat orangish in colour 460. So, we are looking at this range because the liberated ion will have lower colour. So, absorbance should decrease from this standard. So, maximum decrease is the point

where the measurement is being made. So, 460 is the ideal one in quite of the good spectrophotometers you may get 464, but in ordinary spectrophotometers you may get 460 465 455 like that.

So, we are saying 460 you go because the concentration versus absorbance curve is almost flat in this range not much difference ok.

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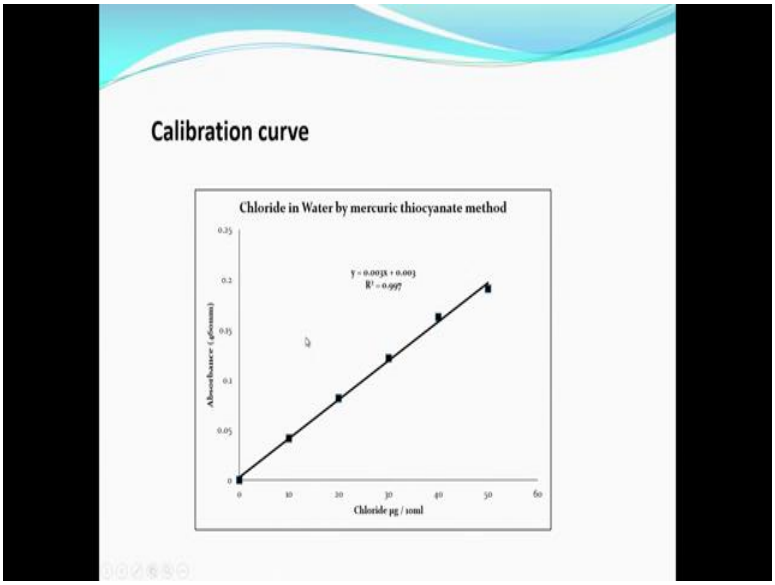

So, this is the calibration curve you can see that the linearity is given by y is equal to 0.003 x plus or minus 0.003 this refers to intersection very less. So, it must pass through the origin, and the concentration the linearity the slope is 0.997 almost one therefore, it is approximately at 45 degree angle to the sample.

So, we will stop here and look at other parameters in the next classes, I would like you to remember as far as possible the reagents reaction conditions at least for water analysis, and I urge you to read this colorimetric methods of analysis by E B Sandell as well as volumetric this Vogel. So, thank you very much we will continue our discussion in the next class for other pollutants.

Thank you.