Atomic and Molecular Absorption Spectrometry for Pollution Monitoring

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Lecture - 31
Fluoride

Greetings to you. Let us start where we have left off in the last class that is the determination of different parameters for water quality monitoring. So, yesterday we had seen 2 methods - one is that of boron and another is chloride.

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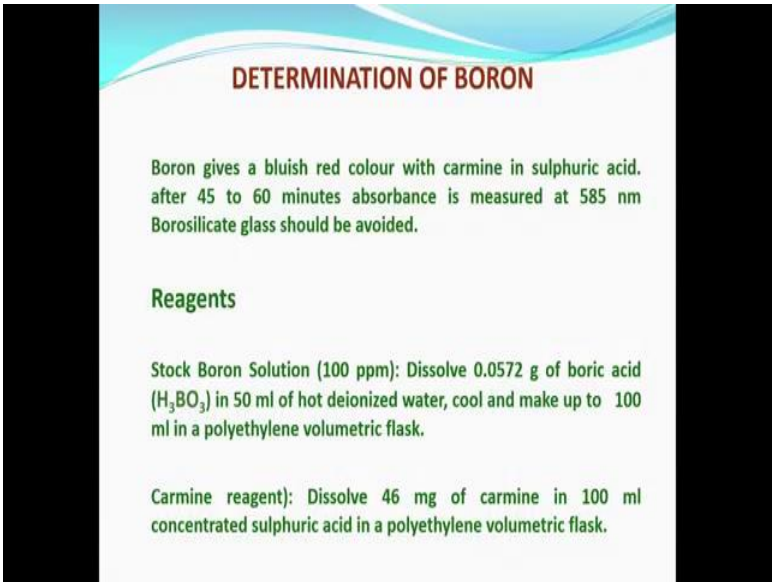

In Boron what we had discussed was the actual method chemical reagent that is required to determine boron that is carminic carmine. And chloride also we had discussed using the mercury thayo cyanide procedure.

Now, if you remember what we had discussed I had told you that carmine is dissolved in concentrated sulphuric acid, as a reagent and that is added to the water to develop the color and which is measured at 585 nanometers etcetera. And then we had the prepared the calibration curve also. I had told you that the reagent cook book value is approximately is 0.31 plus or minus 0.01 absorbance. And this value we are able to say we with absolute certainty for this method because of the use of spectrophotometer which is accurate with respect to the wavelength plus or minus 2 nanometers; that means,

if you are measuring at 586 you may be measuring at 584 or 580. So, 588, and the absorbance will not change much especially if within plus or minus 2 nanometers. And I had recommended a sample volume of 1 ml and if you remember I had also discussed that we have to worry about the interferences, but I did not discuss the interference of other metals or other concomitants in fluoride in boron as well as in chloride.

One reason for this is that when the reagent concentration itself is in concentrated sulphuric acid. There are very few reagents that will precipitate that will not dissolve in concentrated sulphuric acid. So, now, 99 percent of the interferences do not occur whenever we carry out a spectrophotometric determination in high acid concentrations. With respect to therefore, we have not spent enough time to discuss about the interferences for this method. And then I have we had discussed that if you recommended sample volume this sample value is from what you analyze first this is apart from the standard. So, along with the standard you have to run the sample and then get your you the typical quantity this can varying.

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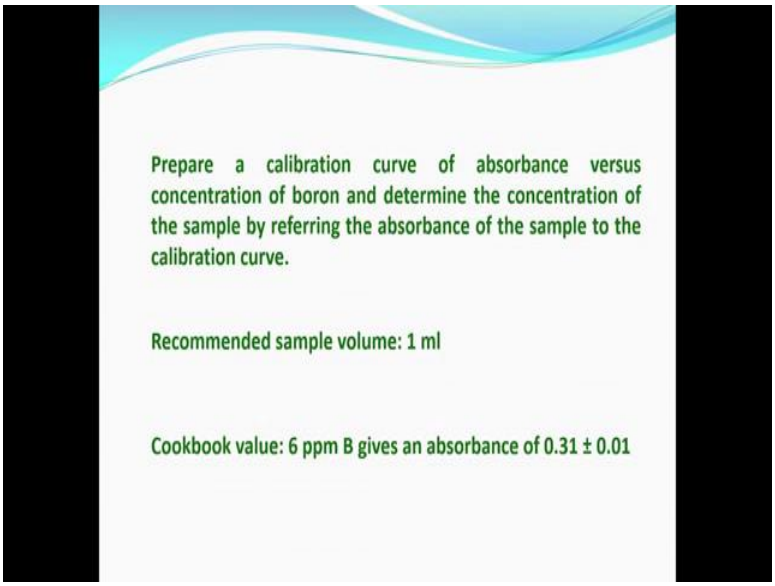

If I say recommended sample volume is 1 ml it means it is only a recommended sometimes if the boron concentration is lower you can take higher concentration also, but remember that the final volume should be 10 milliliters only.

So, sometimes if the concentration is higher, in the given sample, you may have to choose lower volumes depending upon the calibration curve. So, whenever you take any

arbitrary sample you just have to make sure that your absorbance value should be well within the calibration curve. Then the result will be very reliable that is understood.

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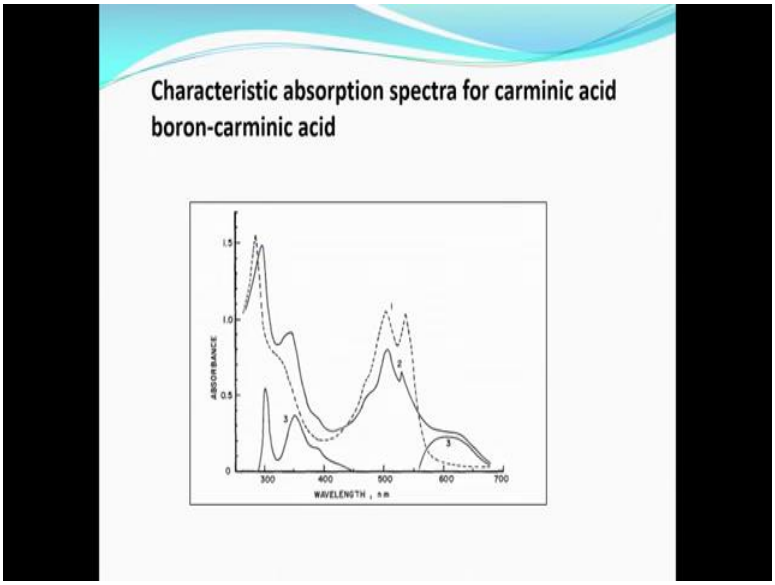

So, we had also I had also shown you a curves like this and 586 is somewhere here. So, the difference between the blank and sample is always very high here and reproducible. So, the choice of the wavelength measurement for absorbance is also a slightly complicated matter, but if there are if the peaks are very few unlike this carmine you will not have much difficulty in choosing.

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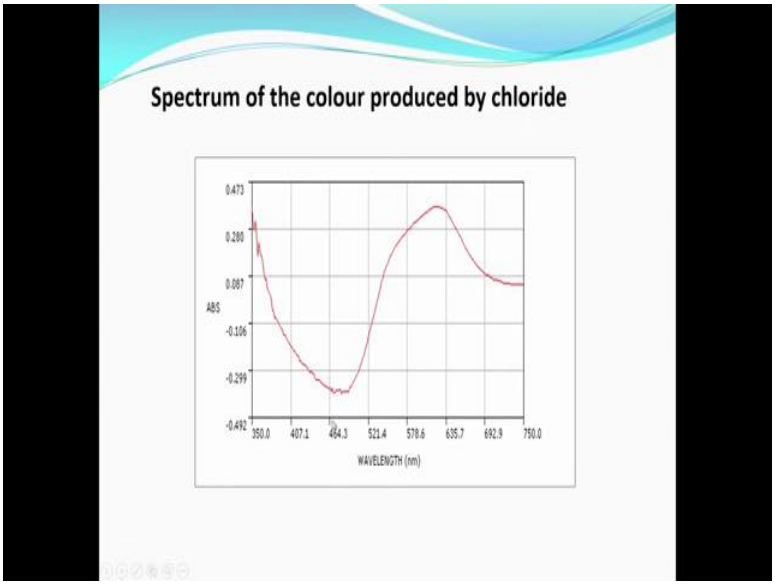

For example, when we go to chloride you can see that the there is only one peak here. There is one trough that is around 460 you can see that absorbance between 460 and 510 may be this is 460 and this is 520 this is half of it, is approximately 490. Around 490 between 460 and 4 90 absorbance does not change much. So, that is how we fix the wavelength. So, the absorbance should not change much. So, even if there is an error of wavelength by about 5 6 nanometers you can see that the absorbance is not changing much here at all.

So, that is the trick we normally employ especially whenever we have the molecular peaks are very less in number 1 or 2 peaks etcetera. It is very easy for us to fix the measurement wavelength. So, again in this case the chloride itself is a good dissolver, lot of chloride salts are soluble in water etcetera. So, the whatever is not soluble you will not have it in the sample in the dissolved form.

Therefore, I have not discussed the interference of other metals in this case. So, preceding further.

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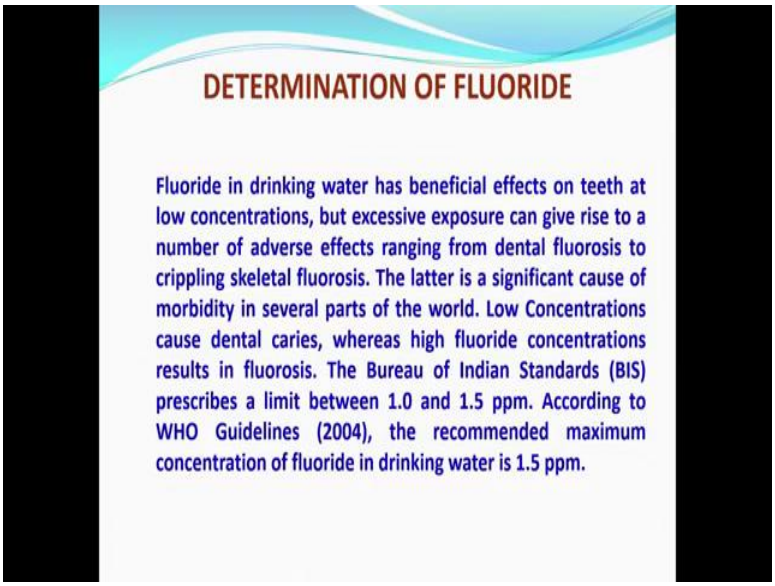

We can take a look at the next one that is determination of fluoride. Now there are lots of things to be said for fluoride. Fluoride is an anion which is not uniformly or widely distributed in nature. Basically it is because there is not much a natural role for fluoride in the natural cycle of things.

For example, if we need if we are talking of boron or something like that, there is a natural need in the there are there are sinks as well as the absorption points. So, there will be a natural cycle through which a dissolved metal will be recirculated through soil water and then animals and then again back to the soil water etcetera. So, that is the regeneration cycle. So, for any element that is required in our day to day metabolism almost all the elements have some sort of a cycle.

And this cycle must be completed in all aspects with respect to generation sink and then precipitation coming into the system out of system. What do you mean by system it is an environment? Suppose we are talking of DDT. We spray take the DDT spray it in the on the crops and then from the crops it gets into the fruit is or grains or etcetera, and then the cows and other animals eat it we also eat the grains etcetera with our excreta, it enters the natural environment of soil and water and whenever it falls on the soil it will get it will get dissolved and washed away into the water ways from the water ways. Again people drink it animals drink it and then the same thing is used for agriculture, again it you know that kind of natural cycle is always established, whenever there is an element in the nature which is regularly used required in the metabolism

So, the fluoride on the other hand yesterday also I had mentioned that it is not part of the natural cycles of the elements in the environment. Normally whenever a fluoride comes on to the surface, it creates some sort of imbalance it has to be treated. So, normally fluoride is found in the rocks, underground and then whenever we dig a bore well or whenever some naturally calamity happens the fluoride will come out into the atmosphere comes and settles on the dust on the soil etcetera.

So, there are always natural calamities. Especially what it is called especially the spewing of the fire from the soil etcetera, I have forgotten the name, but it is very simple this thing. So, mountains spilling fire that is what I mean. So, smoke etcetera forest fires many of these things will spill fluoride into the environment from the bowels of the earth. So, it comes into the environment again it gets into the cycle, but it is not part of our body human body metabolism therefore, fluoride is a pollutant. So, fluoride in drinking water has some beneficial effects. Infact most of our bones and other things catch the fluoride whenever we show an intake of fluoride in the form of water milk any other liquid etcetera.

So, if you remember people use tooth in toothpaste fluoride. There used to be toothpaste called as binaca fluoride. And doctors use fluoride mercury etcetera for dental filling. So, many of the fluoride compounds enter into the atmosphere through several industrial processes. And other natural means especially with respect to industrial processes, I have to tell you that chlorophloro carbons are one of the most important environmentally undesirable chemicals, which are produced in millions of tons which are used in refrigerants. They all enter into the atmosphere reach the atmosphere from the atmosphere they take part in expanding the ozone hole, through which ultra violet rays come and then damage the environment human beings etcetera. So, fluoride is always specially implicated in the environmental as an environmental pollutant.

So, excessive exposures doctor some doctors say a little bit of fluoride is beneficial with for the teeth, but excessive exposure can give rise to a number of adverse effects. Ranging from dental fluorosis to crippling skeletal fluorosis. Actually there are never we take out drinking water from the bore wells in several parts of India Rajasthan Tamil Nadu Andhra Pradesh Maharashtra Rajasthan and several other places, there is lot of fluoride underground and through the bore well the fluoride comes on to the environment and the bore well water contains lot of fluoride. And low concentrations normally cause dental caries, but higher concentrations if you look up the literature and the google, you just hit fluorosis you will come across several millions of hit is where people are affected by high concentration of fluoride in drinking water. So, Kolar then Madanpalli and then several parts of Rajasthan Madhya Pradesh and several other states nearly about I should say about 40 to 45 percent of Indian subcontinent is affected by high fluoride concentrations.

So, high fluoride concentration results in nervous disorders and skeletal disformation. So, I can show you number of things on the google you can also you are also encouraged to look at the fluorosis problems. And therefore, the there is a very high requirement of fluoride analysis in the effluent as well as in drinking water. The bureau of Indian standards prescribes a limit of 1 to 1.5 ppm in drinking water. In Indian standard is 1 ppm who standard is world health organization who that standard is 1.5 ppm. And permissible limit of concentration of fluoride in drinking water is 1.5 ppm; that means 1.5 micro grams per ml or 1.5 milligrams per liter.

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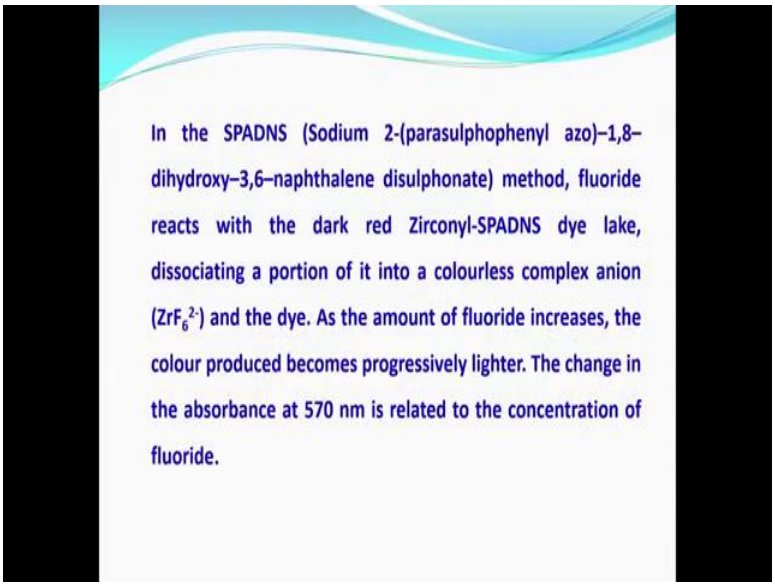

So, we can look at it from the analytical point of way how do we go about doing the analysis of fluoride. The chemical analysis of fluoride is normally accomplished using a reagent called as sodium 2 parasulphonyl azo 1 3 dye hydroxyl 3 6 naphthalene disulphonate.

You can imagine it is a fairly complex reagent, organo chemicalry organic reagent and, but it is available in large quantities because of the importance of fluoride in drinking water. So, this is known as in short it is known as SPADNS. So, I have written here the formula you do not have to remember it for the sake of examination or something like that, but the in short form if you go to market and chemical suppliers and you say you want SPADNS then it is easy to get the chemical.

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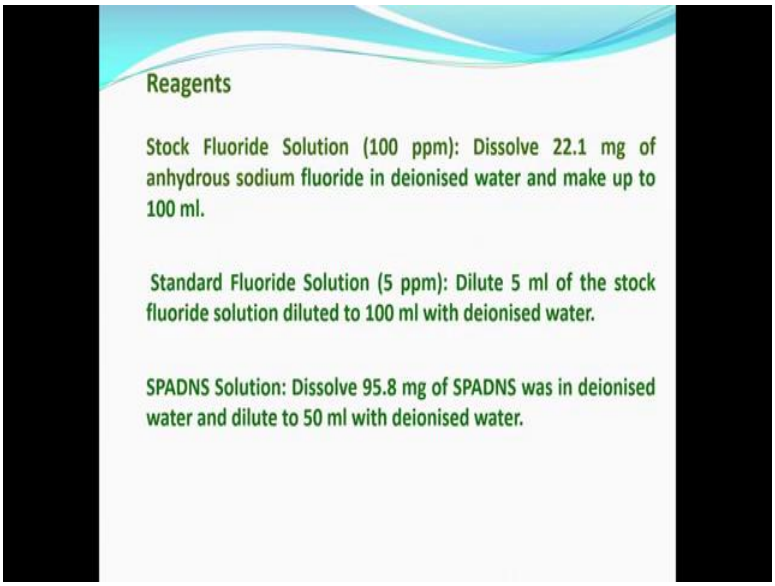

So, the principle of this method is that the fluoride this complex SPADNS reaches reacts with zirconium to form a red dye. I can give you the structure of this.

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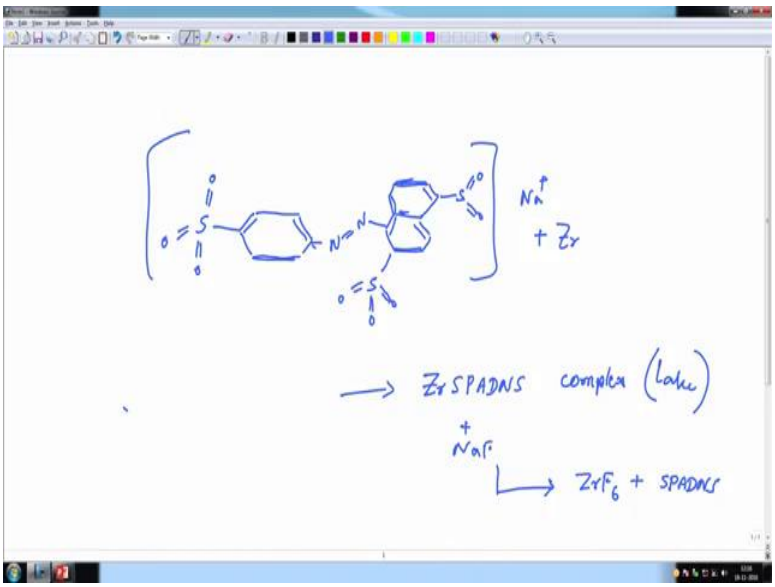

It is a fairly complex structure. It is a sulphonic acid. Fairly complex structure like this and then a benzene ring, then there is nitrogen, fairly complex organic structure. This is not there. This is a single bond and then another ratio 3 h group and there is one more. So, 3 group then this is the structure and then N a plus ns this is always in the form of cation.

So, this compound will react with zirconium to give you zirconium SPADNS complex. Actually this is not a complex, but this is a lake. So, it is red in color and whenever I take the so, zirconium SPADNS complex I add water containing fluoride this will release Zr F6 plus SPADNS. So, the logic is if I take lot of. So, if I take lot of zirconium SPADNS complex, add a little bit of fluoride that is our sample containing fluoride, then what happens the fluoride will complex with zirconium releasing the SPADNS. So, the zirconium SPADNS complex is red in color whereas, zirconium fluoride is color less.

So, whenever there is fluoride, there will be the intensity of zr SPADNS will be less. So, that is the basic principle how the fluoride is determined. Going back to this analysis what we want to tell you is as the 0 red zirconyl SPADNS dye lake is there, that whenever we add fluoride it dissociates part of it and zirconium Zr F6 will fall and the dye will be the concentration a dye will be released as the amount of fluoride increases, the color produce becomes progressive lighter because the red zirconium SPADNS complex will keep on decomposing. So, the change in the absorbance at 570 nanometers is related to the concentration of the fluoride that is the basic principle.

So, what are the reagents how do we go about doing it? It is a very simple formula as I had the discussed earlier what you should prepare is a stock fluoride solution that is 100 ppm is more than enough you can keep it for quite long time also and for that you have to dissolve 22.1 milligram of anhydrous sodium fluoride. You may ask me sir how to weigh 22.1 milligram of anhydrous sodium fluoride? Not to worry there are balances which will weigh up to 0.1 0.1 milligram accuracy. So, if you weigh 22.1 milligram that is quiet 0.01 milligram accuracy people can weigh 22.1 is no problem at all.

So, from these, from 100 ppm fluoride solution, we have to prepare 5 ppm of fluoride. That is 20 times dilution, you just have to take 5 ml of the sample dilute it to 100 ml you have 100 ml of 5 ppm zirconium. So, SPADNS again you have to prepare by dissolving approximately 95.8 milligram of SPADNS in deionized water. It is dissolution know. So, it will dissolve very easily and you have to prepare 50 ml of the deionized water.

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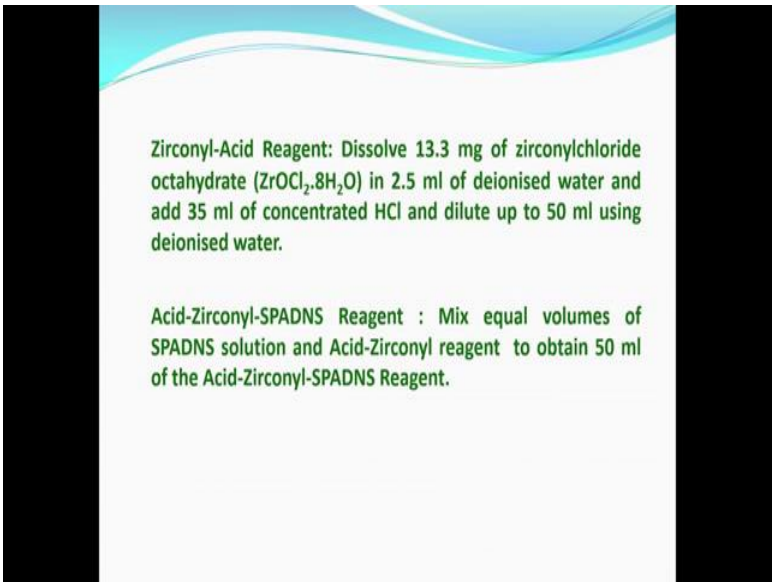

So, then what else you will need you will need, you have to prepare the complex zirconium acid SPADNS complex. For that what you should do is 13.3 milligram of zirconium oxy chloride zirconylchloride octahydrate you have to take, add 2.5 ml of deionized water add 35 ml of concentrated hcl and dilute up to 50 ml using deionized water. All these things are all these reagents whatever I am giving you the recipe, they are all available in text books especially the American the book on the examination a p what is that American water works published book on water analysis apha book it is called it costs about 6 to 8 1000 rupees and all these all these methods have been described there, but not all of them are in my course.

Obviously we have done additional work to bring you the latest, and the most reliable method to get you the right method. So, coming back to this we will go back to the slide and now your next job is to prepare the acid zirconyl SPADNS reagent, that in unique colored lake you have to prepare. For that what you should do is take equal volumes of zirconyl acid and SPADNS we have to mix them and the recipe is given here, you have to add equal volumes and then you will get the colored reagent

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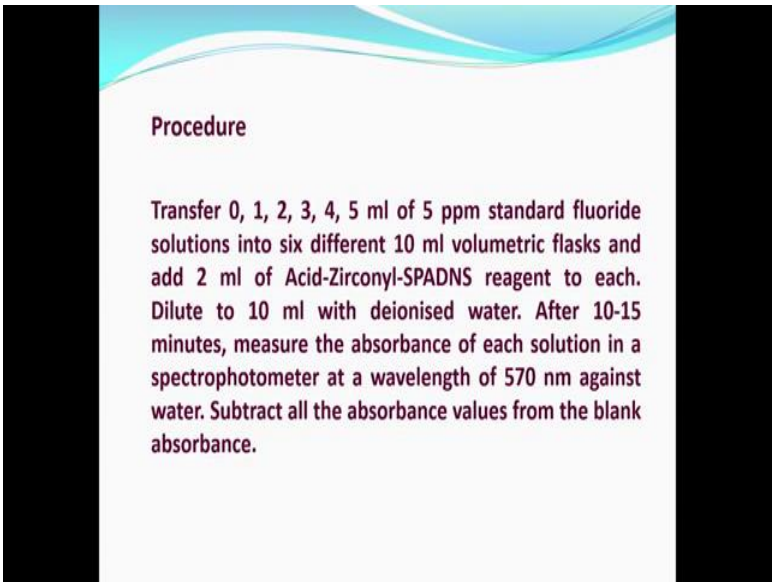

Now, what you should do is the go for the procedure once you have all these things ready. What you should do is transfer 40 to 5 ml of 5 ppm of fluoride, and different volumetric flasks add the reagent 2 ml and then dilute to 10 ml. After about 10 to 15 minutes you see here again I am saying 10 to 15 minutes for the reaction to complete if you do not do it you may not end up with a stable result.

Then you measure the absorbance at 570 nanometers against water you can subtract the absorbance values from the blank because you are going to end up with a negative absorbance.

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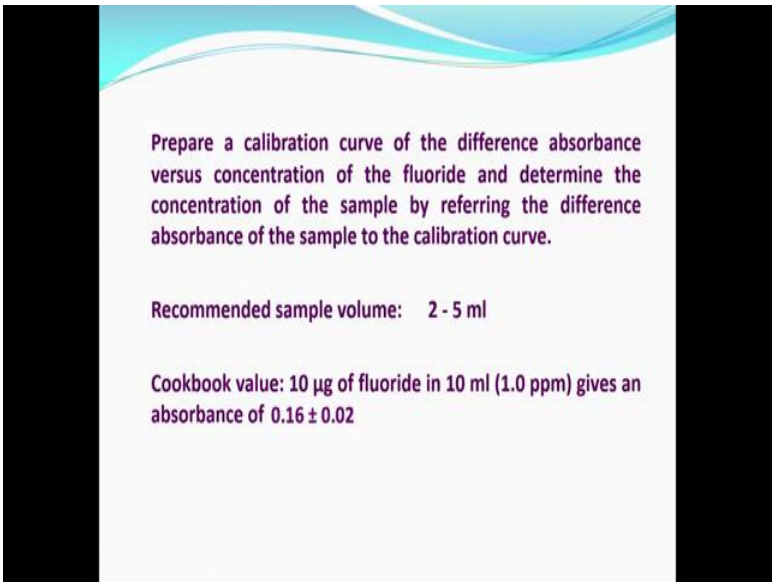

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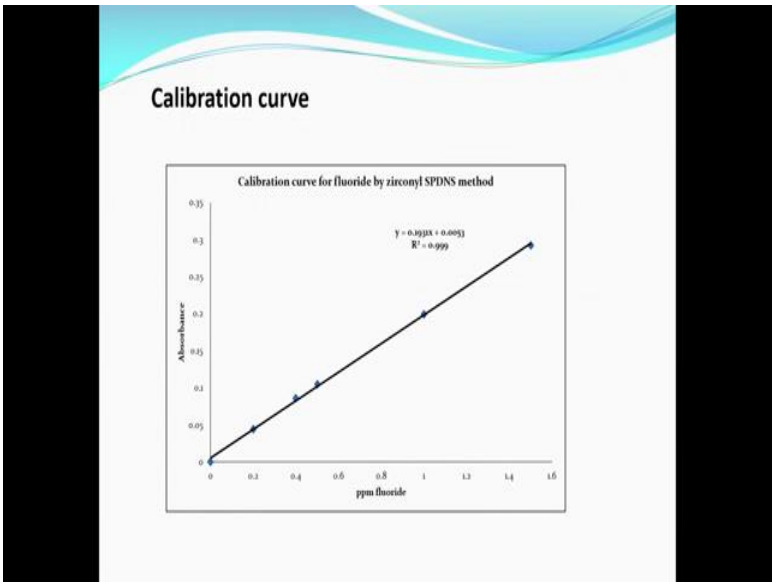

Then preparation of the sample volume etcetera. You can prepare a calibration curve and calibration curve will give you a beautiful curve like this. And then here you can see that I have drawn and the calibration from 0 to 1.6 ppm that is the WHO standard 1.5 ppm. So, when only whenever you stick to these exact recommendations of this procedure, you will end up with a very reliable volume. So, the recommended sample volume should be above 2 to 5 ml depending up on the concentration of the sample. And cook book value should be 10 micro grams in 10 ml that is 1 ppm 1 micro gram in 1 ml is 1 ppm. That absorbance should be approximately 0.14 plus or minus 0.01 absorbance and

if you make your standards properly. You will get this value once you get this value it means you are ready for the actual chemical analysis

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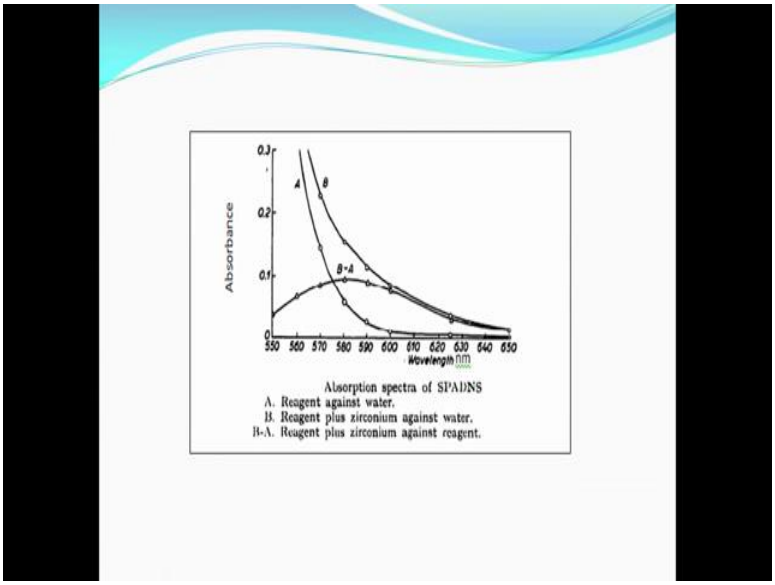

So, now we will I will show you the curves now. The top curve A is a reagent against water; that means, it is it has got a high absorbance and then B is a reagent plus zirconium that is a zirconium SPADNS this is the curve against the wavelength. So, the lambda max is somewhere around 570. This is the lambda max I have not drawn it higher, because we have a requirement of having absorbance less than 0.3 ppm 0.3 absorbance. So, around 560 570 is this thing.

So, suppose you subtract B from A, B minus A is your zirconium Zr F6 formed sample curve. So, that has got a lam x of maximum lambda of around 580 nanometers. So, you are measurement volume should be between 5 around 580 that is the maximum plus or minus 5 nanometers this side that side does not matter. So, you will be in a position to determine fluoride up to plus or minus 0.1 ppm requirement is 1 ppm, but your capability would be 0.1 ppm.

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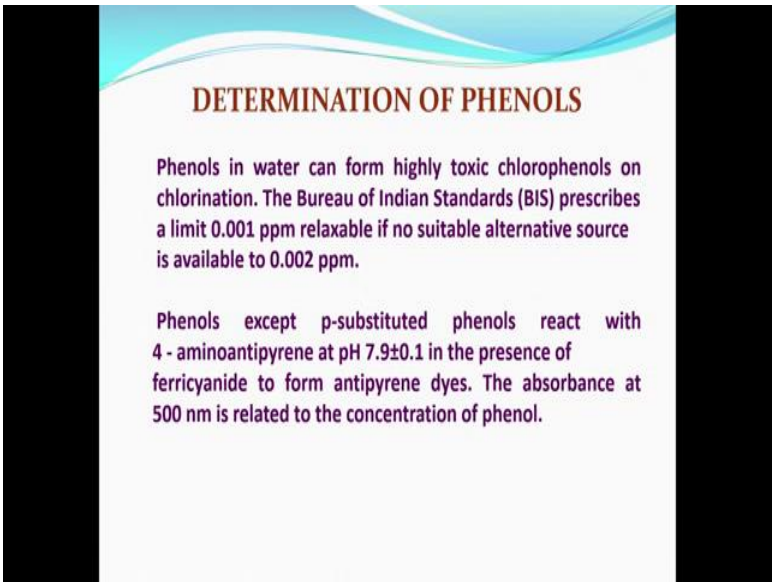

So, this is the calibration curve, and once you have this fluoride you will not have any problem with the determination of fluoride. Again I am not discussing the interference of all the metals, but we have evaluated number of chemicals ionic species and nonionic species. And here I can only tell you that the there is no interference at all from iodide cobalt manganese magnesium all in 100 ppm and then nitrite chloride sls iron copper cadmium iron etcetera lead nickel etcetera. So, the there are some interference substances. For example, tartaric acid: there is certain amount of interference phosphate interferes to some extent edta again as I have been telling you that edta could be one of the natural chemical available in waters river waters etcetera, that could lead to certain amount of interference, but that can be taken care of because up to 50 ppm of edta is tolerated in this method.

Similarly, chromium is tolerated up to 20 ppm, and molybdenum up to 10 ppm. Boron up to 10 ppm bromide and silver up to 100 ppm they can be tolerated. So, depending if you I am not going to give you the details in the ppt, but if you look up any of the text books for these things you will be able to appreciate that fluoride can be determined in presence of several interfering elements. So, thank you very much we will continue our discussion after in the next session.

Thank you.