Atomic and Molecular Absorption Spectrometry
for Pollution Monitoring
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Lecture – 39
Nitrate, chromium

So, we were discussing about zinc, lambda max etcetera 620 and 520 negative also we can determine.

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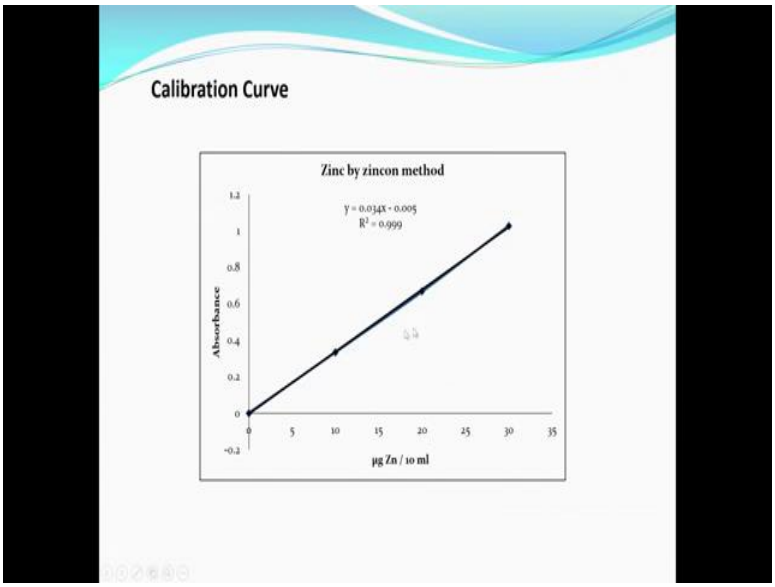

And then I showed you this curve zincon 10 20 30 ppm you can happily determine up to 30 ppm, but it is on the higher side. So, the lambda you can 10 1 ppm should be fairly good enough for your requirement, for water monitoring and then the least square feet is the very good straight line passing through the origin with about 45 degree slope and R square value is 0.999 which means it is a very reliable method.

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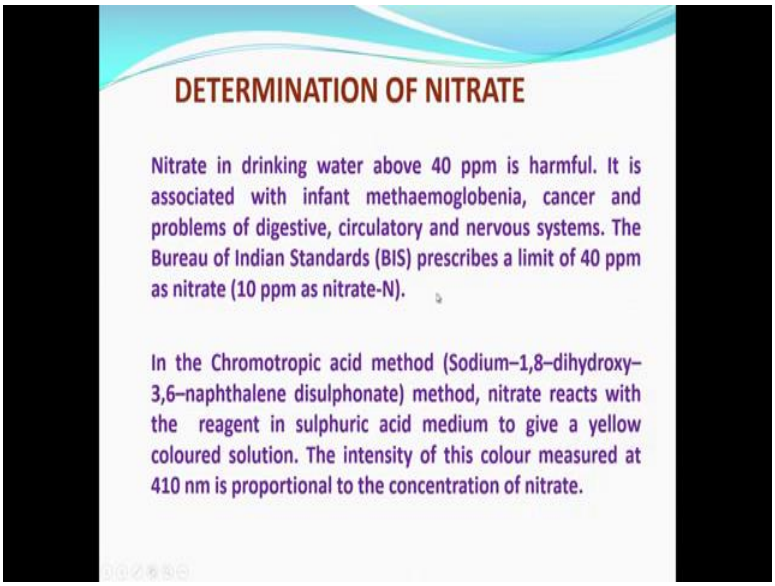

Now, we will move on to another two parameters, that is determination of nitrate. So, I would like to tell you that of late nitrate has become a very important component in drinking water quality, it has assumed more important earlier it was not, but nowadays because of the effect of nitrate causing the infant methemoglobinemia, that is a type of blue baby syndrome; nitrate is being implicated in the disease of methemoglobinemia and it is also been implicated in cancer and problems of digestive, circulatory and nervous systems. The problem is not because of nitrate is there in more higher quantities, but the nitrate in our day to day life is becoming higher. So, the threat of nitrate in the drinking water is increasing day by day for example, in normal river waters or surface waters or pond waters, well water you will not come across high quantities of nitrate, but because of the presence of other elements in drinking water like fluoride, chronide, chromium, arsenic etcetera. Most of the Indian government is sanctioning reverse osmosis units all over India ok.

So, the reverse osmosis units are intended for removing the toxic elements like fluoride and then arsenic etcetera, but the principle of reverse osmosis implicates the rejection of about 30 to 60 percent of water which is known as reject water, remaining 50 to 60 percent is permeate water which is useful for drinking. So, the reverse osmosis works on the principle of essential diffusion through a membrane and the permeate will be having very less concentration of the toxic metals, but the reject will have correspondingly increased anions and cations. So, if you get about 50 percent of drinking water as an RO

permeate, remaining 50 percent you will have to waste. The problem is in the remaining 50 percent of the water the concentration of the elements will increase several fold, and the importance of nitrate comes from this fact.

That the nitrate content quite often increases in the reject RO reject which people are forced to utilize for the day to day purposes; also nitrating is an a industrial process and then all these effluents containing nitrate nitride etcetera they all end up getting oxidized into nitrate, and the concentration of nitrate increases and it is also an industrial product coming from soaps and other things other cosmetics, and the nitrate concentration keep on increasing in the effluent water or surface water or the pond water, bore well water etcetera. So, at the concentration of nitrate normally should not exceed 40 ppm. In 90 percent of the cases if you are using water directly for drinking the concentration would be very less may be 2 ppm, 3 ppm, 5 ppm it does not pose a threat, but wherever there is a treatment system involving the RO reverse osmosis.

Now, a days you should remember that almost every household in India is having a home RO system, as well as in industrially we employ large quantities of RO systems for industrial purposes. So, it has been because of its implication in several diseases, the importance of determination of nitrate has increased several fold and bureau of Indian standard prescribes a limit of about 40 ppm as nitrate, out of which 10 ppm should be as nitrate nitrogen. The other forms of nitrogen in drinking water would be nitrite nitrogen and ammoniacal nitrogen and several other types of nitrogen, but nitrate nitrogen should be less than 10 ppm as nitrate nitrogen, and 40 ppm of nitrogen nitrate in drinking water is definitely harmful you should not be drinking.

So, there is a wonderful method for the determination of chromium for a sorry; for the determination of nitrate the reagent is chromotropic acid, chromotropic acid is nothing, but the sodium salt of 1 8 dihydroxy 3 6 naphthalene disulphonate, that is a organic reagent and almost specific for a nitrate. The nitrate reacts with the re with this reagent and sulfuric acid medium to give a yellow colour complex, the intensity of the colour if it is yellow colour without my telling it should be you should remember that it should be around 400 to 410 nanometers should be the lambda max. So, we look at the first slide of this which is called which sort of presents in before.

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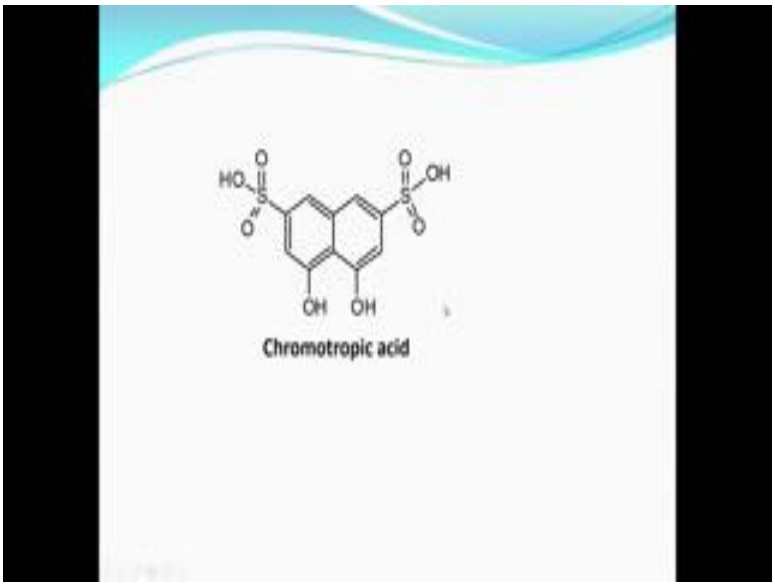

You all the idea that I have presented for this nitrate introduction that should serve as introduction and this is the structure of Chromotropic acid.

You can see that it is a naphthalene ring and then both are aromatic and which 2 S O, 3 O H groups and 2 OH groups, the complexation with nitrate will happen with the removal of water from with these from these OH groups. So, there will be some sort of ring closure and the colour will be shifted to the bathochromic side.

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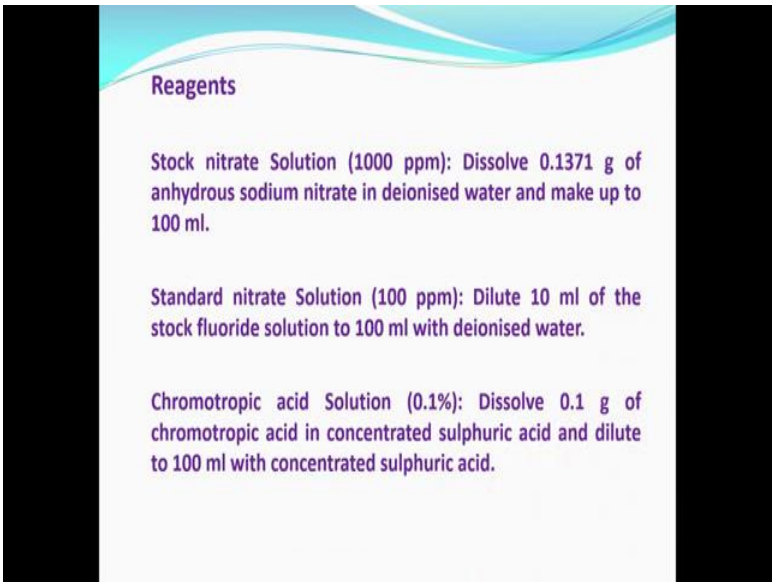

And that is how the determination of nitrate is completed using the spectrophotometric finish. Now the other things become very simple because we have sort of standardized that we prepare up to 100 ppm of sodium nitrate solution, we prepare stock using 0.137gram of sodium nitrate, we have to remember that most of the sodium salts are soluble in water. So, there are no specific instructions for you to design sodium nitrate, same thing is true with respect to dilution we simply dilute 10 times, you will end up with sodium nitrate and chromotropic acid you have to prepare 0.1 percent it is available across the shelf.

But only problem is you have to dissolve the Chromotropic acid in concentrated sulfuric acid, and you have to dilute also with concentrated sulfuric acid this is somewhat hazardous.

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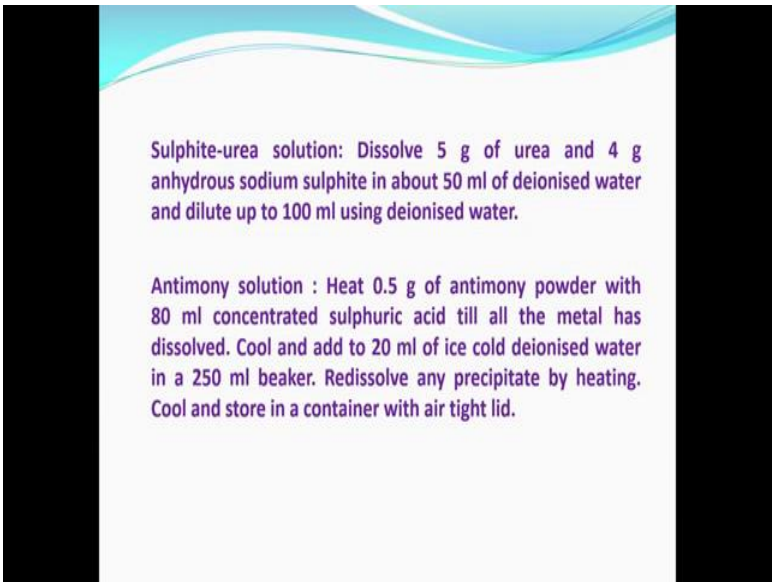

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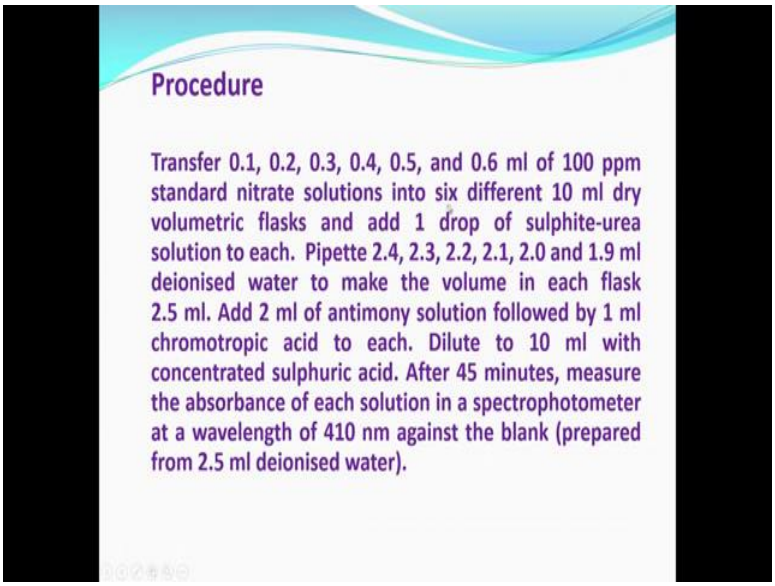

I think most of you are aware that concentrated sulfuric acid you should be very careful in handling, and wherever it is a very highly corrosive liquid, and it is part of the hazardous nature of the chemical laboratory that is you want to determine Chromotropic acid there is spectrophotometrically you have to live with the fact that you have to use concentrated sulfuric acid, with all the associated precautions. Now you need complexing agent especially in this area for the determination of nitrate, for that you have to use urea as well as sodium sulphite in about 50 ml of deionised water and dilute up to 100 ml.

Some times what happens is the sodium sulphite is a reducing agent. So, we have to add prepare about standard nitrate solutions using 0.1 to 0.6 ml of 100 ppm into different flask, and one drop of sulphite urea solution to it and pipette about 2.4, 2.3 etcetera to make them 10 ml. So, the dieonised water to convert everything in to 2.5 ml. So, then we have to add this antimony solution followed by 1 ml of chromotropic acid solution, and after about 45 minutes the colour develops and you have to measure the absorbance of its solution at 410 nanometers against the prepared blank. This is a very simple procedure I do not have to read you the procedure, but still for the rake for the sake of record I will do like such concessions has been the procedure so far.

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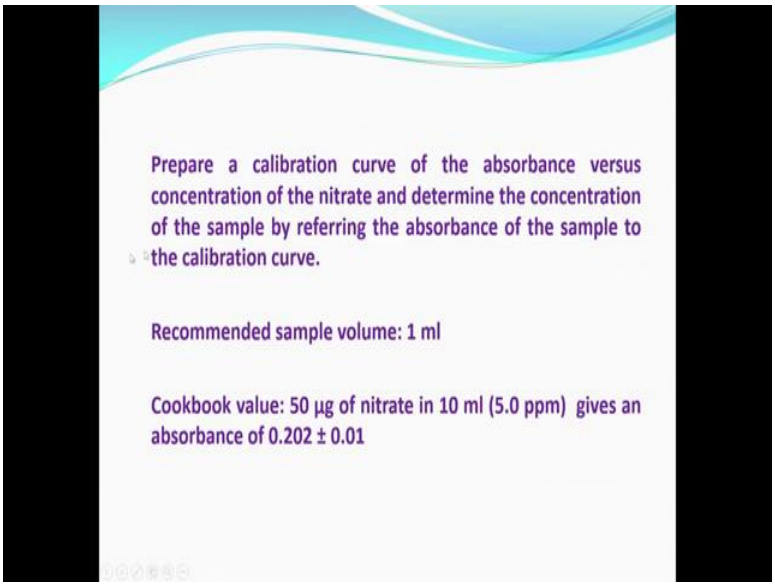

So, we can prepare a calibration curve of the absorbance verses concentration of nitrate, and this the cookbook where recommended by volume is 1 ml, and cookbook value for 50 microgram is 10 ml that is 5 ppm that gives an absorbance of about 0.202 plus or minus 0.01 that is 0.19 to 0.1.

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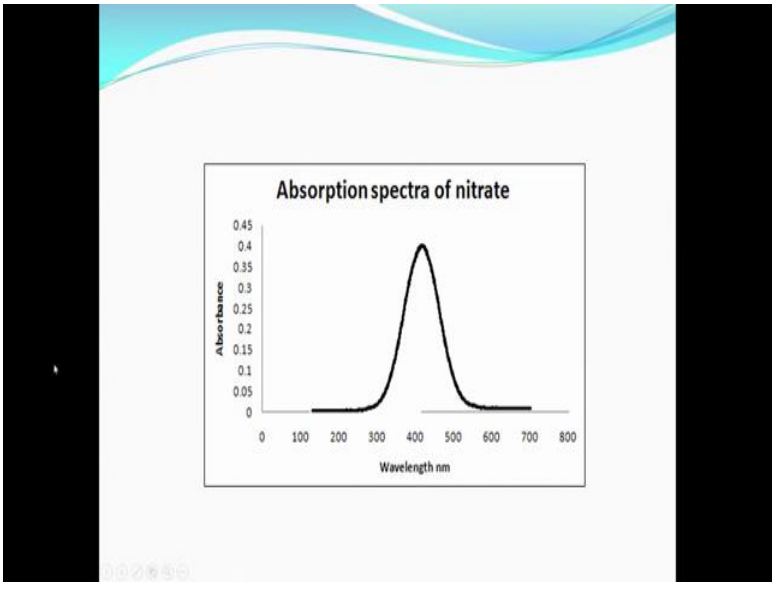

You should be able to get without any problem with ordinary spectrophotometers either it is prism or greater prism or grating or a even a simple calorimeter, because 410 is usually covered in most of this spectrophotometer calorimeters also. There are several

pocket calorimeters available and in the last class I will talk to about portable and other small devises that dedicated devices that can be used for such things. So, there is this is absorption spectra of nitrate and that is the absorbance, where is in you can see that lambda max is around 400 ton it is not very broad monocular peak.

So, you should be have a fairly good spectrophotometers for the measurement even though calorimeters have been used for such purpose; but when you use a calorimeter for measurement of nitrate in chromotropic acid, you need an interference filter that will give you more accurate value than the in normal colour glass filter etcetera. So, that is the only thing I wanted to tell you with respect to this absorption of spectra, absorption spectra and this is the calibration curve for chromotropic acid. You can see that it is a fairly good fit the up to 60 ppm, and the absorbance in what I am presenting here does not exceed 0.4, we have found and above this absorption the curve will bent towards x axis. So, we have to maintain the linearity we have fixed it up to 60 ppm that is 60 micrograms in 10 ml that is 6 ppm, and you can see that the linearity is quite good 0.995 even though it is not the least square feet number 0.995 is not very good.

We normally say 0.997 to 999 is a very good curve, but it is a acceptable as far as we are concerned within plus or minus for 2 3 micrograms errors, I think this should be quite eminently suitable for the determination of nitrate in the by the chromotropic acid method ok.

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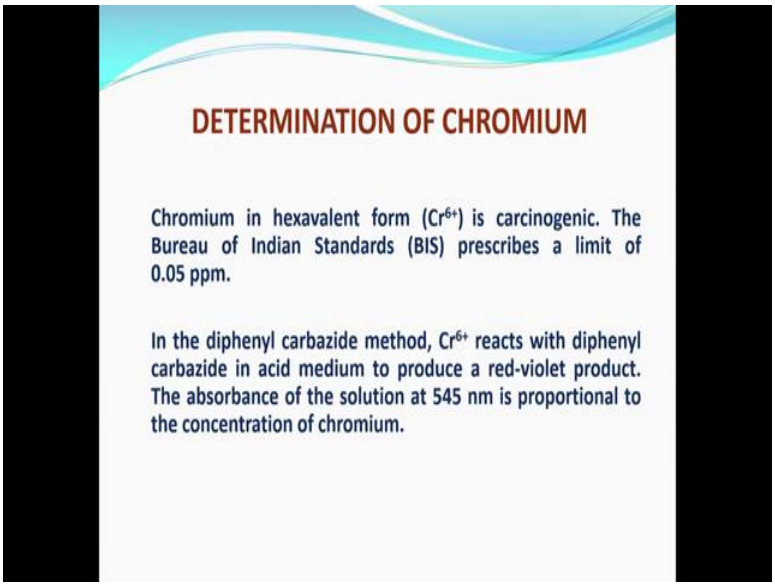

So, this brings me to I would also like to add the effect of nitrate on the other elements for example, the interference in nitrate you can expect quite a lot for example, anions you may not, but definitely some of the metal ions you can expect for example, fluoride does not interfere up to 200 ppm, and then chloride does not interfere up to 200 ppm where we have tested most of them for 200 ppm because even in soils etcetera.

We will not come across higher concentrations, then manganese does not interfere magnesium does not interfere, nitride does not interfere, chloride does not interfere ammonium iron copper all these things are up to 200 ppm will not interfere. Among the cations iron, cadmium, vanadium, antimony, zinc, sulphite, cobalt, nickel, arsenic and mercury they do not interfere up to 200 ppm; that means, this procedure is essentially specific for nitrate. So, without any complications in the procedure we can say that typically we can determine go ahead and determine without much experience also you will get fairly accurate values if you want to determine in soil or drinking water or anything it is essentially for us especially, the for the small children iron and nitrate containing materials are slightly dangerous. So, this information should help you how to determine the nitrate using a chromotropic acid method, a very best one of the best methods I have over come across and typically a reliable method that is all I can tell you at this stage.

Now, the next element on my list is chromium. So, again I would like to tell you that chromium is a very very very celebrated element as far as toxicity is concerned, we know that the chromium is industrially a very important element very widely distributed in in the nature. So, in the soil also it is there in fairly descent quantities, but most of the chromium in the soil is not available to us as a labile compound; that means, whenever it rains or something like that chromium salts do not dissolve, and then flow into an into the surface waters, but chromium is a very important industrial metal, it is required for the production of stainless steel vessels, stainless steel reactors and then chromium plating is one of the most well-known industrial method for the determination of bright surfaces, which are neutral to several chemicals. And they are also sort of corrosion resistant elements chromium, so chromium coating does not result in serious corrosion.

But on the flip side chromium is a carcinogenic element especially hexavalent chromium that is chromium 6plus is carcinogenic; chromium 3 is not carcinogenic that is trivalent chromium. Unfortunately the in the in the environment under suitable circumstances

chromium 6 gets converted into chromium gets oxidized in to convert in to chromium 6 therefore, there is a limit for the determination of chromium in the effluent the normal effluent concentration is about 0.05 ppm. So, the determination of chromium in industrial effluents is a very very important process, 90 percent of all governments in India and other countries put a restriction on the concentration of chromium in the effluents; in the industrial effluents and drinking water also we do not want very high concentration of chromium.

So, with this introduction I would like to take you to the analytical aspects of chromium. So, the diphenyl carbazide method is very celebrated method for the determination of hexavalent chromium, diphenyl carbazide in acid medium reacts to produce a red violet compound it is inner complex this will not there in the text, but for your information I want to you to study the structure of chromium and diphenyl carbazide complex. Feagul and other books usually described the preparation of diphenyl carbazide complex and structural studies also, and in the diphenyl carbazide method chromium 6 react with diphenyl carbazide in acid medium to produce a red violet complex the absorbance is around 545 nanometer.

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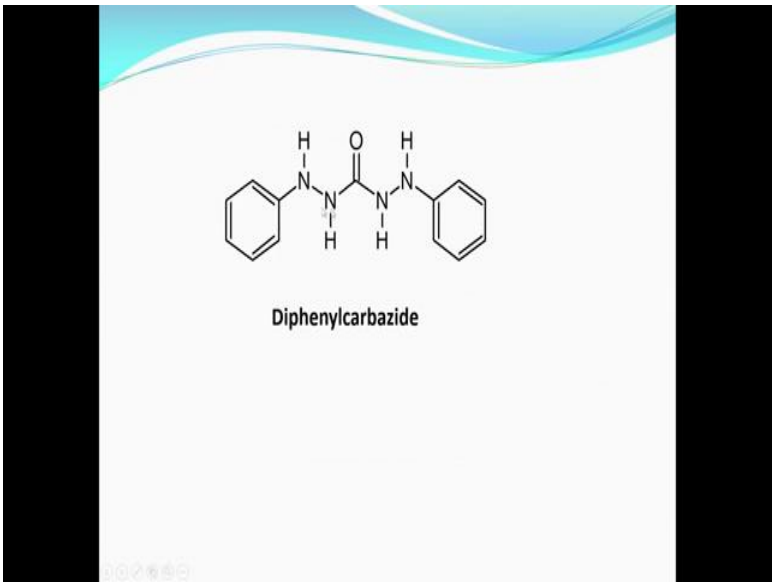

That is somewhat violet in colour slightly bluish violet in colour, this is the diphenyl carbazide we can see that that it is a diagrammatic ring structure with N H N H O N H N H this thing diphenyl carbozole is also one of the similar structures.

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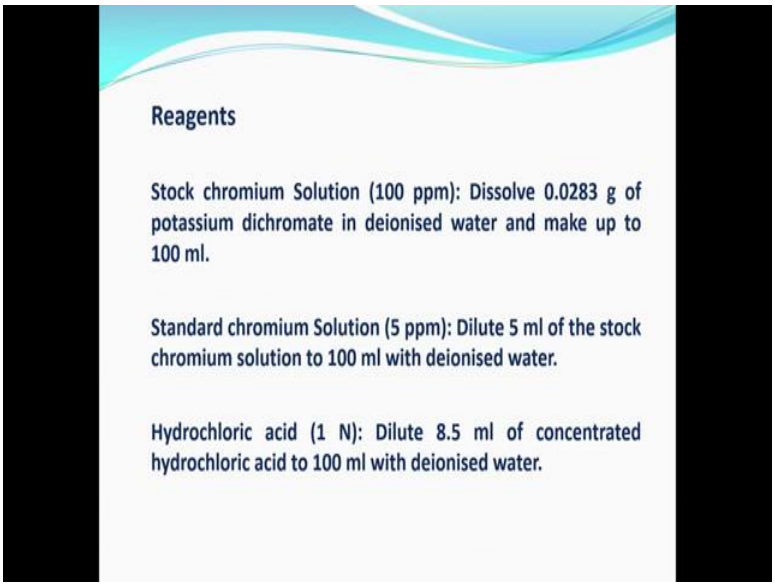

And the reagents; what we need is basically so chromium solution and diphenyl carbazide solution you need some sort of buffer to prepare the final work in the final working solution to around p H 4. So, stock solution I am recommending you pre handle very less chromium even in your day to day life. So, we recommend 100 ppm is more than enough for your stock solution, you can you have to dissolve 0.083 gram of potassium dichromate deionised water very highly soluble in water, and several the colour of the complex even 100 ppm would be quite dark yellow color.

In fact, the several industrial areas in in and around Bangalore whenever you dig a well around bore well even up to 150, 160 degree feet, you get chromium containing water up to 160 ppm 150 to 160 range you will get. So, that is all dark yellow colour in this thing, but for all our studies chromium we can prepare up to 100 ppm, then we can prepare this standard working chromium that is 5 ppm that should be allow that should be you dilute 5 ml that is about 20 times dilution, and hydrochloric acid we need about 100 ml. So, one normal should be more than enough.

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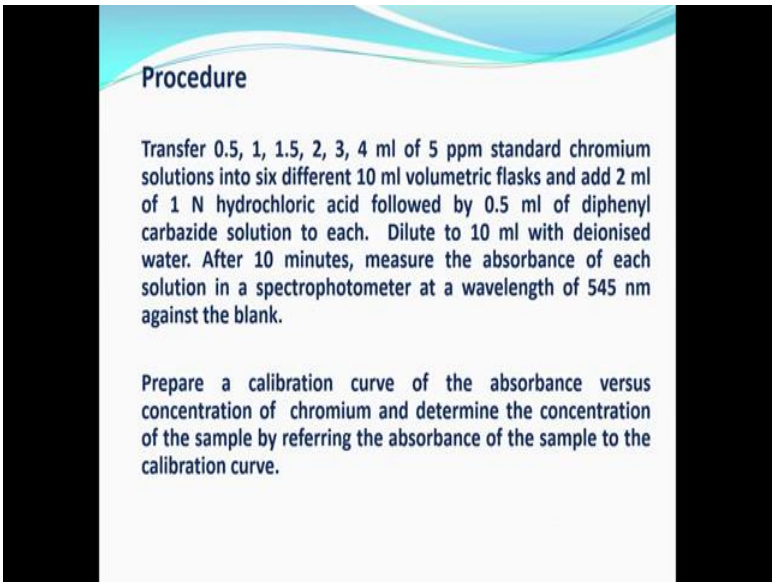

The procedure is to transfer up to 5 ppm to 10 ml volumetric flask, and at 2 ml of hydrochloric acid followed by 0.5 ml of diphenyl carbazide solution to it. The diphenyl carbazide we have to dissolve it in methanol normally it is not easy to prepare a dissolve in any water, so certain amount of methanol has to be incorporated up to 50 percent for the solution.

So, 0.5 ml of 1 percent should be more than enough diphenyl carbazide and allow it for about some 10 minutes measure the absorbance at 545 nanometers ;then you can prepare a calibration curve followed by all other parameters that we are we usually normally look at.

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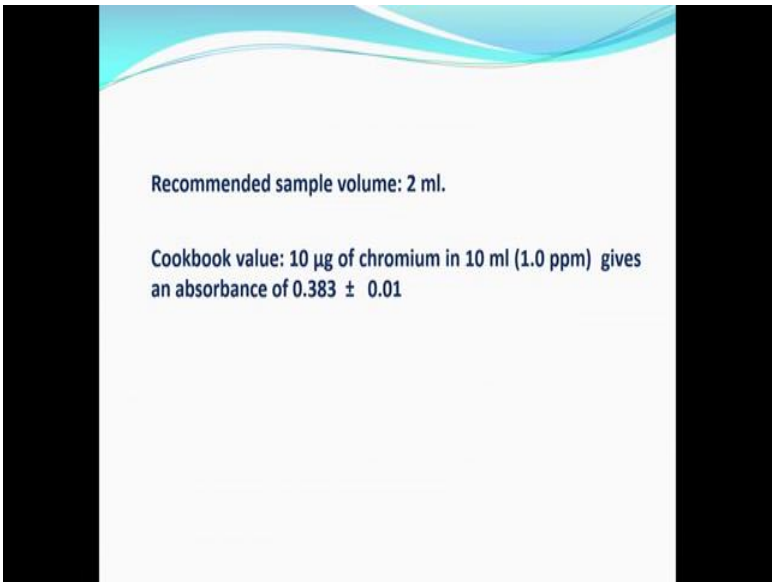

So, recommended sample volume is 2 ml, a cookbook value of about 10 microgram of chromium in 10 ml should give you an absorbance of about 0.383 plus or minus 0.01 absorbance very reliable method and very celebrated method.

Most of the text books do describe this experiment as a standard text standard text book as well as for practicals many M.sc students etcetera engineers use this method very routinely, and this value has been obtained in number of occasions by all researchers and the lambda max, here I am showing you the lambda max of these two solutions over there bottom one, what do you see here is the reagent blank.

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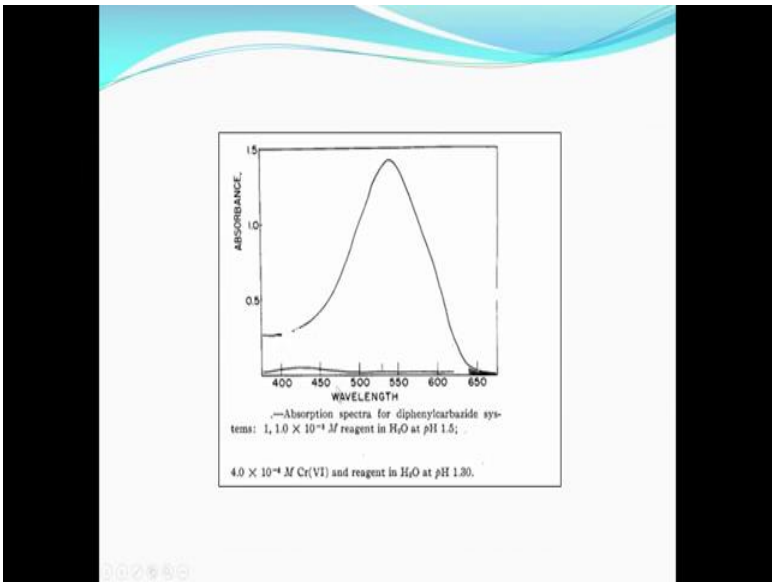

And the top one is the absorption spectra for diphenyl carbazide chromium complex, you can see that around 540 the curve is fairly broad plus or minus 2 3 nanometers does not make much difference to the sensitivity of the method. So, basically the method is applicable to several industrial samples and the method can be adopted for routine analysis ok.

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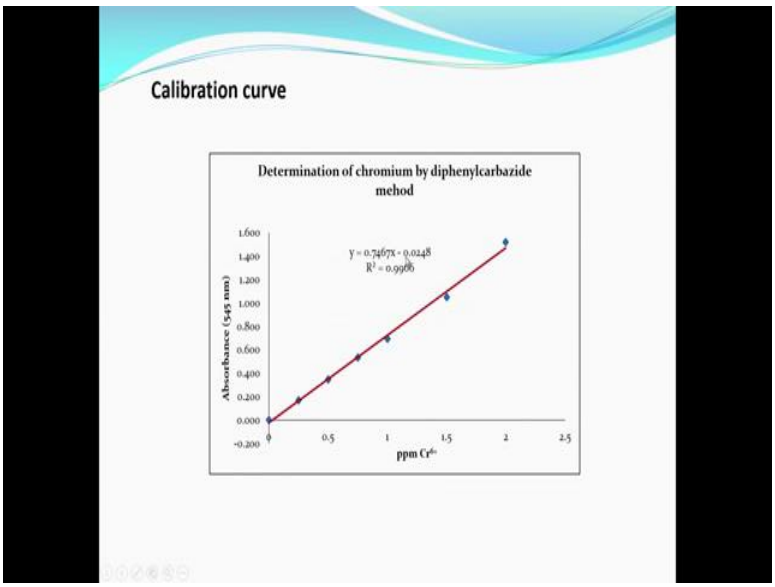

So, this is the calibration curve, you can see that the linearity is up to 2 ppm. So, if my absorbance value is about 0.4 with respect to at 0.5 ppm, 0.04 would be or drinking water level testing.

So, 0.05 ppm should give us 0.04 absorbance, which is quite high with respect to drinking water, but what we can do you we can take a higher sample and instead of 1 ml you can take 5 ml and then you can bring it to descent level for measurement between 0.2 and 0.8; that is a proper that is the aim of all experiments with respect to relative concentration error.

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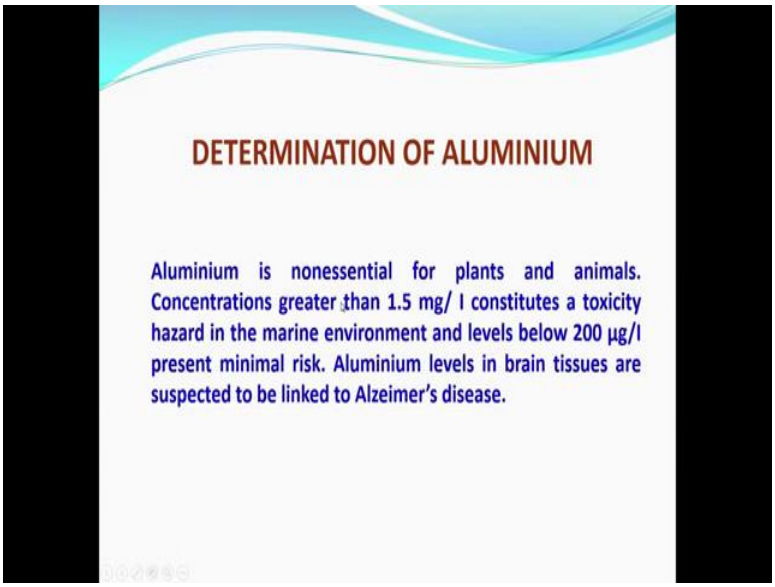

So, that completes our discussion about aluminum, I will do a small introduction regarding the determination of aluminum and I have not informed you about the interference of chromium. Before I proceed to aluminum I would like to talk to you about the interference of chromium other elements in chromium, in general the we are normally also worried about the anions especially whenever we are using azide and other chemicals for spectrophotometry, we normally worry about the anions: among the anions hydride bromide co do not interfere, hydride and bromide do not interfere with up to 100 ppm.

Remember for our in cookbook value we are preparing 1 ppm. So, 100 times this concentration in if the iodide is more, it will not interfere. When the same thing is true with respect to bromide and then what about chloride? I would like to ask you such

questions especially in the examination, because I am not mean I do not normally tell about the interference of chloride in this method, but you have to think about the procedure because if I am using one normal HCL for the adjustment of p H or around p H 0.2 or point something or 2 normal HCL; obviously, it means that chloride will not interfere, same thing will be true of sulphate also. So, if the acidity is high we would be either using chloride or sulphate, but if it is nitrate I may be slightly worried because nitrate nitric acid have got an oxidizing property.

So, a nitrate nitric acid may cause some moment of interference by destroying the diphenyl carbazide reagent. So, in this such tricks we normally employ in most of the examinations and, but if you remember the procedure if you look at the procedure carefully, you can answer many of these questions without any problem. So, in this method chloride does not interfere, sulphate does not interfere, nitrite does not interfere that is nitric acid will not interfere; and cobalt, magnesium and iron and copper iron up to 100 ppm will not interfere, but copper reduces the absorbance about 0.297 that is instead of 0.38 you are getting about 0.29; that means, there is some amount of interference whenever there is copper.

So, we try to reduce this by decreasing the concentration of copper to see how long at what level the interference of copper becomes negligible; when then what we do is we reduce it to 10 ppm, 50 ppm like that until we reach the equivalent volume. So, if I say that up to 5 ppm if the absorbance is within plus or minus 0.03 nanometers it is not interfering. So, 10 percent we can make it. So, up to 5 ppm we do not have any problem with respect to this thing, but unfortunately chromium copper even in 5 ppm it gives an absorbance of 0.533 instead of 0.38; 5 ppm level that is equivalent level. So, we can draw two conclusions from this one is copper definitely interferes, but if the interference of copper is with the formation of another compound another complex, then the another complex we by increasing the concentration of the reagent we may be able to overcome the interference.

But if the concentration is if the copper is having a preferential interaction with diphenyl carbazide, preventing the formation of chromium complex then we should definitely call it interference, but if it is structured it can be reproducible. Copper is one such case where 5 ppm will definitely give lower result, but it does not interfere in the whenever you have 5 ppm it will give the same result; that means, the interference of copper can be

factored into the calibration of chromium. So, this point I wanted to convey to you regarding the interference of this, and then I also wanted to talk to you about triton, and triton is again a serious interference because up to 100 ppm it gives you very less absorbance less than more than 10 percent change, but 10 ppm it is same problem, but around 5 ppm I do not have much problem. Fortunately in most of our river waters the absorbance is always lower in in the concentration of triton x 100 in our river water is less than 5 ppm.

So, but at the same time it is important for us to look at the concentration of chromium; so concentration of triton x 100 in for the determination of chromium. So, I want to make a statement here that up to 5 ppm we do not have any problem. If you have triton in the river surface waters triton x 100 that is a nonionic surfactant triton x 100. So, aluminum we do not have any problem up to 100 ppm we do not have any interference. So, the idea is you can determine fairly confidently if you know the metrics components of the chromium effluent.

So, drinking water definitely 0.05 is the limit, we do not have a choice we have to go determine the chromium content. So, this is I have I think I already covered this aspect by the lambda max etcetera, and then this is also there I already discussed this. Now in the next class what I would like to do is discuss the determination of aluminum, and another one or two elements which I feel are important for you if you wish to pursue a career in spectrophotometry or analytical science.

So, thank you very much we will continue our class in the next meeting. So, have a nice day.