Atomic and Molecular Absorption Spectrometry for Pollution Monitoring

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Lecture – 34
Magnesium

We are continuing our discussion on the determination of magnesium. I wanted to show you the structure of titanalum. It is a fairly complicated structure.

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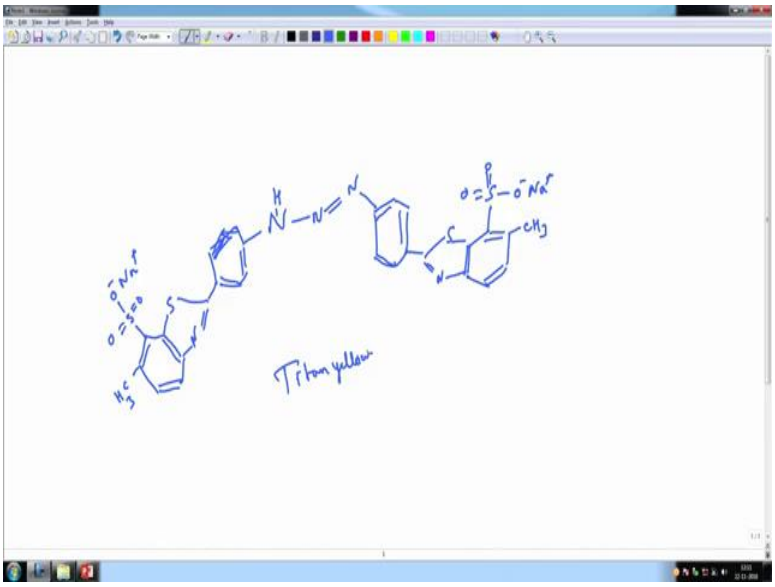

But I wanted to show it to you. It is an again triazodi. This is Sulphur group. This is nitrogen group. And then we have a double bond here, followed by another aromatic ring. And again we need sulphonate groups here. O minus Na plus and this is a CH 3 group. We also have to have a similar structure on this side. That is after NH a benzene ring that is the benzene ring. And then at the para position, we have a similar structure, one is Sulphur one is nitrogen followed by a benzene ring. Again followed by SO 3 Na group this is S 3. So, this is titan yellow.

So, what is important is we have this kind of organic substances that are usually present in our analytical kitty. And you can see that this structure is a fairly typical of organic reagents, in almost all analytical reagent most of them are triphenyl methane dyes and

then they will be azodies and then amines like then. So, the higher the molecular weight the greater is the chromophore. So, the greater the chromophore the better will be the colored reaction, but again it all depends upon how the organic moiety will complex with the metal ion. So, it is as I have said earlier it could be pH dependent also. And the complex structures the structure of the complexes are studied by coordination chemist and several of these metal and di complexes amine complexes etcetera apart from analytical uses they also have uses as medicines and other things.

So, coordination chemistry is a part of analytical chemistry or analytical chemistry is the part of coordination chemistry and it is very important for us to keep track of the new developments in coordination chemistry to develop new analytical reagents that can be used for chemical analysis also. So, I want you to go back to our discussion on the hydroxylamine hydrochloride etcetera.

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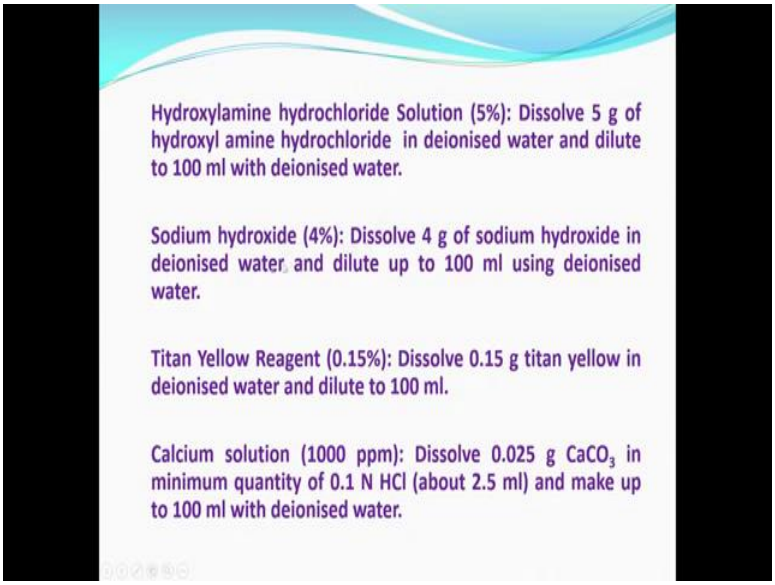

These are the reagents we have been trying to we should prepare and as I have told you the reaction continuous.2 completions only, around pH 12 and we add calcium as a precaution to ensure that there would not be any interference from calcium. And we have to transfer reagents one to 6 ml 10 ppm solution.

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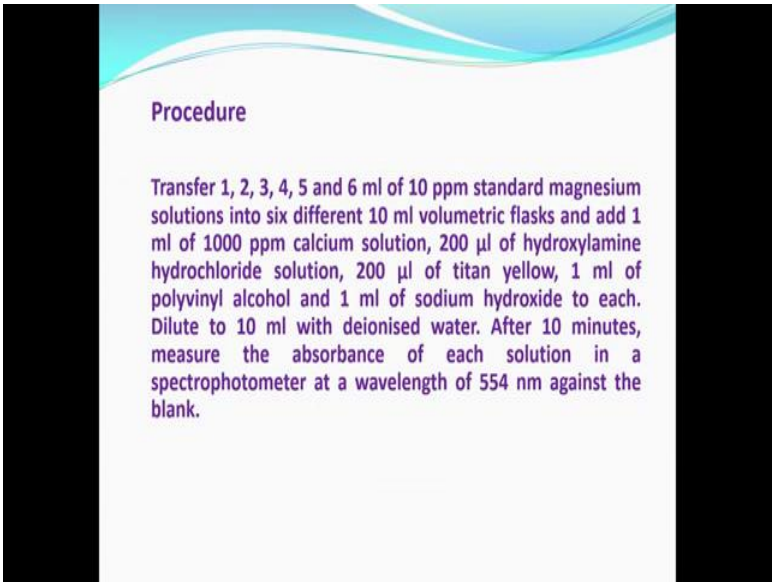

And then 200 microliter of Shydroxylamine hydrochloride and 200 and microliter of titan yellow etcetera 1 ml of polyvinyl alcohol and 1 ml of sodium hydroxide.

Now, whenever I tell you that you have to use so many microliters. You do not have to really worry about the use of micro pipettes. Basically glass pipettes are available in for 1 ml. So, they are all calibrated with 0.1 0.2 0.3 ml. So, 100 micro liter would be 1.1 ml. So, if I say 200 microliters if you do not have a micro pipette each micro pipette will cost you around 2000 rupees or between 1000 and 2000. High end micro pipettes will also cost you around 45 to 50000 etcetera. So, you do not have to really worry about whether you have a micro pipette or not. You can use ordinary glass pipettes of 1 ml calibration. There are micro pipettes are available in 1 ml, 2 ml, 5 ml, 10 ml 25 ml etcetera glass pipettes. So, you can use them. So, you really do not have to worry about micro liter when I say you can use this unless it is 4 or 5 microliters or 10 micro liters. You know for that sampling you may need microliters and for that there are other ways of doing it.

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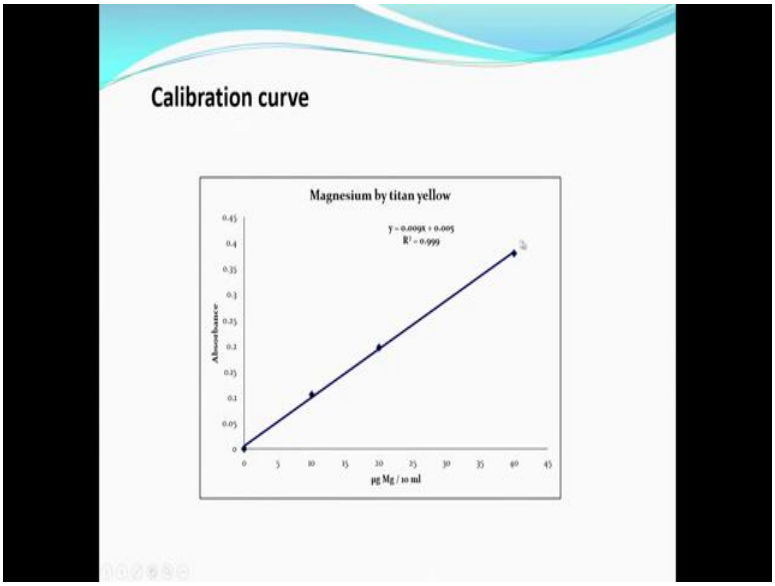

So, with this assurance I want to continue our discussion and you have to prepare a calibration curve. And the calibration curve will look like this. Titan yellow see up to 40 ppm I have the calibration. So, a linear calibration you can see that the correlation is very excellent, the linearity given by R square is 0.999 that is a very good response. That is the recommended sample volume is 1 ml.

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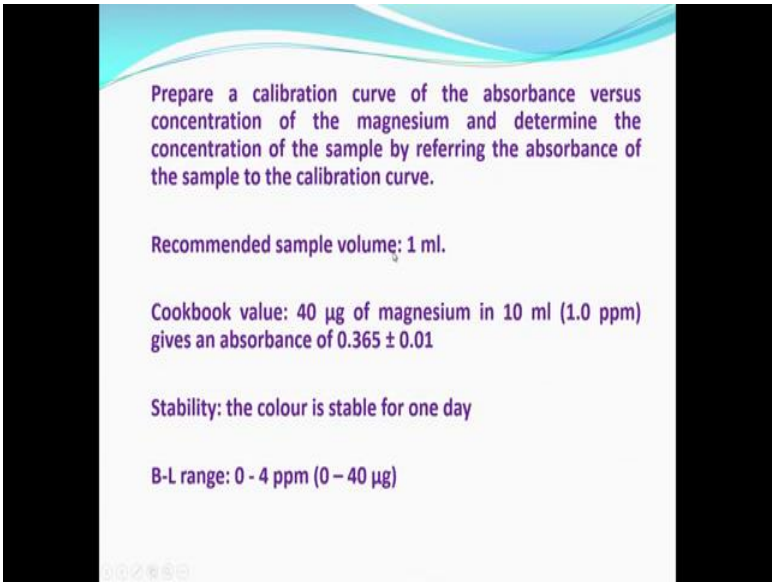

Then cook book value. I am recommending that you take about 40 microgram of magnesium as a standard in 10 ml. And that should give you an absorbance of about 0.365 plus or minus 0.01; that means, 0.37 or 0.3 8 0.34 to 0.3 8 if you get absorbance you are in in good hands.

So, stability the colour is stable for one day; that means, you have enough time to measure the absorbance, and beer lamberts law is applicable to from 0 to 4 ppm. So, what is actually the measurement wavelength? Measurement wavelength is 554. From our knowledge of electromagnetic radiation, we can imagine that the colour would be something like magenta, magenta colour that is approximately that of potassium permanganate.

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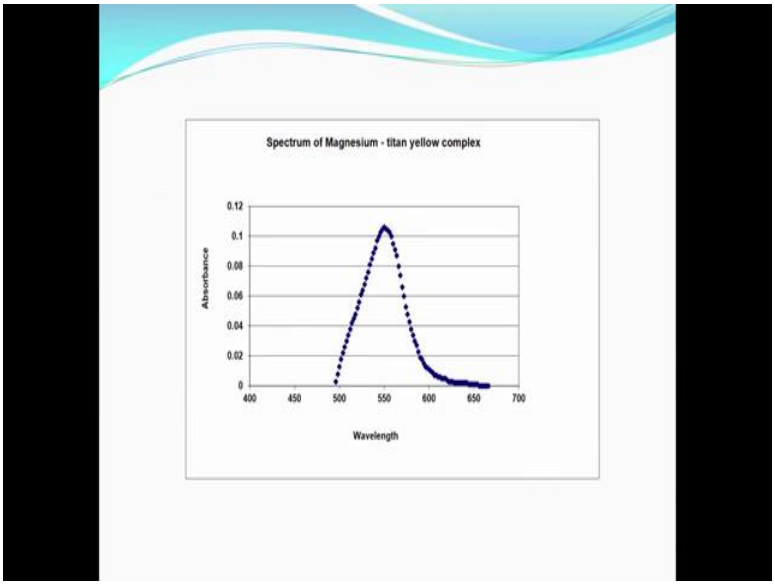

So, this is the lambda max, spectra absorbance spectrum of the sample, and you can see that there is only one peak that is against the blank of course, against the blank you still we have a wonderful method for the determination of magnesium.

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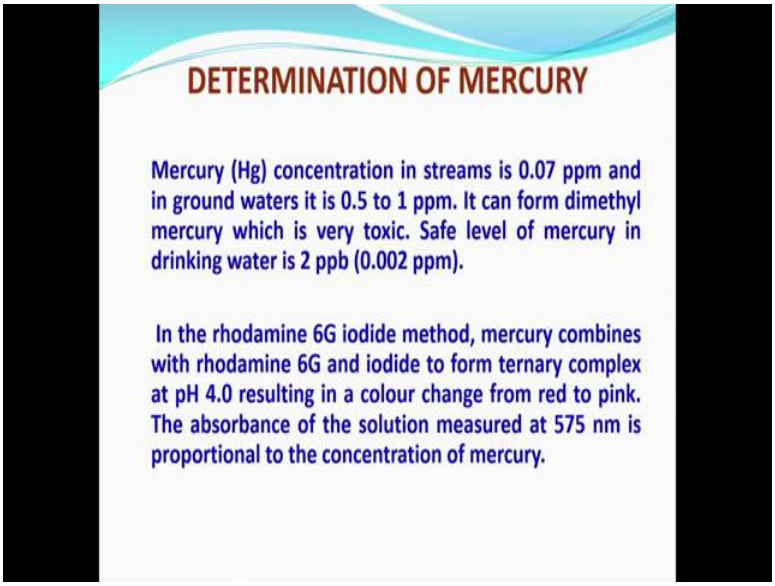

So, this figure I have already shown you. And now we move on to the determination of mercury. Now again mercury is one of the most dreaded element in the environment. Mercury is there everywhere. In the laboratory yes it is there, in the at homes it is there, in hospitals it is there, because doctors use mercury bulbs to measure your blood pressure and mercury is emitted in number of industrial operations for example, burning of coal it contains mercury. Sea water contains mercury, where ever is there is even high ways people have determined mercury from the petro chemical burning along the high way you can determine mercury lot of it. And mercury is a carcinogenic it is a very well implicated in it minamata bay disease. I do not know how many of you have heard about the minamata bay disease, but mercury has been implicated.

Normally mercury is present in water as inorganic mercury. Methyl mercury or phenyl mercury, so there was this company preparing making benzaldehyde and the somewhere around 1950 and they used to let out the organic waste containing mercury into the sea. So, the fishes use to collect the mercury in their gills and then even in their body and Japanese as you as many of us know are found of sea food they used eat these fishes and as a result mercury content in their body went up and people were afflicted with neurological disorders. Lot of problems with neurology blood pressure etcetera and it plays on the brain also if it is there in our body.

So, mercury is not only implicated by minamata bay disease, the problems of mercury where well known even in the medieval century. In the earlier somewhere in the medieval centuries people used to make tall hats if you have seen an old English films medieval English films. Ladies and gents used to ware tall hats and those hats were fitted with feathers. And the compound used to fit the feather to the hat was a mercury compound. And this mercury compound used to disintegrate and then get into the atmosphere and then get into the atmosphere etcetera that is one part, but the guy who prepares this hat those guys used to in just mercury, because mercury is having a very high vapor pressure even at room temperature. That is why we do not allow mercury to be spilled on the laboratory floor. So, even at laboratory floor they vapor pressure of mercury is about 0.31. That is very high compared to any metal.

So, we should not be breathing mercury at all. And anything that contains mercury more than even in the coal ash and other things it is dangerous. I request all of you to be very careful with respect to mercury in your day to day life also. Doctors use mercury as regular filler in the teeth and that is because inorganic mercury is not so, dangerous, but organic mercury is. So, that is phenyl mercury and methyl mercury, but we cannot guarantee that the mercury in our teeth or somewhere, when it is used as in the dental carries. What is the guarantee that it will not dissolve with the food what all we take coca cola, this that acid food acids etcetera, and it may get into our system? And it used to get it will damage cause damage.

Now, coming back to this hat business. Mercury the people who used to make the hats used to get affected by the mercury and the neurological disorders. Basically neurological disorder means it effects the mind. So, people go mad. So, the disease associated with mercury in the 17 and 1600 1700 ad was known as Mad Hatter's Disease. So, people who used to make hats they used to go mad, and those people used to get mad haters disease, but of course, we know now that it is the mechanisms etcetera there are several thousands of applications, research publications. And then for mercury action etcetera and with this introduction I would like you to understand how to go about determination of mercury.

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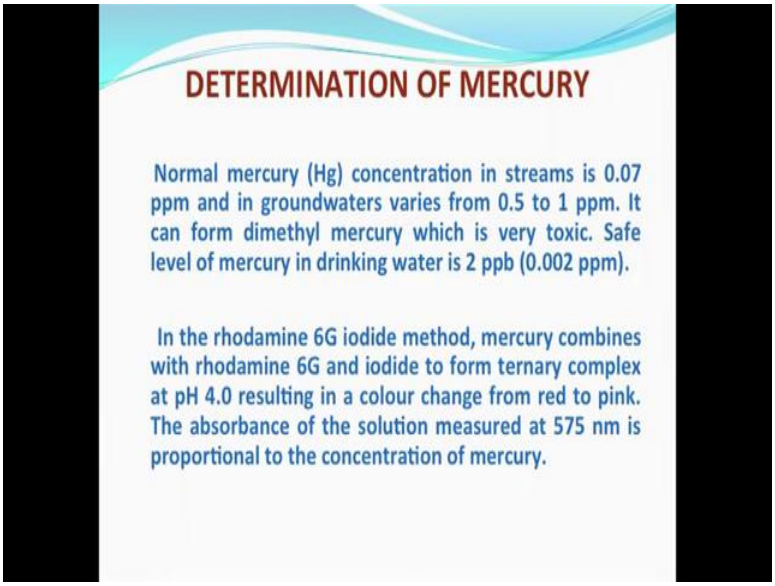

So, normal concentration of mercury in streams is 0.07 ppm. And ground water it varies from 0.5 to 1 ppm. It can form dimethyl mercury which is very toxic and safe level of mercury in drinking water is 2 ppb that is 0.00 2 ppm. So, mercury is usually not determined by spectrophotometry. We have try to address this problem in our application in spectrophotometry because in higher concentration it can definitely be determined let us see how we are proceeding regarding the mercury.

Now, what I wanted to tell you was this mercury is determined by rhodamine 6G and iodine. It forms again a tri ion pair complex with mercury rhodamine 6G and iodide. It forms a ternary complex around pH 4 resulting in a color change from red to pink the absorbance of the solution is measured around 575 nanometers. And it is proportional to the concentration of mercury.

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So, with this small introduction let us look at how to go about analyzing mercury. There are several kit is available for the determination of mercury even in the environment; that means, without using all these you can use lead acetate paper, you can use lead acetate paper and if there is mercury will form a mercuric acetate and you can coat it with dip it with sulphide solution and mercuric suplhide will precipitate it will give a black colour.

So, mercury has also got another problem another property basically, it forms amalgams with many metals. So, whenever you are handling mercury, it is very important for you to be aware of the dangers of mercury. So, coming back to the reagents we have the stock solution of mercury. You should not keep mercury in glass vessels. So, prepare 0.1000 ppm in a plastic bottle and standard mercury working solution is 5 ppm, that is 0.5 ml of the stock solution dilute, it with 100 ml. Now I think most of you are familiar with how to prepare the reagents. So, if it is it is a simple arithmetic involving dilutions.

So, buffered iodide solution, here we have made a slight modification, what we do is we add buffer and iodide solution together. So, it is a citrate citric acid buffer and edta also. So, we add about 24 grams of 2 citric acids 12 gram of sodium citrate, potassium iodide and sodium thiosulphate and 0.466 gram of disodium; that means, we are using 2 one complexing agent that is edta followed by citric acid citrate buffer. So, adjust to pH 4 and standardize pH meter and you can dilute at up to 250 ml. Rhodamine 6G is again a

tri phenyl methane dye. I do not have to tell you what is a tri phenyl methane dye now I suppose, but still I want to give you the structure of rhodamine 6G because I have been talking about rhodamine 6G. Similar structures, but still you should not get confused rhodamine, for example, between rhodamine B and rhodamine 6G we have lot of similarity because all of them are triphenyl methane dyes.

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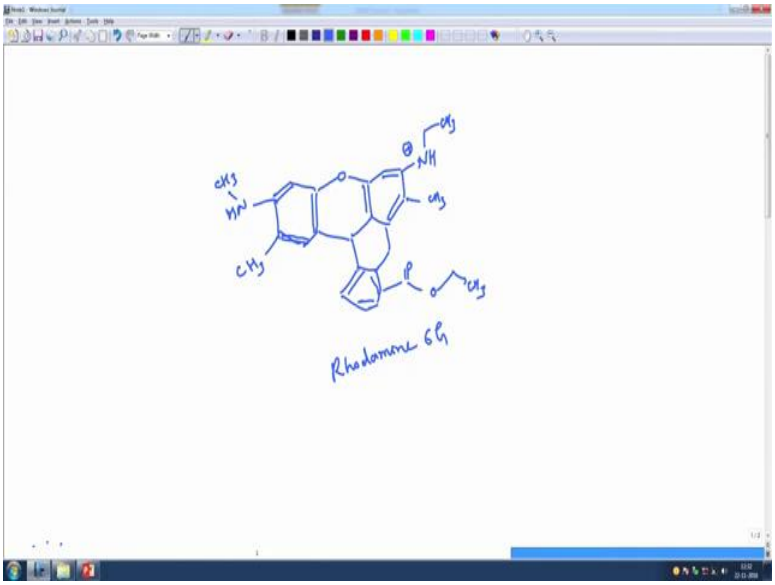

Again rhodamine 6G is a fluorescent solution pink solution and it is structure is something like this. Then again this is also an aromatic ring followed by NH CCH 3 NCL, that is NH CH 3 this should be plus, and then this is CH 3 group then we have one more benzene, ring sort of a semi benzene ring it is. It is not here actually how do I eliminate colour. You can look up the structure in a regular, this is again a benzene ring and then this is oxygen and CH 3 group, and then this is CH 3.

And here again NH CH 3 to this compound I have referred earlier in my talk on interference from about when I was talking about fluorescence, I have talked about this compound and we can this at chemical is again available across the shelf it is regain in a dye which is used for dying the colors, dying the cloths. Pink you know fluorescent pink colour if you see anywhere on the road you can see the; you can imagine that it would it could be 99 percent rhodamine 6G. It is also used in the printing of notes etcetera very widely used dye and assuming that you have all those solutions you have to prepare 1000

ppm mercury, and then 5 ppm is your working solution, then the iodide solution etcetera I have already told.

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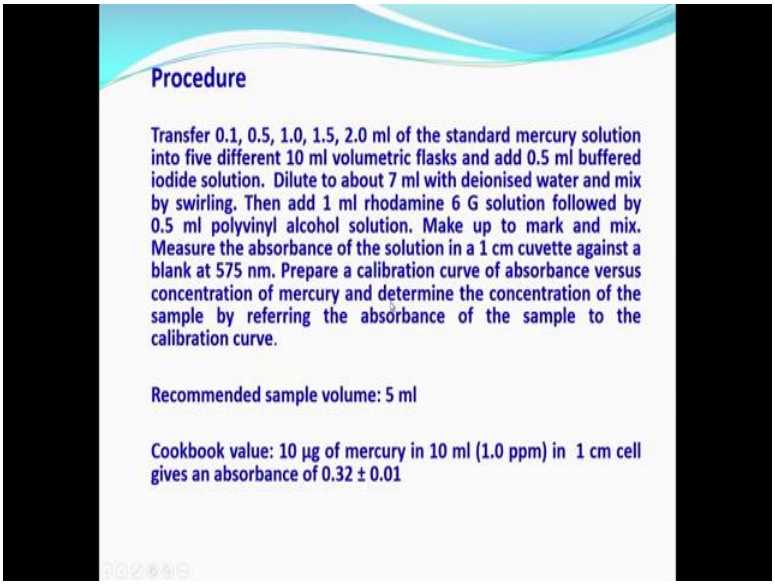

Once you have this you prepare add 0.1 to 2 ml of the standard mercury solution. And 10 ml of the solution add buffered iodide solution, followed by dilution again adding 1 ml of rhodamine 6G, and 2 stabilize you have to add 0.5 ml of polyvinyl alcohol solution, then other things are fairly simple. That is you have to make up to the mark and mix measure the absorbance of the solution in one centimeter cuvette at 575 nanometers. You have to prepare a calibration curve as usual and refer the absorbance of the sample to the calibration curve.

Now, this is the calibration curve. We can see that up to 10 micrograms in 10 ml that is 1 ppm. You should get an absorbance of about 0.03 absorbance. So, this would be the approximately 2 ppm 2 micrograms will give you 0.1 absorbance, 0.07 or something it is a fairly good decent number and it would not bring you to 0.1 ppb current standards, but you will come across several situations were mercury will be in ppm level. At least ppb level this calibration works in ppb level parts per billion level.

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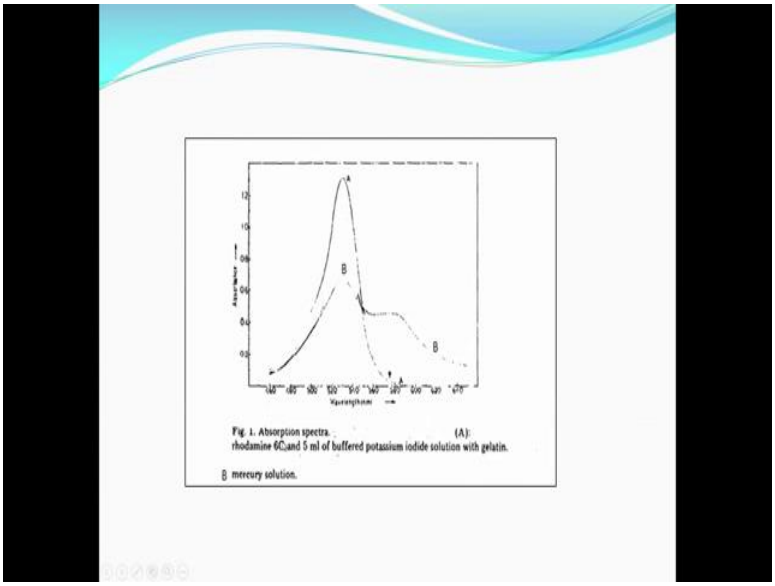

So, this is the absorption spectra of rhodamine 6G and buffered iodide solution with gelatin that is a. This is the absorption and the complex is having a lambda peak somewhere around 575 a small shoulder peak. That is a basically it is a chromophoric shift. This chromophore is extending on the, it is a bathochromic shift. So, the absorbance at this wavelength that is around 520 goes down and then an additional peak will shoulder peak will appear around 575, but around 575 the rhodamine 6G peak is almost 0 having shows 0 absorbance. So, this is the difference what we are measuring around 575. So, B is the mercury solution that is rhodamine 6G buffered solution gelatin or polyvinyl alcohol followed by mercury.

So, recommended sample volume is about 5 ml. So, even if it contains 0.2 ppm you should still end up with the calibration with a value of about 0.3 5 and 0.32 basically, but does not matter. So, 1 ppm is 0.32 0.01 ppm is 0.03 absorbance. So, 0.03 you can you can measure up to 0.09, 0.1 absorbance perfectly if you take 3 ml of the solution.

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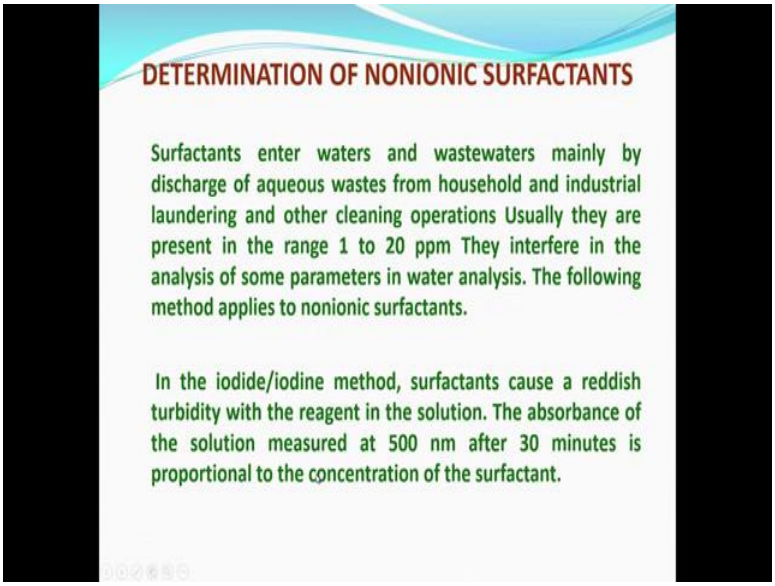

So, we would like to we will not say anything more about the mercury, because they are normally mercury absorption is done by hydride generation atomic absorption spectrometry. That if time permit is if I offer you one more course I may talk to you about atomic absorption spectrometry also, but there are other methods of doing the determination of mercury with icp, but in comparison even though the method is not. So, sensitive like atomic absorption or cold vapor mercury absorption or icp or hydride generation icp. Still the spectrophotometric method normally gives you fairly decent values using this method. We have applied this method to number of samples and I am very happy to tell you that this method has been developed in our laboratory, and we have applied it to several systems.

So, going back coming on to the new system that is nonionic surfactants. That is the next parameter of water analysis, but before that I have to tell you about the interference of the rhodamine 6G method. So, with normally if it is extraction you will not find many interferences because mercury complex gets extracted and you can determine the complete the determination using the available by simple extraction you can separate it from the matrix, but what is important is in the aqueous solution how much it can tolerate that gives you the that gives you the value of the method.

So, I am happy to tell you that lithium magnesium calcium etceteras alkali and alkaline metals normally do not interfere because most of them are soluble in water and colorless. So, manganese ion manganese cobalt transition metal elements manganese cobalt copper etcetera they do not interfere. And at this stage I must tell you that the interference is tested around 100 ppm it is if your we are working with about 1 ppm the concentration of the interference will be 100 times more than that.

So, all the data what I am giving you is approximately 100; that means, zinc cadmium silver chromium and many of these elements arsenic chloride bromide iodide chlorate sulphate nitrite silicate phosphate fluoride etcetera, they do not interfere including lead antimony and serium. So, surfactants they do interfere because of the formation of micelles and platinum interferes by basically, platinum and palladium they do interfere, but chances are 99 percent of the time you may not be able to you will not be getting mercury along with platinum and palladium especially in drinking water.

So, I am giving away almost a full proof method for the determination of mercury using rhodamines 6 g and iodide. And that is aqueous system. So, the whole analysis can be completed within half an hour if you have all the reagents ready with you. So, that brings me to another system that is we will discuss about surfactants, nonionic and ionic surfactants.

Generally, in all municipal waters, especially river waters and then surface waters ponds etcetera, all of them are contaminated with surfactants. Nowadays anything that we use to wash our cloths will contain surfactant. So, most famously known as lab linear alkyl benzene and lab sulphonate labs that is linear alkyl benzene sulphonate there are basically 3 types of surfactant. One is cationic surfactants another is anionic surfactant and another is nonionic surfactant. So, the cationic surfactants are not. So, much used in washing machines and soaps etcetera, but anionic surfactants definitely are used because their counterpart ion would be sodium. So, sodium sulphonate sodium lignosulphonate and then linear alkyl benzene sulphonate sodium salt all these things are being are being used in surfactants, that makes them highly soluble in water as well as the make them an essential component of all our river waters, if we do not treat them.

In fact, I must tell you that 99 percent of our water treatment problems arise from the presence of surfactants, in the in our city municipal wastes whenever we take bath, we let out lot of surfactant present in our bathing soap. Whenever we wash we let out and 99 percent of the cosmetics that we use creams and other things moisturizers all those things will contain surfactants. Today surfactant industry is one of the biggest contributor to the water problem in our industry.

So, with this introduction, I want to continue your discussion on the determination of nonionic surfactants. So, ionic surfactants it is very easy for us to determine and several methods are there, but nonionic surfactants are not defined. So, all of them as a together they can be a classified as nonionic and we can go for the determination.

So, with this introduction I want you to take a look at this slide. Surfactants enter waters and wastewaters mainly by discharge of aqueous wastes from household industrial laundering. And other cleaning operations they are present in the arrange of 1 to 20 ppm even in our rivers the interfere in the analysis of some parameters in water analysis and the typical method is iodine iodide method they cause a reddish turbidity with a reagent in the solution. The absorbance of the solution is measured around 500 nanometers; that means, it is a red colored complex, that can be measured after about 30 minutes and the absorbance is proportional to the concentration of the surfactant.

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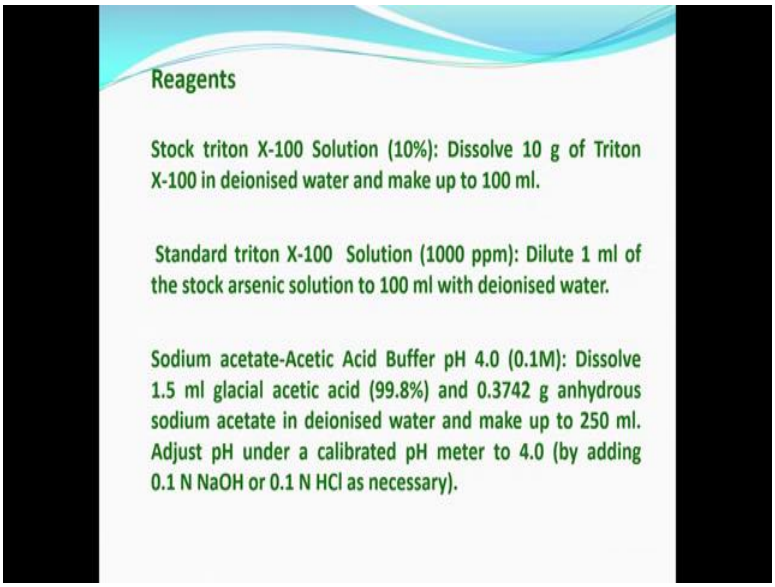

Now, most of the surfactants are represented as triton X-100. This is a very common nonionic surfactant and available across the shelf. And it is also used in industrial samples and you have to prepare 10 gram of that in to make up to 100 ml that is 10 percent and standard triton, you have to prepare 1000 ppm and you need a buffer of Acetic acid acetate buffer that makes it around 4.

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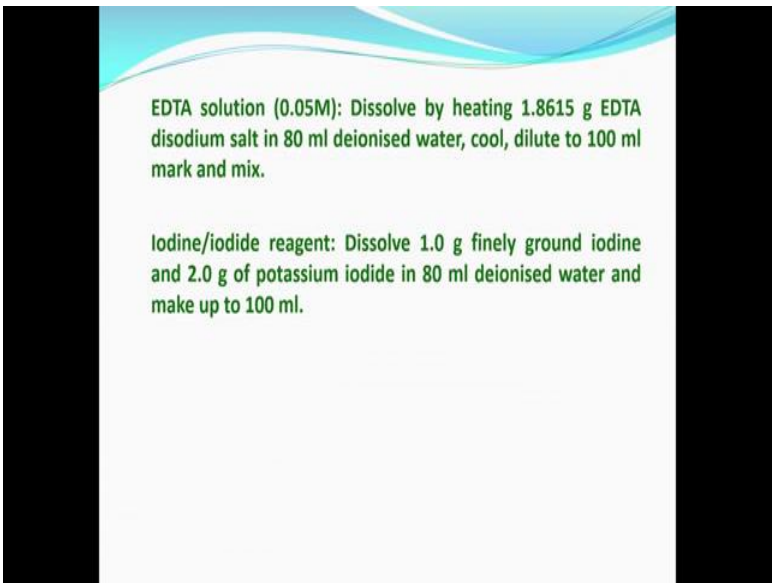

And then we need to complex that is edta 0.05 molar and iodide iodine reagent. What you have to do is actually it is the iodine, but iodine does not dissolve in water. So, what we do is we prepare a solution of iodine in potassium iodide, which is why I have written here that you have to dissolve one gram of finely ground iodine and 2 gram of potassium iodide in 80 ml and dilute it up to 00 ml.

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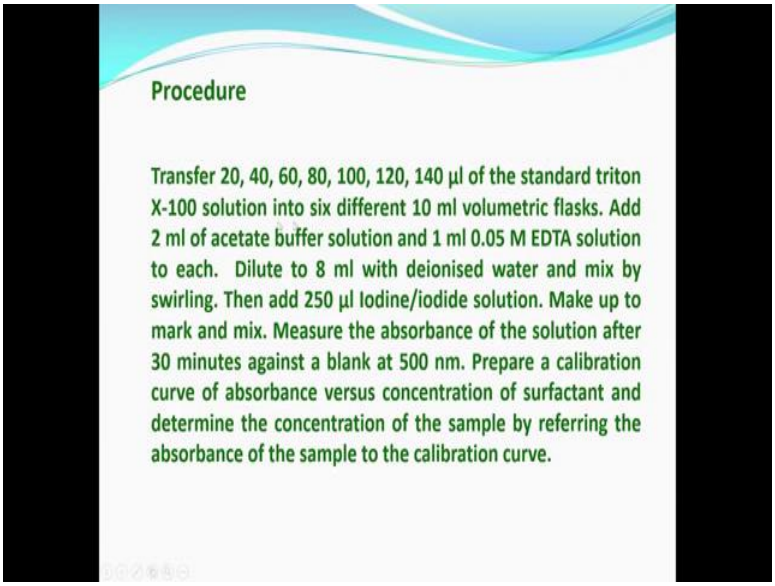

And then the procedure is very simple nowadays, now I think most of you are familiar with procedure, that is you take some quantity of the standard sample and in 10 ml add buffer add 1 ml of edta dilute to 10 ml, and then add iodine iodide solution make up to the mark and mix then the complex will form only thing is after the complex forms we have to worry about how long it is stable, that that will be around 30 minutes and we have to measure a blank. So, measure against the blank also prepare a calibration curve very wonderful calibration curve you will get.

For example, look at this complex, what is a linearity value R square 0.998, up to 100 ppm.

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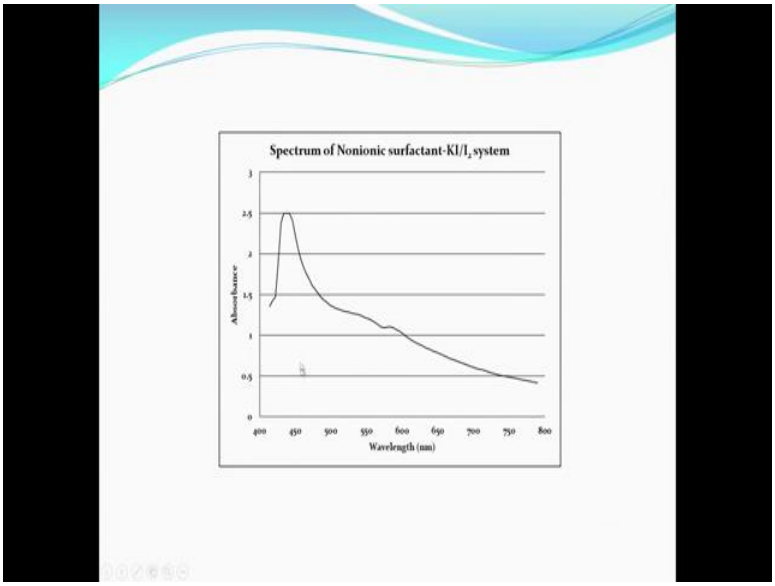

We can determine very easily at 500 nanometers that is red colour and then this is the complex 400 450 and we are recommending 500. Because it is potassium iodate iodide also has some amount of absorbance in this solution.

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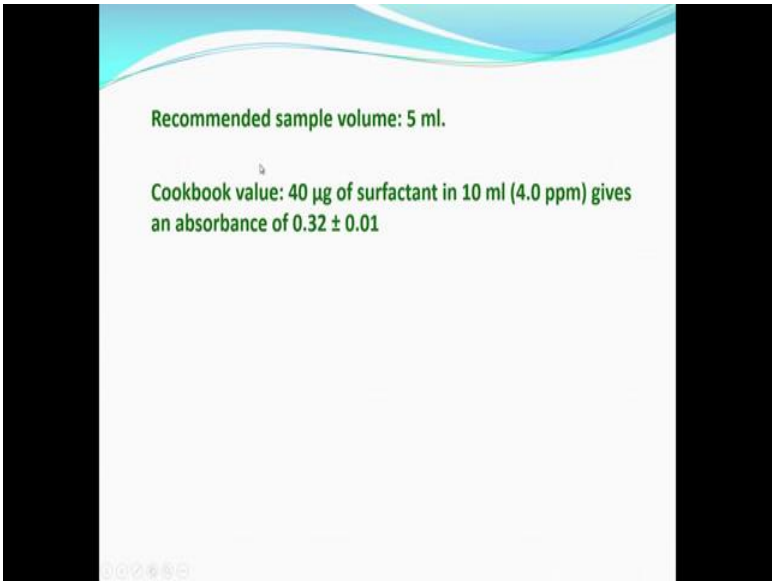

And cook book value is 5 ml of the sample you can take along with your standards what we had recommended, and you can go for a cook book value of about 40 micro grams should give you an absorbance of about 0.32 plus or minus 0.01. I think all of you must

of noticed by now. That most of our absorbance values are working up to are within 0.8 that is less than the relative concentration error.

So most of the time our absorbance linearity ends up around between 0.5, 0.4, 0.3 etcetera, but it does not mean that it is it ends only there, with reasonable error you can extend it up to 0.8 and up to 2 absorbance also. This we have already discussed earlier, but it depends upon the accuracy again. So, the accuracy what you achieve is something phenomenal for example, if 40 microgram of the surfactant gives you 0.32, 10 micro grams will give you 0.08 approximately that is 1 ppm. 1 ppm of this the surfactant will give you 0.08 absorbance a very easily determinable quantity in spectrophotometer; what you need is only a simple spectrophotometer with 350 to 750 nanometer capability.

So I have already shown you these figures. And I will not say more about these analyses because you will your fine I am giving you most of the details in the course as well as I am giving you the references and you can look up other methods also for comparison. I taught you how to determine the how to compare the different analytical methods by means of sandal sensitivity or the detection limit that is approximately 0.004. So, even if you determine 3 times the standard value that is 0.012 that itself is a great achievement.

So, I hope this course will continue to give you insights into the determination of different parameters which we will continue in the discussion, we can continue in our next classes.