Atomic and Molecular Absorption Spectrometry for Pollution Monitoring

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Lecture – 37
Cadmium, copper, lead

Continuing our discussion on the water parameters, we will now discuss about cadmium. So, cadmium is again one of the most important chemical. It is a carcinogenic it is poisonous it is toxic, but it is industrially a very important element. Especially the gold people who manufacture gold ornaments etcetera they use cadmium as one of the alloying element to fix the jewelry, pearls etcetera to gold and soldering a gold soldering etcetera. And it is one of the important element the average abundance of cadmium in the earth's crust is approximately 0.16 ppm.

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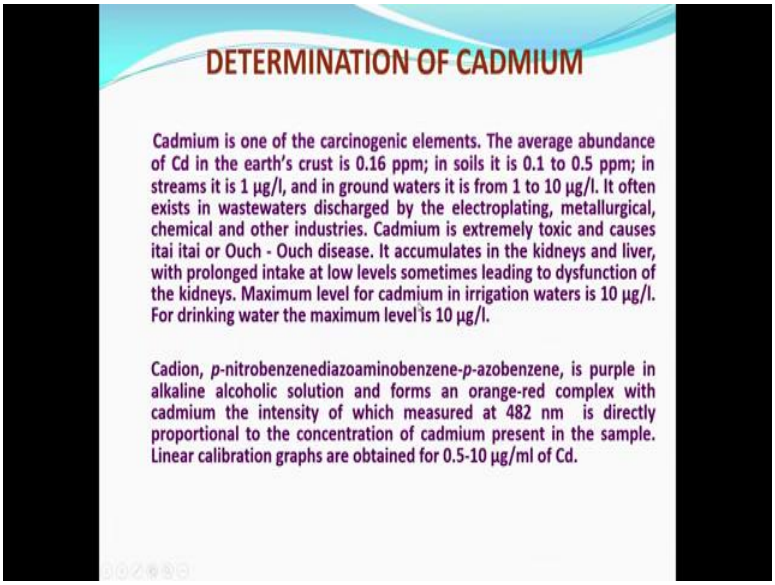

In soils it is again widely distributed and the concentration varies from 0.1 to 0.5 ppm, but you need not get worried about cadmium because it is held in the matrix crystal matrices, and it is not easily available in day today a crop agricultural business etcetera, not for the plants in streams it is approximately about 1 microgram per liter that is about point per ppb parts per billion. No one points per billion. And in ground waters it is

varies from one to 10 microgram per liter that is 10 ppb. So, it often exists in wastewaters discharged by electroplating.

One of the cadmium is cadmium plating is widely popular and it is extremely used in metallurgical industries chemical industries and other industries also. So, cadmium is an extremely toxic and causes a disease known as itai itai and this cadmium, itai itai disease is similar to the one I had described to you during our discussion on mercury. Mercury causes a similar disease which attacks the central nervous system, that is known as minamata bay disease. And in cadmium it is a similar ache disease that attacks the central nervous system. It is known as itai itai disease i t a i - itai itai basically it means ouch ouch in English and in many Indian languages.

So, people who were afflicted regarding the cadmium say contamination, where use to shout like this. And the cadmium also comes from the fish. So, people who eat fish and fish contaminated with cadmium are the cause of itai itai disease. Basically it accumulates in the kidneys and liver, but prolong intake at lower levels sometimes leading to the dysfunction of the kidneys etcetera are very common. So, maximum level for cadmium in irrigation water is 10 micro gram per liter that is 10 ppb parts per billion for drinking water it is micro optimum level is 10 microgram per liter.

So, with this introduction, I would like to tell you that there is a specific reason for cadmium that is known as cadion. It is para nitrobenzene diazoaminobenzene para azobenzene, it that is the chemical name of the reagent and it is perfectly alkaline solution and forms and orange red complex with cadmium. And orange red complex means we can we should immediately imagine that the lambda max should be somewhere around for between 475 and 500. The optimum for this complex is 482 nano meters.

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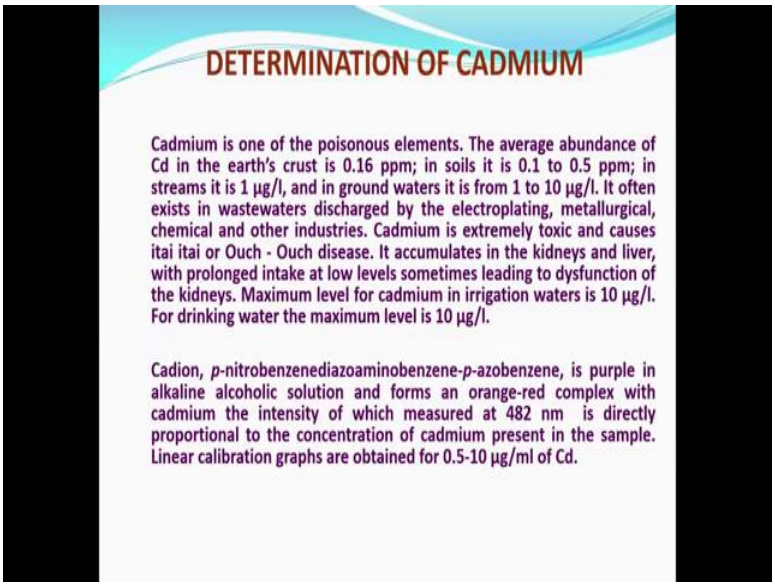

So, it is directly proportional to the concentration of cadmium present in the sample if we are working within the beer lamberts law range. And the linear calibration curve that is beer lamberts law range is 0.5 to 10 micro gram per milliliter of cadmium.

That means it 10 ppm is the determination limit, but we are saying 10 micrograms is per liter is the limit in drinking water. So, spectrophotometry is not an ideal method for the determination of cadmium for drinking water purposes, portability purposes. Because it is 10 times the spectrophotometric limit is 10 times higher than this. So, normal method for the determination of cadmium is in reusing atomic absorption or icp, but here what happens is if we are able to concentrate about 1 liter to 100 ml or 1 liter to 10 ml then the concentration will automatically increase and come in this range 10.5 micro gram per milliliter it should be possible and to determine the cadmium.

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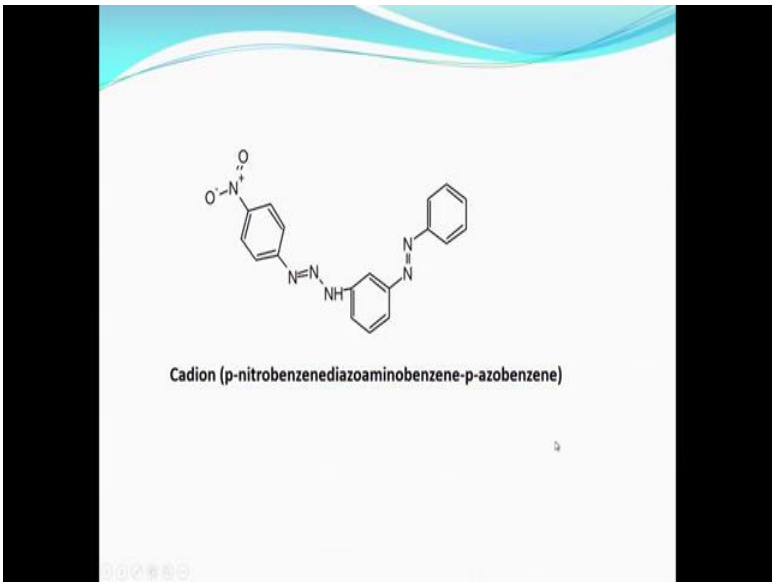

So, this is the reagents structure cadion para nitrobenzene diazoaminobenzene para azobenzene. And this this is the structure this is nitrite group para nitro and on the para.

There is azo group and then one more amino and benzene ring and then one azo group. So, in this forms a complex with cadmium. The details of the complex can be obtained from the other reference books what I have described earlier, or you can recap the sandal book, e b sandal calorimetric methods of determination third edition.

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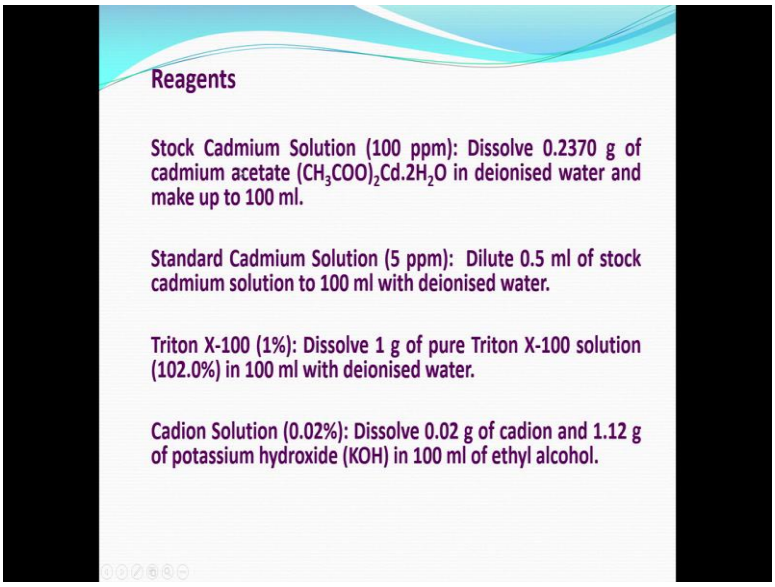

Now, with this introduction I do not want to go into too much of details of this. Because stock cadmium solution we prepare 100 ppm details are given here. So, what we use is not cadmium chloride or something, but cadmium acetate. So, if you use cadmium acetate here stock solution will be fairly stable. And standard calibration is standard cadmium we can prepare it by 5 ppm and they you need triton X-100 again it is a nonionic surfactant.

You can dissolve one gram of pure triton X-100 in 100 ml and that is a triton cadion solution. Cadion is available across the shelf in from many industrial houses laboratory suppliers and you can prepare that in potassium hydroxide solution and 100 ml of ethyl alcohol.

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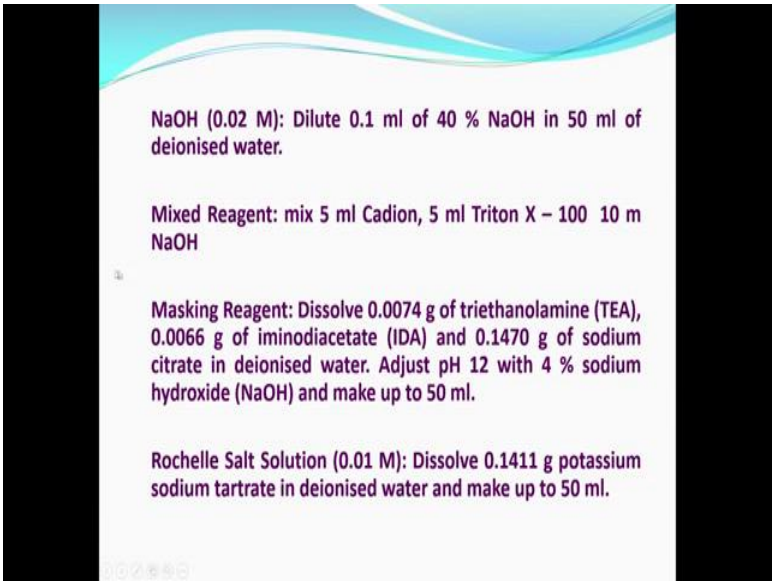

So, you also need sodium hydroxide 0.02 molar of and the actual reagent is a mixture of 5 ml cadion 5 ml triton X-100 and 10 ml of NaOH. So, you need a masking agent because the reaction proceeds in alkaline medium, and the masking agent is triethanolamine again as usual because in alkaline medium we will need triethanolamine as a complexing agent triethanolamine is a beautiful complexing agent for many matrix including iron. And then iminodiacetate it is another complexing agent and sodium citrate citric acid, it works as a complexing agent in an acidic medium.

But sodium citrate works as complexing agent in alkaline medium. So, you can adjust the pH ti 12 with 4 percent sodium hydroxide make it up to 12 to 50 ml then you also

need potassium sodium titrate in the deionized water and make up to 50 ml for the complexation reactions because many metals interfere in the determination of cadmium.

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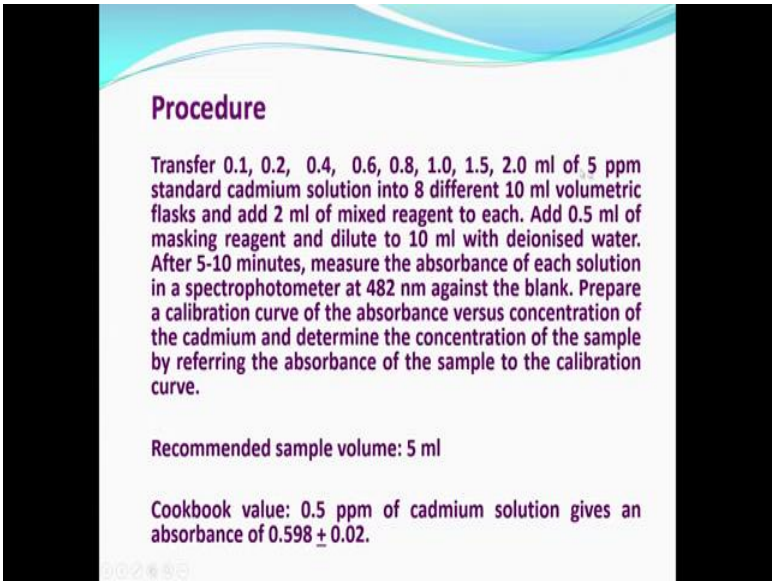

So, procedure is very simple. We can transfer up to 5 ppm standard cadmium, and then you add mixed reagent 2 ml masking agent that is triethanolamine and dilute it measure the color at 482; that means, again the color is approximately orange red complex. So, you can prepare a calibration curve of up to ppm and then recommend sample volume is 5 ml, if you want to determine in drinking water or industrial waters cookbook value 0.5 ppm should give you about 0.598 plus or minus 0.02.

So, if you dilute it 0.05 ppm that is 5 ppb should give you about 0.05 and 0.06 absorbance. That is also quite well within the range. So, using this reagent we have brought the determination of cadmium to spectrophotometric level, with the current pollution control index. So, that is the achievement what we have done here in this case by the use of triton X-100. So, this is the spectrum of the complex.

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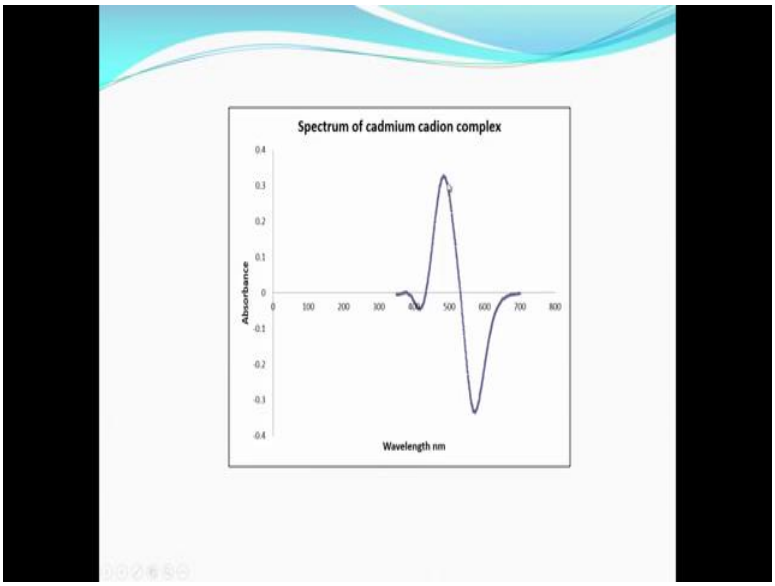

And the lambda max is somewhere around 482. And then this negative peak is for carry on excess carry on normally in most of this spectrophotometric procedures we use excess carry on or excess reagent to account for the complex formation whenever the concentration is higher.

So, this is the calibration curve you can see that we have a very good linearity and the linearity R square volume is 0.966 it is which is fairly good.

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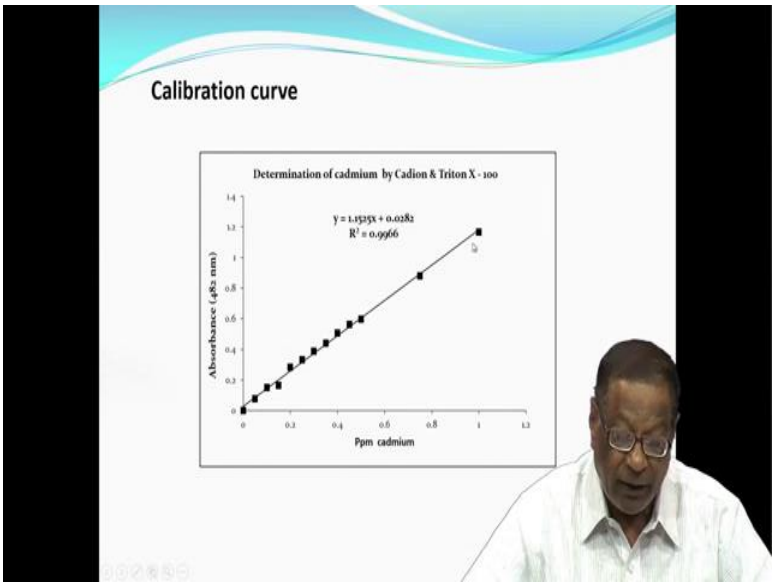

So, you can see up to 0.2 ppm or even 0.1 ppm it is gives you an absorbance of about 0.2 that makes it a method preferred method compiled to atomic absorption all because we have been trying to use triton X-100, as one of the reagents, and this is a modification we have done to the actual system and it is very easy to determine cadmium by this method.

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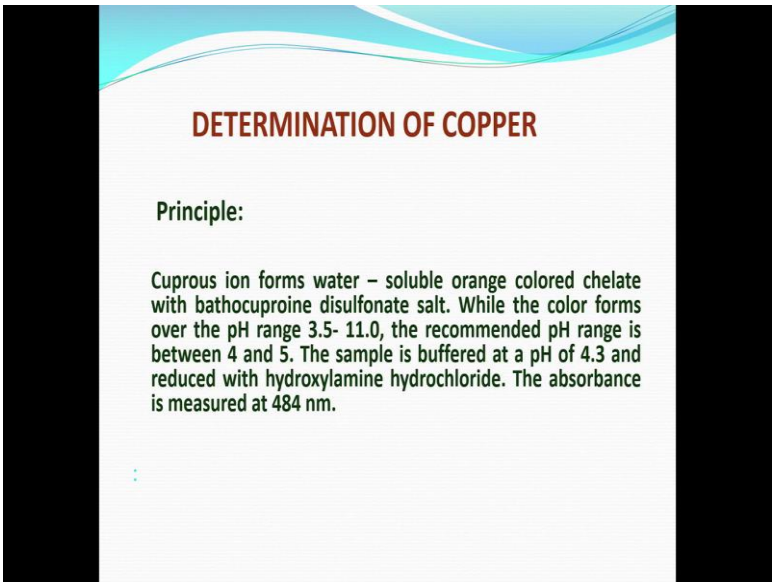

So, now I would like to move on to another parameter that is copper. And regarding the copper, I have to tell you that copper is also a fairly widely distributed element in the nature.

I would like to I have forgotten to add let us go back to cadmium again because I wanted to talk you about some of the interferences in cadmium. So, let us go back to cadmium a little bit, and in in this method this is a cadmium method the fluoride chloride bromide sulfate nitrate etcetera they do not interfere because most of them are in the a most of the time the reaction is carried out in alkaline medium, but aluminum does not interfere, but it forms a yellow colored complex. Therefore, aluminum is not it is not possible to determine, but around 100 ppm aluminum can be tolerated. And nickel also interferes and then cobalt copper almost all these elements interfere cobalt copper zinc vanadium and then antimony all these things interfere lead does not interfere, but around for that is only around 500 ppm. Basically interference means it is an absorbance value which is not expected or which is much more than plus or minus 10 percent of the standard cookbook value now in this cadmium.

We have put 0.598 as cookbook value; that means, if everything is 10 times that is 0.06 we call it interface. So, if I reduce the concentration by about 10 times if I get within the range within plus or minus 10 percent we call it as non-interfering. In that aspect in that mind I have to tell you that boron led and arsenic chromium do not interfere in the determination of cadmium. So, ferric again approximately 50 ppm range that is 5 ppm it does not interfere whereas, interfere always because in alkaline medium whereas, precipitate as hydroxide. So, that is not it is not a problem because it would have in your case whenever you have ferrous sample ferrous, I earn in you water sample it would have precipitated all you have to do is just filter it and use it for the determination. Then silver up to 100 ppm does not interfere mercury up to 100 ppm does not interfere manganese interferes.

And then molybdenum in presence of masking agent that is Rochelle salt because cadmium and molybdenum sometimes occur together therefore, we have recommended Rochelle salt, for the complexation of this molybdenum and manganese also interferes up to 10 ppm, but with Rochelle salt as a complexing agent it does not interfere. Now this is regarding the all this what I have said. So, far is regarding the interference in cadmium. So, again I will go back to copper. The determination of copper I was telling you that it is there present in the soil, in wide quantities. And most of the soils are normally having iron cobalt nickel in very low quantities, iron will be maximum silica will be maximum aluminum will be maximum. Apart from this some soils are rich in other micronutrients like copper zinc and then manganese all these boron etcetera, but the value in terms of metallurgy metallurgically they are not of much significance because they are all in ppm levels so, but the God has made them micronutrients. So, that wherever these chemicals are there this metals are there in slightly higher quantities the plant growth will be profuse. So, the copper is also a fungicide.

Several copper sulfide copper oxychloride etcetera is used as fungicides in coffee and other plants in horticulture as well as agriculture. And then copper industrially copper is a very important chemical. It is used in electro plating 99 percent of electro plating work is done with copper. And the cuprous iron normally a copper is not a pollutant in actual sense, but again imparts some sort of a raw paste to the water.

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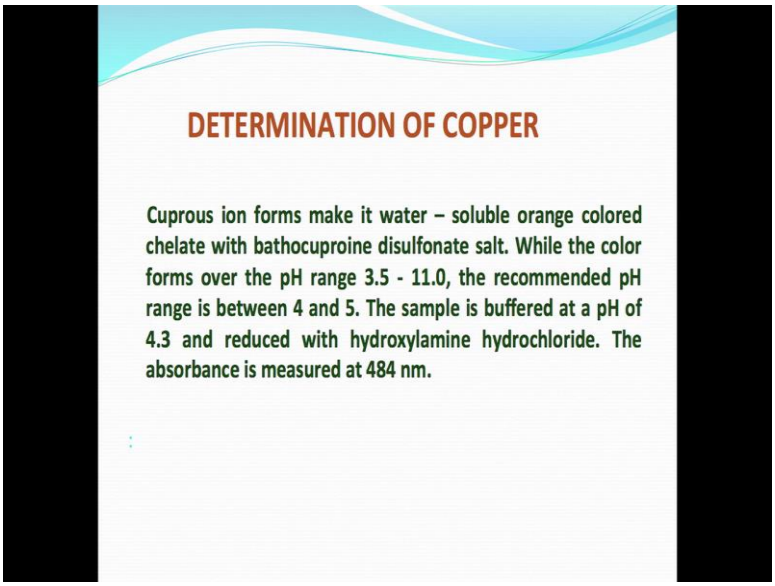

So, the there is a limit for the determination of copper, which I have already explained to you in the beginning and the regarding the chemistry of this principle is cuprous ion forms water soluble orange colored complex with bathocuproine disulfonate salt.

So, bathocuproine is a very preferred reagent almost specific and lovely chemical for the determination. So, the color forms in the range with an over a very wide range that is 3.5 to eleven, but the recommended pH range is 4 to 5 because we want to complex the many metals which may interfere using simple chemicals like edt a N t a etcetera. The sample is buffered at a pH of 0.3 and it is reduced with hydroxylamine hydrochloride because copper cuprous is the cuprous forms the complex with bathocuproine not the cupric. So, absorbance is again measured around 484; that means, the color is somewhere orangish red color.

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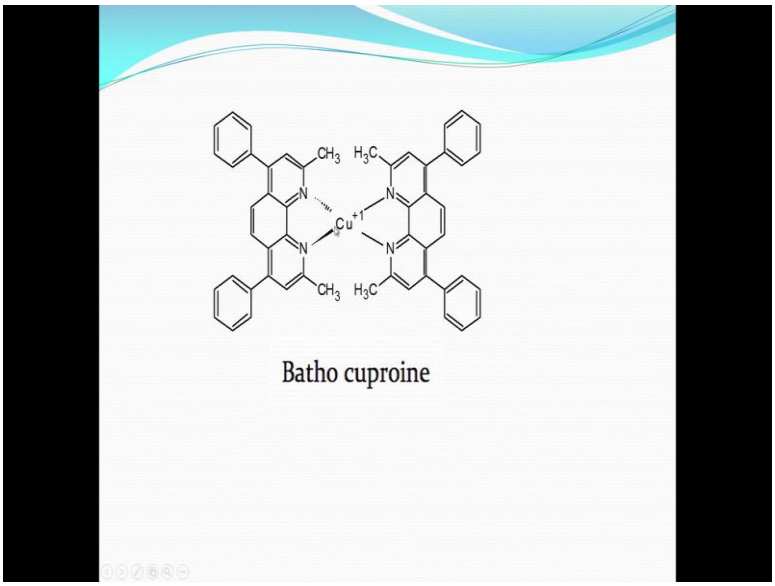

So, this is a very interesting sub complex this is the copper complex with batho cuproine. We can see that batho cuproine is having nitrogen groups here, and then this is like periphery.

See it is sort of tetrahedral complex, but it is like a periphery group there may be one or 2 bondings, above the plane of the formation of this copper. And this is the structure of bathocuproine copper complex. So, then as I had explained to you more the number of rings more would be the chromo phone more would be the color. So, this is basically sort of charged transfer complex only because in the most of them are electron donating groups.

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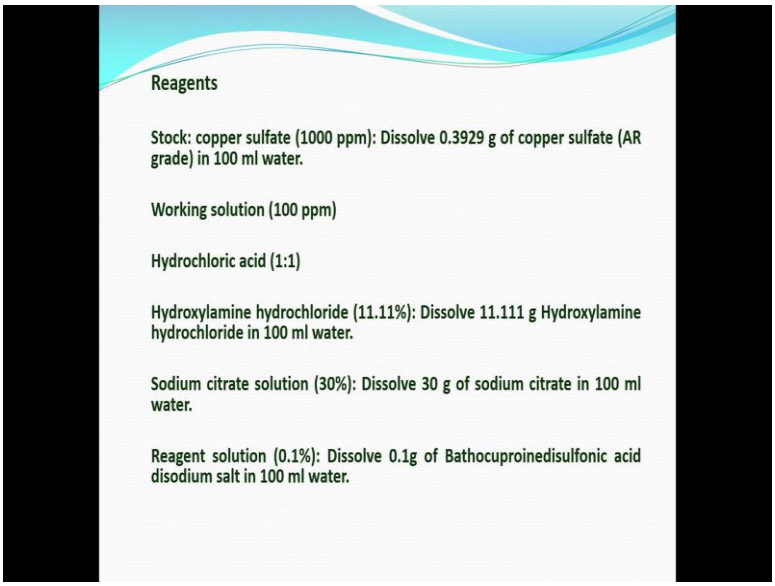

They all they for nitrogens and there are very few bonds between these 2. And the method is applicable to the determination of copper for over a long range. So; obviously, the reagent preparations etcetera I have do not have to give spoon feed you, but as usual our copper sulfate should be stock solution should be around 1000 ppm that you can desolate by 0.1 0.39 gram of copper sulfate you know N l R grade.

Of course in 100 ml of water your working solution can be about 100 ppm and we would also need hydrochloride acid hydroxide hydrochloride about 11 percent and sodium citrate, you will need about 30 grams about 100 ml that is about 3 percent 30 percent and reagent solution should be 0.1 gram bathocuproine sulfonic acid.

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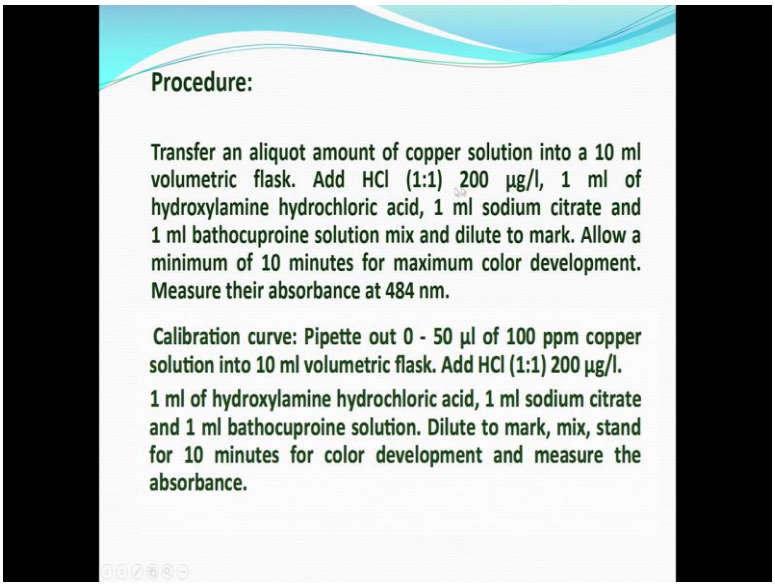

So, procedure is very simple transfer in aliquot into 10 ml volumetric flask add HCL approximately 200 micro liters and 1 ml of hydroxylamine hydrochloride 1 ml of sodium citrate and 1 ml of bathocuproine solution mixture and you can dilute to the mark. So, our usual practices allow it for some time, and dilute to only up to use on develop only in 10 ml and calibration curve is linear up to 50 micro liters, 0 to 50 micro liter in 10 ml volumetric flask that works up to about 5 ppm, that is 5 micrograms in 10 ml that is of 15 micrograms in 10 ml that is 5 ppm.

And all other things are fairly simple and the recommended volume is 2 ml, cookbook value is 1 ppm gives you about 0.21 plus or minus 0.01.

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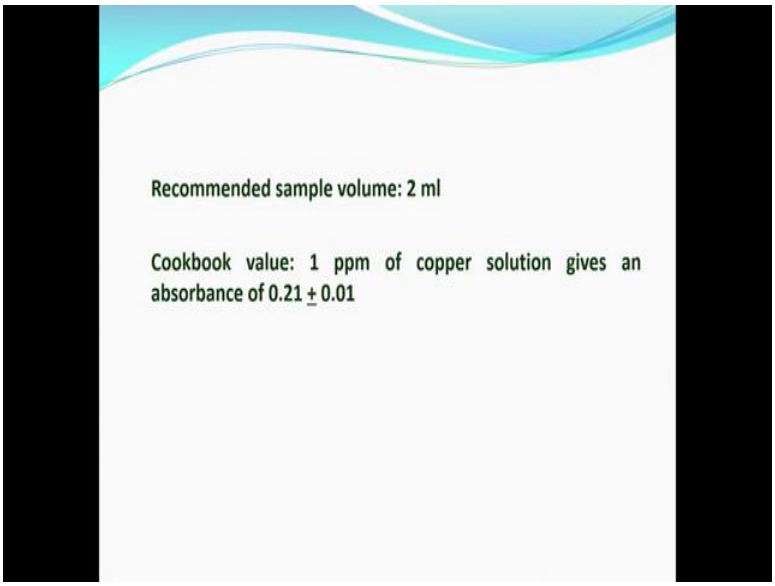

The significance of this is if you want to determine copper you prepare all the reagents and take 1 ppm copper and if you get 0.1 plus or minus 0.01 absorbance your procedure is correct, your reagents are correct your pipettes are correct and you can go ahead with the sample preparation with these sample analyses.

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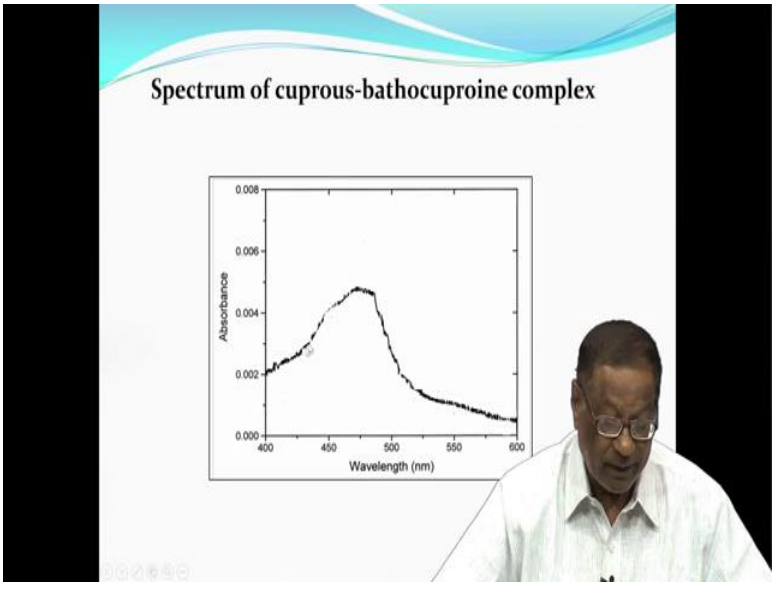

So, this is the spectrum of the complex very simple good nice spectrum bathocuproine, somewhere around 480 fairly stable at the top; that means, you have a slightly wide range for measurement means you can use a colorimeter also. We do not need only a

spectrophotometer for the determination of copper. So, calibration curve wonderful calibration curve with a linearity index of 0.999.

And we can see that up to 50 micro retain the absorbance is almost about 0.9 and according to our relative error concept we should not be more than point 8 or 0.9. So, I think copper by bathocuproine is a fairly good method for the determination every analytical laboratory can have this bathocuproine in their talk.

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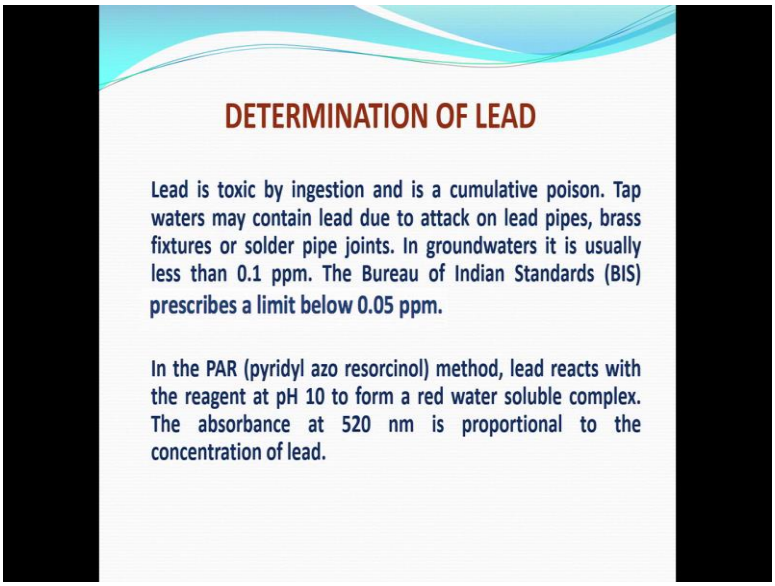

Next I want to talk to you about the interference. Before I proceed to lead, among interferences I would like to tell you that the cadmium suffers interference from I d a, but around 1000 ppm up to 1000 ppm it does not interfere. And same thing is true with chloride fluoride sulfate etcetera because the analysis is being done in alkaline medium. So, many of these things will not precipitate. Phosphate bromide etcetera, nickel up to 100 ppm does not interfere and then zinc up to 10 to ppm does not interfere vanadium up to 500 no problem. And then antimony up to 250 no problem. Yes, chromium at ferric ferrous etcetera up to 50 ppm there is no problem.

That means equivalent quantities of chromium nickel etcetera they can be tolerated for the determination of bathocuproine. So, it is a very interesting to work with bathocuproine as a reagent for spectrophotometric determination of copper. Now I would like to proceed for the determination of lead. Now there are lots of things to be told about lead. For example, the lead is an element which is known to human beings since 10th

century AD. We have been using lead in variety of forms and it is widely distributed in nature, it is lead is toxic by nature. And the maximum use of lead is in the preparation of in the petrol. Since in the last century and only since last 10 years we have moved away from the lead culture, that is lead use to be added to petrol as an anti-knocking agent, not for diesel, but only for petrol nowadays since it is last 10 years in the lead has been removed from the petrol formulation.

Instead we are using MTBE methyl tert butyl ether, but still most of the lead that was being used in petrol is distributed in the environment even now. And most of the soil it has been as a because it gestures compound it has precipitated all over the world. And every soil sample and every plants sample is contaminated with lead as of now, and including the human beings who consume the agricultural products from the soil as well as the non-vegetarian people who are dependent upon the terrestrial animals for their food. So, lead is toxic by injection, it is a cumulative poison; that means, if once the lead enters into your body it keeps on adding and stored getting stored in the body, until it starts causing problem. The toxicological nature of lead has been widely documented and right now as of now the lead is part of our body and all of us are contaminated with lead it is very difficult to find any human any person without lead in his body.

Most of the lead is already there in the blood. So, tap waters may contain lead due to attack on lead pipes brass fixtures and solders etcetera. Lead has been used as a solder material since quite long time. So, there is no escape from the contamination of lead as far as human beings are concerned. So, we have to be very careful with respect to the lead contamination and toxic effects of lead. In ground waters the concentration of lead is usually less than 0.1 ppm. So, the bureau of Indian standards prescribes a limit of 0.05 ppm that is 5 micro of the 5 na picograms 5 nano grams in water. And we have chosen this pyridyl azo resorcinol method lead reacts with this reagent at pH 10 to form a red water soluble complex. The absorbance lambda mats are at 520 nanometers that is and it is proportional concentration of lead.

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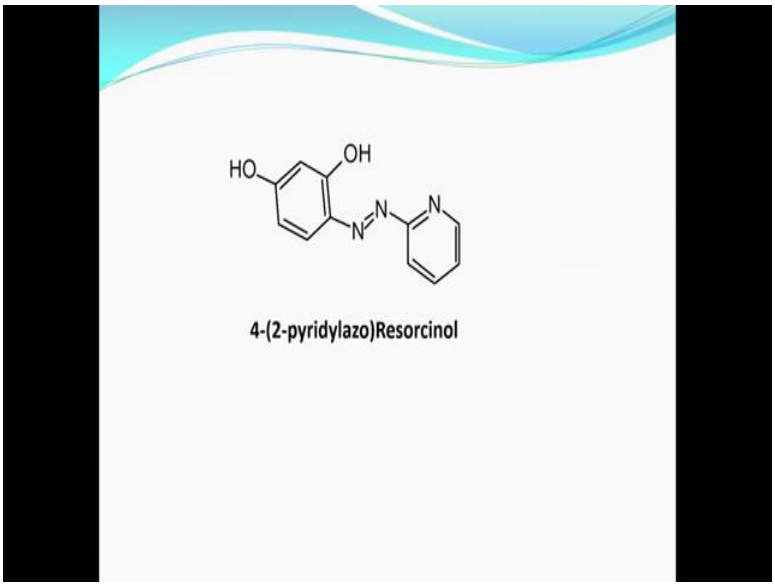

So, this is 4 2 pyridyl azo resorcinol, a very good azo reagent and then N N group is the functional group. There is an O H here there is one O H, and there is an N N group and metal complex can form here using this nitrogen or there are 2 O H groups. There can be complex formation here or between this O H, and this nitrogen all these are stereo specifically controlled reactions. And usually this reaction has been studied excellent over a period of time by several excellent researchers, and most of the methods using this hydrochloride pyridyl azo resorcinol are organic in nature, that is the final product of the complex is normally extracted in to organic solvents and then analysis is completed usually in organic solvent early.

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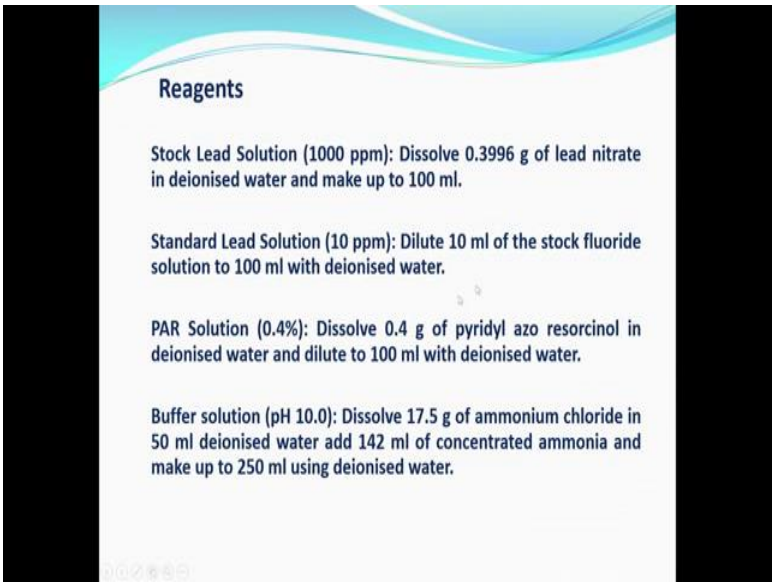

Now, we have modified this procedure using only aqueous finish. So, the reagents include preparation of lead sample that is around 1000 ppm and then you can prepare standard lead solution of 10 ppm.

That is working solution and you have to usually prepare lead in plastic bottles not in glass. And 4 2 pyridyl azo resorcinol that is par solution par 0.4 percent you can dissolve it in deionized water, very easily solvable. And the reaction is alkaline medium as usual, especially for this this kind of azo dye products. And we have to prepare a buffer of about pH 10. The details are given here on the ppt. And the procedure involves transfer of up to 10 ppm in standard solution in 10 ml volumetric flask.

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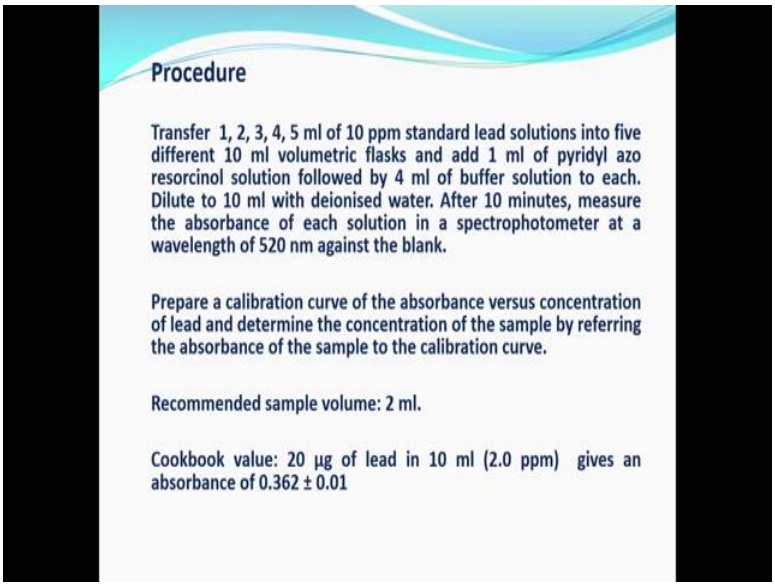

I will add reagent followed by buffer the 4 ml etcetera. Those details are will not go in turn, but we have to measure the lambda max at 520 nanometers the recommended volume is 2 ml and cookbook value for 20 microgram lead in 10 ml that is 2 ppm it gives an absorbance of about 0.362 plus or minus 0.01 absorbance. So, that works out to in 10 ml that is 2 ppm, but the limit is 0.5 ppm. So, this procedure is not really applicable for drinking water with that standard specification.

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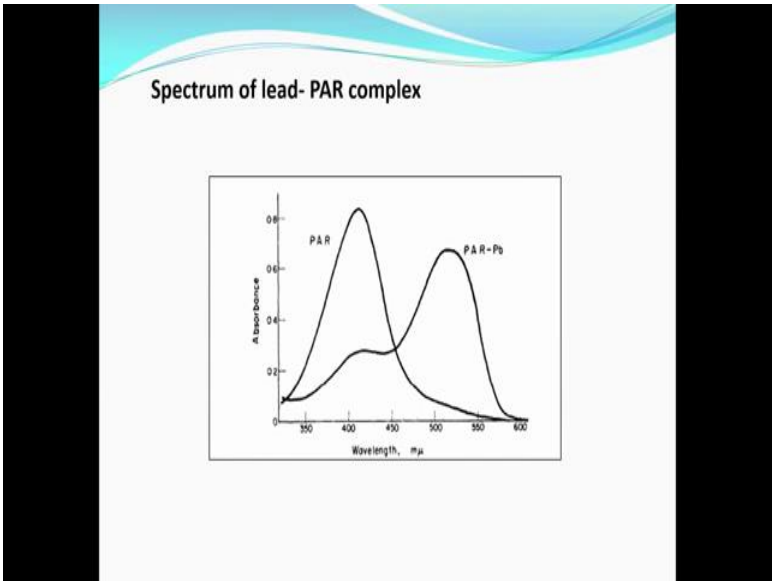

So, but still we have included at this because there are several industrial affluent and water samples you will have to analyze especially with respect to lead and wherever the concentration is higher than 2 ppm or higher than 0.2 ppm. For example, this is 2 ppm is 0.36 0.2 ppm is 0.036. So, 0.036 is imminently measurable in in drinking water etcetera, if the concentration exceeds, but applicability you can use this for pass or fail test. So, that is the beauty of spectrophotometric, whether the method is applicable directly to the quantitatively or one not can first determine the quality determined qualitatively whether the concentration is exceeds or not.

So, the spectrum par is here par and lambda max this there is a big bathochromic shift from 400 to 550 wonderful reagent. And this is somewhat orangish yellowish and this is red in color. And the lambda linearity is verifiable up to 50 ppm where it goes up to 0.9 and the linearity index that is R square value will be 0.99 8; that means, it is a very good straight line passing through the origin.

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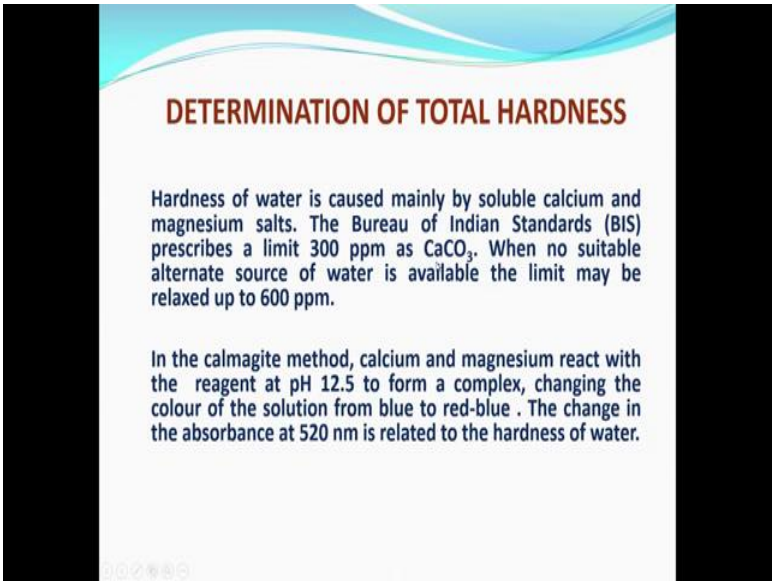

So, know it is possible to determine the concentration of lead in drinking waters etcetera, but the interference of par is a matter of concern because 4 2 pyridyl azo. I have told you most of this azo dye react with many metals. So, lead pyridyl azo resorcinol also is not an exception to this rule is, but we can take hard from the fact that fluoride chloride etcetera does not interfere, but fluoride does interfere does not interfere up to 5 ppm, but higher values it forms a complex with lead. So, it is not very good cobalt, magnum,

magnesium, nitrate, etcetera do not interfere up to 100 ppm that is 20 times the concentration.

So, we have also may always made a point to test for sodium lauryl sulfate that is most of the detergents in the aqueous in the streams, that is around 10 ppm it does not interfere and the iron cobalt copper etcetera they are all of them will interfere even at 100 ppm level. So, we have to work make sure that the lead is separated from these elements. So, that is iron copper and then vanadium anti-vanadium etcetera. And sulfate citric acid etcetera they do not interfere up to 100 ppm level. So, then there is phosphate also does not interfere edt does not interfere. So, up to 50 ppm and aluminum etcetera can be tolerated up to 50 ppm. So, in general the method is applicable to for the determination of lead if the quantities of the interference are within the equivalent range. If any of these metals are metals and anions cations and anions exceed 100 ppm more than 50 ppm we will have to think about how to go about analyzing, but such situations are fairly rare.

So, with this introduction, I will complete our discussion on lead, and in the next class we will determine and we will see how we can go about determining the total hardness and other parameters.

Thank you.