Atomic and Molecular Absorption Spectrometry for Pollution Monitoring

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Lecture - 35
Nonionic surfactants, iron, phosphate

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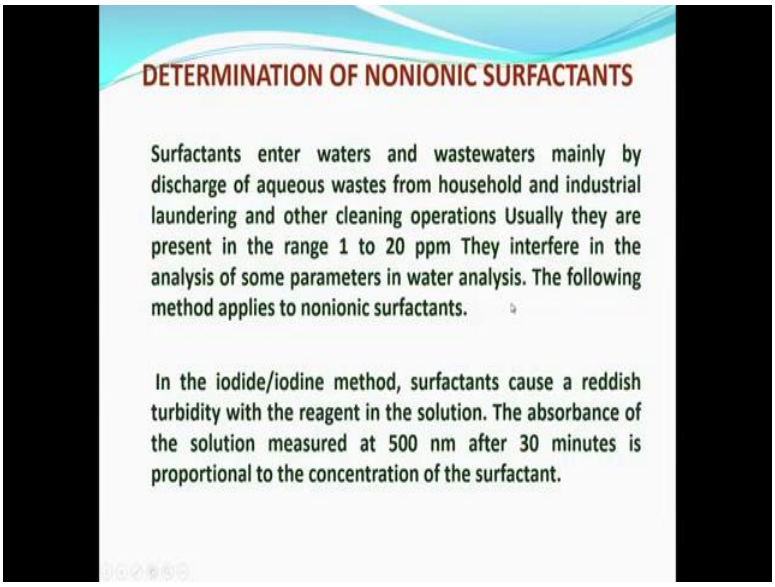

Greetings to you, we are on the 17th lecture of this 20 hour program. Last class I was teaching you about the determination of nonionic surfactants.

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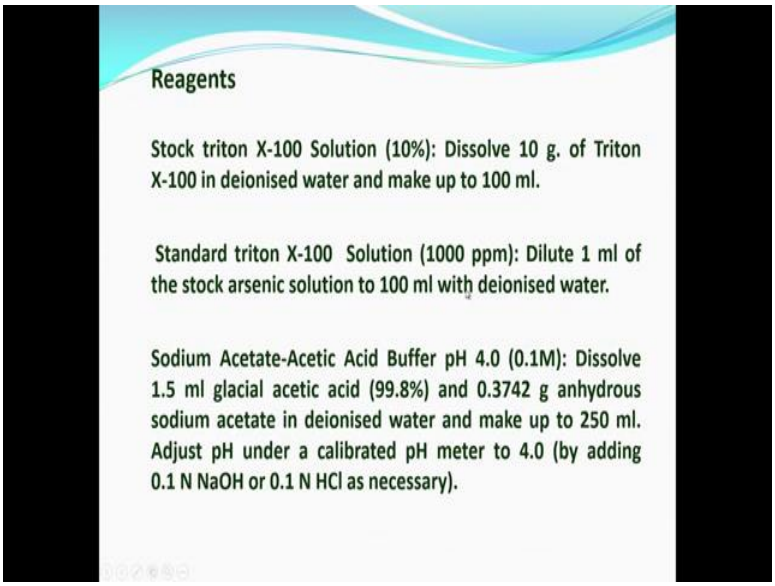

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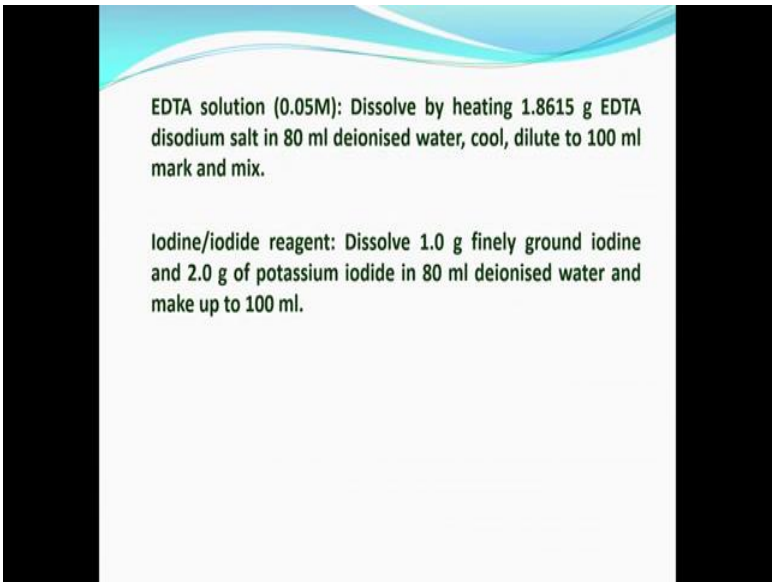

And as I was telling you that now a day's everywhere there are surfactants entering in your water analysis, without going into too much of the detail I would like to show you this slide.

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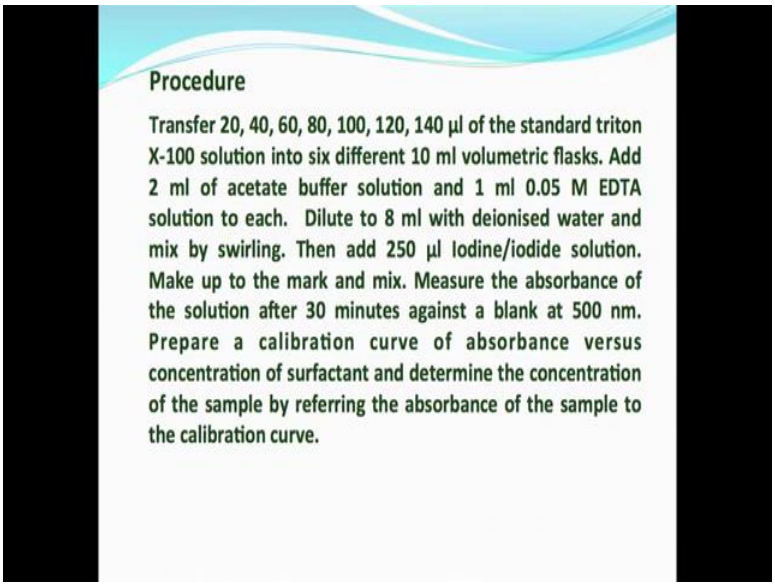

And next slide I had there, showed to you the preparation of the reagents, and then this is the continuing the same vein we prepare all other reagents, and this is the procedure we had stopped somewhere here.

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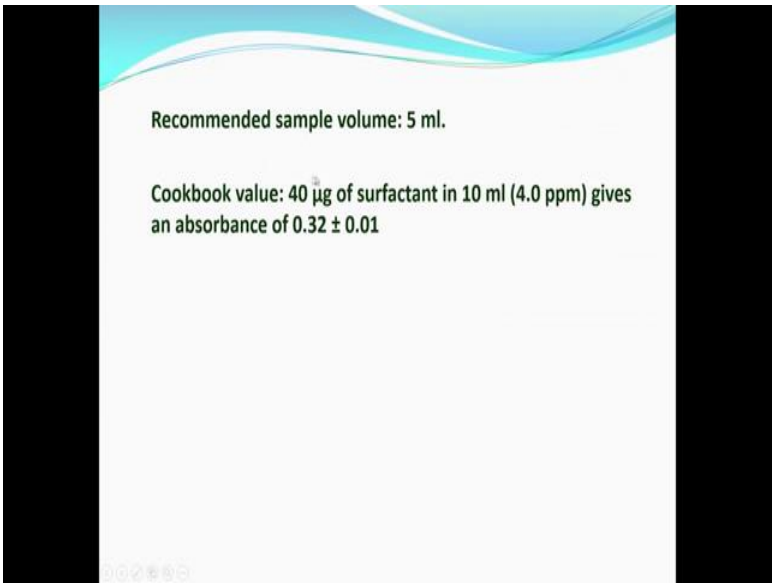

Where, I had indicated that the recommended sample volume is about 5 micro litre 5 ml, and cookbook value for 40 microgram of the surfactant you should get if everything is in order, and 10 ml if you have this kind of surfactants standard value, it should give a an absorbance of about 0.32 plus or minus 0.1 at about 500 nanometers.

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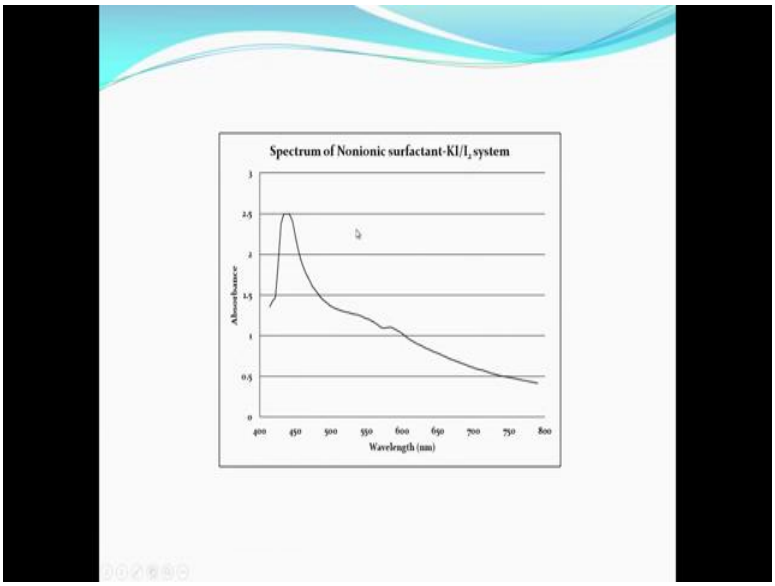

So, this is the spectrum of nonionic surfactant and k i iodine system, you can see that the peak is somewhere around 400 here, but we are choosing somewhere around 500 I think.

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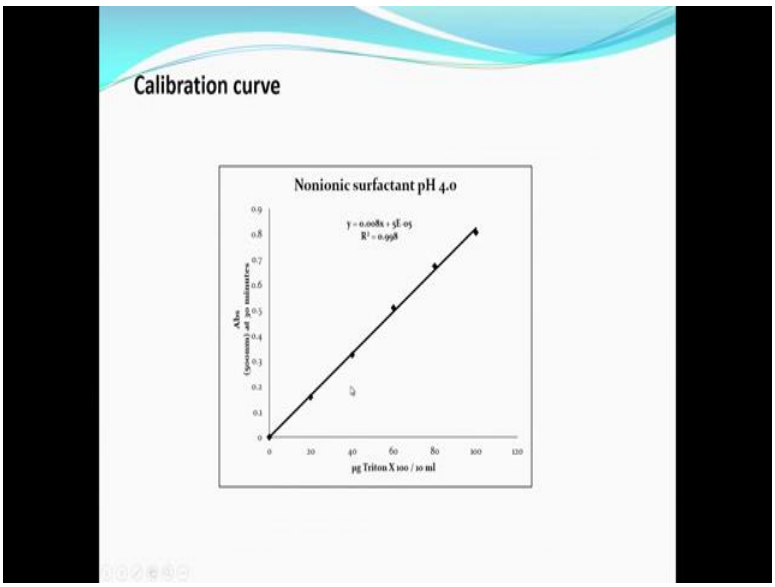

For measurement and this is the linearity curve, beer lamberts law passing through the origin and the linearity is wonderfully covered with r square value, when you were your getting 0.998 so; that means, the curve is highly reliable.

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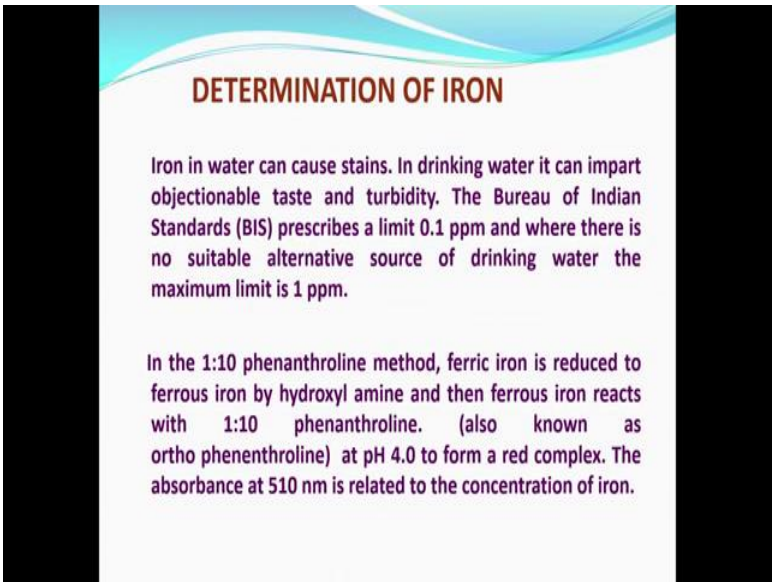

Now, we will move on to the interferences; in interferences normally what we would like to look at as I have told you are the number of elements and since I am not going to present it to you here. I would like you to record here the interferences of different elements and that is lithium, boron, magnesium, calcium, copper, cobalt, manganese all these ions do not interfere. First I give you normally the non interfering, and that you also includes nickelous ion, zinc ion, chromic chrome that is chromium, 3 aluminium ferric, f e 3 plus, arsenous, chloride; does not interfere bromide, iodide, chloride etcetera do not interfere, sulphate does not interfere, nitrate nitrite etcetera do not interfere edta. In general except any of the metal ions that we had tested in normal hello are you able to record me if I show my.

No, the shirt you are wearing is this thing.

What?

Blue.

So?

Background it glitters a lot.

What should I do?

We just want or put the pip.

Ah.

We just cannot put the pip.

Ok.

It glitters a lot.

Can you put on the side?

No sir it glitters.

Oh, I should have known that.

Ah the thing is background is black.

Yes.

You are wearing it the same similar colour.

Oh.

Only the face will be normal. This thing will be a glittering a lot.

Um.

It will have some distinct lines and something.

So, what to do?

We can continue without this thing sir the picture in (Refer Time: 04:39).

Um you have a shawl or something.

No sir.

It is there no.

That thing no. It is the bigger one its full of dust.

Dust.

Junk. You can just continue like that.

You do not have a coat.

No sir (Refer Time: 05:16) nothing.

Give me your sweater.

This one.

You wear only t shirt.

No I do not wear t shirts.

Inside you do not have.

No.

Only banyan alright we continue like this.

Yes, sir sure.

Fine, that is why I got confused the when even when I am showing this your

No I was really doing like to doing that this thing.

Ok.

It was not up to a glittering was more.

[FL]. So, now, we continue our discussion on the determination of other parameters, that is let us have, let us talk about iron. Iron in water can cause stains in drinking water it imparts a certain objectionable taste and turbidity, the bureau of Indian standards prescribes a limit of about 0.1 ppm, where there is no suitable alternative source of drinking water the maximum limit is 1 ppm. So, iron as such does not have any deleterious effect on the health of the health of fauna, but in general the, it is not desirable whenever you wash cloths containing iron it leaves stains etcetera.

So, the best method for iron is the determination of iron using one tenth phenanthroline and this is a very old method very well tried and tested method. And here we have to

remember that it is a ferrous ion that reacts with one tenth phenanthroline and not the ferric ion. So, ferric ion is usually in all drinking waters whenever you come across, because they are all exposed to oxygen and atmospheric dissolved oxygen and atmospheric oxygen, most of the iron salts are dissolved as ferric.

So, it is important for us to first reduce the ferric ion to ferrous and then we should react it with one-tenth phenanthroline. It is also known as orthophenanthroline and that pH 4 it forms a red complex, the absorbance at 510 nanometer is related to the concentration of the iron.

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This is the structure of 1, 10 Phenanthroline, and the complex will form ferric ferrous complex will form a bond with both these nitrogen's forming a complete ring structure. So, this is the one of the most celebrated inorganic organic reagents for the determination of iron and it is a text book for almost all standard text book experiment at right from pre university level to M.sc level.

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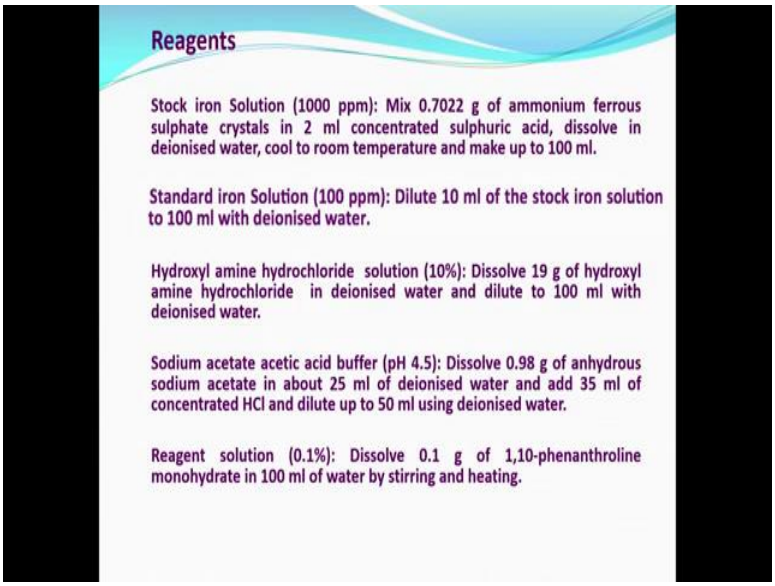

So, the reagents we have as I have already told you that we have reduced everything to 100 ml, maximum stock solutions and I am giving you the details here 0.7022 gram of ammonium ferrous ammonium sulphate. Crystals we have to dissolve it in sulphuric acid; that means, it has to be highly acidic the acidity comes down most of the ferric and iron ferrous as well as aluminum, they all precipitate and we will not have any test result to show. And standard ion solution we have to prepare about 100 ppm, and hydroxyl amine hydrochloride you will need to reduce ferric to ferrous. So, that concentration I have given here and then we have to prepare sodium acetate acetic acid buffer of pH 4.5 f for that also you have to dissolve about 0.98 gram of anhydrous sodium sulphate in about 25 ml in deionized water, add 35 ml of concentrated HCL dilute up to 50 ml that is a very standard procedure. But here it is you have a ready reference for using the preparing the sodium acetate acetic acid buffer, and then the you have to dissolve one tenth Phenanthroline also in the same way, but you have to dissolve it in water you can add a little bit of alcohol for easy dissolution of course, it requires a little bit of heating and stirring.

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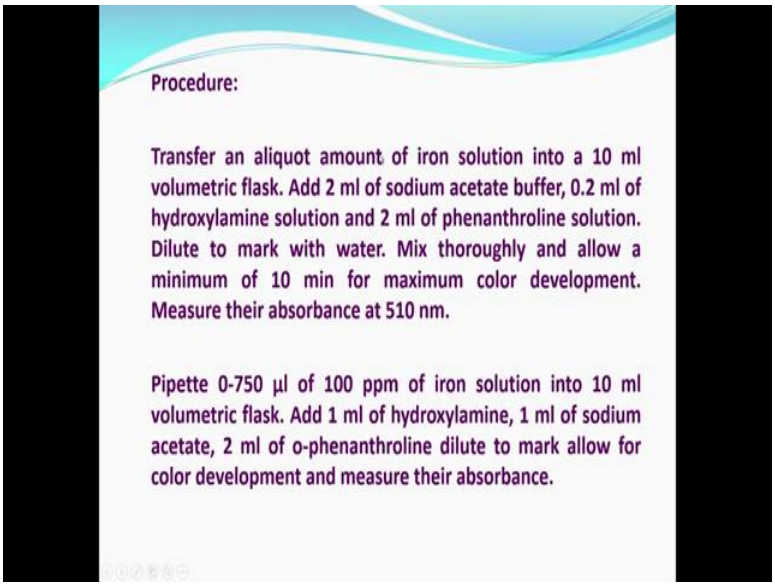

So, because it is a very simple test you have add according to the reagents what I have given here, 10 ml at takes 2 ml buffer, 2 ml hydroxylamine hydrochloride, 2 ml of orthophenanthroline and you have to dilute with mark to the mark with water followed by addition of your sample and then lamda max is at 510 nanometers, you have to pipette about 0 to 750 microliter of 100 ppm sample solution, into 10 ml volumetric flask this is for the standard.

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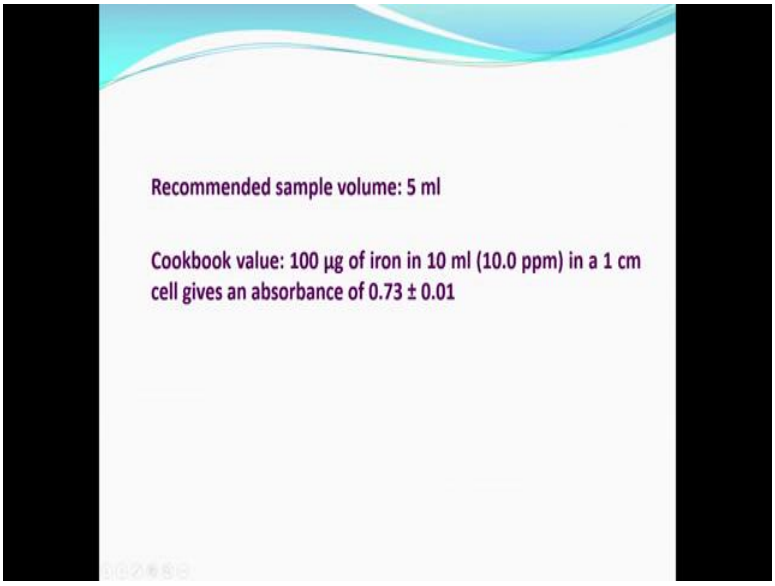

So, if you add all these reagents as I have indicated here, you will have a good curve that is good measurement numbers and the recommended sample volume is about 5 ml and cookbook value for 100 micro gram of iron in 10 ml, that is 10 ppm in 1 centimeter cell is approximately 0.73 plus or minus 0.01 nanometer, 0.01 absorbance only sorry not nanometer, but it is absorbance.

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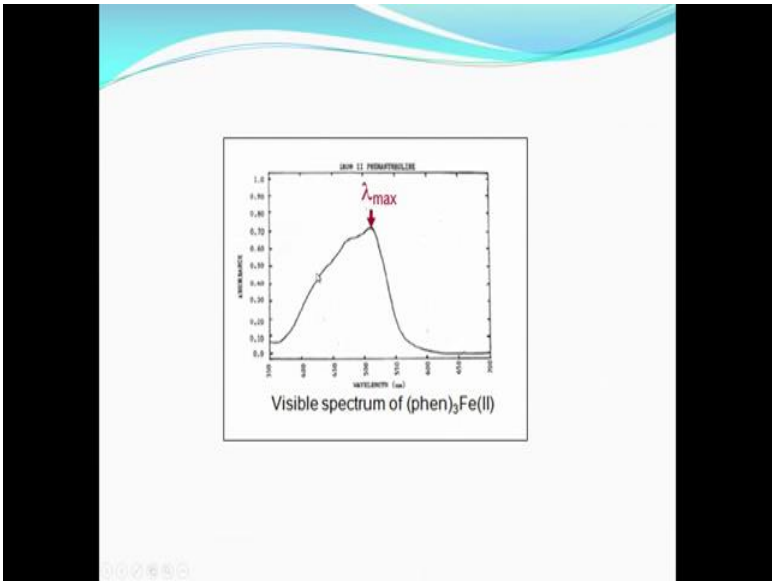

So, this is the complex measured against its own blank usually blank is colourless in this case, and we have a lambda max around 510 or 520 would be the most ideal one, and the calibration curve as you can see from this curve is very good up to 150 micrograms in 10 ml that is 1.5 ppm. So, it is very sensitive method.

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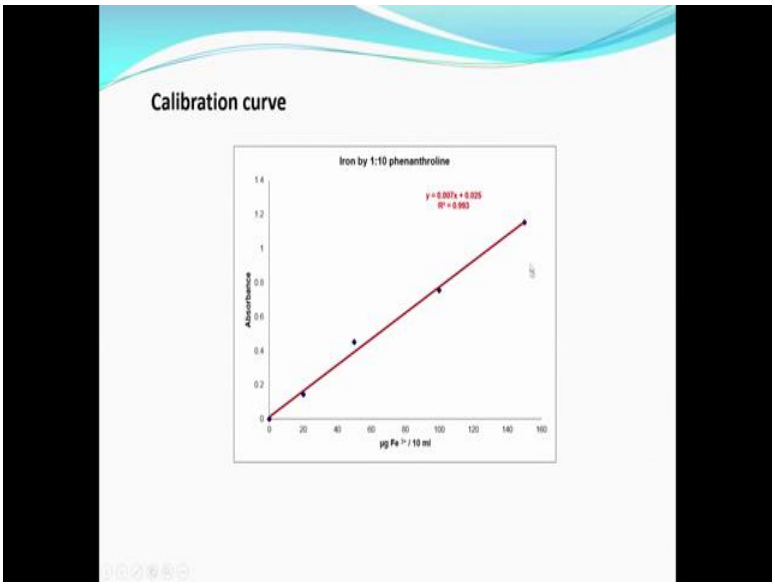

There are other sensitive methods also using potassium thiocyanate very good method directly for the determination of ferric, but there are lot of interferences in the ferric thiocyanate method; where as in ferrous orthophenanthroline there are not there is not much interference and we also note that they r square value for this that is the linearity index for this is 0.993 not very good, because in good spectrophotometric procedures we expect between 0.997 to 0.998, 0.993 is not a very good one, but it has nothing to do with the method as such, it is a characteristic of the reagent or the complex and the complex is stable indefinitely for almost up to 6 months you do not have to worry about it.

Now, I would like to give you some information about the interference of the other elements, and I have to tell you that magnesium, lead fluoride, manganese, iron, iodine, aluminium, sulphate, nitrate, phosphate, tartrate, chloride, vanadium, molybdenum borate, sodium lauryl sulphate, and tritonic (Refer Time: 14:06) did not interfere, but then what sort of things will interfere in this method? Those include antimony, nickel bromium, zinc some of the transition metal ions, which also are capable of forming cyclic complexes with orthophenanthroline. And then EDTA interferes by forming a stronger complex, which does not permit iron orthophenanthroline complex to be formed.

So, you cannot use EDTA to mask the other elements in this case. So, then DTPA that also interfere that is another complexing agent, cadmium interferes, cobalt interferes etcetera some of these interferences can be overcome by reducing the concentration, but some of them can be overcome by using citrate citric acid buffer, that we are already using here to remove the possible interferences. So, I have a limit of nickel toleration, that is up to 100 microgram of nickel can be can be tolerated in the method, and cadmium also can be tolerated up to 50 micrograms that is in presence of 1 ml of citric acid citrate buffer.

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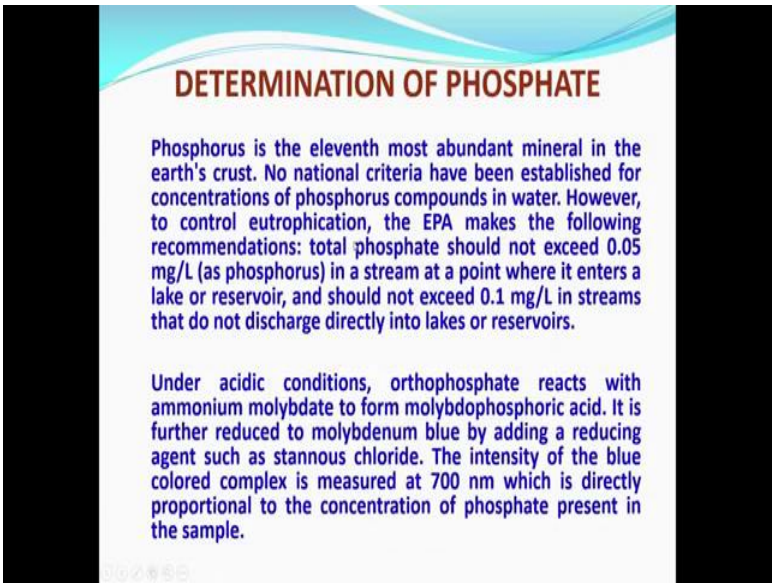

So, I want to give you another method that is the determination of phosphate; in the phosphate ion phosphorous is one of the most abundant mineral in the earth’s crust and no national standard criteria have been established for concentration of phosphorous compounds in water. The reason is we use phosphate all over the world for agriculture as well as in some other industrial applications and phosphate is used as a fertilizer, and it is closely it is a biologically essential element, but it has got its own problems in the environment especially if nitrogen and phosphorous are there in the effluent or in a water body there will be something known as the algae and other forms will plant forms will proliferate, and once the algae finish their life time they all become dead mass, and this dead mass keeps on increasing reducing the life of a water body.

So, most of the water tanks in villages must be guarded against phosphate; so the to control eutrophication phosphate should not exceed more than 0.05 milligram per liter that is 5 ppm in a stream, at a point where it enters a lake or reservoir and it should not exceed 0.1 milligram per liter that is these in streams, and these norms are normally followed very strictly with respect to the effluent industrial effluent especially from industries as well as municipality municipal effluents.

So, what are the typical reactions of phosphate, how do we go about determining the phosphate in a given sample. The best method is arseno molybdo phosphoric acid method it is normally orthophosphate reacts with ammonium molybdate to form molybdo phosphoric acid, and it is reduced to molybdenum blue by adding a reducing agent such as stannous chloride. The intensity of the blue colored complex is measured at 700 nanometer which is directly proportional to the concentration of the phosphate present in the sample; a very simple method required in several applications and several laboratories, organic laboratories, inorganic laboratories as well as in agricultural universities, and factory affluent monitoring, a very important it is also used as a special component in most of our washing machines, in washing powders detergents washing powders etcetera there is lot of phosphate usage, and that makes it a bit tricky especially because the most of the washed phosphate ends the ends up in the river water systems.

So, these are the reagents what all we need is phosphate solution, standard phosphate solution 10 ppm, you can prepare 100 ppm and 10 ppm standard stock solutions and then all are all the solutions are soluble in water.

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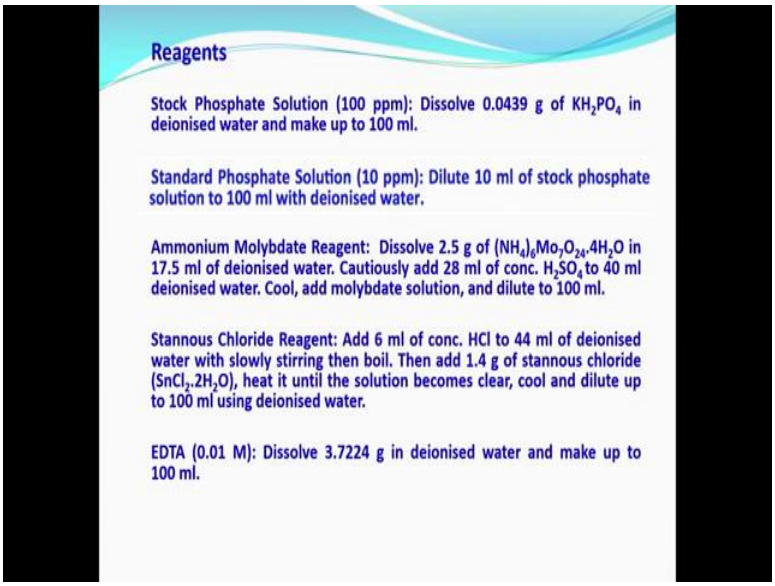

So, then you have to prepare ammonium molybdate reagent, that is available across the shelf and you have to dissolve it in deionized water, add about 28 ml of concentrated sulphuric acid and then cool and add dilute 200 ml. Stannous chloride is another important reagent which is a reducing agent. So, you have to dissolve stannous chloride with in concentrated HCL, and slowly you have to stir and boil etcetera this is a little tricky part if you do not have very good stannous chloride, you will end up with a little bit of difficulty therefore, I suggest you practice it quite a 2-3 times on smaller volumes, and see whether you get clear solutions if the pH is not correct then you will end with a heap of precipitate, which will be which will go waste especially of stannous hydroxide; and then we need EDTA for the complexation of the typical elements present in water and that you prepare by dissolving 3.72 gram in deionized water and make up to 100 ml.

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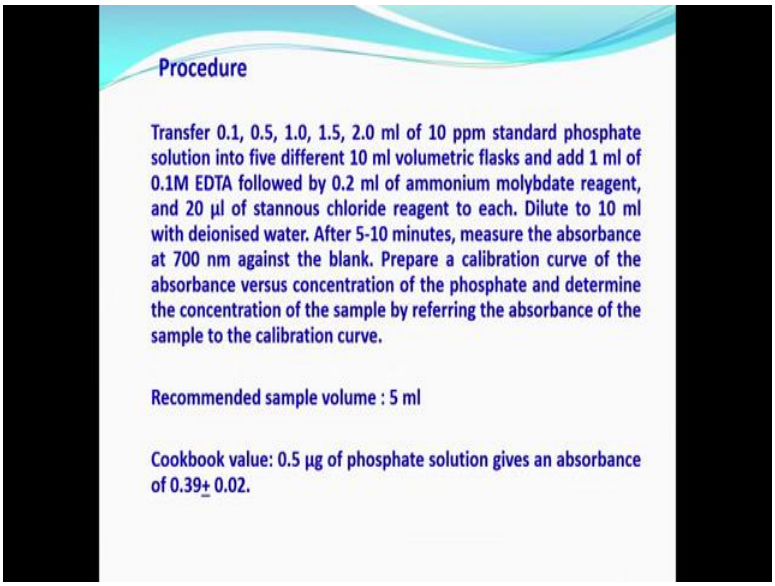

So, the procedure involves 0 to 10 ppm of standard phosphate solution, followed by addition of 1 ml of 0.1 molar EDTA that is a complexing agent we add first only along with the sample; and then we add about 0.2 ml of ammonium molybdate reagent followed by 20 micro liter of stannous chloride reagent to each. So, dilute to 10 ml with deionized water, and after about 5 to10 minutes you can measure the absorbance at 700 nanometer against a typical blank.

So, this should be followed by calibration curve and they form it can be an recommended sample volume is about 5 ml, and the cookbook value for you for phosphate is 0.5 microgram phosphate solution should give an absorbance of about 0.39 plus or minus 0.02 in10 ml of the final solution.

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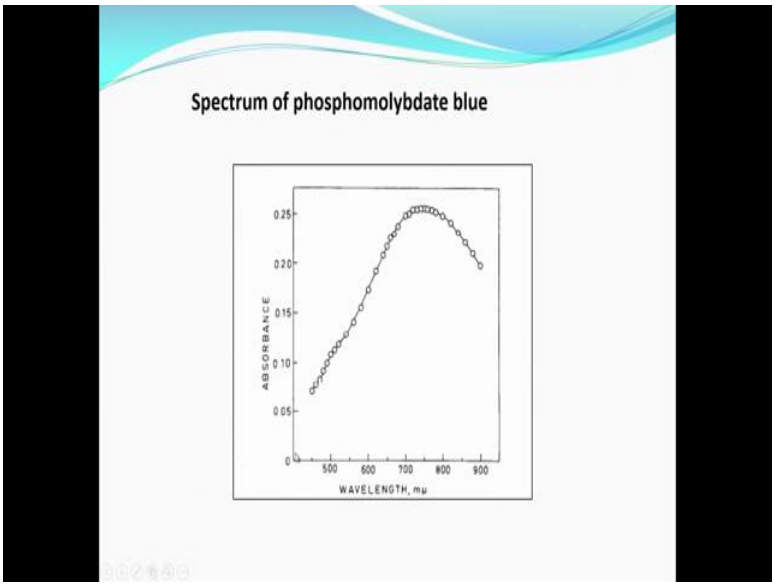

So, this is the spectrum of phosphomolybdate phosphomolybdate blue and you can see that the lamda max is somewhere around 700, it is fairly flat in the maximum maxima region. So, you can use even a coloury meter for the determination instead of a spectrophotometer.

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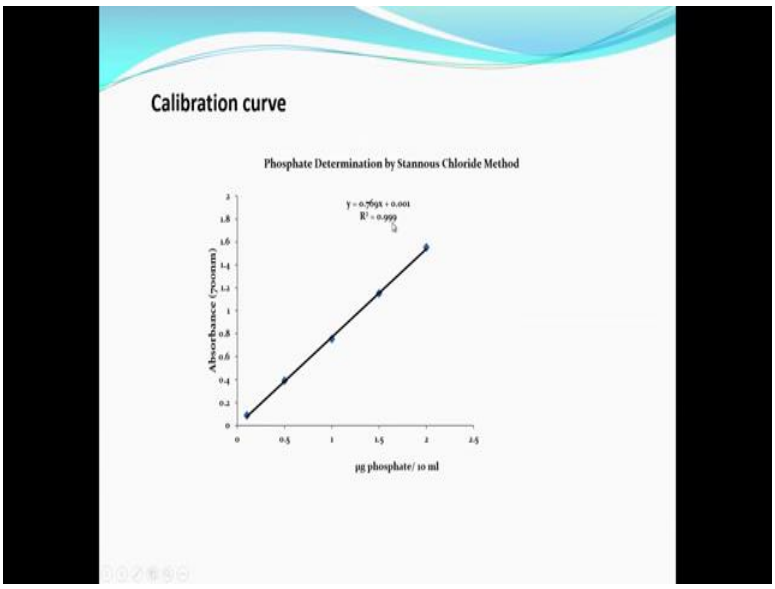

And this is how the calibration curve looks and we have a fantastic correlation that is linearities 0.999, and this is one of the best method as far as my experience goes for the

determination of phosphorous, because the concentration is always within this range especially in a storm water and river water pond water etcetera.

So, many times my students have completed this analysis very regularly, and we have always ended up with the recommended absorbance range that is 0.39, and now I would like to show you some of the interferences that are expected. So, you may note that nickel does not interfere, usually 100 fold range cobalt, nickel, copper, copper does not give any color there is certain definitely some amount of interference, and zinc gives interference molybdenum all these things interfere many of the metals for example, calcium, magnesium etcetera in about 100 fold excess, they do give white and blank precipitate.

For example, led gives a black precipitate, bismurth gives a white precipitate etcetera and among the anions not much interference is expected, because a chloride, bromide, iodide and fluoride sulphate, nitrate EDTA SLS etcetera they do not interfere, but of course, SLS interferes and for those things we have to we have tried almost all complexing agents, and what we find is tenfold excess gives you certain amount of interference, but still it is not very good so, but equal amounts there are no interferences from aluminium, magnesium, molybdenum etcetera antimony, but antimony, bismurth etcetera they do precipitate. So, they give interference, but they precipitate as hydroxides not as a complex.

So, tenfold fluoride etcetera in tenfold excess does not interfere, and then we have tried couple of complexing agents for example, glycine as a 1 ml of 0.1 molar, glycine we have tried and in glycine also we found that most of the cobalt copper etcetera they do become turbid, but equal amount of phosphate does not give any interference for example, if the concentration of phosphate is around 30 to up to 2 ppm 2 or 3 ppm the interference will not be there. So, copper, cobalt, zinc, cadmium etcetera they do not interfere especially if the interference is very less, because these elements are not there in presence of in the in the almost the same quantities you will not usually come across.

So, same thing, but to our this may found that the phosphate there is certain amount of interference which we could not remove that is arsenic. Even 0.5 ppm arsenic keeps on interfering and 100 ppm level yes to we could manage it to some extent. So, with this

interference data I would like to conclude about the stannous chloride, and the next element on my radar is nitrite.

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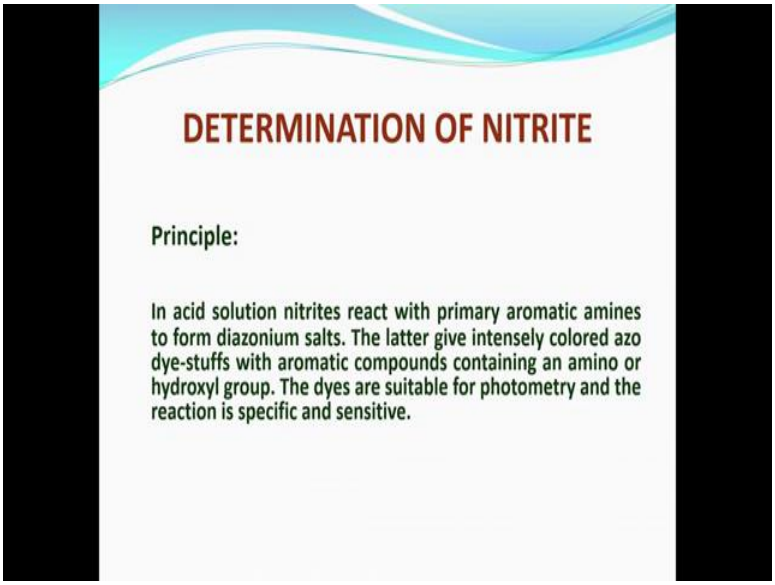

Nitrite is one of the important interfering element present in water, not desirable because it reacts with primary aromatic amines, and then nitrites are implicated in the blood reaction with heamoglobins, and they do give carcinogenic complexes give rise to generation of certain carcinogenic substances therefore, nitrite has become important pollutant to be determined very regularly with in a drinking water.

So, with this introduction I would like to say that the in acid solution nitrites do react with primary aromatic amines to form diazonium salts, very standard organic chemistry reaction and the latter give intensely colored azo dye stuff, with aromatic compounds containing an amino and hydroxyl groups. So, these dyes are suitable for photometry, and the reaction is specific and very sensitive. We will continue our discussion after about in the next class.

Thank you.