

**Atomic and Molecular Absorption Spectrometry
for Pollution Monitoring**

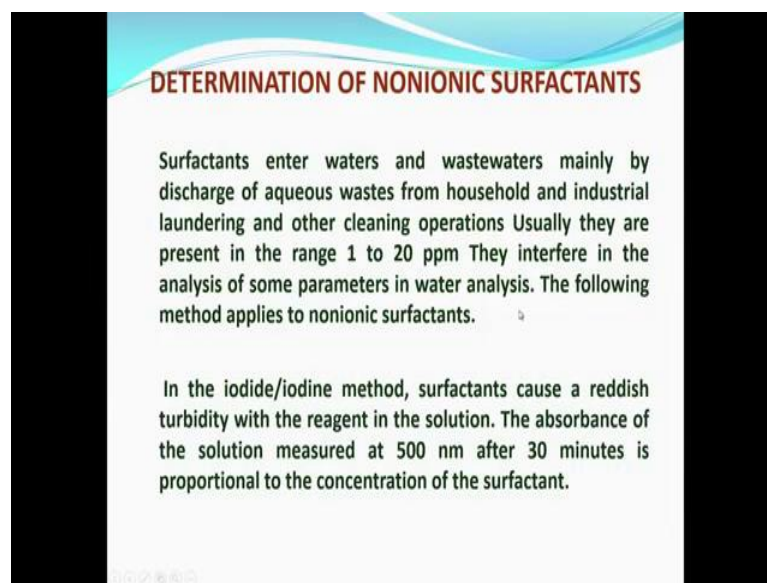
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Indian Institute of Science, Bangalore**

Lecture - 35

Nonionic surfactants, iron, phosphate

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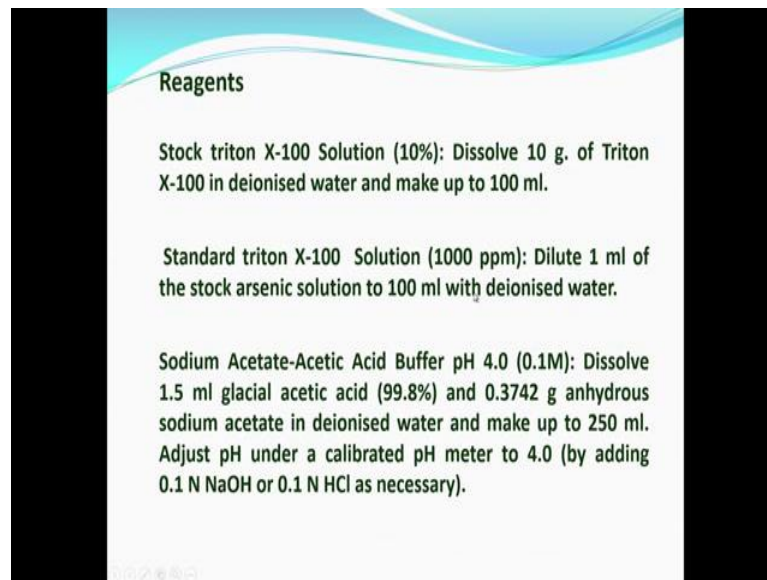
DETERMINATION OF NONIONIC SURFACTANTS

Surfactants enter waters and wastewaters mainly by discharge of aqueous wastes from household and industrial laundering and other cleaning operations. Usually they are present in the range 1 to 20 ppm. They interfere in the analysis of some parameters in water analysis. The following method applies to nonionic surfactants.

In the iodide/iodine method, surfactants cause a reddish turbidity with the reagent in the solution. The absorbance of the solution measured at 500 nm after 30 minutes is proportional to the concentration of the surfactant.

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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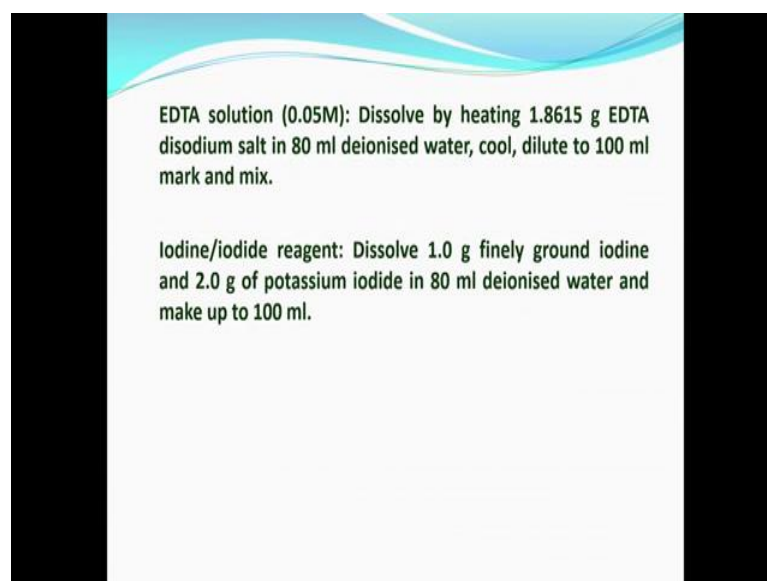
Reagents

Stock triton X-100 Solution (10%): Dissolve 10 g. of Triton X-100 in deionised water and make up to 100 ml.

Standard triton X-100 Solution (1000 ppm): Dilute 1 ml of the stock arsenic solution to 100 ml with deionised water.

Sodium Acetate-Acetic Acid Buffer pH 4.0 (0.1M): Dissolve 1.5 ml glacial acetic acid (99.8%) and 0.3742 g anhydrous sodium acetate in deionised water and make up to 250 ml. Adjust pH under a calibrated pH meter to 4.0 (by adding 0.1 N NaOH or 0.1 N HCl as necessary).

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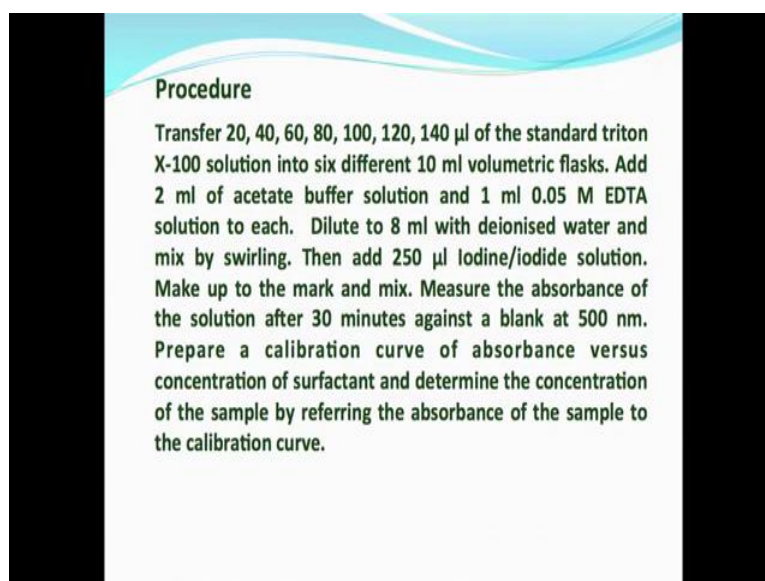


EDTA solution (0.05M): Dissolve by heating 1.8615 g EDTA disodium salt in 80 ml deionised water, cool, dilute to 100 ml mark and mix.

Iodine/iodide reagent: Dissolve 1.0 g finely ground iodine and 2.0 g of potassium iodide in 80 ml deionised water and make up to 100 ml.

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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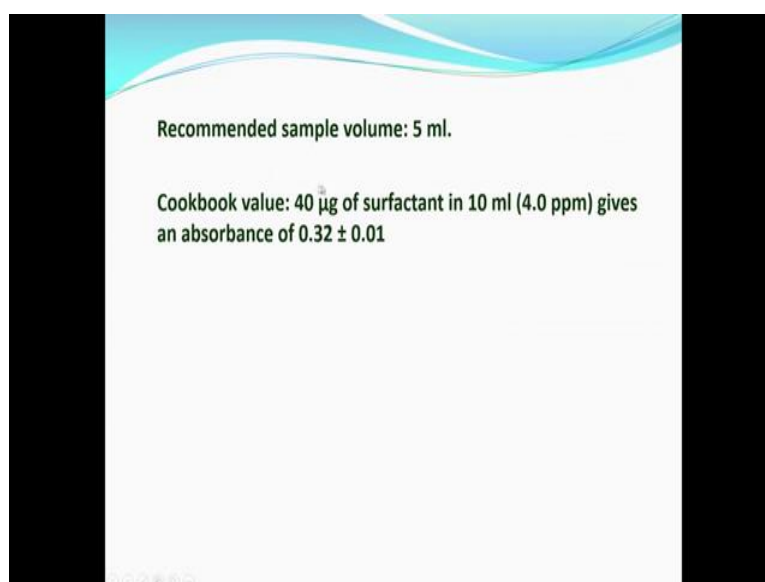


Procedure

Transfer 20, 40, 60, 80, 100, 120, 140 μl of the standard triton X-100 solution into six different 10 ml volumetric flasks. Add 2 ml of acetate buffer solution and 1 ml 0.05 M EDTA solution to each. Dilute to 8 ml with deionised water and mix by swirling. Then add 250 μl Iodine/iodide solution. Make up to the mark and mix. Measure the absorbance of the solution after 30 minutes against a blank at 500 nm. Prepare a calibration curve of absorbance versus concentration of surfactant and determine the concentration of the sample by referring the absorbance of the sample to the calibration curve.

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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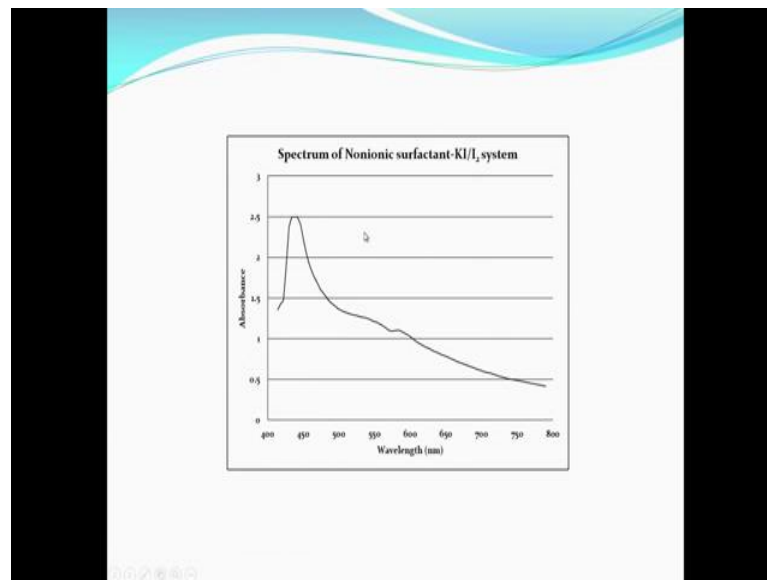


Recommended sample volume: 5 ml.

Cookbook value: 40 μg of surfactant in 10 ml (4.0 ppm) gives an absorbance of 0.32 ± 0.01

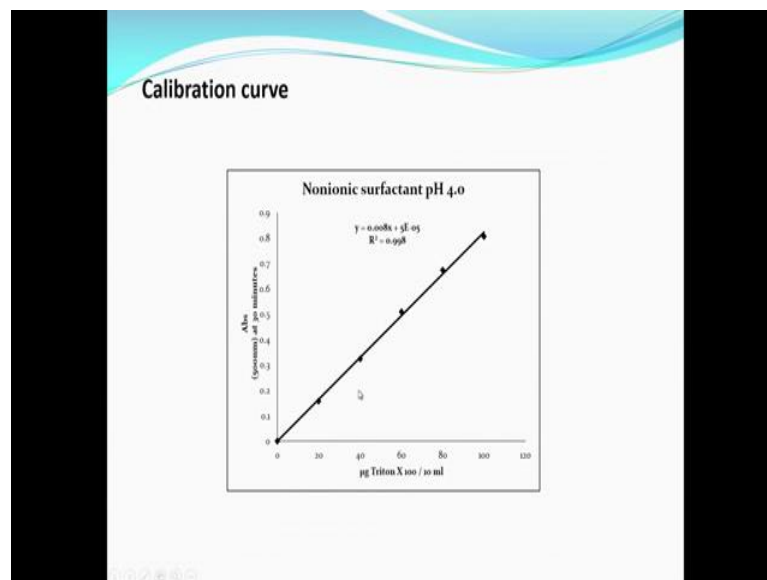
Where, I had indicated that the recommended sample volume is about 5 micro litre 5 ml, and cookbook value for 40 microgram of the surfactant you should get if everything is in order, and 10 ml if you have this kind of surfactants standard value, it should give a an absorbance of about 0.32 plus or minus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

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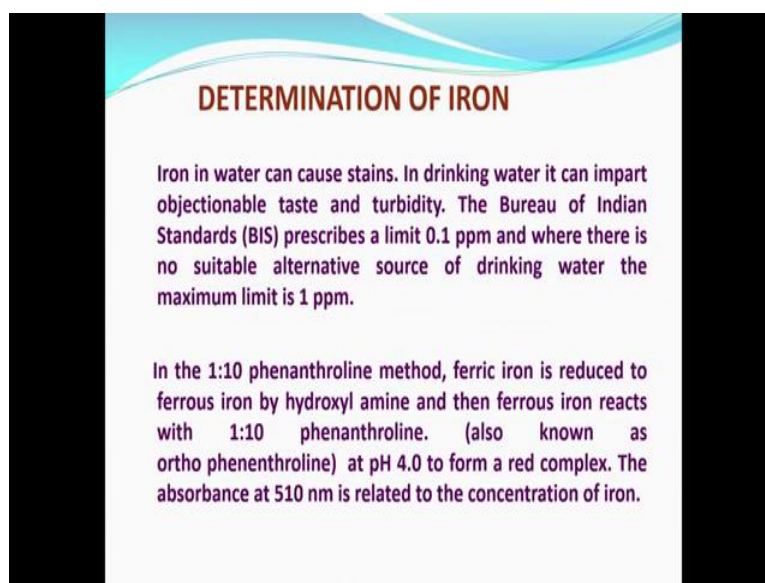
So, this is the spectrum of nonionic surfactant and k i iodine system, you can see that the peak is somewhere around 400 here, but we are choosing somewhere around 500 I think.

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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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DETERMINATION OF IRON

Iron in water can cause stains. In drinking water it can impart objectionable taste and turbidity. The Bureau of Indian Standards (BIS) prescribes a limit 0.1 ppm and where there is no suitable alternative source of drinking water the maximum limit is 1 ppm.

In the 1:10 phenanthroline method, ferric iron is reduced to ferrous iron by hydroxyl amine and then ferrous iron reacts with 1:10 phenanthroline. (also known as ortho phenanthroline) at pH 4.0 to form a red complex. The absorbance at 510 nm is related to the concentration of iron.

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, Fe^{3+} , 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.

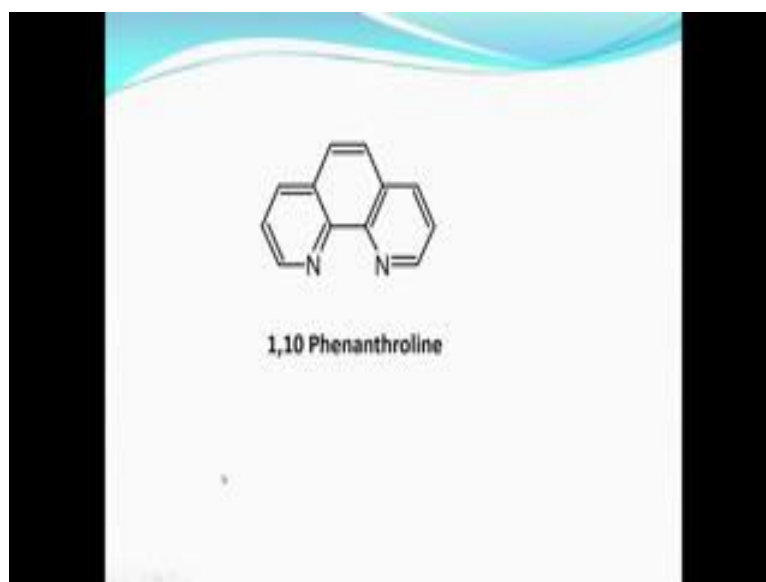
[FL]. So, now, we continue our discussion on the determination of other parameters, that is let us have, let us talk about iron. Iron in water can cause stains in drinking water it imparts a certain objectionable taste and turbidity, the bureau of Indian standards prescribes a limit of about 0.1 ppm, 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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Reagents

Stock iron Solution (1000 ppm): Mix 0.7022 g of ammonium ferrous sulphate crystals in 2 ml concentrated sulphuric acid, dissolve in deionised water, cool to room temperature and make up to 100 ml.

Standard iron Solution (100 ppm): Dilute 10 ml of the stock iron solution to 100 ml with deionised water.

Hydroxyl amine hydrochloride solution (10%): Dissolve 19 g of hydroxyl amine hydrochloride in deionised water and dilute to 100 ml with deionised water.

Sodium acetate acetic acid buffer (pH 4.5): Dissolve 0.98 g of anhydrous sodium acetate in about 25 ml of deionised water and add 35 ml of concentrated HCl and dilute up to 50 ml using deionised water.

Reagent solution (0.1%): Dissolve 0.1 g of 1,10-phenanthroline monohydrate in 100 ml of water by stirring and heating.

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 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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Procedure:

Transfer an aliquot amount of iron solution into a 10 ml volumetric flask. Add 2 ml of sodium acetate buffer, 0.2 ml of hydroxylamine solution and 2 ml of phenanthroline solution. Dilute to mark with water. Mix thoroughly and allow a minimum of 10 min for maximum color development. Measure their absorbance at 510 nm.

Pipette 0-750 μl of 100 ppm of iron solution into 10 ml volumetric flask. Add 1 ml of hydroxylamine, 1 ml of sodium acetate, 2 ml of o-phenanthroline dilute to mark allow for color development and measure their absorbance.

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.

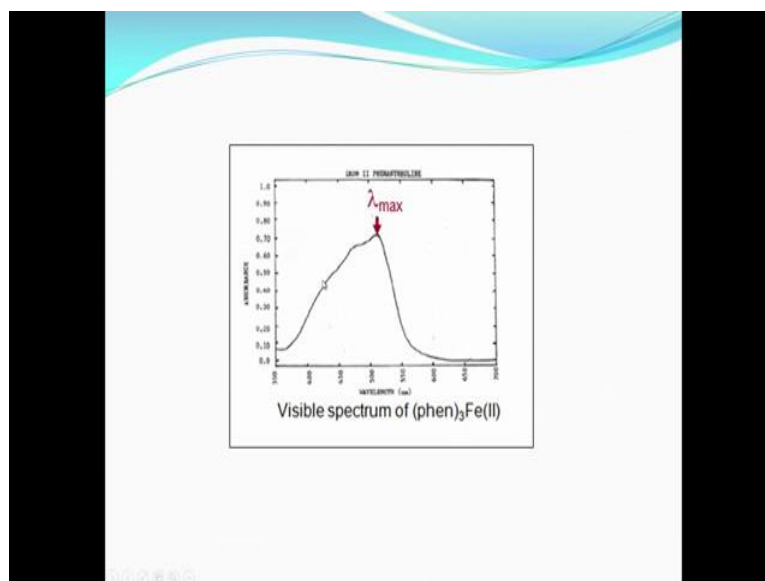
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Recommended sample volume: 5 ml

Cookbook value: 100 μg of iron in 10 ml (10.0 ppm) in a 1 cm cell gives an absorbance of 0.73 ± 0.01

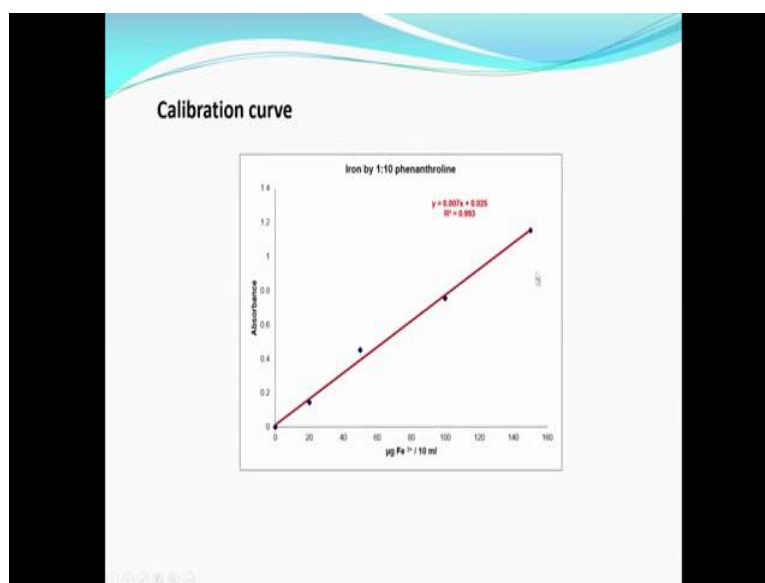
So, if you add all these reagents as I have indicated here, you will have a good curve that is good measurement numbers and the recommended sample volume is about 5 ml and cookbook value for 100 micro gram of iron in 10 ml, that is 10 ppm in 1 centimeter cell is approximately 0.73 plus or minus 0.01 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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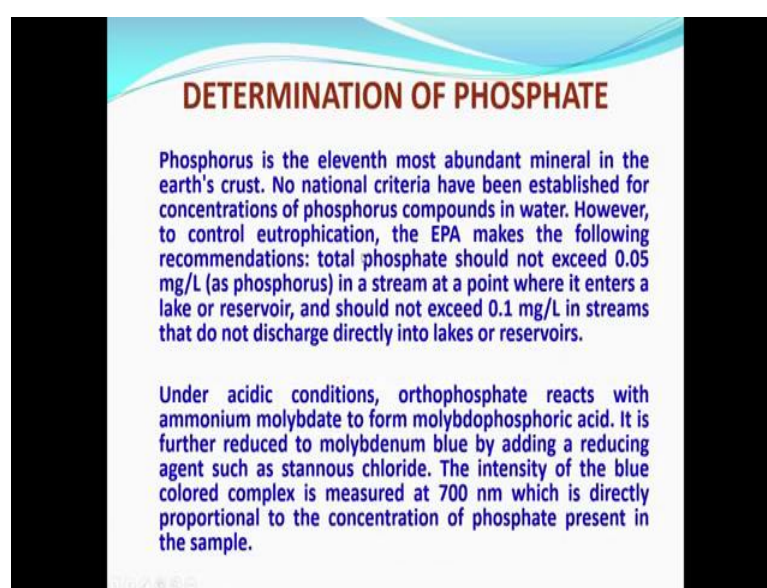


There are other sensitive methods also using potassium thiocyanate very good method directly for the determination of ferric, but there are lot of interferences in the ferric thiocyanate method; where as in ferrous orthophenanthroline there are not there is not much interference and we also note that 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 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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DETERMINATION OF PHOSPHATE

Phosphorus is the eleventh most abundant mineral in the earth's crust. No national criteria have been established for concentrations of phosphorus compounds in water. However, to control eutrophication, the EPA makes the following recommendations: total phosphate should not exceed 0.05 mg/L (as phosphorus) in a stream at a point where it enters a lake or reservoir, and should not exceed 0.1 mg/L in streams that do not discharge directly into lakes or reservoirs.

Under acidic conditions, orthophosphate reacts with ammonium molybdate to form molybdophosphoric acid. It is further reduced to molybdenum blue by adding a reducing agent such as stannous chloride. The intensity of the blue colored complex is measured at 700 nm which is directly proportional to the concentration of phosphate present in the sample.

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 arsenomolybdophosphoric acid method it is normally orthophosphate reacts with ammonium molybdate to form molybdophosphoric 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 effluent 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 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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Reagents

Stock Phosphate Solution (100 ppm): Dissolve 0.0439 g of KH_2PO_4 in deionised water and make up to 100 ml.

Standard Phosphate Solution (10 ppm): Dilute 10 ml of stock phosphate solution to 100 ml with deionised water.

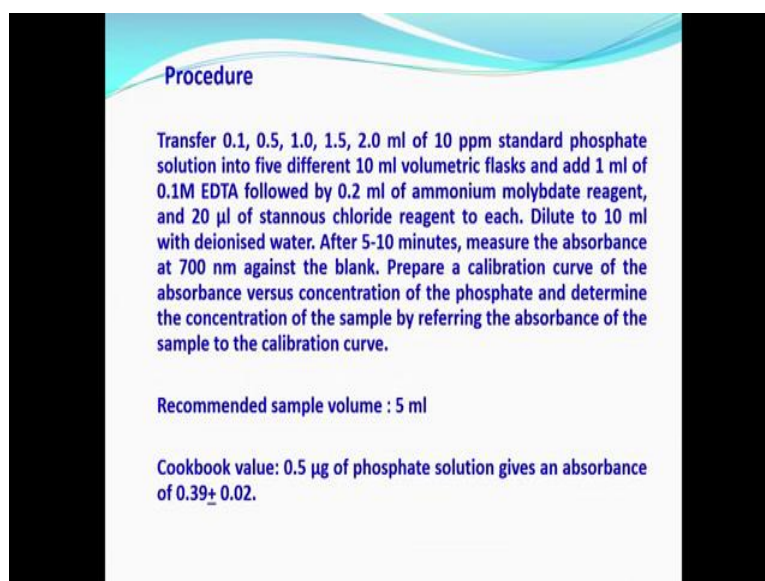
Ammonium Molybdate Reagent: Dissolve 2.5 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ in 17.5 ml of deionised water. Cautiously add 28 ml of conc. H_2SO_4 to 40 ml deionised water. Cool, add molybdate solution, and dilute to 100 ml.

Stannous Chloride Reagent: Add 6 ml of conc. HCl to 44 ml of deionised water with slowly stirring then boil. Then add 1.4 g of stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$), heat it until the solution becomes clear, cool and dilute up to 100 ml using deionised water.

EDTA (0.01 M): Dissolve 3.7224 g in deionised water and make up to 100 ml.

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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Procedure

Transfer 0.1, 0.5, 1.0, 1.5, 2.0 ml of 10 ppm standard phosphate solution into five different 10 ml volumetric flasks and add 1 ml of 0.1M EDTA followed by 0.2 ml of ammonium molybdate reagent, and 20 μ l of stannous chloride reagent to each. Dilute to 10 ml with deionised water. After 5-10 minutes, measure the absorbance at 700 nm against the blank. Prepare a calibration curve of the absorbance versus concentration of the phosphate and determine the concentration of the sample by referring the absorbance of the sample to the calibration curve.

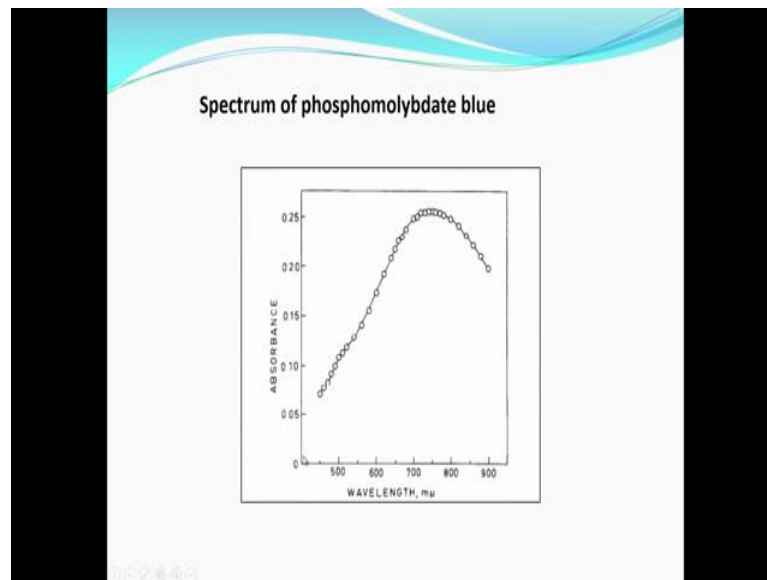
Recommended sample volume : 5 ml

Cookbook value: 0.5 μ g of phosphate solution gives an absorbance of 0.39 ± 0.02 .

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 to 10 minutes you can measure the absorbance at 700 nanometer against a typical blank.

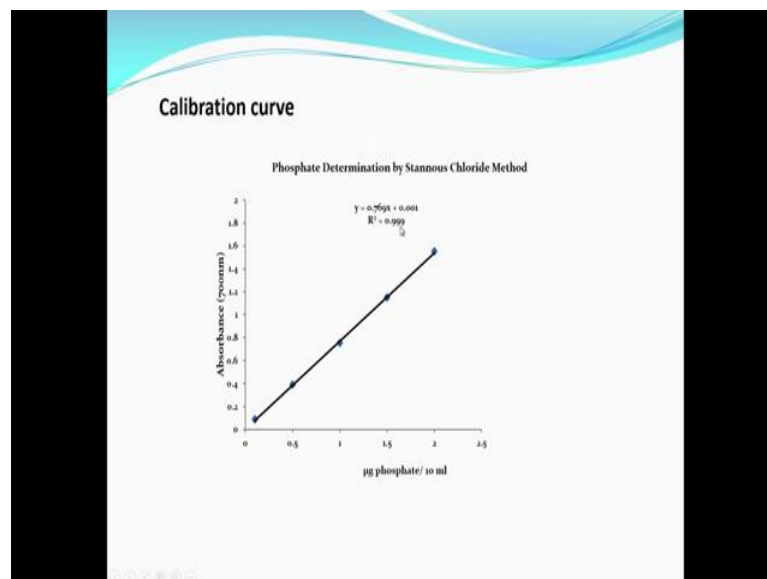
So, this should be followed by calibration curve and then from it can be a recommended sample volume is about 5 ml, and the cookbook value for you for phosphate is 0.5 microgram phosphate solution should give an absorbance of about 0.39 plus or minus 0.02 in 10 ml of the final solution.

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So, this is the spectrum of 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, lead gives a black precipitate, bismuth 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, bismuth 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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DETERMINATION OF NITRITE

Principle:

In acid solution nitrites react with primary aromatic amines to form diazonium salts. The latter give intensely colored azo dye-stuffs with aromatic compounds containing an amino or hydroxyl group. The dyes are suitable for photometry and the reaction is specific and sensitive.

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 hemoglobins, 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.