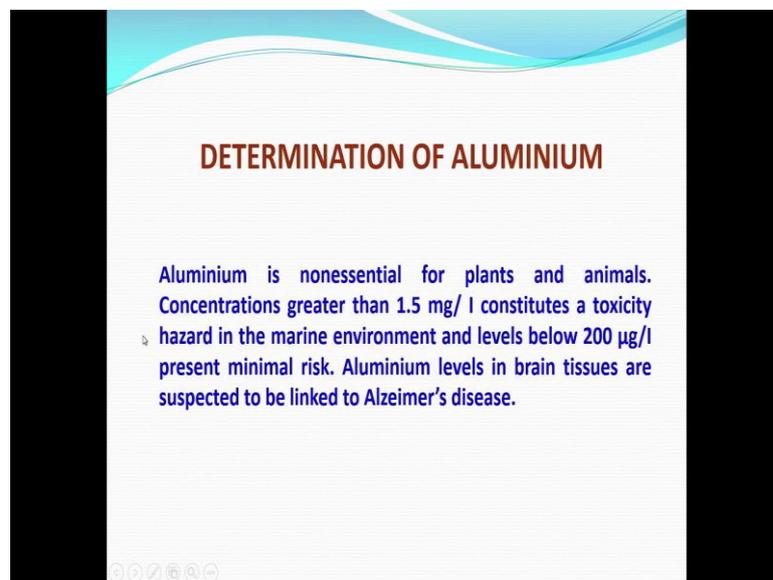


**Atomic and Molecular Absorption Spectrometry
for Pollution Monitoring
Dr. J R Mudakavi
Department of Chemical Engineering
Indian Institute of Science, Bangalore**

**Lecture – 40
Determination of aluminum, cyanide, sulphate**

Greetings to you today we will discuss about 4 elements that is aluminium and sulphate, cyanide and ammonium; these 4 ions are normally determining in the effluent samples and we will start with aluminium.

(Refer Slide Time: 00:44)



DETERMINATION OF ALUMINIUM

Aluminium is nonessential for plants and animals. Concentrations greater than 1.5 mg/l constitutes a toxicity hazard in the marine environment and levels below 200 µg/l present minimal risk. Aluminium levels in brain tissues are suspected to be linked to Alzheimer's disease.

Regarding aluminium, I want to tell you that aluminium is a nonessential element for both plants as well as animals, but aluminium is very very widely distributed in the nature in the soil and in the air also, in the air we breathe there is about 20 to 25 ppm the parts per billion ppb level of aluminium in the background. So, aluminium is very widely distributed therefore, it is important that all we have to understand about the toxicity of aluminium.

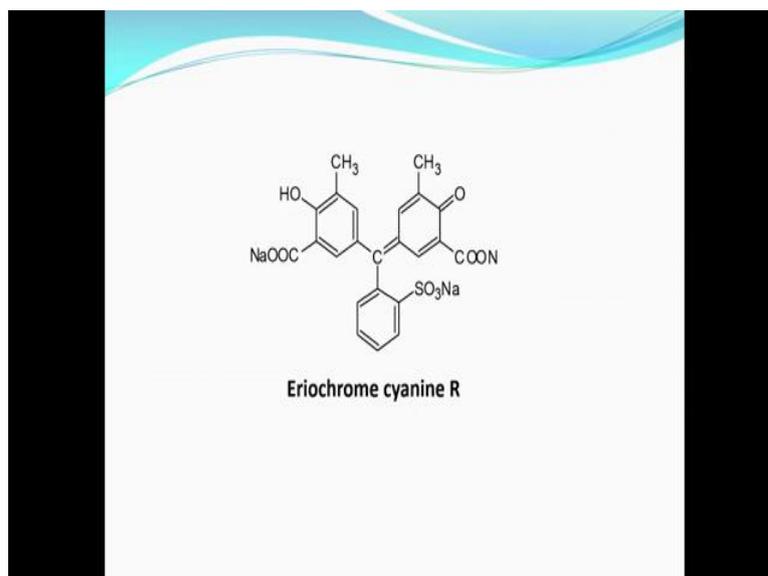
Normally concentration is greater than 1.5 milligram per liter constitutes a toxicity hazard in the marine environment; that means, in high salt solutions if the aluminium is more than 1.5 milligram per liter, then it causes toxicity in the marine animals like fish and other things algae plant environment as well as animal environment, and even in

small reevaluates normally aluminium precipitates around pH 5 also pH 5, 6 more than pH 3 it will start precipitating and when the watery pH is about 5 or 6 or 7 you may not find much dissolved aluminium in that. But you will find that most of the aluminium has been precipitated at the bottom of the reverse and reevaluates, and if there is not much force in the water movement most of the bottom is covered with aluminium hydroxide precipitate. And the pH of the near the bottom of a flowing stream changes quite often depending upon the input and there are lot of animals which are floating very near the bottom a protozoa, bacteria and several other things and many animals are in that in that area within 2 to 3 millimeter of the bottom, within 2 to 3 millimeter height of the water from the bottom would be expose to high aluminium concentrations.

So, that can become toxic the aluminium at that level and then it can cause a disturbance in the natural cycle of the plant and animal life. So, levels below 200 microgram per liter present minimal risk. So, aluminium level aluminium has been quite practically in implicated in Alzheimer's disease. So, normally people who drink from aluminium cans they are high risk people for Alzheimer's diseases etcetera especially if you are in the habit of drinking Coco cola or something from aluminium cans, it should be slightly worried about the dissolved aluminium levels in the human body.

So, aluminium levels in brain tissues are suspected to be link to Alzheimer's disease. So, I will show you the first slide now that is that contains all the ideas what I have given you and we normally use aluminium also as a highly industrial product usually aluminium is used in industries for roofing etcetera may aluminium is very common, it is corrosion resistant normally it has a coating of aluminium oxide on the surface when expose to the air and provides a very safe environment for the corrosion resistance. So, normally aluminium is also used as a for esthetic purposes, for windows and things like that and the wasted aluminium vessels are use for cooking and that also could be one cause for Alzheimer's disease and therefore, it is important that we determine aluminium very low levels.

(Refer Slide Time: 05:51)



So, aluminium is normally determined using Eriochrome cyanine (Refer Time: 00:00), this is a triphenylmethane substance dye and it has got SO₃Na groups that makes it solubilize it very easily, and then it has got about COH groups and CON groups and CH₃, CH₃ like that quite possible to complex metals using these links CH₃ oxygen and there is one more here etcetera, and the complex structure of the complex you can look up in the inner standard text books.

(Refer Slide Time: 06:32)

Reagents

Stock aluminium solution (1000 ppm): Dissolve 1.758 g of A.R. aluminium sulfate in 100 ml water.

Working solution (100 ppm): 0.1 ml of the stock solution to 100 ml with deionised water

Sulfuric acid 0.02 N H₂SO₄: Add 300 µl of concentrated sulphuric acid to 100 ml water to get approximately 1 N sulphuric acid. Dilute 1 ml of this to 50 ml with deionised water.

So, to determine aluminium what we do is normally we go for 1000 ppm, stock solution which is prepared by dissolving 1.75 gram of aluminium sulphate, and working solution should be approximately 100 ppm.

Sulfuric acid should be approximately 0.02 normal and this you can prepare up to 100 ml and, but before you use it should be diluted to 50 ml with deionised water.

(Refer Slide Time: 07:16)

Buffer Reagent (0.3 M): Dissolve 13.6 g of sodium acetate trihydrate $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$ in 50 ml deionised water and add 4 ml of glacial acetic acid. Make it up to 100 ml and adjust the pH to 6.

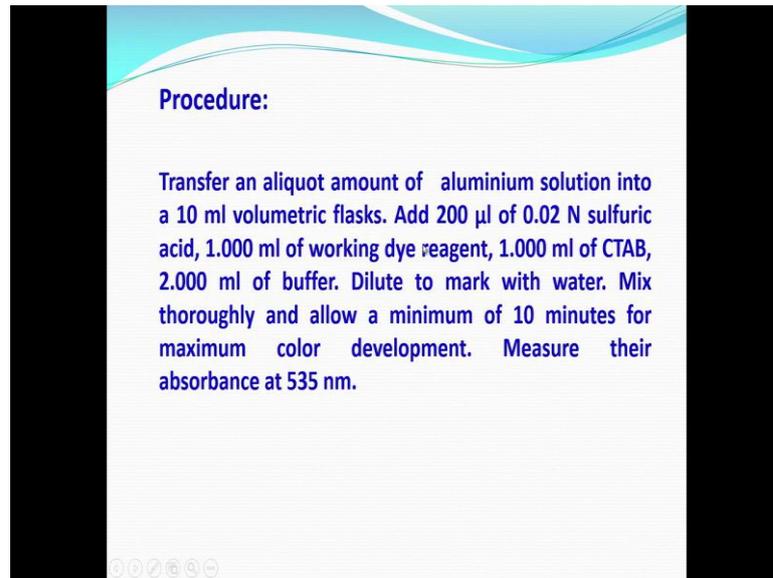
Erichrome cyanine R (0.015%): Dissolve 0.015 g of Erichrome cyanine R in 5 ml of deionised water and add (1:1) acetic acid adjust the pH to 3. Make it 100 ml with water.

CTAB solution (0.1%)

And then you also need a buffer of sodium acetate acetic acid that is around pH 4, the buffer concentration should be approximately about 0.3 molar. So, you can prepare the dissolved you can by dissolving sodium acetate in 50 ml and add a 4 ml of glacial acid as you can make it and then use it. Erichrome cyanine R is a available across the shelf it is a very good dye for clothes also, and you have to dissolve 0.015 gram of erichrome cyanine R in 5 ml of deionised water.

So, what we have done is usually in sets of aluminium determination there will be a formation of some sort of lake; that means, a sort of precipitate may be obtained and as you know precipitate is not good for spectrophotometry. So, what we have we done is in this case we are asking you to prepare cetyl trimethyl ammonium bromide, that is CTAB it is a cationic surfactant you have to prepare 0.1 percent of CTAB that is that we keep the small precipitates particles in solution. So, that is the modification we have done to the standard method.

(Refer Slide Time: 08:43)



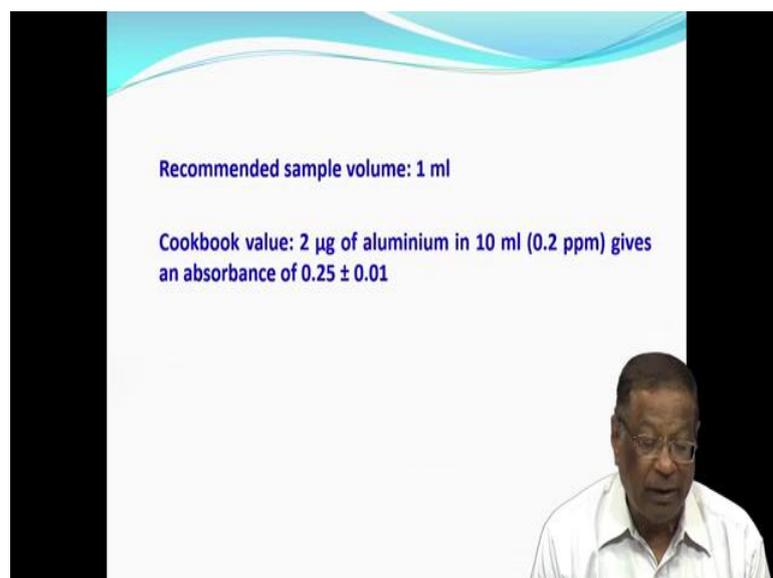
Procedure:

Transfer an aliquot amount of aluminium solution into a 10 ml volumetric flasks. Add 200 μ l of 0.02 N sulfuric acid, 1.000 ml of working dye reagent, 1.000 ml of CTAB, 2.000 ml of buffer. Dilute to mark with water. Mix thoroughly and allow a minimum of 10 minutes for maximum color development. Measure their absorbance at 535 nm.

And then the procedure is very simple now, if you have all the reagents all you got to do is take the standard solutions aliquot of aluminium in 10 ml standard flask that as usual.

Then you add 200 micro liter of sulfuric acid, 1 ml of working dye 1 ml of CTAB and 2 ml of buffer, and then you have to add your reagents and the aluminium. You also need the complex gives you an absorbance at 535 nanometer, that is again it is a sort of purple red colour.

(Refer Slide Time: 09:25)



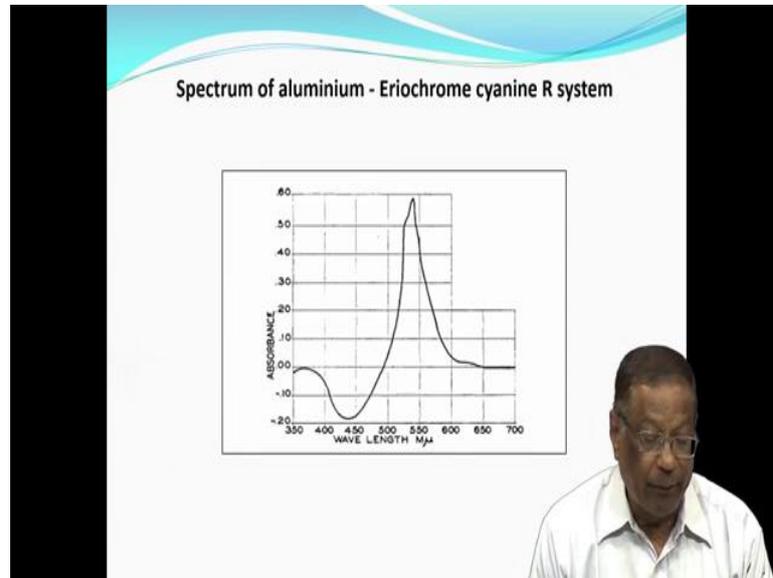
Recommended sample volume: 1 ml

Cookbook value: 2 μ g of aluminium in 10 ml (0.2 ppm) gives an absorbance of 0.25 ± 0.01



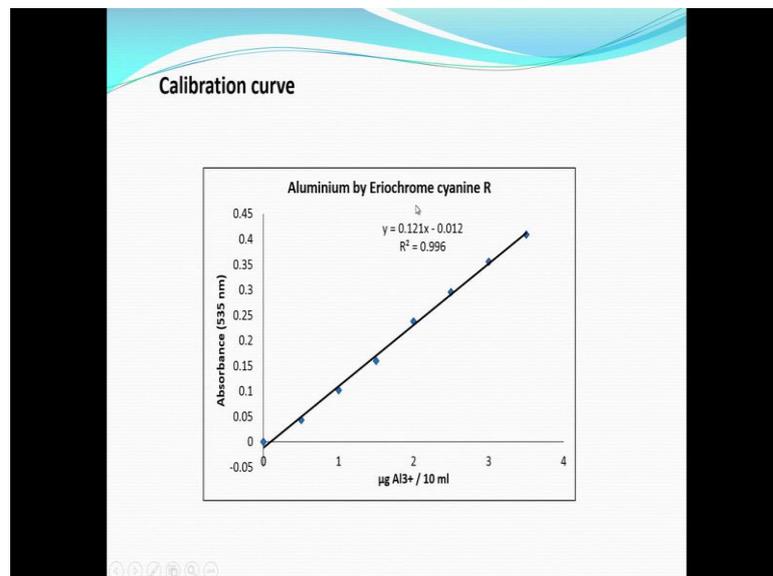
So, recommended sample volume is 1 micro liter, 1 milliliter and in the cookbook value for 2 microgram of aluminium in 10 ml that is 0.2 ppm should give you an absorbance of about 0.25 plus or minus 0.01 absorbance.

(Refer Slide Time: 09:49)



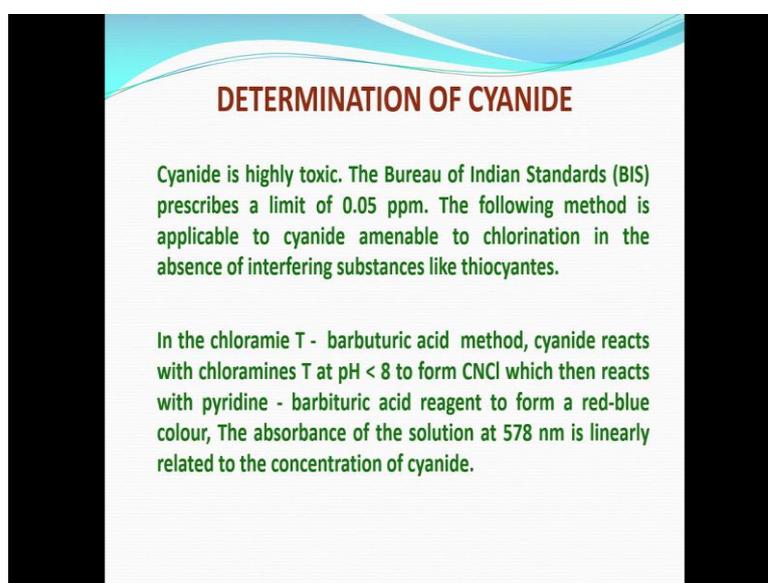
So, this is the spectrum of aluminium that is aluminium and Eriochrome cyanine R complex this spectrum has been taken against a blank, because I am showing you only one figure and at the against the blanks you can see that there is a lambda max around 525 or so, and the let us say around 535 you are getting the lambda max.

(Refer Slide Time: 10:24)



And the calibration curve will show you aluminium Erichrome cyanine R are complex follow Beer Lambert's law up to 3.5 micrograms in 10 ml, that is a fantastic improvement over the extraction procedure, but the linearity is also fairly the least square index R^2 gives you a value of approximately 0.996 which means that the method is very sensitive, and follows a good line which gives you a good linearity which means the results will be highly dependable. So, I would also like to add here that the method needs to be standardized every time, because this colour is not very stable for long time. So, every time you have to prepare a standard and then do their determination.

(Refer Slide Time: 11:38)



DETERMINATION OF CYANIDE

Cyanide is highly toxic. The Bureau of Indian Standards (BIS) prescribes a limit of 0.05 ppm. The following method is applicable to cyanide amenable to chlorination in the absence of interfering substances like thiocyanates.

In the chloramine T - barbituric acid method, cyanide reacts with chloramines T at $\text{pH} < 8$ to form CNCl which then reacts with pyridine - barbituric acid reagent to form a red-blue colour, The absorbance of the solution at 578 nm is linearly related to the concentration of cyanide.

So, that brings me to the another parameter that is cyanide. Cyanide is a parameter of importance and everybody knows that cyanide is a highly poisonous chemical very difficult to handle, you are not allowed to keep it in the laboratory unless you are trained to handle it, but cyanide has got a very varied uses in our day to day industrial life we may not be using it much in normal circumstances, but cyanide is a very important plating chemical. So, cyanide people using doing plating will employ kilograms of cyanide and then there is another process that is known as nitriding, many of the industrial chemicals in a metals which are part of the machines they have to provide very hard surface.

So, this hard surface should be a few microns. So, may be 1 or 1.5 millimeters of something like, that and that kind of surface is prepared by taking the metal and dipping it in a cyanide solution and then melt it melt the cyanide salt and keep the

cyanide salt melted for about 5 to 6 hours or 10 hours according to the procedure which imparts hardness to the metal surface that is known as nitriding. So, the nitrogen combines with the higher particles on the surface that is that will give you a nitride metal surface. So, that is also a very important aspect of industrial life, and I have seen people who use nitrate cyanide in kilogram quantities with bare hands, of course that is not a very good practice.

Because any cut in the hand or something like that you are handling the cyanide a person may die, and cyanide the action of cyanide is known to occur through the replacement of oxygen by cyanide in the hemoglobin. As we know hemoglobin is a preferring like structure with iron in the center and then on 4 sides parallel on the same plane nitrogen perforin groups are there on the top there is another nitrogen group bound to a proton and at the bottom it is a oxygen and carbon dioxide oxygen and carbon dioxide.

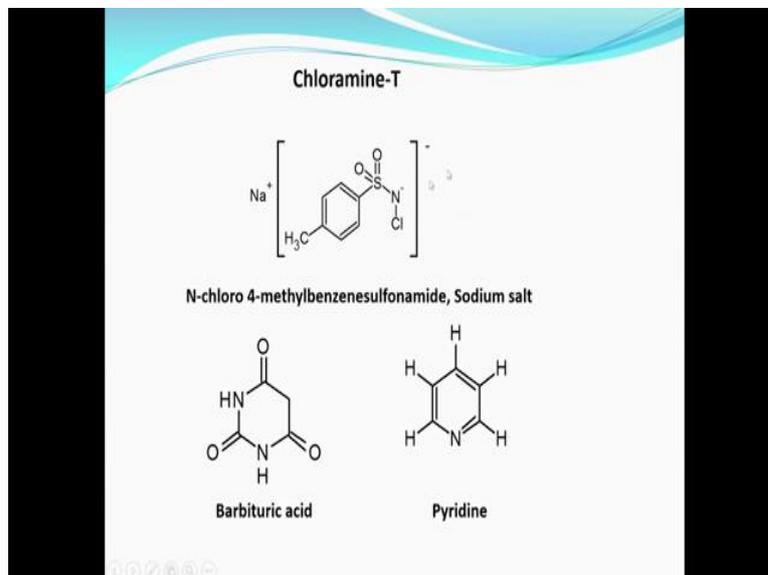
As we breathe in we take up oxygen and oxygen goes and sits a attaches itself to iron and then we as we breathe out the carbon dioxide will be exited from the same spot. So, carbon dioxide and oxygen normally are exchangeable in a red blood cell in our body; now if I have some cyanide in the in my body the cyanide will go and attach it at the play attach it to iron complex hemoglobin complex at the bottom where oxygen should have been there, and cyanide attaches itself so strongly that it would not give chance for oxygen to attach itself; that means, cyanide has to go oxygen has to come in. So, this equilibrium is disturbed, once it is disturbed, it becomes irreversible and a person will die of asphyxiation.

So, the reaction is very fast and people say that they are not been able to determine the taste of cyanide also, because before it is determined the person will die. So, a cyanide we have to worry about in the environment because especially from electro plating industries and metal finishing industries. So, the my slide shows you that exactly the same in same information that is highly toxic, the BIS prescribes a limit of 0.05 ppm the following method is a applicable to cyanide that is amenable to chlorination in the absence of interfering substances like thiocyanates.

So, the normal method is in the used chloramine T and barbituric acid, where cyanide will react with chloramine T at pH less than eight to form cyanogen chloride. This then reacts with pyridine barbituric acid reagent to form a red blue colour the absorbance of

the solution at 578 nanometer is usually related to the concentration of cyanide very simple and straight forward method all the reagents are available across the shelf.

(Refer Slide Time: 17:42)



And this is the chloramine T complex reagent it is sodium chloramine T, NA plus chloramine T minus this chloramine T is nothing, but N chloro 4 methylbenzenesulfonamide is sodium salt and this is the structure of barbituric acid that is NH NH, and pyridine reacts pyridine is a very simple chemical.

(Refer Slide Time: 18:23)

Reagents

Chloramine T Solution (100 ppm): Dissolve 1.0 g of chloramine T in deionised water and make up to 100 ml. (Stable for 1 week)

Sodium hydroxide Solution (4 %): Dilute 4 g sodium hydroxide in deionised water and make up to 100 ml with deionised water.

Sodium hydroxide Solution (0.16 %): Dilute 4 ml of 4 % sodium hydroxide with deionised water to 100 ml.

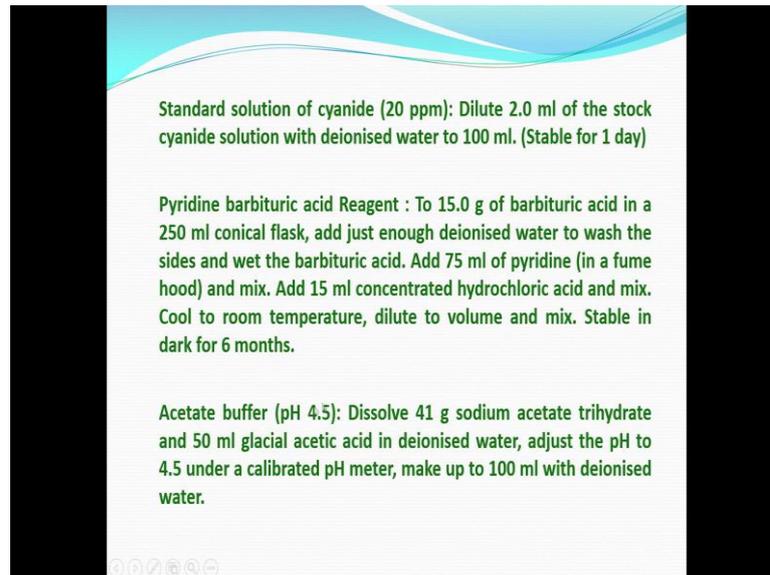
Stock cyanide Solution (1000 ppm): Dissolve 0.2510 g of potassium cyanide in 4 ml of 4 % sodium hydroxide solution and dilute to 100 ml with deionised water. (Stable for 1 week)

Just like benzene where instead of the sixth carbon atom there is only one nitrogen there. So, the reagent chloramine T is prepared by dissolving one gram of chloramine T. It is available in quite large quantities; it is an industrial chemical also, and you can dissolve it in water to make up to 100 ml. Normally chloramine T solutions are stable for about one week; that means, every week you have to prepare fresh chloramine T if you want to determine cyanide. So, it is also important that you prepare about sodium hydroxide of 4 gram of sodium hydroxide in deionised water with about 100 ml solution you can prepare, and from this you have to prepare 0.16 percent of sodium hydroxide again.

Because normally you can straight away prepare 0.16 percent sodium hydroxide also, but the procedure according to us what we feel is 4 percent sodium hydroxide is quite stable, and the 0.16 percent you can determine as an when you need it. So, for every experiment you can just do this dilution and sodium cyanide is the standard chemical you have to prepare 1000 ppm and dissolve it potassium cyanide is available in the market and you have to dissolve it in 4 percent of sodium hydroxide solution and dilute to 100 ml; that means, the cyanide solution should be in alkaline medium. So, if the cyanide is in acetic medium it will release hydrogen cyanide gas and it which may cause problem of toxicity.

So, one has to be very careful how you store your cyanide in the laboratory also. So, standard working solution you can prepare up to 20 ppm that is no problem, and pyridine barbituric acid reagent you have to prepare separately taking barbituric acid as well as the pyridine; what you should do is dissolve about 15 gram of barbituric acid in 250 ml conical flask just add enough deionised water to keep the barbituric acid in solution that is quite soluble in water. And then you have to add about 75 ml of pyridine and that you should do in a fume cupboard, because pyridine vapours are also are not good for breathing. So, only the all these procedures you have to handle in a fume cupboard and you have to take adequate precautions for preparing the solutions and as well as handling the solutions.

(Refer Slide Time: 21:30)



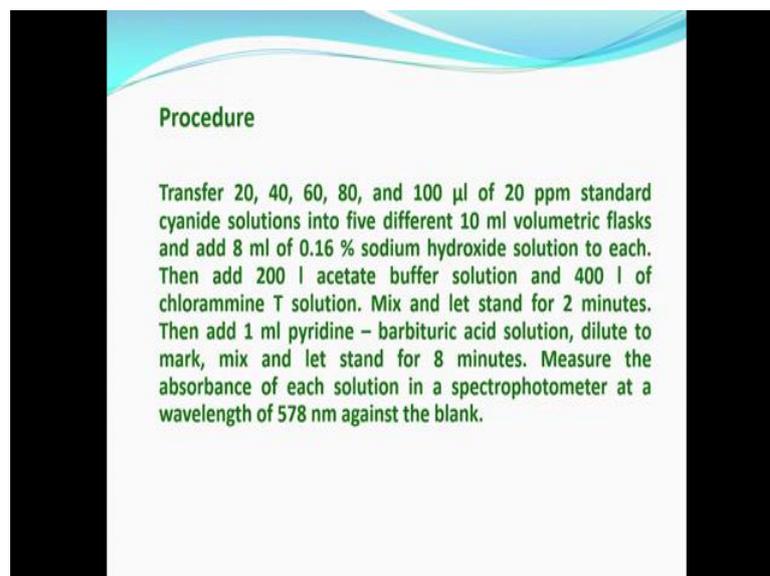
Standard solution of cyanide (20 ppm): Dilute 2.0 ml of the stock cyanide solution with deionised water to 100 ml. (Stable for 1 day)

Pyridine barbituric acid Reagent : To 15.0 g of barbituric acid in a 250 ml conical flask, add just enough deionised water to wash the sides and wet the barbituric acid. Add 75 ml of pyridine (in a fume hood) and mix. Add 15 ml concentrated hydrochloric acid and mix. Cool to room temperature, dilute to volume and mix. Stable in dark for 6 months.

Acetate buffer (pH 4.5): Dissolve 41 g sodium acetate trihydrate and 50 ml glacial acetic acid in deionised water, adjust the pH to 4.5 under a calibrated pH meter, make up to 100 ml with deionised water.

So, we can add a little bit of concentrated hydrochloric acid also and cool to room temperature dilute to volume mix and stable, but once you prepare this it is stable for about 6 months. Then you need to prepare a acetic acid acetate buffer that is sodium acetic acid you can take trihydrate and mix in the proportions mentioned here that is 41 gram as well as sodium acetate trihydrate and 50 ml of glacial acetic acid. So, under using these things you can make up to 100 ml and start preparing the procedure is you take 20 to 100 micro liter of 20 ppm standard cyanide in different flask.

(Refer Slide Time: 22:14)

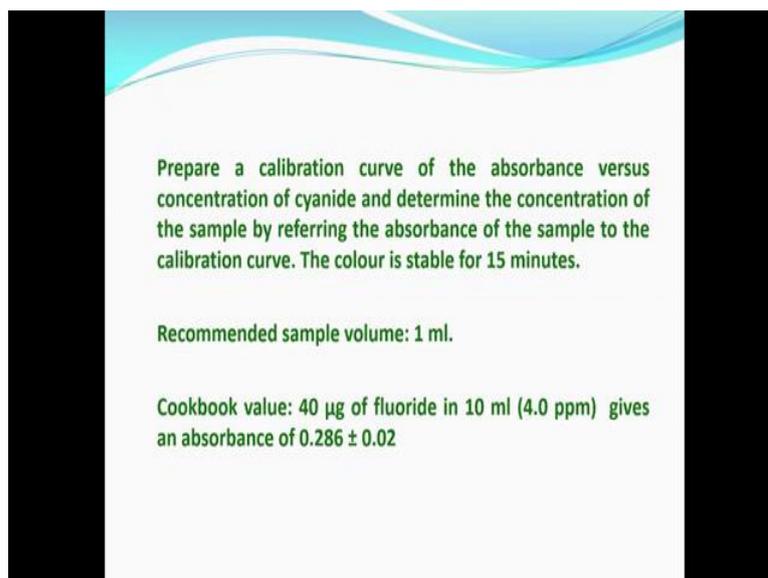


Procedure

Transfer 20, 40, 60, 80, and 100 μ l of 20 ppm standard cyanide solutions into five different 10 ml volumetric flasks and add 8 ml of 0.16 % sodium hydroxide solution to each. Then add 200 μ l acetate buffer solution and 400 μ l of chloramine T solution. Mix and let stand for 2 minutes. Then add 1 ml pyridine – barbituric acid solution, dilute to mark, mix and let stand for 8 minutes. Measure the absorbance of each solution in a spectrophotometer at a wavelength of 578 nm against the blank.

And add the sodium hydroxide 0.16 percent, and add about 200 micro liter of acetic buffer, 400 micro liter of chloramine T and mix them and let them stand for 2 minutes then add your 1 ml pyridine barbituric acid solution. So, dilute it to the mark mix and let stand for about 8 minutes. So, you have to measure the absorbance at 578 which means the complex should be somewhat bluish in colour.

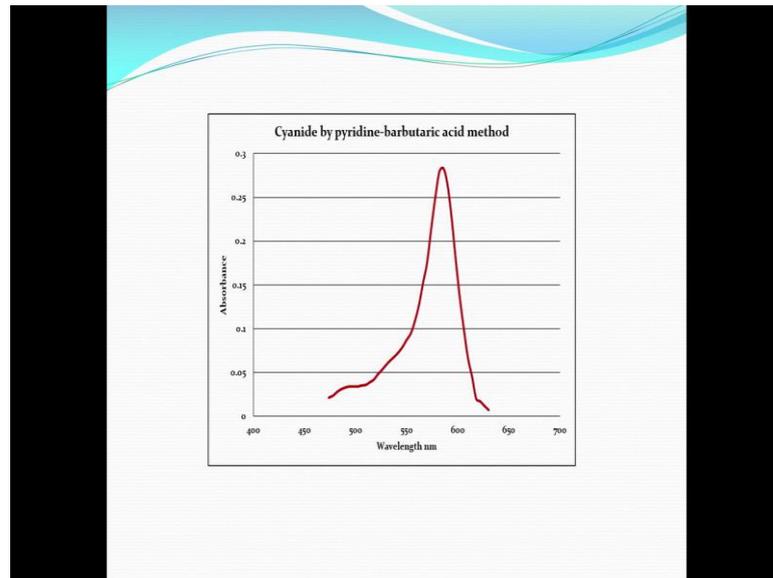
(Refer Slide Time: 22:51)



So, we have to prepare a calibration curve of the absorbance verses concentration of cyanide and you can determine the concentration of the sample by referring to the calibration curve as usual.

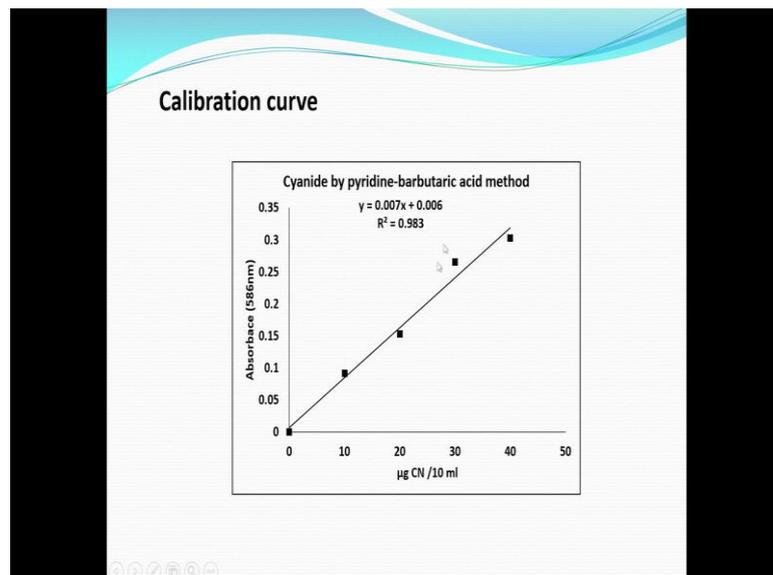
So, nothing very specific about it, but one thing you should remember is the colour is stable for about only about 15 minutes; that means, it does not give you the procedure does not give you enough time to keep the sample and measure at your with convenience it is better you should measure this in colour within 15 minutes and recommended volume is about 1 ml. So, cookbook value for 40 microgram gives an absorbance of about 0.286 grams absorbance not grams.

(Refer Slide Time: 23:49)



And the cyanide pyridine barbituric acid method will show you lambda max, spectrum shows like this that is a spectrum taken against the blank. So, you can see that it gives a very sharp peak somewhere around 560, 570 which I have mentioned in my previous slide, that is at what is a wavelength that is 578 nanometers. So, that will give you fairly good sensitivity and this is the linearity curve for cyanide not very good in terms of linearity.

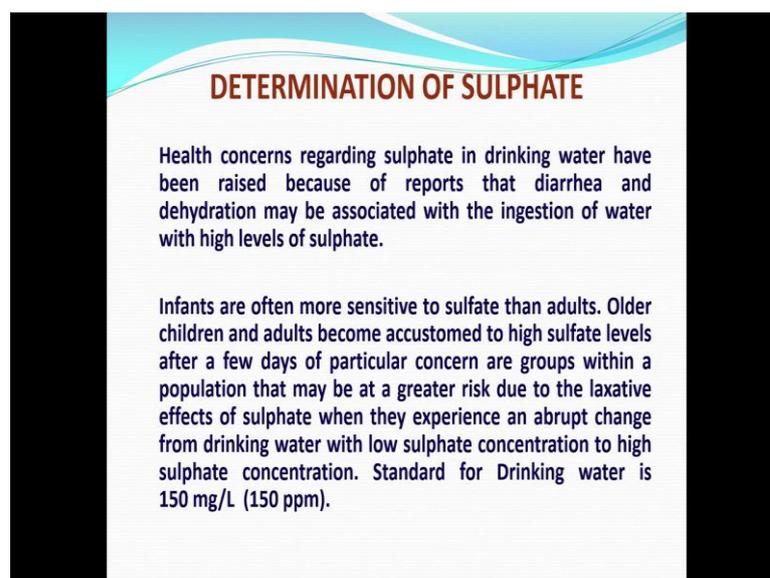
(Refer Slide Time: 24:40)



Because R square value is approximately 0.983, but if you are determining to 10micrograms in 10 ml that is 1 ppm should give you an absorbance of about this much. So, 0.5 ppm should be able to get about 0.05 absorbance which should be fairly as far as the method is concerned which should work for most of the industrial applications without any dilution that is the beauty. So, now, I will continue a explaining about the determination of sulphate. Determination of sulphate is very important I do not have to mention to you that sulphate is not a pollutant in the normal sense.

But sulphate is there everywhere just like chloride sulphate is there in the soil, it is there in the water, it is there in the air we breathe and most of the automobile exhaust in the environment (Refer Time: 26:16) sulfur dioxide which gets converted into the into sulphate in the atmosphere, whenever there is rain or something like that the sulphate will combine with some of the metal ions in the air and then sulphate will rain forming sulfuric acid also as well as some other metal salts and sulphate is implicated in acid rain. So, that is that follows a naturally therefore, sulphate is there all around us again and sulphate regarding health concern, I should tell you that it does not cause you any problem as such, but higher level of sulphates usually end up giving you irritation because there was the taste of water is not does not the taste of water is not good when it contains high levels of sulphate.

(Refer Slide Time: 27:22)



DETERMINATION OF SULPHATE

Health concerns regarding sulphate in drinking water have been raised because of reports that diarrhea and dehydration may be associated with the ingestion of water with high levels of sulphate.

Infants are often more sensitive to sulfate than adults. Older children and adults become accustomed to high sulfate levels after a few days of particular concern are groups within a population that may be at a greater risk due to the laxative effects of sulphate when they experience an abrupt change from drinking water with low sulphate concentration to high sulphate concentration. Standard for Drinking water is 150 mg/L (150 ppm).

So, health concerns regarding sulphate in drinking water have been raised because of reports that sometimes diarrhea and dehydration may be associated, but it is not proven yet with the induction of water contain in higher levels of sulphate, as of now what we would like to remember is more than 200 ppm of sulphate in drinking water is not good. So, whenever you take a water some drink water from a bore well, chances are you may have high higher levels of sulphate if the water is drawn from about 2 more than 200, 300, 400 feet then the sulphate will be in higher quantities. So, that is one reason why most of the drinking water has to be monitored for sulphate.

So, there is another possibility that the people are sensitive with to sulphate even with small quantities of sulphate with respect to age it has something to do with the age infants are usually very sensitive to sulphate than the adults. So, older children and adults become accustomed to high sulphate levels, but children it is a bit of problem. So, after a few days of particular concern there are groups within a population that may be at a greater risk than others, this happens because of the laxative properties of the sulphate. So, an abrupt change from the water what you drink is always could be a cause for indigestion and diarrhea.

Now, many people do not recognize it as one of the reasons for sulphate and it is not so easily detectable nor it is proven, but chances are there if you the water what you are drinking suddenly it characteristics you move to some other town other place and then start drinking that water, there will be a problem of this water causing you diarrhea. Sulphate is also not very good with respect to laundry, the industrial municipal water river waters contain about 60 to 80 ppm of sulphate, and higher than that is not really good. We will continue our discussion of sulphate in the next class.