Atomic and Molecular Absorption Spectrometry for Pollution Monitoring

Dr. J R Mudakavi

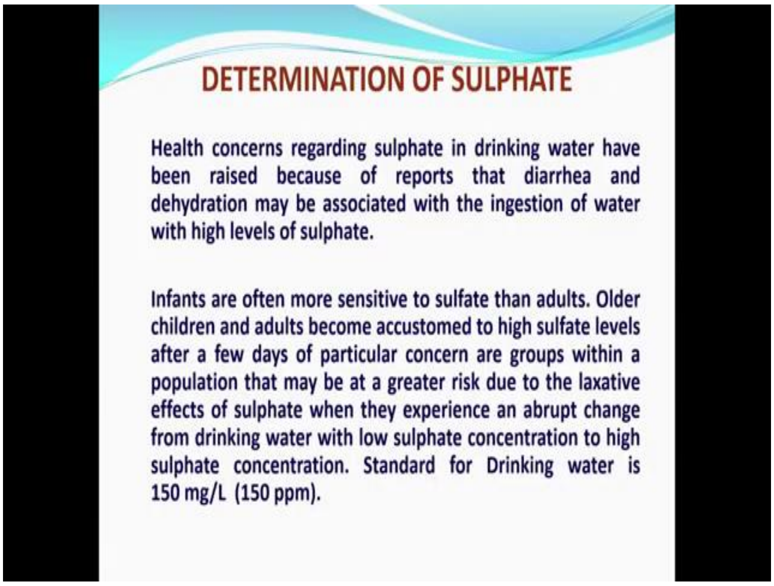
Department of Chemical Engineering

Indian Institute of Science, Bangalore

Lecture – 41

Sulphate, ammonia, Conclusions

(Refer Slide Time: 00:24)



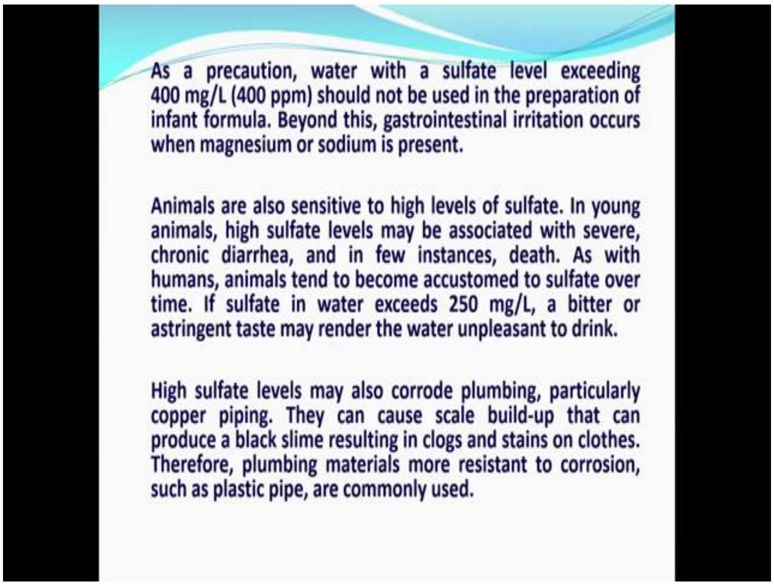
DETERMINATION OF SULPHATE

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, we are discussing about sulfate and I was telling you that 200 up to 200 ppm is usually allowed according to the WHO standard and, but the normal standard for drinking water is about 150 milligram per liter, that is 150 ppm.

(Refer Slide Time: 00:40)



As a precaution, water with a sulfate level exceeding 400 mg/L (400 ppm) should not be used in the preparation of infant formula. Beyond this, gastrointestinal irritation occurs when magnesium or sodium is present.

Animals are also sensitive to high levels of sulfate. In young animals, high sulfate levels may be associated with severe, chronic diarrhea, and in few instances, death. As with humans, animals tend to become accustomed to sulfate over time. If sulfate in water exceeds 250 mg/L, a bitter or astringent taste may render the water unpleasant to drink.

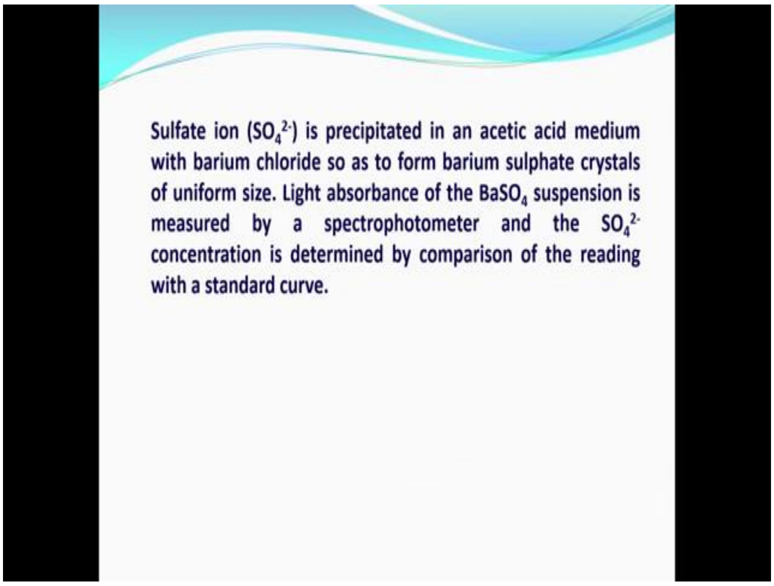
High sulfate levels may also corrode plumbing, particularly copper piping. They can cause scale build-up that can produce a black slime resulting in clogs and stains on clothes. Therefore, plumbing materials more resistant to corrosion, such as plastic pipe, are commonly used.

So, normally as precaution water with sulfate level exceeding 400 ppm should not be used in the preparation of infant formula, because I was telling you that infants are more prone to go through to sulfate abuse, and we have to make sure that the water use for infant feeding etcetera should not contain so much of sulfate.

So, beyond this gastrointestinal irritation also occurs and magnesium and sodium are present which are the common constituents of water. So, animals are also sensitive to high levels of sulfate, in young animals sometimes high sulfate levels are associated with severe chronic diarrhea and in few circumstances death also higher concentration, but only with younger animals. So, just like humans animals tends to become a custom to sulfate over time.

So, higher sulfate does not really result in problems, but if the sulfate level exceeds 250 milligram per liter, the bitter taste will continue and astringent effect you know astringent effect means somewhat undesirable effect taste it may render the water very unpleasant to drink. So, high sulfate levels also cause plumbing particularly copper in copper piping, they can cause scale build up that can produce a black slime resulting in clogs and stains produces stains on the clothes etcetera. So, most of the plumbing materials are resistant to corrosion such as plastic pipe so, to avoid that PPO plastic pipe, but it does not do away with the problem with sulfate.

(Refer Slide Time: 03:04)

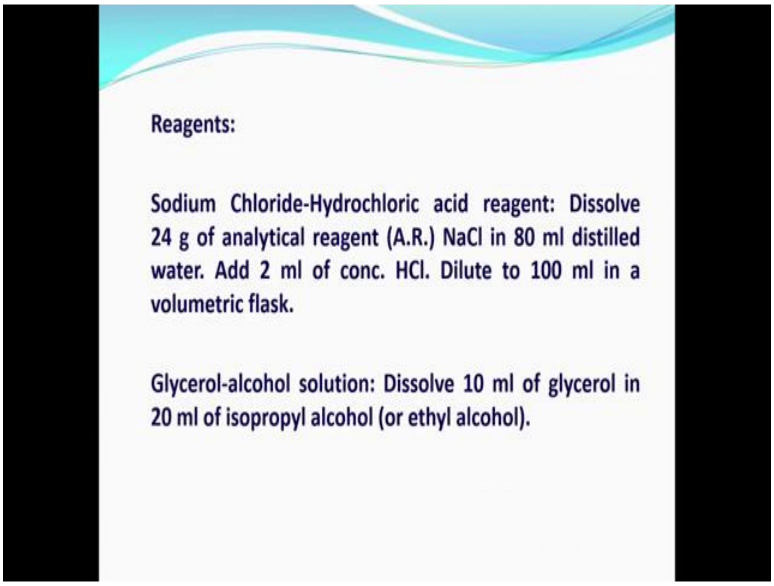


Sulfate ion (SO_4^{2-}) is precipitated in an acetic acid medium with barium chloride so as to form barium sulphate crystals of uniform size. Light absorbance of the $BaSO_4$ suspension is measured by a spectrophotometer and the SO_4^{2-} concentration is determined by comparison of the reading with a standard curve.

So, sulfate ion is normally precipitated in acetic acid medium with barium chloride; this is a very standard procedure for the preparation of for the determination of barium sulfate, it is a very high school level chemistry barium sulfate is highly insoluble in water and acetic acid medium helps in producing barium chloride good crystals of uniform size. So, normally light absorption of the absorbance of barium sulfate suspension is measured by a spectrophotometer and the sulfate concentration is determined by comparison of the reading with a standard curve. See the problem with determination of sulfate is the normal method for precipitation of sulfate is by gravimetry and there are number of other methods also for the determination of sulfate.

But in ppm level you have to work harder to because the precipitate may not be in a weighable form we may not get enough of the sample to precipitate. So, the method that method has been modified using spectrophotometry its not done by us, the method is already there what we have done is we have try to downsize the whole operation to smaller volume so that the experiment can be carried out at a faster with less use of chemicals.

(Refer Slide Time: 04:49)



Reagents:

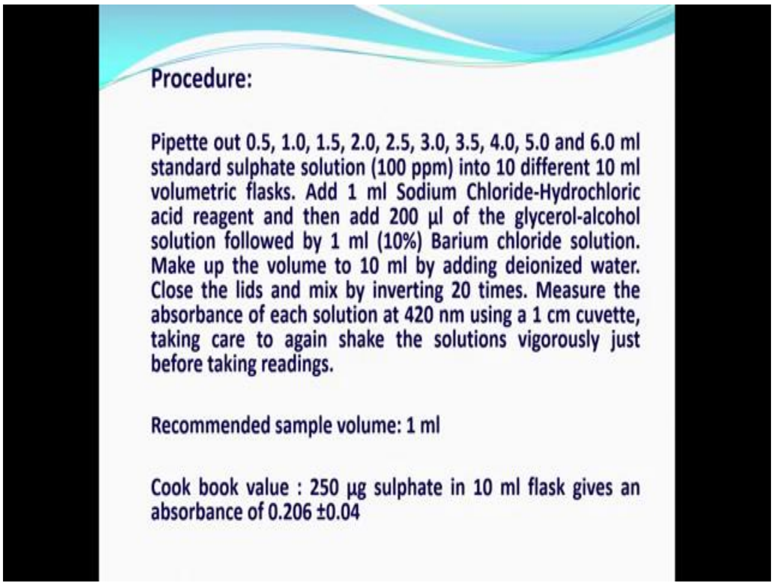
Sodium Chloride-Hydrochloric acid reagent: Dissolve 24 g of analytical reagent (A.R.) NaCl in 80 ml distilled water. Add 2 ml of conc. HCl. Dilute to 100 ml in a volumetric flask.

Glycerol-alcohol solution: Dissolve 10 ml of glycerol in 20 ml of isopropyl alcohol (or ethyl alcohol).

So, these are the reagents what we need we just need sodium chloride and hydrochloric acid reagent, we have to dissolve 24 gram of sodium chloride in 80 ml of distilled water, add 2 ml of concentrated hydrochloric acid to 100 ml volumetric flask, then you also need a glycerin glycerol alcohol solutions, this solution is required to keep the precipitate in suspension form; because I have already explained in turbidimetric methods during our discussion on the instrumentation, I had mentioned to you that any gravimetric method can be converted into a spectrophotometric method provided the precipitate in kept in solution.

So, the same principle here there I have mentioned that any precipitate can be kept in suspension using a viscous liquids, sometimes polyvinyl alcohol you can use or you can use glycerin or you can use glycerol alcohol solution like this, only to increase the viscosity and to ensure that the precipitate does not settle down during the measurement. So, there is a only purpose while we use glycerol alcohol solution in the determination of sulfate. So, the procedure is very simple all you have to do prepare out standard sulfate solution in 10 different flask, volumetric flask add 1 ml of sodium chloride and hydrochloric acid reagent.

(Refer Slide Time: 06:45)



Procedure:

Pipette out 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 5.0 and 6.0 ml standard sulphate solution (100 ppm) into 10 different 10 ml volumetric flasks. Add 1 ml Sodium Chloride-Hydrochloric acid reagent and then add 200 µl of the glycerol-alcohol solution followed by 1 ml (10%) Barium chloride solution. Make up the volume to 10 ml by adding deionized water. Close the lids and mix by inverting 20 times. Measure the absorbance of each solution at 420 nm using a 1 cm cuvette, taking care to again shake the solutions vigorously just before taking readings.

Recommended sample volume: 1 ml

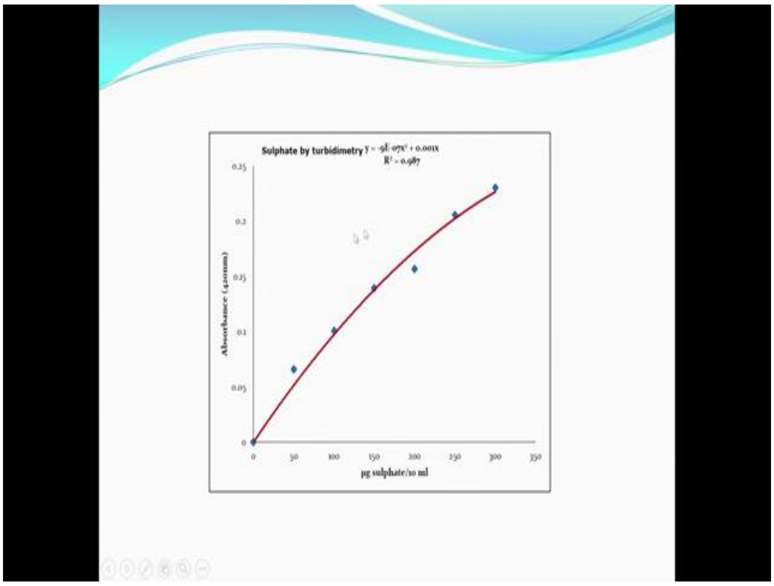
Cook book value : 250 µg sulphate in 10 ml flask gives an absorbance of 0.206 ±0.04

So, add up to 200 micro liter of the glycerol alcohol solution followed by 1 ml of the barium chloride solution. So, the barium chloride will react with the sulfate present in the sample to give you barium sulfate and the alcohol glycerol solution will help you to keep the solution in tact that is no precipitation should occur. So, we have to what we should do is close the lids and mix it by inverting 20 times. So, the conversion of this 20 times mixing is only arbitrary, you can mix it 40 times 50 times at say any number of times, but the requirement is you should be able to mix it in a reproducible manner, if you have a solution like this all you should so is do it like this in a very very reproducible manner so that precipitate will not grow in size also because that will result in more of scattering radiation not the absorbance radiation.

So, if you are able to do this exactly for each of the sample as well as blank, you should be able to measure the absorbance because this precipitate will remain in solution it will be of uniform size the scattering will be less, and all these properties we can observe. So, this is a only method among the water treatment chemicals water parameters I am recommending as a spectrophotometric method even though many of them can be followed by using this, but it depends upon the ingenuity to adopt. I am only giving you an example here, but any precipitation method can be used for the spectrophotometric application.

So, then suppose when do that then you measure the absorbance of each solution at one 420 nanometers. So, it is a white colour solution they basically. So, it does not matter which wavelength you use, but 420 seems to be fairly good wavelength, there is no hard and fast rule that you should only 420 nanometers, you can use any of the wavelengths available on the spectrophotometer as for as white precipitance are concerned. So, if the recommended sample volume is a approximately 1 ml because the concentration wave may be vary from 250, 50, 100 like that and then cookbook value for we have prepared cookbook value for 250 milligram of sulphate in 10 micro liter 10 m l, that is about 25 microgram ppm that should give you an absorbance of about 0.206 plus or minus 0.04; that means, the allowance here plus or minus 0.04 indicates that for a turbidimetric methods we should keep a larger allowance for accuracy.

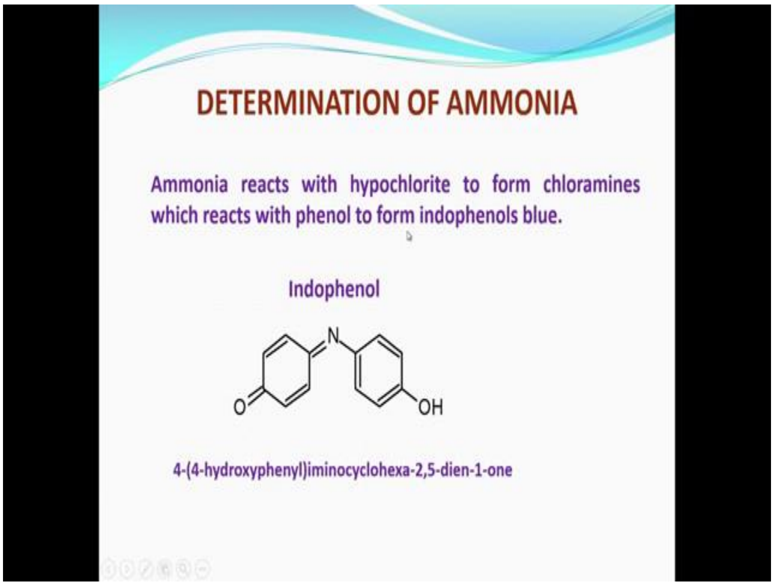
(Refer Slide Time: 10:07)



So, this is a method again I want to draw your attention to the calibration curve; the calibration curve is not at all linear, but it does not its necessary that it should be linear this is one classic case where the calibration can be non-linear and, but if it is reproducible we should be able to use it for our purpose.

Now, the r square value; obviously, will not be very good if you want to fit it into a linear quadratic equation, but 0.987 value what we have got, and if you are able to reproduce a any of the results with a reasonable accuracy you should be able to go ahead and complete the chemical analysis with a spectrophotometric finish, you otherwise there are many other methods one can go depending upon the accuracy required.

(Refer Slide Time: 11:14)



DETERMINATION OF AMMONIA

Ammonia reacts with hypochlorite to form chloramines which reacts with phenol to form indophenols blue.

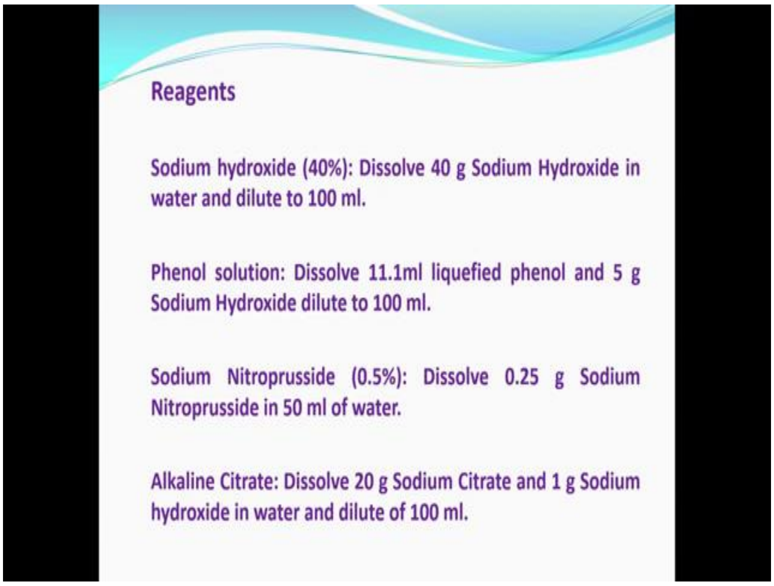
Indophenol

4-(4-hydroxyphenyl)iminocyclohexa-2,5-dien-1-one

So, I want to stop our discussion on sulphate at this level, and then we move on to ammonia this will be the last of the parameters which I will be discussing with you for water quality monitoring. So, we will not take much time regarding the determination of ammonia, but as an as prior information I have to tell you that ammonia is again everywhere, and it is there in the air water we breath to some extent and chloramines are being used in water treatment and then chloramine t and etcetera they all they are used ammonia is an industrial chemical, it also used as a medicine, in many of the Vicks and other substances which you smell when you have a cold, and industrially ammonia is produced in several millions of tons every year and ammonia is being transported across the country for several purposes.

But if there is a leakage of ammonia it will leads to sort of toxic acid effects on the people who are exposed to that, and what I would like to tell you is this reaction with indophenol ammonia reacts with hypochlorite to form chloramines, which react with phenol to form indophenol blue. So, in this is a structure of indophenol that is with a chiton group and nitrogen and then there is AOH group this is a technically 4 4 hydroxyphenyl iminocyclohexa 2,-5 dien 1-one ok.

(Refer Slide Time: 13:09)



Reagents

Sodium hydroxide (40%): Dissolve 40 g Sodium Hydroxide in water and dilute to 100 ml.

Phenol solution: Dissolve 11.1ml liquefied phenol and 5 g Sodium Hydroxide dilute to 100 ml.

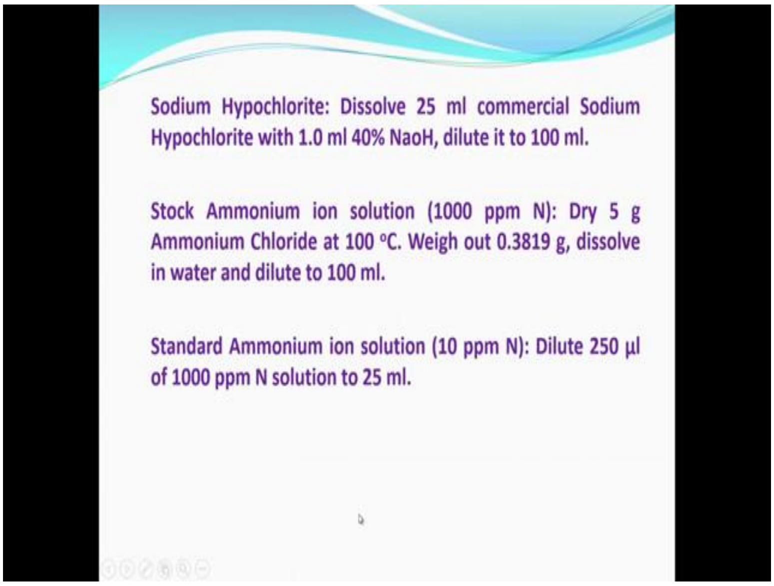
Sodium Nitroprusside (0.5%): Dissolve 0.25 g Sodium Nitroprusside in 50 ml of water.

Alkaline Citrate: Dissolve 20 g Sodium Citrate and 1 g Sodium hydroxide in water and dilute of 100 ml.

So, the reagents required for this are sodium hydroxide because the reaction proceeds in alkaline medium it is good also, you have to dissolve forty gram of sodium hydroxide and dilute to 100 ml you need phenol, phenol is available across the shelf and 11.1 ml liquefied phenol and 5 gram of sodium hydroxide can be dilute to 100 m l.

And then you need sodium nitroprusside, 0.25 gram of nitroprusside in 50 ml of water and then you also need alkaline citrate citric acid citric acid buffer approximately about in alkaline medium. So, that is we have to add sodium hydroxide in water so and dilute to 100 m l.

(Refer Slide Time: 14:05)



Sodium Hypochlorite: Dissolve 25 ml commercial Sodium Hypochlorite with 1.0 ml 40% NaoH, dilute it to 100 ml.

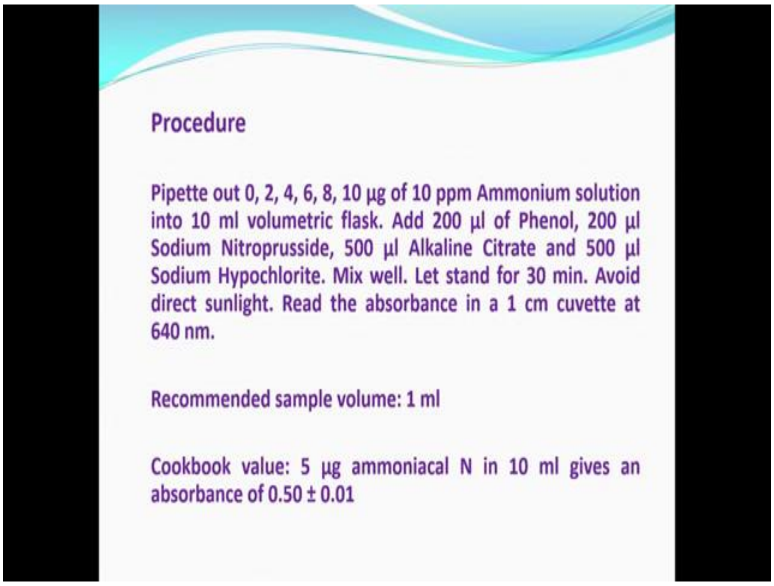
Stock Ammonium ion solution (1000 ppm N): Dry 5 g Ammonium Chloride at 100 °C. Weigh out 0.3819 g, dissolve in water and dilute to 100 ml.

Standard Ammonium ion solution (10 ppm N): Dilute 250 µl of 1000 ppm N solution to 25 ml.

So, you also need sodium hypochlorite just chemical available across the shelf you have to dissolve 25 ml of commercial sodium hydrochloride hypochlorite, with 1 ml of 40 percent N A dilute it to 100 m l. Then stock ammonium solution we can prepare by ammonium chloride, we have to weigh out 0.3819 gram dissolve it in water, and dilute to 100 m l; standard ammonium solution working that is working solution.

We have to prepare 10 ppm that should be more than enough; the reaction is we have to prepare 250 micro liter of 1000 ppm solution and to 25 m l.

(Refer Slide Time: 14:59)



Procedure

Pipette out 0, 2, 4, 6, 8, 10 µg of 10 ppm Ammonium solution into 10 ml volumetric flask. Add 200 µl of Phenol, 200 µl Sodium Nitroprusside, 500 µl Alkaline Citrate and 500 µl Sodium Hypochlorite. Mix well. Let stand for 30 min. Avoid direct sunlight. Read the absorbance in a 1 cm cuvette at 640 nm.

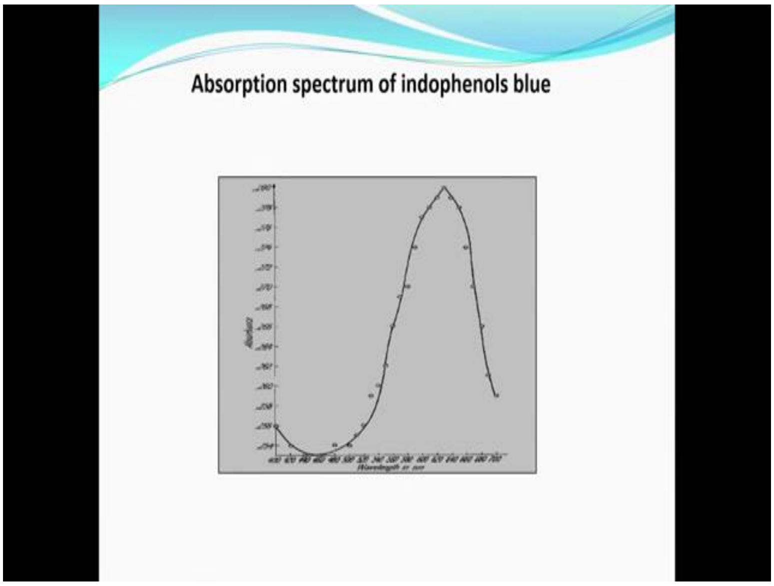
Recommended sample volume: 1 ml

Cookbook value: 5 µg ammoniacal N in 10 ml gives an absorbance of 0.50 ± 0.01

And the procedure involves pipette out up to 10 ppm solution in 10 ml volumetric flask, add phenol, Sodium Nitroprusside alkaline, citrate and Sodium Hypochlorite all you have to do is mix well and let stand for about 30 minutes indophenol will develop and only thing I want to tell you at this point is we should do it in diffuse light do not do it in sun light conditions. So, we can read the absorbance of 640 that produces a very bright blue colour solution.

And recommended volume is 1 ml for your sample and cookbook value for 5 microgram of ammoniacal nitrogen in 10 ml gives an absorbance of about 0.50 that is 5 microgram in 10 ml is about 0.5 ppm. Point 5 ppm in (Refer Time: 15:57) giving an absorbance of 0.50 is a very good sensitivity.

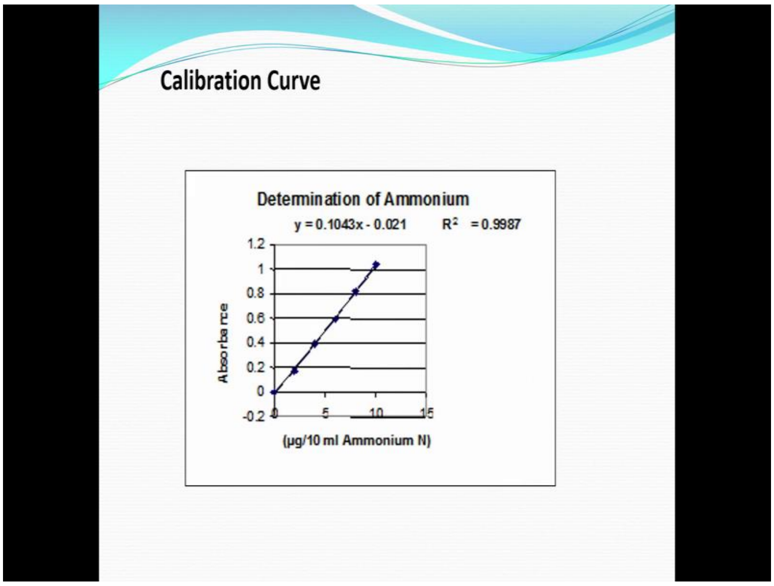
(Refer Slide Time: 16:06)



Absorption spectrum of indophenols blue

So, this is the absorption spectrum of the complex versus a blank standard blank without ammonia, and you can see that the method has got a fairly good sensitivity around 620 640 we should be able to get a correct absorbance.

(Refer Slide Time: 16:32)



Calibration Curve

And this is the calibration of ammonium ion in water, you can see that it goes through this origin and up to 1 ppm you can get a fairly good linearity. Least square fit gives you an r square value of about 0.987 which is fairly good I should say, and I would like to tell you that this completes our course on the monocular absorption methods using spectrophotometry, and related techniques for pollution water pollution monitoring. What I have try to teach you in this course is a very important aspect that very simple chemistry can be used two advantage to monitor the environment around us at the levels prescribed by the central government or any other government agency for the environment.

So, this whole course what I had divided into basically three parts; first one is the theoretical part which has I have given gone in detail telling you about the structure of the atom and how molecules and molecular orbital theory etcetera can be used, to advantage regarding the spectrophotometric that is that has lead the basis of spectrophotometry. Then I have in gone in to the theoretical aspects of spectrophotometric technique, that is transition from bonding and nonbonding orbitals and regarding the whether we can we should be able to convert a given structure and predict where the lambda max can be obtained.

I have also discussed with you the instrumentation in great detail regarding the spectrophotometry and the associated techniques that is modular techniques which can be added to spectrophotometer, they are including gravimetry sorry including the turbidimetry, nephelometry, luminescence spectrometry etcetera; and I have also discussed with you a little bit of about reflectance spectroscopy that is for paints etcetera.

And then in part two what I have done is I have selected about 21 parameters for water quality monitoring, and explain to you how these parameters can be monitored using spectrophotometry; basically the whole thing is an exposition of spectrophotometric technique to you so that once you are able to go through this course you will feel very very familiar with any spectroscopic this spectrophotometric technique, you will also be able to design new experiments based on the course content what I have given here. So, I hope you have enjoyed the course and the one more outcome of this course is I have given you a cookbook containing how to prepare the solutions even though the last part is may be slightly boring to you, because it is a sort of repetitive last 5 course classes I have take taken you through 21 parameters, and how to prepare the solution etcetera that should serve you as a cookbook itself.

So, if you move on to work you do not have to look for sources of information anywhere else unless you need. So, this is what I try to teach you, I hope you have enjoyed the course and I have also enjoyed the teaching you this course and it has been a rewarding experience for me and wish you all the best [FL] all the best.

Thank you very much.