Atomic and Molecular Absorption Spectrometry for Pollution Monitoring

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Lecture - 33
Arsenic, Free Chlorine

Greetings to you, we are starting our class with the determination of water parameter; drinking water parameters for arsenic, I will also take a look at some other methods that are there along with arsenic some other parameters like chlorine and free chlorine, etcetera. In general what we would like to say about arsenic is it is a carcinogenic element. Arsenic there is lot of problem with arsenic 5 that is arsenic invalency 5, arsenic 3 is not that bad, but in general arsenic whenever it is there in solution, it may get oxidized to arsenic 3 to arsenic 5. So, the danger of arsenic is always there it is environmentally not considered safe at all and it has basically no physiological role in the human metabolism or animal metabolism.

Unfortunately, the arsenic has become part of our system already even though it has no physiological role; that means, it has; it does not take part in any human metabolic process; that means, it is not an essential element, it is not a micro nutrient, it is not a an element that is present in large that should be present in large quantities also.

So, unfortunately evidence against arsenic has been piling up in the environment and all over the world, there is a general awareness of the dangers of arsenic in the environment. Arsenic is used in number of applications including thin films etcetera. It is also used as a food preservative, grain preservatives and then it is used in paints especially in marine paints and in marine paints what happens is the arsenic coating paint peels off and then it enters the water and then it is consumed by the fish and other marine animals that disturbs the hormone ratio of male and female hormone ratio in all elements.

So, the productivity of the fish and dolphins etcetera keeps on coming down and there are lot of accidents of a arsenic also in the recorded in the history recent history of about 30 to 50, years arsenic deaths have been reported, arsenic leakages have been reported and recently in Pakistan 176 people have died due to arsenic and in Manfred on, Italy there was a huge arsenic accident; arsenic release basically which rendered the an area of about 110 kilometer useless for and they had to shut down all the human habitation and other livestock etcetera, remove from the system, even now there are traces of arsenic in and around and arseno molybdateas and arseno arsenic compounds, organo arsenic compounds have been there in use ever since last 50-60 years and the most disturbing trend is even in India, arsenic is being found in drinking water especially in Bengal, Bihar that a Dhanbad area and nowadays in south also for example, Dodballapur in Karnataka near Bangalore many of the industrial estates etcetera are releasing arsenic knowingly or unknowingly in the water ways and there seems to be a little problem with respect to arsenic in the drinking water.

All over the world drinking water standard for arsenic is 0.01 ppm that is about 1 nano gram. So, you can imagine what would be the demands on arsenic determination in the environment in the air as well as in the drinking water because even in if the arsenic enters in drinking water it may lead to imposex problems that is sex hormone ratio changing because of arsenic. So, there is a general awareness and there is a requirement of; for the determination of arsenic in the environment as well as water.

Now, basically arsenic occurs naturally being 20th most it is a 20th most abundant element in the Earth’s crust its highly toxic and carcinogenic it occurs as arsenide as well as arsenate the arsenate is plus 5 oxidation state safe level is 0.01 ppm following method we have developed a method for the determination of arsenic using rhodamine B.

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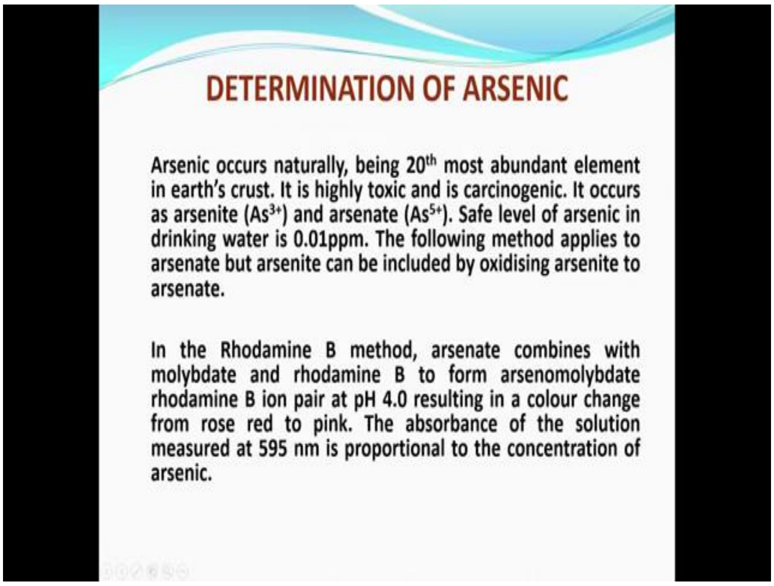

DETERMINATION OF ARSENIC

Arsenic occurs naturally, being 20th most abundant element in earth’s crust. It is highly toxic and is carcinogenic. It occurs as arsenite (As^{3+}) and arsenate (As^{5+}). Safe level of arsenic in drinking water is 0.01ppm. The following method applies to arsenate but arsenite can be included by oxidising arsenite to arsenate.

In the Rhodamine B method, arsenate combines with molybdate and rhodamine B to form arsenomolybdate rhodamine B ion pair at pH 4.0 resulting in a colour change from rose red to pink. The absorbance of the solution measured at 595 nm is proportional to the concentration of arsenic.

Usually we have developed a method for determination of arsenic using rhodamine B that is a tri phenyl methane dye and in this method, arsenite combines with the molybdate and rhodamine B to form arseno molybdate rhodamine B ion pair the optimum pH is 4 that results in a color change from rose red to pink, the absorbance of the solution is usually measured at 595 nanometers that is it is follows Beer Lambert’s law and it is the absorbance is proportional to the concentration of arsenic.

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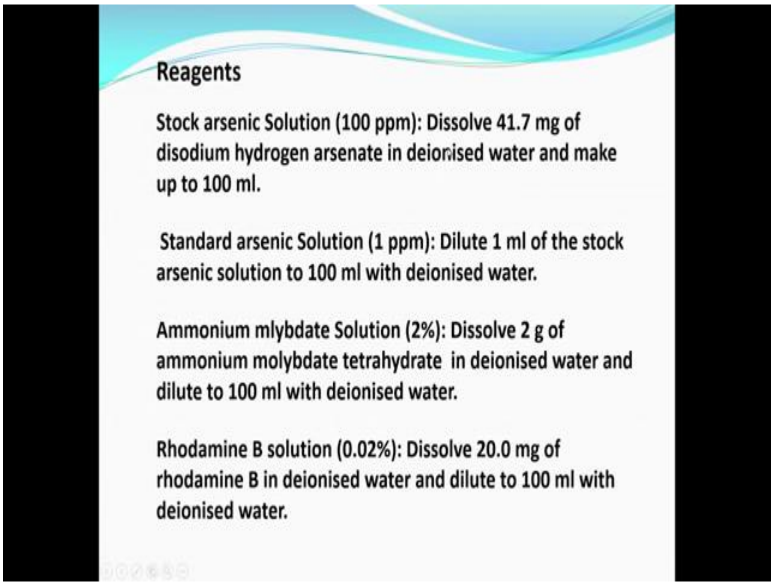

Reagents

Stock arsenic Solution (100 ppm): Dissolve 41.7 mg of disodium hydrogen arsenate in deionised water and make up to 100 ml.

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

Ammonium mlybdate Solution (2%): Dissolve 2 g of ammonium molybdate tetrahydrate in deionised water and dilute to 100 ml with deionised water.

Rhodamine B solution (0.02%): Dissolve 20.0 mg of rhodamine B in deionised water and dilute to 100 ml with deionised water.

Now the reagents the very simple you can prepare stock arsenic 100 ppm by dissolving 41.7 milligram of disodium hydrogen arsenate, in deionized water and make up to 100 ml then working solution would be 1 ppm that is you have to dilute 100 times it goes without saying that all the dilutions etcetera in spectrophotometry should be done with very good quality water that is a dm water of about 10 raise 2 minus 18 micro moss conductivity; that means, very less dissolved salts also should be there.

Now, you can prepare ammonium molybdate solution of 2 percent for that you have to just dissolve ammonium molybdate that is available its available as a tetrahydrate in deionized water and diluteto 100 ml. Now rhodamine B is a dye usually it is available in kilogram quantities all over the all over India it is a cloth dye basically to make the colored to make the cloths look red and pink etcetera, but it is also a good chemical reagent analytical reagent that is available as a chemical available with chemical stores and of course, you when we buy from chemical stores what we mean is it is available as a 99.99 percent purity.

So, that is the idea of using rhodamine B. So, for that we have to just dissolve 20 milligram of rhodamine B in deionized water and dilute to 100 ml.

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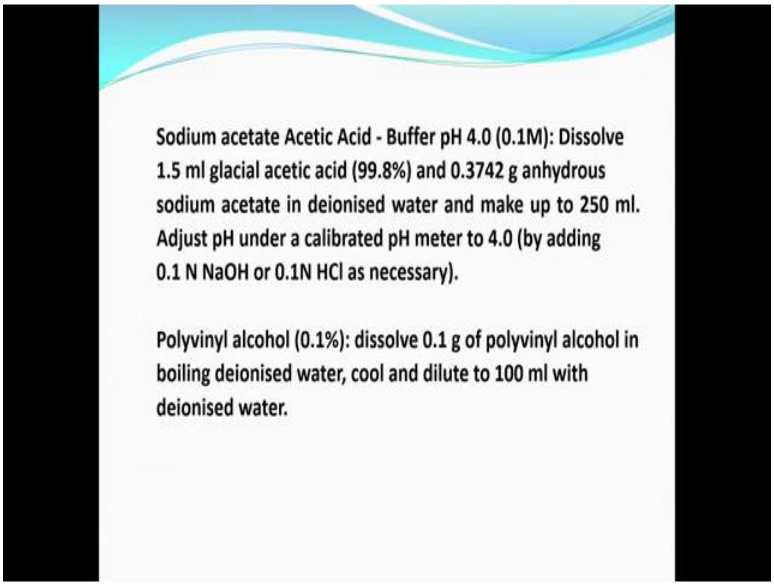

Sodium acetate Acetic Acid - Buffer pH 4.0 (0.1M): Dissolve 1.5 ml glacial acetic acid (99.8%) and 0.3742 g anhydrous sodium acetate in deionised water and make up to 250 ml. Adjust pH under a calibrated pH meter to 4.0 (by adding 0.1 N NaOH or 0.1N HCl as necessary).

Polyvinyl alcohol (0.1%): dissolve 0.1 g of polyvinyl alcohol in boiling deionised water, cool and dilute to 100 ml with deionised water.

Now, the procedure sodium you also need sodium acetate and acetic acid buffer of pH 4 and for that you have to dissolve 1.5 ml of glacial acetic acid and 0.3742 gram of anhydrous sodium acetate in deionized water make up to 250 ml, you have to adjust the pH to 4 and you we have modified the earlier this method used to was worked for extraction now we have modified to with a an aqueous finish.

So, for that what we have done is we have dispensed with the extraction organic extraction reagent and we are we are recommending polyvinyl alcohol 0.1 percent as a stabilizer. So, ion pairs are normally stabilized using a thick viscous solutions of polyvinyl alcohol glycerol glycol etcetera and we have found that polyvinyl alcohol is fairly good reagent and you have to just have to dissolve 0.1 gram in 100 ml cool, it we have to heat it otherwise it will not dissolve.

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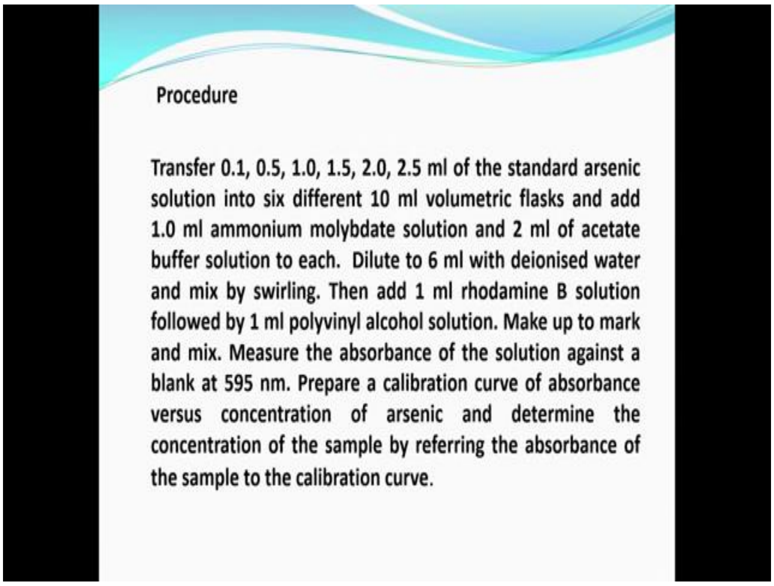

Procedure

Transfer 0.1, 0.5, 1.0, 1.5, 2.0, 2.5 ml of the standard arsenic solution into six different 10 ml volumetric flasks and add 1.0 ml ammonium molybdate solution and 2 ml of acetate buffer solution to each. Dilute to 6 ml with deionised water and mix by swirling. Then add 1 ml rhodamine B solution followed by 1 ml polyvinyl alcohol solution. Make up to mark and mix. Measure the absorbance of the solution against a blank at 595 nm. Prepare a calibration curve of absorbance versus concentration of arsenic and determine the concentration of the sample by referring the absorbance of the sample to the calibration curve.

So, what the idea is you prepare 0.1 to 2.5 ml of the standard arsenic solution and add 1 ml of molybdate solution add 2 ml of acetate buffer and then you have to dilute it with 6 ml of deionized water and mix by swirling and you have to add 1 ml of rhodamine B followed by polyvinyl alcohol solution to stabilize the color. Now all you have to do is remaining procedures are all fairly simple now the; I do not have to tell you that you have to dilute it up to 10 ml and measure the absorbance against a blank again, blank is necessary because it is also red in color and as I have told you molecular peaks normally overlap each other. So, the color of the blank must be subtracted from the color of the sample.

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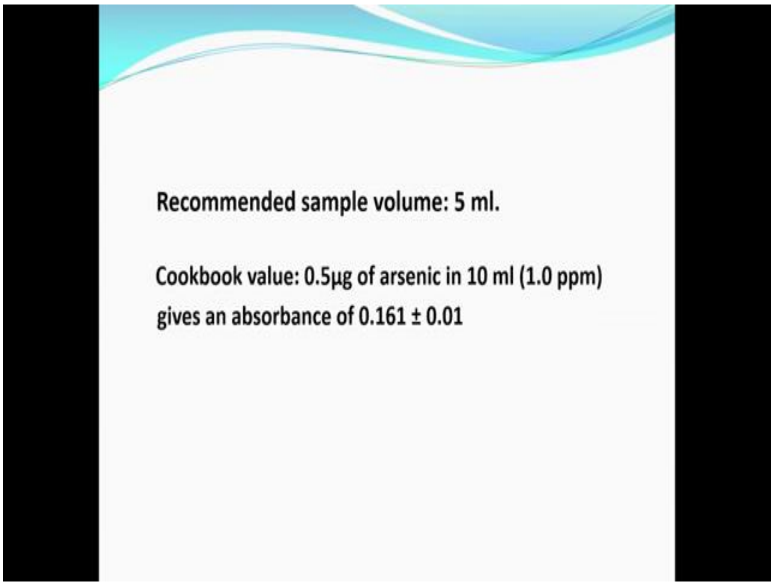

Recommended sample volume: 5 ml.

Cookbook value: 0.5µg of arsenic in 10 ml (1.0 ppm) gives an absorbance of 0.161 ± 0.01

So, you have to prepare a calibration curve and it recommended sample volume can be up to 5 ml because what we want to do is we have to determine concentration of arsenic in 0.01 ppm. So, if you take 5 ml 0.01 into 5 would be 0.05 micrograms of arsenic and that will if you take a cook book value 0.5 microgram of arsenic in 10 ml that is a 1 ppm gives you an absorbance of about 0.161, 2.0 plus or minus 0.01 absorbance.

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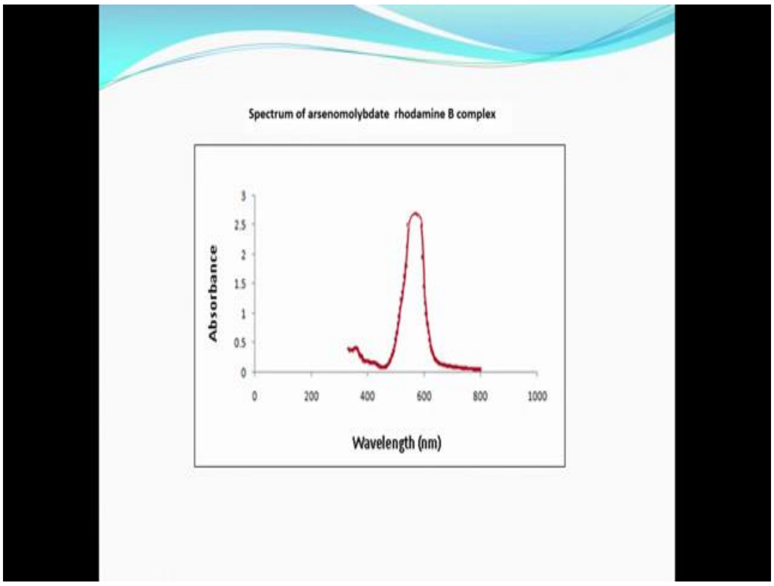

Spectrum of arsenomolybdate rhodamine B complex

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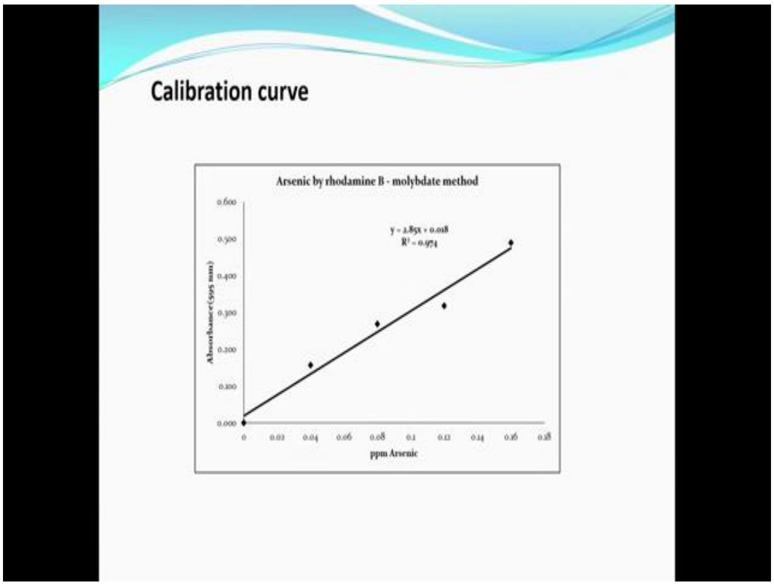

Calibration curve

So, this is the arsenic absorbance lambda it is a fairly simple complex this is drawn against the blank and arsenic calibration curve is already here you can see that up to 2.16 ppm you can determine arsenic. So, 0.1 would be somewhere here, but if you take larger quantities you can make it come on the calibration curve.

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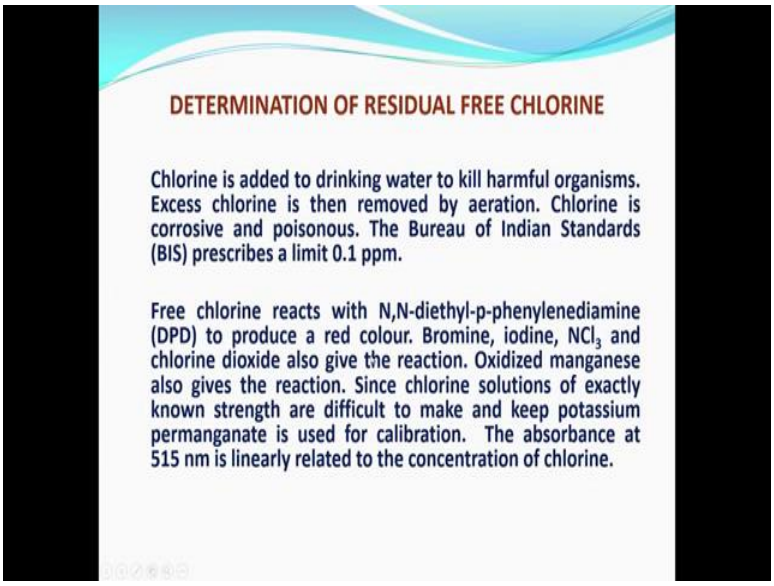

DETERMINATION OF RESIDUAL FREE CHLORINE

Chlorine is added to drinking water to kill harmful organisms. Excess chlorine is then removed by aeration. Chlorine is corrosive and poisonous. The Bureau of Indian Standards (BIS) prescribes a limit 0.1 ppm.

Free chlorine reacts with N,N-diethyl-p-phenylenediamine (DPD) to produce a red colour. Bromine, iodine, NCl_3 and chlorine dioxide also give the reaction. Oxidized manganese also gives the reaction. Since chlorine solutions of exactly known strength are difficult to make and keep potassium permanganate is used for calibration. The absorbance at 515 nm is linearly related to the concentration of chlorine.

So, that completes our discussion on arsenic of course, there are other methods of determining arsenic by marsh test which is the conversion of arsenic into arsenic hydride and that arsenic hydride can be dissolved in water and then treated with a try phenyl methane dye with a spectrophotometric finish at ppb level. So, there are several methods, but for the time being we are recommending this if this method does not work because of the combinations etcetera then you will have to look at arsenic hydride method coming back to arsenic I am very happy to tell you that our research shows us, our research shows that there are no interferences from about 100 ppm concentrations from any of these except serium which decolorises the rhodamine B itself. So, serium is an oxidant and surfactants also interfered to some extent.

So, the details you can have it from the published method it is available in the literature and I recommend you to go into details of this method or get in touch with me whenever you need some consultation with for analysis especially of arsenic in drinking water or any other thing and now we move on to the determination of residual free chlorine. This is a fairly important method because free chlorine is usually added as a disinfectant in several water waste water treatments especially even for municipal waste water what people do is they collect river water and a pond water, surface waters and then ground water they collect it and then treat it with a lamer or something like that to precipitate all the dissolved solids to precipitate aluminum iron etcetera most of the dissolved solids are separated and then it is treated with chlorine for disinfection.

So, normally 0.1 ppm excess chlorine is added to the determination of in the determination method because chlorine kills the micro; kills the bacteria and other pathogenic microorganisms and that is why it is a very important parameter for the determination of water quality usually a slight excess of chlorine is maintained in drinking water, but the chlorine monitoring is also essential in several other occasions where waste water and city municipal city waste water is treated for the before they let out in to the water ways.

For example in Delhi approximately a 20 percent of water is only being treated before is it is let out in to Jamuna River. So, remaining 80 percent we hope that it gets diluted and then concentrations come down below the detection limit, but another application what I always foresee is the small establishments require chlorine determination especially in swimming pools etcetera. So, in swimming pools if the chlorine content is high people get eyes become red and there will be some slight toxic reactions a therefore, it is very important that chlorine should be determined if we do not add chlorine in swimming pool normally what happens is the chlorine will lead to chlorine will, if it is absent it will the swimming pool water will be contaminated very fast and you will not be able to swim without treatment. So, the most of the swimming pools have got water treatment facility that is basically a recirculation facility with a dosing of chlorine.

So, chlorine is a very important parameter I want you to note from this slide that it is basically added to kill harmful organic organisms excess chlorine can be removed by aeration, but again that is a question of practice how much we want to retain basically chlorine is also corrosive poisonous etcetera, but still we do not have a very viable and cheap cheaper method of disinfection then chlorine in therefore, it is used in most of the industrial process and municipality water supplies all over India and world also all over the world also the bureau of Indian standards prescribes a limit of 0.1 ppm of a chlorine.

So, this residual free chlorine normally the chemistry of this reaction is it reacts with an di methyl para phenylenediamine DPD it is a short for short in short produce a red color; obviously, all halogens like bromine iodine nitrogen tri chloride and chlorine dioxide all these things give this reaction oxidized manganese gives thus a similar reaction. So, we have to assume that all these bromine iodine etcetera if they are present, they will interfere in the analysis of free chlorine.

Since chlorine solutions of exactly known strength are very difficult to make because we have to dissolve chlorine gas in water and it is very difficult to prepare solutions of exact strength. So, and what we need you what we do is we prepare a chlorine solution and potassium permanganate is used for calibration. So, the absorbance at 515 nanometers is linearly related to the concentration of chlorine.

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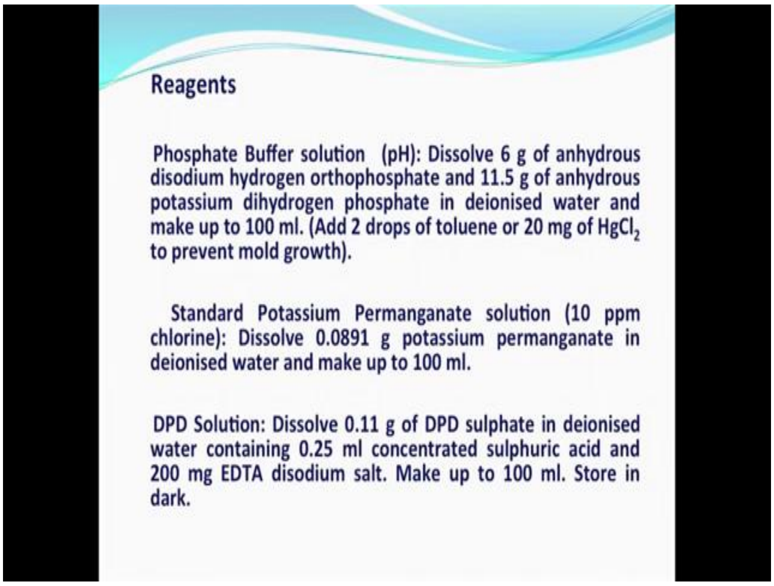

Reagents

Phosphate Buffer solution (pH): Dissolve 6 g of anhydrous disodium hydrogen orthophosphate and 11.5 g of anhydrous potassium dihydrogen phosphate in deionised water and make up to 100 ml. (Add 2 drops of toluene or 20 mg of $HgCl_2$ to prevent mold growth).

Standard Potassium Permanganate solution (10 ppm chlorine): Dissolve 0.0891 g potassium permanganate in deionised water and make up to 100 ml.

DPD Solution: Dissolve 0.11 g of DPD sulphate in deionised water containing 0.25 ml concentrated sulphuric acid and 200 mg EDTA disodium salt. Make up to 100 ml. Store in dark.

So, reagents very simple reagents phosphate buffer you have to dissolve 6 grams of disodium hydrogen orthophosphate and potassium dihydrogen phosphate that is the mixture we have to dissolve it in deonised water make it to 100 ml sometimes we do add 2 drops of a toluene or 20 milligram of mercury chloride in all solutions in organics solutions to prevent the mold growth. So, this is not necessary if you want to add if you want to determine the chlorine immediately, but if you want to prepare and keep it for use the buffer for long time then I recommend that you add about 2 drops of toluene or 20 milligram of mercury chloride to prevent the mold growth then other things are very simple standard potassium permanganate you have to use and that details are given here 0.0891 gram of potassium permanganate and DPD solution you need that also I have given you details and to prevent interference from the other metal ions I am recommending here that you use 200 milligram of EDTA while preparing this DPD solution itself.

So, you do not have to separate normally people add EDTA to complex the interfering elements, but here as a precaution I am assuming that you will have water sample from municipality etcetera and there will be definitely other metal ions therefore, I am recommending the DPD itself can be prepared using this EDTA and in the reaction mixture EDTA will complex with the metal ions and DPD will be reacting with chlorine of course, I do not have to tell you that you have to store it in the dark DPD is a darkly dark colored solution.

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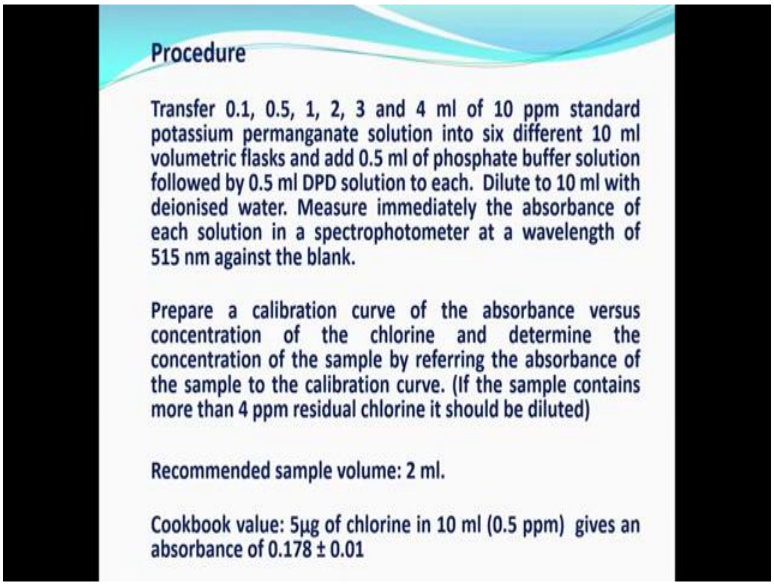

Procedure

Transfer 0.1, 0.5, 1, 2, 3 and 4 ml of 10 ppm standard potassium permanganate solution into six different 10 ml volumetric flasks and add 0.5 ml of phosphate buffer solution followed by 0.5 ml DPD solution to each. Dilute to 10 ml with deionised water. Measure immediately the absorbance of each solution in a spectrophotometer at a wavelength of 515 nm against the blank.

Prepare a calibration curve of the absorbance versus concentration of the chlorine and determine the concentration of the sample by referring the absorbance of the sample to the calibration curve. (If the sample contains more than 4 ppm residual chlorine it should be diluted)

Recommended sample volume: 2 ml.

Cookbook value: 5μg of chlorine in 10 ml (0.5 ppm) gives an absorbance of 0.178 ± 0.01

And the calibrationcurve is up to 4 ppm 4 ml of 10 ppm that you can use and you use along with that and add 5 ml of phosphate buffer followed by DPD and dilution etcetera as usual 10 ml.

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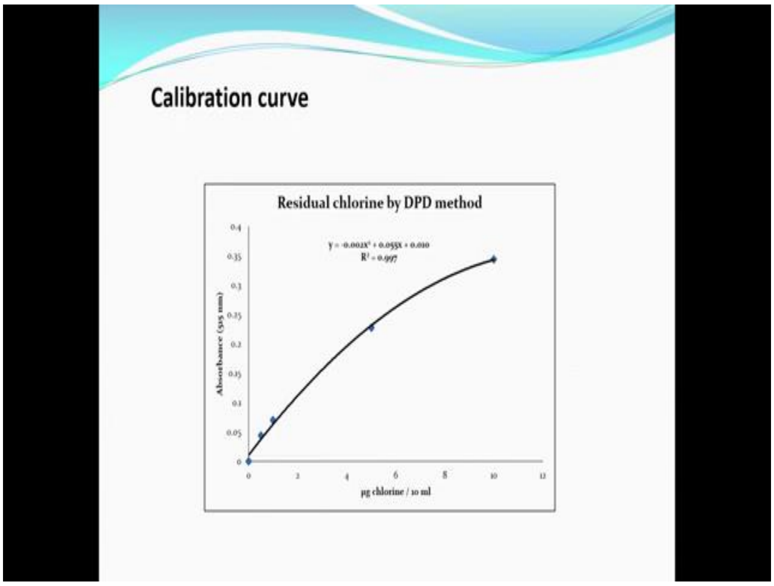

Calibration curve

And you have to prepare a calibration curve the calibration curve is not linear, this is a very very classic example of a non-linear absorbance relation with the analyite very very classic example, but the results are reproducible, so we take it that we can use this, but if you fit it with a quadratic equation you will end up with a R square value of about 0.997.

So, that is a nice thought and the recommended volume is 2 ml. So, the cook book value if you use 5 microgram of chlorine in 10 ml that is 5 divided my 10 is 0.5 ppm that should give you an absorbance of about 0.178 plus or minus 0.01. So, if you go back we can you know that we the required standard is 0.1 ppm and we are getting 0.5 ppm should give you 0.178. So, 0.1 should give you approximately 0.03. So, you can take 5 ml.

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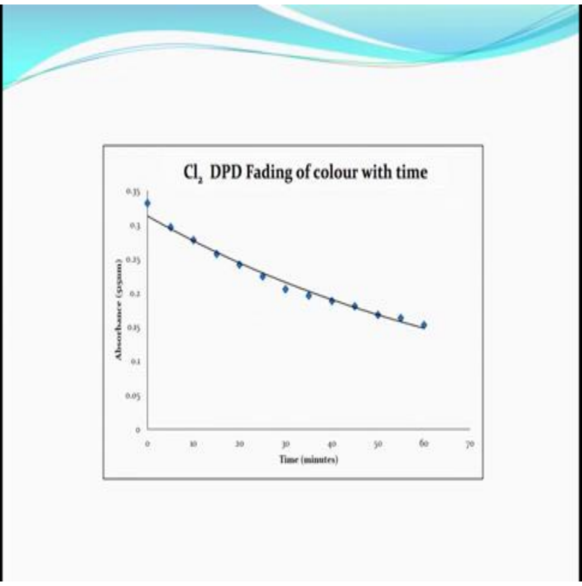

So, that works out approximately the straight away application of the method within the working standards.

Now, here I am showing you one more figure that is chlorine is determined by the fading of the color not by addition of the color. So, I have given you a figure here fading of the color is not a very very nice thought because it keeps on fading because chlorine is an oxidizing agent therefore, we have made a curve or a we have established a relationship of absorbance versus time you can see that the curve the absorbance is not stable at all. So, you have to fix up the time when you want to measure yes therefore, the time becomes a critical element in the absorption method. So, what we have said here is the absorbances, you keep the time constant between each measurement for each measurement you have to maintain the same time gap between the measurement. So, that should take care of the variation in the analysis.

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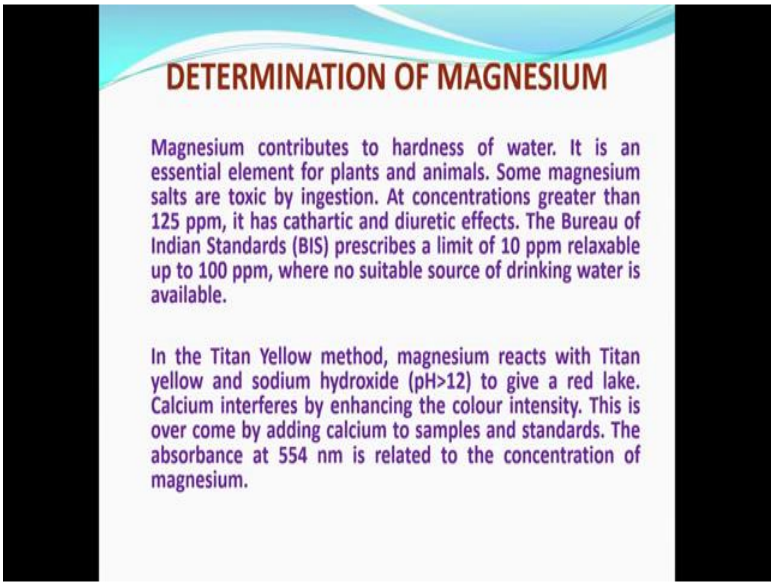

DETERMINATION OF MAGNESIUM

Magnesium contributes to hardness of water. It is an essential element for plants and animals. Some magnesium salts are toxic by ingestion. At concentrations greater than 125 ppm, it has cathartic and diuretic effects. The Bureau of Indian Standards (BIS) prescribes a limit of 10 ppm relaxable up to 100 ppm, where no suitable source of drinking water is available.

In the Titan Yellow method, magnesium reacts with Titan yellow and sodium hydroxide (pH>12) to give a red lake. Calcium interferes by enhancing the colour intensity. This is over come by adding calcium to samples and standards. The absorbance at 554 nm is related to the concentration of magnesium.

Now, I would like to move on to the determination of magnesium in this I will just give a some sort of introduction because especially for magnesium what is important is the it is a ubiquitous element it is a micro nutrient it is present in sea water it is present in bore well water it is present in drinking water therefore, it is very important that magnesium should be determined not that magnesium is having great problem with metabolism, but magnesium sulphate along with calcium sulphate imparts hardness to the water. So, I think all of you know what is hardness it is the foaming capability of water therefore, it is if the water is hard, it becomes very difficult to wash the cloths etcetera and many of you if you would are using hard water you would also notice that in on the vessels etcetera there will be scales formation because magnesium will not go away by washing with water.

So, as and as you keep on washing the vessels will keep on collecting scales of magnesium sulphate therefore, magnesium becomes a tricky element especially magnesium and calcium they are most dreaded elements in heat exchangers whenever you use a hard water all the as the water evaporates the scales will form calcium sulphate and magnesium sulphate will form along with the silica present even if it is in ppm level magnesium and calcium will form magnesium silicate and calcium silicate and as we know the chemistry of silicates is nothing, but the chemistry of cement.

So, cement itself is made of calcium and magnesium silicates and you can imagine we build the buildings is, with cement. So, it is not easy to destroy cement it may develop cracks or something like that that is different, but it is not easy to dissolve calcium and magnesium silicates and they always form the scales. So, magnesium contributes to the hardness of water it is an element essential element for plants and animals some magnesium salts are toxic by some magnesium salts are toxic by ingestion and the concentration is greater than 100 ppm it has some there is some evidence of cathartic and diuretic effects.

So, the Bureau of Indian standards prescribes a limit of 100 ppm relaxable 10 ppm it is relaxable up to 100 ppm where no suitable source of drinking water is available. So, we have; we are presenting you here the titan yellow method where magnesium reacts with titan yellow and sodium hydroxide above pH 12 that gives a red lake of course, we should expect that as an alkali and alkaline earth metal all those metals will interfere. So, in the determination of calcium magnesium will interfere and in the determination of magnesium calcium interferes. So, calcium interference is recorded by enhancement in the absorbance. So, this is overcome by adding calcium, we can add calcium itself to the standards and the lake absorbance maximum is at 554 that is related to the concentration of magnesium.

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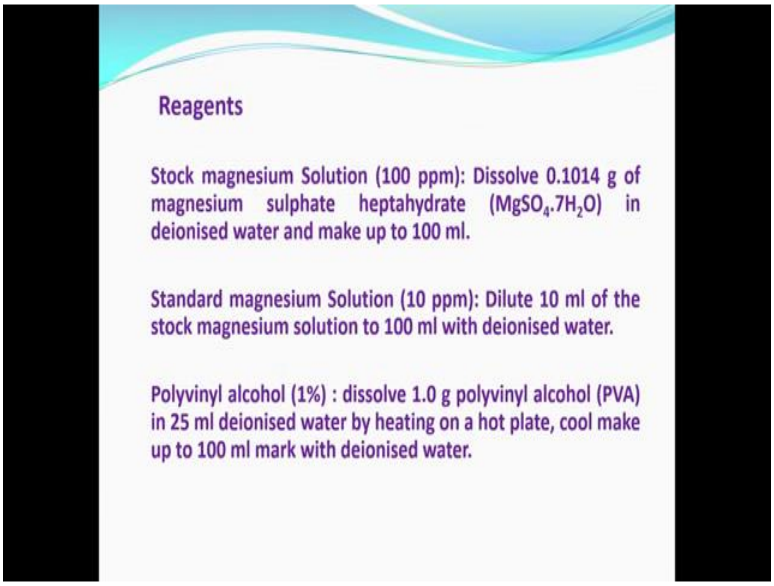

Reagents

Stock magnesium Solution (100 ppm): Dissolve 0.1014 g of magnesium sulphate heptahydrate ($MgSO_4.7H_2O$) in deionised water and make up to 100 ml.

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

Polyvinyl alcohol (1%) : dissolve 1.0 g polyvinyl alcohol (PVA) in 25 ml deionised water by heating on a hot plate, cool make up to 100 ml mark with deionised water.

So, reagents we include stock prepare stock magnesium 100 ppm and then dilute it to 10 ppm and then polyvinyl alcohol again as I have been telling you that we add it to stabilize the precipitate or lake. So, usually 0.1 percent is more than enough. So, here we dissolve 0.1 gram of poly vinyl alcohol in 25 ml of the water; deionized water followed by 100 ml of a dilution to 100 ml that also you will have to prepare daily or regularly on and off because over period of time polyvinyl alcohol becomes very thick and you may not be able to pipette out. So, that is a problem. So, we recommend that polyvinyl alcohol should be prepared daily fresh.

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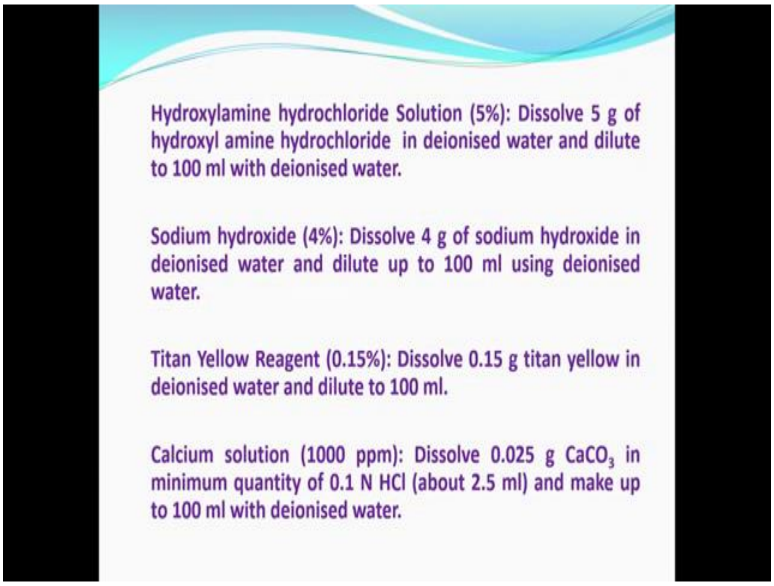

Hydroxylamine hydrochloride Solution (5%): Dissolve 5 g of hydroxyl amine hydrochloride in deionised water and dilute to 100 ml with deionised water.

Sodium hydroxide (4%): Dissolve 4 g of sodium hydroxide in deionised water and dilute up to 100 ml using deionised water.

Titan Yellow Reagent (0.15%): Dissolve 0.15 g titan yellow in deionised water and dilute to 100 ml.

Calcium solution (1000 ppm): Dissolve 0.025 g $CaCO_3$ in minimum quantity of 0.1 N HCl (about 2.5 ml) and make up to 100 ml with deionised water.

So, you also need hydroxyl I mean hydro chloride solution that is again you can prepare 5 percent sodium hydroxide, you can you need 4 percent and that is weight by weight and then titan yellow reagent is 0.15 gram of titan yellow you need and calcium solution you have to stock is 1,000 ppm.

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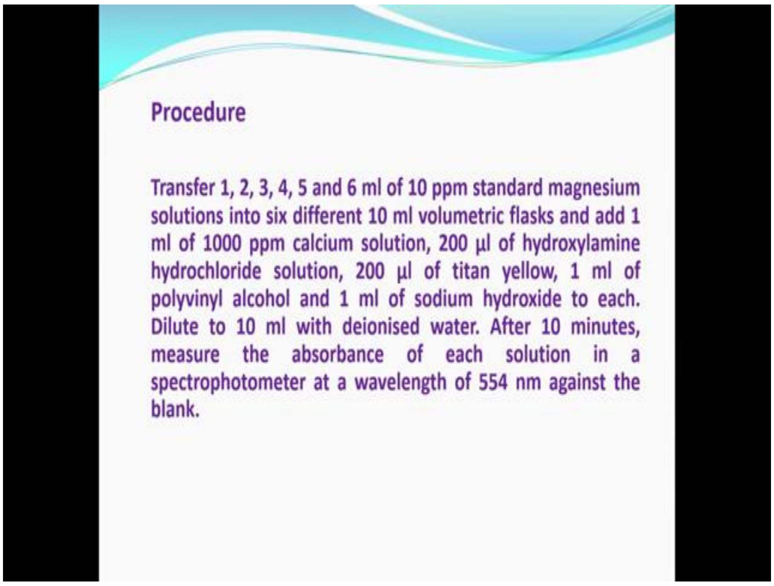

Procedure

Transfer 1, 2, 3, 4, 5 and 6 ml of 10 ppm standard magnesium solutions into six different 10 ml volumetric flasks and add 1 ml of 1000 ppm calcium solution, 200 µl of hydroxylamine hydrochloride solution, 200 µl of titan yellow, 1 ml of polyvinyl alcohol and 1 ml of sodium hydroxide to each. Dilute to 10 ml with deionised water. After 10 minutes, measure the absorbance of each solution in a spectrophotometer at a wavelength of 554 nm against the blank.

And you can dilute it and working solution should be 10 ppm. So, we will continue our discussion after about in the next class.

Thank you.