Atomic and Molecular Absorption Spectrometry
for Pollution Monitoring
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Lecture - 38
Total hardness, zinc

Greetings to you. Let us continue our discussion on the water parameters especially drinking water parameters using spectrophotometry. Already covered about atrium parameters which include anions and cations and today I am talking about the other parameters that is total hardness. You may wonder what is this hardness, total hardness to do with spectrophotometry. Usually total hardness of water is caused by the presence of calcium and magnesium salts.

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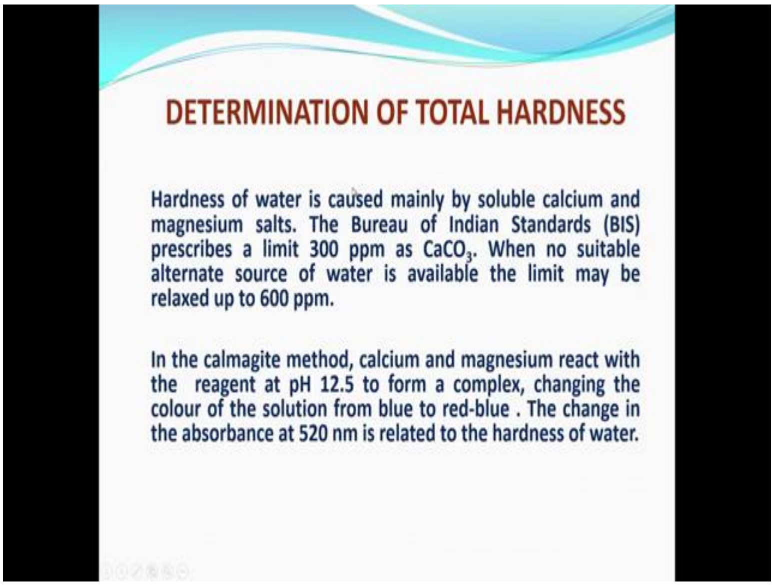

And the solubility of calcium and magnesium salts are quite good and the presence of these salts leads to the presence of these salts causes the water to taste very hard.

You do not feel like drinking it and then when you want to wash the clothes it will keep on taking the soap, but it will not produce any lather, as you know lather production there is a an essential characteristic whenever you want to wash your clothes, basically lather is a type of a foam with very large surface area and whenever we want to wash the clothes with the soap, the lather will catch the particles dust particles and other things and then the clothes will get brighter or get cleaner. So, hardness has got about another property that is it cannot be used in several industrial processes such as cooling and heating because as the water evaporates the soluble salts will precipitate and coat on to the inside of the cooling tubes which are made of copper or iron and presence of a little bit of silica will produce calcium silicate and magnesium silicates.

The both these salts are essentially like cement because cement is also a silicate and as we know cement building etcetera last for 100s of years and so, the silicate salts also will last for several years unless you remove them mechanically the presence of silicates on the inside of the heat exchange tubes causes low temperature movement, that is low temperature transform and that causes the requirement or to increase the heat requirement will increase.

So, from the industrial point of view also presence of hardness cause in chemicals like calcium magnesium are more desirable. Hardness of water the is measured as ppm parts per million of calcium carbonate become magnesium carbonate and several other carbonates and sulphates also cause hardness, but for easy standard in the Bureau of Indian standard; BIS prescribes a limit of about 300 ppm as calcium carbonate and no suitable alternate source of water is available the limit may be relaxed up to 600 ppm, but this works only for drinking water. So, usually hardness is determining by titration with ethylenediaminetetraacetic; ethylenediaminetetraacetic acid as a titration method.

But we are not recommending that what we want to recommend here is the calmagite method. So, in this method both calcium and magnesium react with this reagent at about pH 12.5 to form a color complex, they changes the color of the solution from blue to red blue the change in the absorbance at 520 nanometers is related to the hardness of waters.

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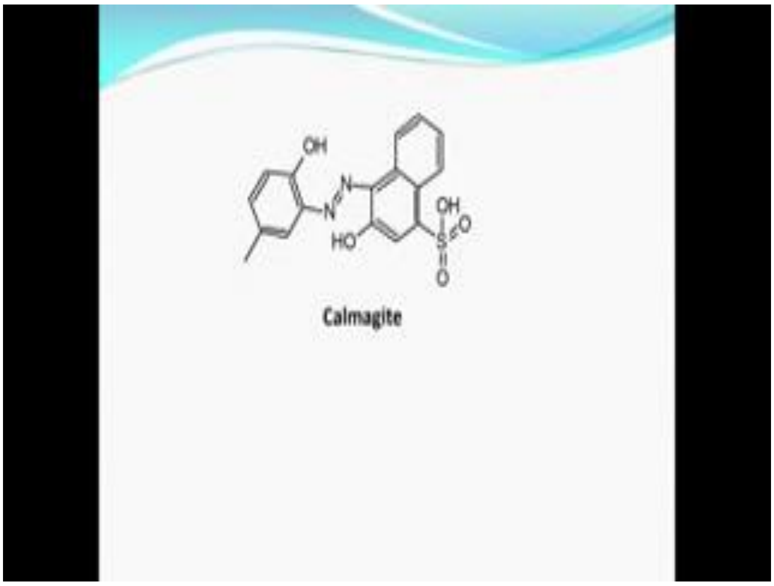

So, this is the structure of calmagite you can see here it is contains 3 benzene rings connected with AZO group and OH group, there is 1 SO 3 group, this SO 3 group helps in solubilizing the salts. So, we does not need to add any sulphate and something like that and this AZO group and this OH group will help form a complex of ring closure using calcium and magnesium here. So, it is basically a question of ring closure reaction and the chronopher will increase the increased chronopher will shift the lambda max to the bathochromic site that is only higher valiance site.

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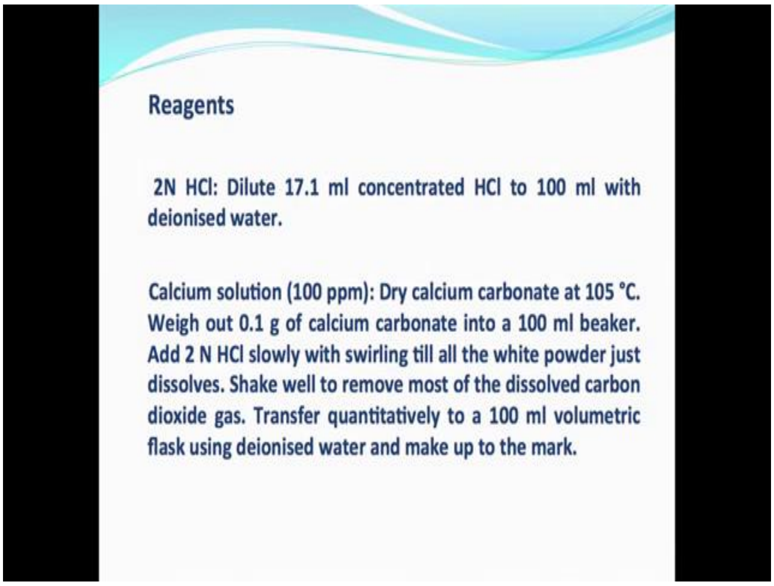

So, calmagite it is also colored, but the complex will be more colored with lambda max slightly towards the right that is at longer wave length. So, the reagents include very simple things now will not going to very much detail about how to prepare the reagents because all the numbers are given here. So, we have to take concentrated HCL and dilute it to 100 ml and you can prepare the calcium solution by you have to dry the calcium carbonate because usually calcium carbonate is associated with water and you have to remove this water and that happens around 105 degree centigrade, you just try to weigh out calcium carbonate into 100 ml beaker, add 2 normal HCL; hydrochloric acid, slowly it swirling till the white powder, just dissolve shake well remove and transfer the quantity into 100 ml volumetric flask and dilute it to 100 ml.

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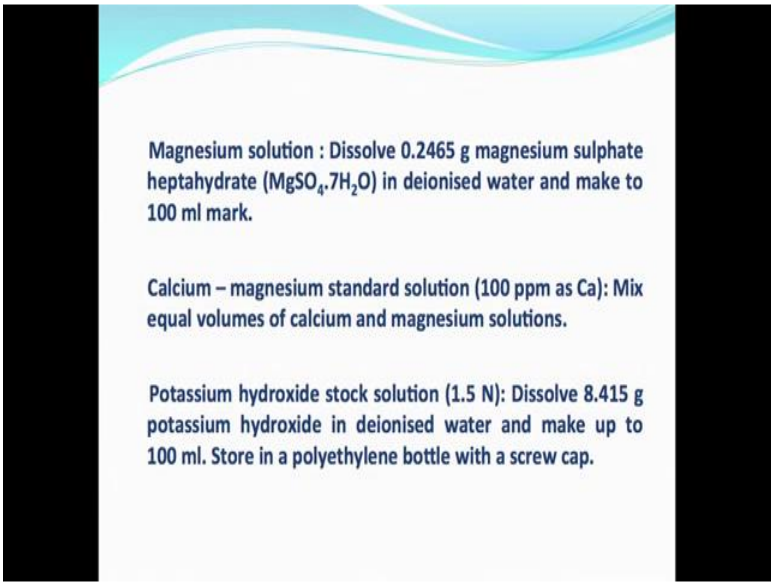

So, that is the standard calcium solution you can also prepare magnesium solution also containing 0.2465 gram of magnesium sulphate heptahydrate that is 7 H2O in deionised water and make to 100 ml for our working reagent with this both calcium and magnesium prepare to prepare 100 ppm equivalent of calcium because sometime magnesium may be there sometimes calcium may be there. So, when we mix equal volumes of calcium and magnesium solutions we get about we get 100 ppm of both, but only as the same concentration. Now since the reaction occurs around pH 12, we need several potassium hydroxide solution and this stock solution is prepared by dissolving potassium hydroxide in dieonised water and make up to 100 ml.

This potassium hydroxide or any other hydroxide as I have been repeatedly telling you we need to dissolve in water, but store in polyethylene bottle with a screw cap. Normally if you store it in glass bottles there is a tendency that water will evaporate and it will form it will be very difficult to remove the bottle to open the bottle this is a practical difficulty.

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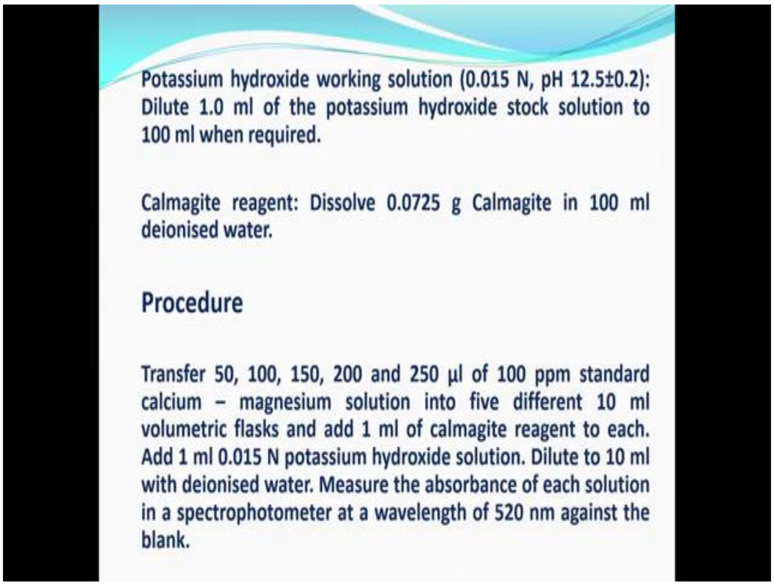

So, potassium hydroxide working solution also you can prepare by adjusting the pH to 12.5 and we have to prepare 0.01 normal potassium hydroxide, for this we have to dilute 1 ml of potassium hydroxide stock solution to 100 ml. So, all these things you can calculate yourself, but I have giving you the details because I want to give you a readymade method because sometimes it takes time for you whenever there is an urgent need for preparation of the reagents you need the ready reference method to work. So, I am straight away taking you with this introduction I am straight away taking you to the determination to the experimental level itself.

So, calmagite reagent also you can prepare by dissolving 0.0725 gram of calmagite in 100 ml deionised water, but this reagent is available in the in the market. So, there is no difficulty in obtaining this calmagite solution now the hardness of a given solution always we measure in about 50, 100s, etcetera that is if you take river water, nowadays in India, you will come across a waters having about 100 to 200 ppm of hardness. Even in river water in bore well it may go up to it depends upon the depth at which bore well water is extracted and there also the range may vary from few 100s to 1500 ppm. So, basically the range should vary from 50 to 500 range.

If we can make a calibration curve using this king of standard, I think we should be in the business. So, what we should do is we normally do not worry about plus or minus ten percent error in measuring the hardness of water. So, we prepare 50, 100, 150, 200 and 250 micro liter of 100 ppm standard solution that is both containing both calcium and magnesium and then you dissolve them and put them in volumetric flask add 1 ml of the reagent dilute by potassium hydroxide solution and measure you just have to measure the absorbance after adding 1 ml of 0.015 molar potassium hydroxide solution, we have just try to dilute it and measure the absorbance of at a wave length of 520 nanometer against the blank dish tells us that the reagent could be somewhat bluish in color reddish red, violet says the right color and as usual.

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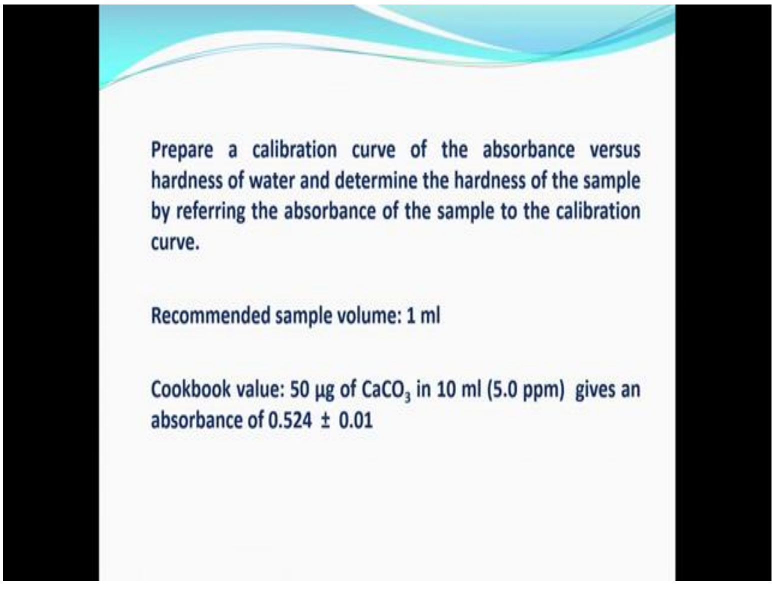

We have to prepare a calibration curve of the absorbance verses hardness of the water and determine the hardness of the sample by referring the absorbance of the with a calibration curve. So, recommend a sample volume is about 1 ml, but this can; this refers to only the standard solution that is if you are take 50 ml in 50 micrograms, it gives you that is about 5 ppm 50 microgram in 10 ml that is 5 ppm, it gives you an absorbance of about 0.524 plus or minus 0.01 that is quite good absorbance and if you get this absorbance with you standard reagents you are in business; that means, all your preparation standard solutions and other things are all.

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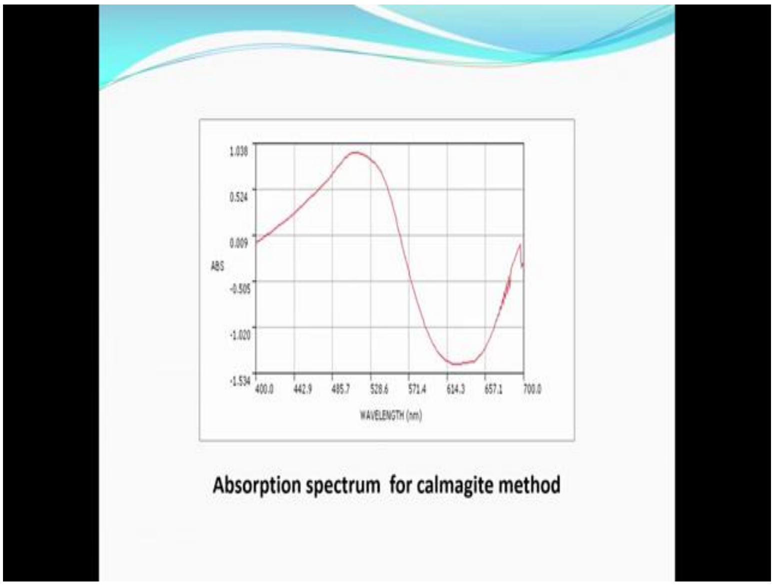

Well under good control, so, I am showing you the absorbance of this calcium magnesium that is complex that is calmagite complex calcium magnesium complex and then the lambda max.

As you can see here is somewhere around 485 this is around 510 to 520, the curve is somewhere flat here in this region not much absorbance range and so, you can be comfortable when you are plus or minus 5 nanometers this side that side that no serious error will be introduced during the measurement.

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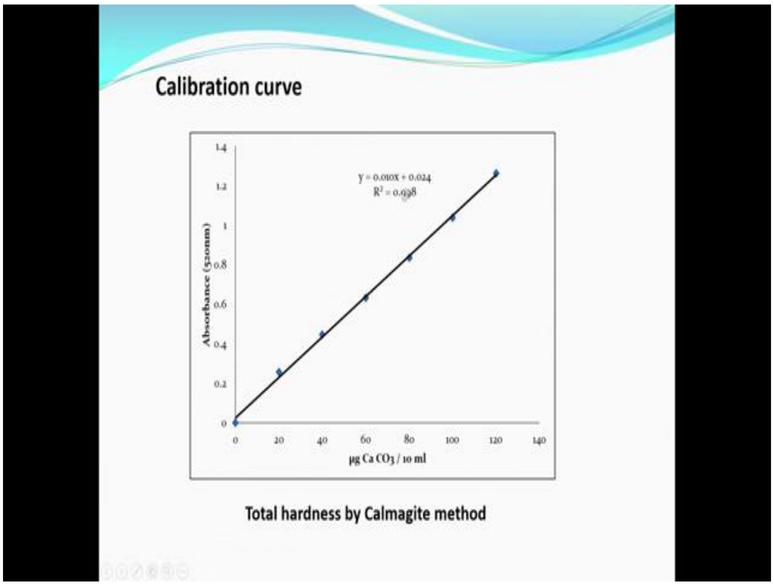

So, this is the calibration curve you can see that the calibration curve is linear, we have done it up to 120 micrograms here, but we can see that we are already very near the end of the absorbance scale that is almost 0.2 to 1.5 as dictated by the relative standard error we should be within 0.2 to 0.8 and that range and here even around 120 ppm, we have absorbance of about 1.3. So, any standard it follows a very nice linear curve.

The least square feet value of r square is 0.998; that means, the method is quite reliable at this thing and of course, you will always be having some amount of in normal circumstances you will be having the hardness not within 50 or 100, but you will your range it may go between 200, 300, 5- 600, 800 to 1500. So, what you should do you do a pilot trial with a with 1 ml of the given sample where calibration curve is done anyway, but the actual sample analysis if you want to determine the hardness of the sample you try it with 1 ml.

If the absorbance is too high then you will have to dilute it accordingly and then try to bring it within 0.2 and 0.8 and multiply it by the dilution factor and you will be able to determine the hardness of water a very simple experiment which can be conducted and completed within half an hour if you have all the reagents and the reagents are all available across the shelf we will not have any worry regarding this analysis of hardness.

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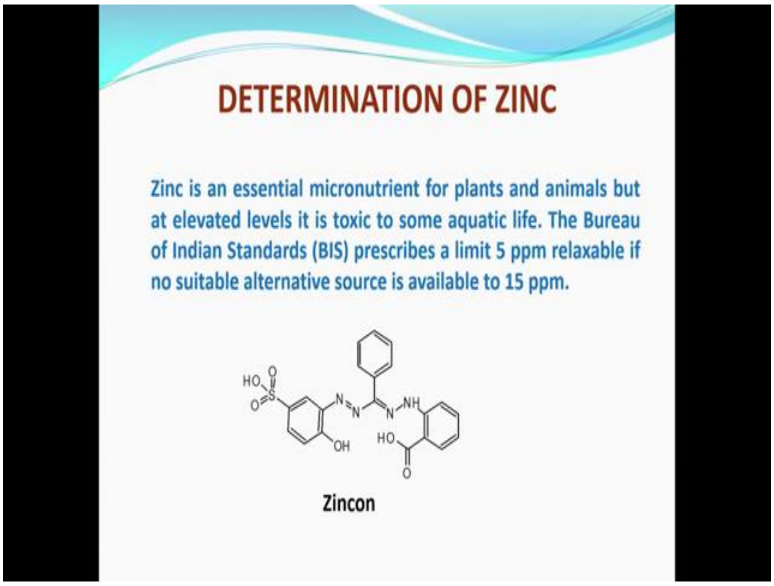

So, now I would like to take you to the determination of zinc, zinc is an essential element of the plants and animals, but elevated levels it is toxic to aquatic life as well as human life, but it that is a very standard statement any chemical that is in excess is toxic that is a fundamental reveal so, but zinc is an a essential micronutrient if you look at some of the soil as well as water content; water samples all over the world you will see that most of the soils and water they do contain certain amount of zinc and that is how it is distributed it is widely distributed element the Bureau of Indian standards prescribes a limit of 5 ppm that is relaxable if no suitable alternative source is available. Then it is up to 15 ppm.

Now zinc is a industrial element also it is used for the determination it is used for anodizing. So, you can see that many of the material around you that is zinc sheets as you might have heard they are all aluminum and iron which are galvanized. So, in galvanization zinc is coated electro electrometrically. So, the zinc is acts as a sacrificial cathode protecting the metal inside the zinc coat and it is also an alloying element brass is known well known example of copper and zinc alloy. So, brass has got a very bright alloy structure color and it is also used and the zinc is also used in give a imparting strength to fibers especially this cellulose fibers if you want to make cloth or something like that using viscose or rayon or something like that then the first the wood pulp is treated with sodium hydroxide and then dissolved in sodium hydroxide.

And then treated with carbon disulfide to remove the lignin and once we lignin is removed the fiber becomes white and this fiber you; fiber is dissolved in carbon disulfide or and then pass through a spinneret containing number of fibers and the spinneret is treated with zinc to give strength to the yarn. So, this kind of yarn is suitable to this strength to the yarn. So, most of the tires of cars, airplanes, cycles, etcetera and clothes what we wear, viscose clothes that is very soft materials, they are all made of viscose rayon which is strengthened with zinc and there are of course, several other kinds of industrial applications for zinc and so it is a widely distributed element as well as widely used element. So, there is no escape from zinc in your day to day life from this because of the origin because of the use of zinc in several industrial applications that we normally come across.

So, the BIS standard prescribes limit of 5 ppm and this is zinc is determined by using a reagent call as zincon, this zincon is a very special organic compound and it is a trigonal of course, and I am not going to give you the actual chemical name because it will run it about 2 pages, 2 lines not 2 pages and but I can tell you that essentially, it is contains SO 3 group, here in this side that helps solubilization there is n n double bond and OH group and NH double NH grouping and then OH group is there is a triton group and 2 3 benzene rings are there. So, because of this there will be complexation of zinc something like inner complex and let us see how the reagent works basically what happens is with this kind of structures we can expect.

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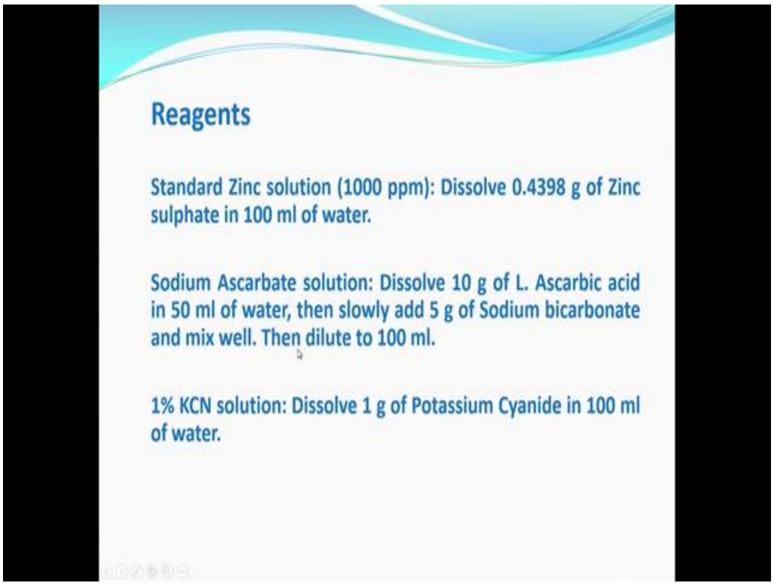

We can expect several types of metals to complex with zincon. So, the trick is there anywhere that we release zinc from the complex leaving others in this solution. So, that trick has been employed here that is why I have chosen zinc also to you in this presentation. So, many other metals including zinc form this, but then we add cycle of zincon to this to remove the zinc and then we monitor the absorbance.

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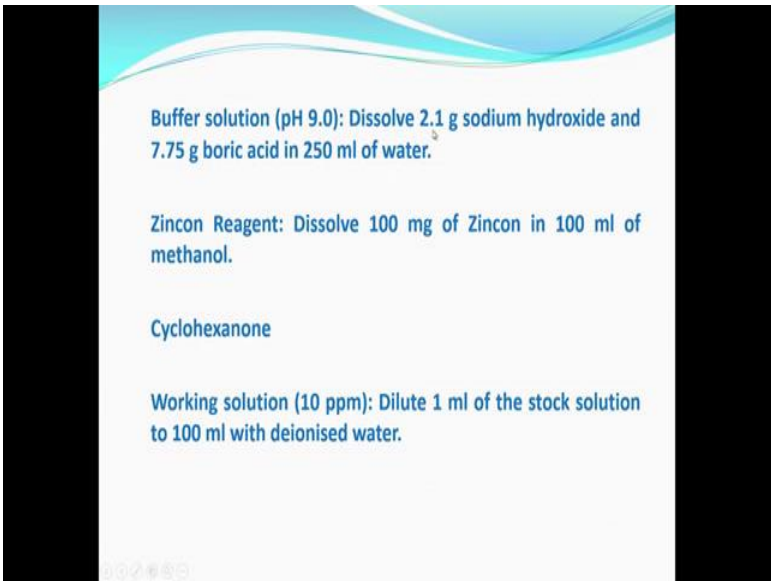

So, the reagents the reaction is carried out around pH nine using sodium hydroxide and boric acid and then zincon reagent is again dissolved in methanol because; obviously, many such compounds having high monocular weight they do not dissolve in water. So, you have to have methanol or ethanol which are miscible with water because you want to develop aqueous methods.

So, the only we know very few organic chemicals which are miscible with water. So, zincon dissolved in methanol and methanol is miscible with water methanol and ethanol among the 2 methanol is cheaper compared to ethanol. So, similarly you can use acetone also, but the rate of evaporation of ethanol acetone is not much higher than methanol. So, the concentration keeps on changing even if you keep it at room temperature. So, we normally recommend dissolution in methanol. So, that is how we prepare that and then standard zinc solution we know how to prepare this are the numbers 0.4398 and sodium acerbate, we have to prepare their using ascorbic acid and adding 505 gram of sodium bicarbonate mixing well this becomes a slightly darker solution and complexing agent is potassium cyanide.

So, there potassium cyanide is a dangerous chemical, but still there are certain situations in the life of any chemist where you cannot avoid the contact with some of these chemicals which are deadly of course, there are other ways of doing zinc analysis, but potassium cyanide is not very unusual lot of laboratories do have it, but you may also able to get it for laboratory purpose the method of the in the laboratory method you should be able to determine the zinc and zincon is as I told you it is easy to prepare working solution we need 10 ppm that is 10 microgram. So, see 1,000 ppm, we need we are preparing and then working solution is 10 ppm. So, that is a very simple calculation.

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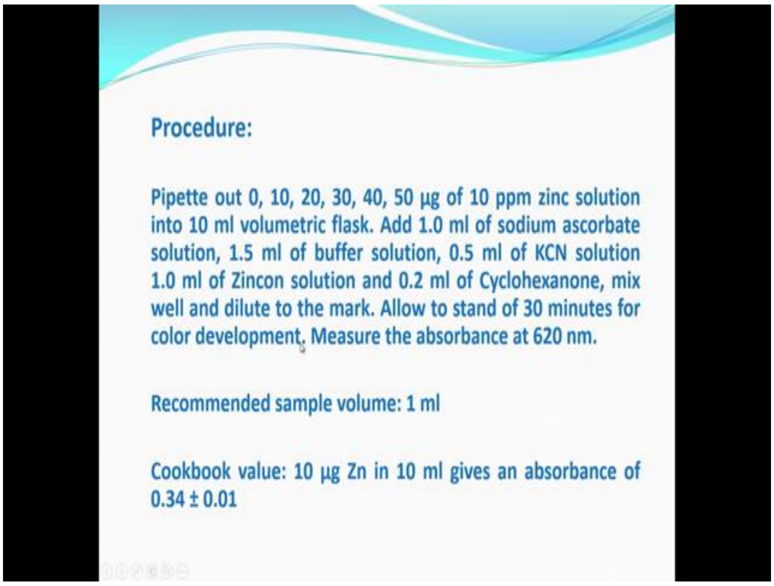

And the procedure involves transferring 0 to 50 microgram of zinc 10 ppm zinc solution that is up to 5 m l, 10 ppm into 5 would be that 50 micrograms and 10 divided by 10 ml is 5 ppm. So, 1 to 0 to 5 ppm is our working range.

And you can had 1 ml of sodium ascorbate solution and buffer solution followed by 0.5 ml of potassium cyanide. So, you can also add 1 ml of zincon solution and after adding zincon solution you have to add 0.2 ml of cyclohexanone this releases the zincon complex zinc complex from the cyanide and that mixes it with zincon. So, you allow it to stand for about thirty minutes at room temperature. So, color develops and you have to measure the absorbance at 620 nanometers further chemistry of this reaction you can study in feagul that is a book I have recommended for almost all spectrophotometric procedures you can also look up third addition of EB sandal colorimetric methods of analysis. So, sample recommended volume is an 1 ml and cookbook value will be for ten micrograms in 10 ml.

That is 1 ppm should give a absorbance of about 0.34 plus or minus 0.01 that is 0.32 to 0.36; 0.33 to 0.35 absorbance that should give you a fairly good control over the experiment if your; all you reagents are good.

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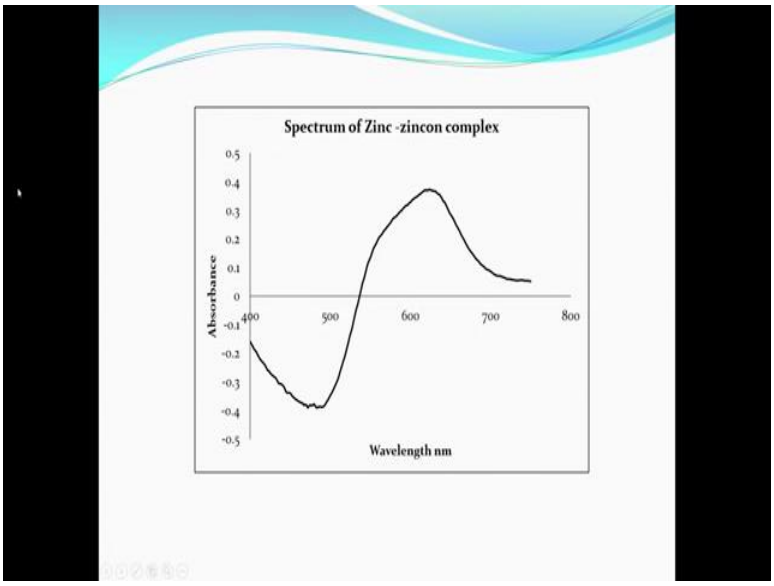

So, this is the lambda max of the spectrum of the lambda spectrum of zincon complex and this I have recommended 620 nanometer. So, if we go back to this complier to this spectrum we can see that lambda max is around 620 or 630 at the lambda max, the peak is fairly broad; that means, again the importance of this situation is plus or minus 2 3 nanometer plus or gives you a fine nanometer range where the absorbance will be almost constant with respect to the zinc concentration around 620. So, whether you are around 625 or 630, it does not matter that it will give permission to work with colorimetric method that is the colorimetric instead of spectrophotometrics.

So, you can determine zinc in all your sample it is an agriculturally important element also because it is a micronutrient, it is also used in pharmaceuticals industries and then it is very easy to determine zinc around this linear here at the back as you look at this curve you can see that there is lot of we usually add excess of the reagent and that reagent compared to when you measure at the blank you will get a negative value also. So, it is not a unusual, but we concentrate on the absorbance difference that is positive. So, we can determine this you can even use this somewhere around 480 that is a negative value that is a amount of zinc that is liberated this also you can also use as a negative parameter, but it is up to it is normally comfortable to use the positive difference between the blank and sample now I would like to tell you about the interference of this method.

So, the interference studies we have conducted earlier and by determining 10 ppms standard that is how we do we take 10 ppm solution in 10 ml that is 1 ppm, we normally go for 1,000 ppm. So, for the ppm we add the interference species and then measure the absorbance. So, if there is more than 10 percent of the absorbance, we conclude that it is a interfering element we did not find any interference from cobalt nickel calcium magnesium sulphate phosphate nitrate and then silver fluoride chloride iodide mercury tartaric acid citric acid and surfactants. So, this shows that the method is very very robust and some interference can be overcome by the addition of citrate and triturate because around pH 12 we will get only citrate acid sodium citrate and sodium triturate and 100 microgram of chromium molybdenum lead antimony arsenic and triton x 100 this is a standard surfactant we normally come across.

So, in the rivers etcetera whenever we use one of the surfactants which I have been telling you and these things did not interfere up to 100 micrograms levels that is 1 ppm of zinc and 100 microgram of the interfering element interfering element or anion or complex of whatever it is, but aluminum, iron, copper and cadmium, they did not interfere up to 5 times that is when you want to determine zinc in 1 ppm up to 5 ppm of any of these elements will not interfere and vanadium limit is a little lower that is up to 2 ppm. It can be tolerated and EDTA and manganese did not interfere; that means, with if EDTA does not interfere, we can always conclude that the method will be robust because EDTA is a very strong complexing agent with several metals that are normally present in drinking water river water lake water pond water and all those things. So, we will continue our discussion in next class.

Thank you.