Atomic and Molecular Absorption Spectrometry for Pollution Monitoring

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Lecture - 36
Nitrite, manganese

Gratings to you, we continue our discussion with the other parameters of water monitoring it applies also to effluent monitoring. So, today I am going to discuss with you about the determination of nitrite. Nitrite in general is a pollutant basically it effects the heart and other tissues.

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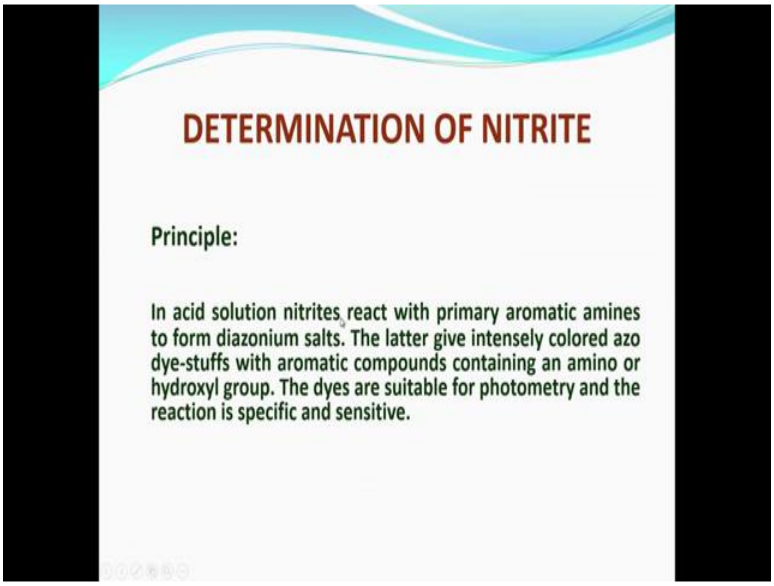

DETERMINATION OF NITRITE

Principle:

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

Especially with the formation of chemicals, which will determining the functioning of the heart, in a acid solution normally. Like nowadays nitrites are there in all water and effluents and whenever there is a problem of a hard water in the country there is a certain amount of softening required and one of the softening method is by RO that is reverse osmosis, and in reverse osmosis the pollutants dissolved salts usually pass through the reverse osmosis membrane RO membrane by diffusion, and then the substances which are having up to 100 Daltons are held in the membrane and the remaining water passes through the RO membrane.

So, in general what happens is the permeate is good water, but the reject concentrates almost all the salts that are rejected and the treatment or disposal of the RO reject is a fairly difficult problem, and in this context the determination of nitrite becomes important. The normal effluent should not contain more than 45 ppm of nitrogen nitrite I mean, and that is why nitrite has become an important parameter for the determination of water, in drinking as well as portability as well as for industrial effluents.

So, the principal is very simple, what happens is you react the sample containing nitrite with the primary aromatic amines to form diazonium salts, this a very well known chemical reaction almost all organic chemist knows, know that nitrites react with primary aromatic amines, and they form the diazonium salts these diazonium salts are intensely colored azonia azo dye stuffs, and whenever they react with our aromatic compounds containing an amino or hydroxyl group the give red color, yellow color, and intense colour substances these dyes are suitable for spectrophotometry and the reaction is very specific and sensitive. That means, almost all nitrites usually end up if you react the end up giving colored dyes whenever you form diazonium salts, and treat them with some aromatic compound containing amino or hydroxyl group; more than 10,000 applications of these techniques have been applied in spectrophotometry, and this is what I am presenting to you is specifically for nitrite.

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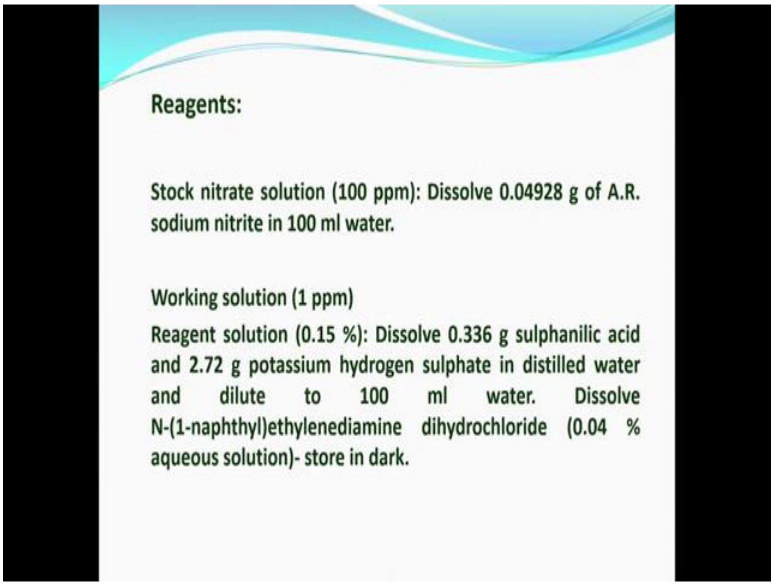

Reagents:

Stock nitrate solution (100 ppm): Dissolve 0.04928 g of A.R. sodium nitrite in 100 ml water.

Working solution (1 ppm)

Reagent solution (0.15 %): Dissolve 0.336 g sulphanilic acid and 2.72 g potassium hydrogen sulphate in distilled water and dilute to 100 ml water. Dissolve N-(1-naphthyl)ethylenediamine dihydrochloride (0.04 % aqueous solution)- store in dark.

So, the reagent solutions are all very simple you need to prepare stock nitrite solution that is about 100 ppm, and your working solution would be 1 ppm. So, all you have to do is prepare 100 ppm and dilute it by dilute it 100 times to prepare the working solutions; this working solution you have to prepare daily. And the reagent solution is a sulphanilic acid solution and it is treated with hydrogen potassium hydrogen sulphate in distilled water and N E DL that is what we call it you have to N-1 naphthylethylenediamine dihydrochloride is a solution and this also you have to prepare, but store in the dark because it is photosensitive reagent.

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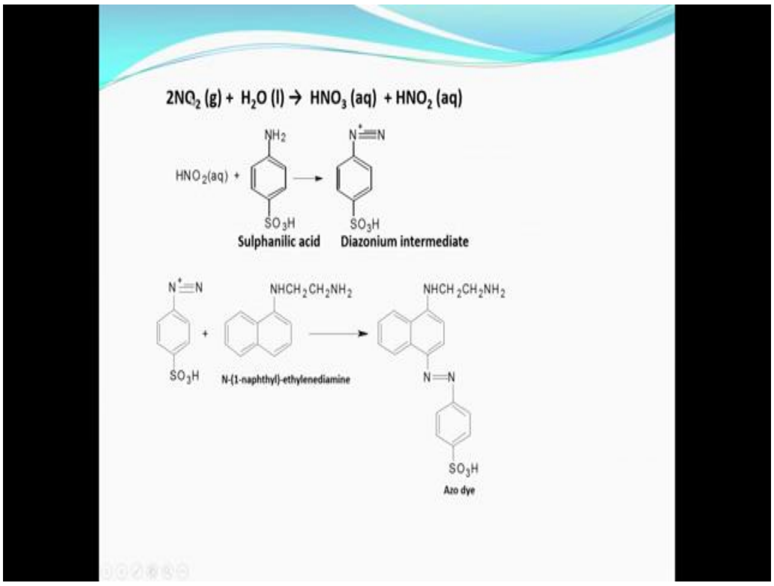

$2NO_2\,(g) + H_2O\,(l) \rightarrow HNO_3\,(aq) + HNO_2\,(aq)$

And then this is the basic reaction, nitrite group will react with water to give you nitric acid and HN 0 2 that is a very simple straight forward reaction that is in presence of oxidizing element, and this H N 0 2 nitrous acid aqueous will react with C 6H 5 SO2 SO3 H that is sulphanilic acid to give you an azo dye.

The azo dye I have I am representing it as N plus and N and then this dye this is known as diazonium intermediate, and this diazonium intermediate is reacted with n onenaphthylethylenediamine, that will that is an simple an addition product and the azo dye is formed.

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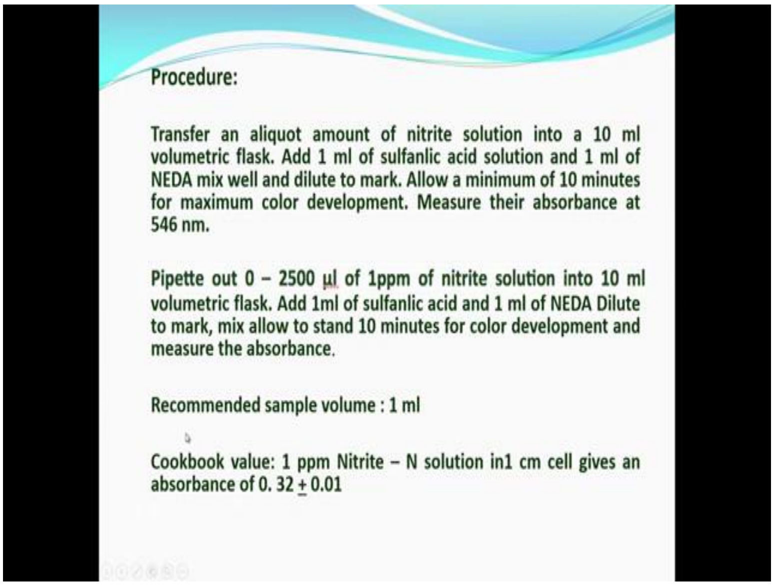

Procedure:

Transfer an aliquot amount of nitrite solution into a 10 ml volumetric flask. Add 1 ml of sulfanlic acid solution and 1 ml of NEDA mix well and dilute to mark. Allow a minimum of 10 minutes for maximum color development. Measure their absorbance at 546 nm.

Pipette out 0 – 2500 µl of 1ppm of nitrite solution into 10 ml volumetric flask. Add 1ml of sulfanlic acid and 1 ml of NEDA Dilute to mark, mix allow to stand 10 minutes for color development and measure the absorbance.

Recommended sample volume : 1 ml

Cookbook value: 1 ppm Nitrite – N solution in1 cm cell gives an absorbance of 0. 32 ± 0.01

This azo dye is intense red in color, and you will have to measure the absorbance of this. So, what we do is we go about doing normal reaction transferring an amount in required amount in 10 ml volumetric flask, and you have to prepare standards from 0 to 2500 micro liter that is approximately 2500 micro grams of nitrite solution in view normally we dilute it in 10 ml volumetric flask, and then we have to add the this works out to about 2.5 ml 2500 ml of the sample and then 1 ml of a sulphanilic acid, and 1 ml of neda solution dilute to mark allow it to stand for 10 minutes and you have to measure the absorbance.

Normally a recommended volume is about 1 ml that is your whenever you have an effluent you should take 1 ml of the effluent, and even for standard you can take 1 ml that is1 ppm. So, one microgram of 1 ml 1 ppm nitrite nitrogen solution in 1 centimeter cell gives you an absorbance of about 0.32 plus or minus 0.01; that means, if you we assume that the instrument sensitivity is 0.004, 10 times dilution would be 0.1 ppm and your detraction limit would be somewhere about 0.001 ppm, 0.01 ppm that is about 10 pica nanograms.

So, it is a fairly sensitive reaction and you can continue looking working with this, very comfortable with almost all waters containing nitrate as a component.

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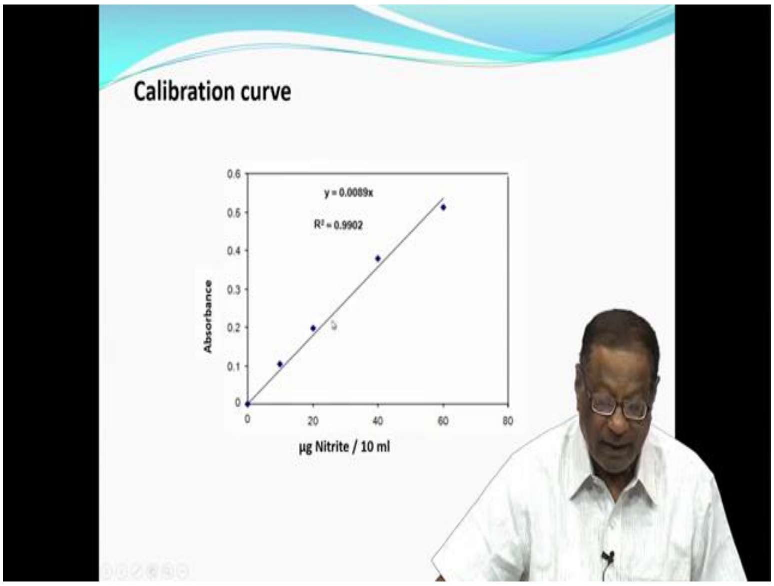

Calibration curve

So, I want to show you this curve that is this is the calibration curve, you can see that the calibration curve is fairly linear and r square is value is about 0.9902 that is the linearity index.

So, it is fairly decent because you are you will be determining 20, 40, 50, 60 micrograms only that is about 6 ppm. So, whenever you have a higher solution you dilute it accordingly and complete the analysis.

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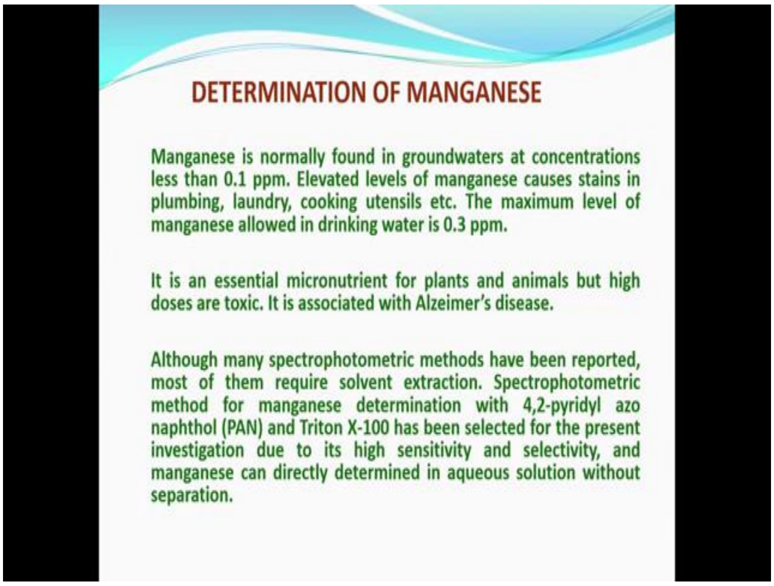

DETERMINATION OF MANGANESE

Manganese is normally found in groundwaters at concentrations less than 0.1 ppm. Elevated levels of manganese causes stains in plumbing, laundry, cooking utensils etc. The maximum level of manganese allowed in drinking water is 0.3 ppm.

It is an essential micronutrient for plants and animals but high doses are toxic. It is associated with Alzeimer's disease.

Although many spectrophotometric methods have been reported, most of them require solvent extraction. Spectrophotometric method for manganese determination with 4,2-pyridyl azo naphthol (PAN) and Triton X-100 has been selected for the present investigation due to its high sensitivity and selectivity, and manganese can directly determined in aqueous solution without separation.

But what I wanted to tell you is nitrite is a very important component it is also used in the industry to for nitriding many of these stainless steel and other metals are used toughened by molten nitrite solution molten nitrite salt, they are exposed and heated to about 900 degree centigrade and the waste nitrite bath will have this nitrite coming into the effluent and also nitrite is a typical industrial effluent also.

So, that completes our discussion on nitrite, and then now we move onto determination of manganese; and regarding manganese I have to tell you that most of you are familiar with manganese in the environment. Potassium permanganate most of you are familiar it is dark violet in color it is an oxidizing agent, and the oxidizing agent it is used in the treatment of water, water treatment; even when the wells around your house are polluted and smell is coming or some organic things are coming in sewage or etcetera, treatment with potassium permanganate is one of the standard method of well water treatment. And also in the laboratory potassium permanganate is used as a oxidizing agent, and it is very well known. And manganese is also normally found in ground waters at a concentrations of about 0.1 ppm, manganese is a very interesting element because it is a widely it is widely distributed in the earth’s crust also.

So, most of the soils have manganese, and there is a requirement of the manganese measurement in the soil and water etcetera because it is a micro nutrient also. So, because it is a distributed widely in the soils, you can come across soils which are having elevated levels of manganese. Now what this manganese do in the environment the problem is elevated levels of manganese cause stains in plumbing, laundry, cooking utensils etcetera. So, it is a very tricky element and manganese is basically very important industrial element it is also used in the alloys, and the maximum level of manganese are allowed in drinking water is 0.3 ppm.

So, it is an essential micro nutrient also for plants as well as animals, but higher doses are toxic. Actually this statement is a little ambiguous whenever we say any element is a micro nutrient it does not mean that only micro nutrient quantities we are exposed, any material whenever it is in excess can become toxic. So, manganese is no exception to this rule, and it is toxic at higher levels and it is associated with alzheimers disease. So, along with aluminium, manganese also people look at the manganese concentration in blood brain and fluid body fluids etcetera. Therefore, it is also industrially very important chemical metal and several methods are there for the determination of manganese, most of them usually requires solvent extraction. So, we have tried to do the analysis by sticking to aqueous solutions that is one of the aims of this program this teaching program, where we want to avoid extraction at the same time permit you to determine the substances in ppm level or within the specified limits by the pollution control board.

So, spectrophotometric method for manganese determination we are proposing this 4 2 pyridyl azo naphthol and triton reagent. Usually there are so many methods for the determination of manganese, why we have chosen this reagent is because 4 2 pyridyl azo naphthol that is known as pan in short, 4 2 pyridyl azo naphthol pan it is a very commonly available organic reagent you can buy it across the shelf. It is very easily available and triton X-100 is another reagent that is beenselected because it is a surfactant, it is a nonionic surfactant and the one of the jobs of triton X-100 is to keep the concentration of the micelles in such a way that it does not precipitate.

So, actually several surfactants are regularly (Refer Time: 14:17) routinely used in spectrophotometry now a days, earlier I have explained this type of reaction whenever we did it with the precipitation stabilization; sometimes we have used polyvinyl alcohol, sometimes we have used gelatin and now I am proposing that we use triton X-100 for the present investigation. Why? Because it affords a very high sensitivity of the reaction, it also gives you selectivity and manganese can be directly determined in aqueous solution without separation from interfering elements, that is one of the advantageous of the determination of manganese.

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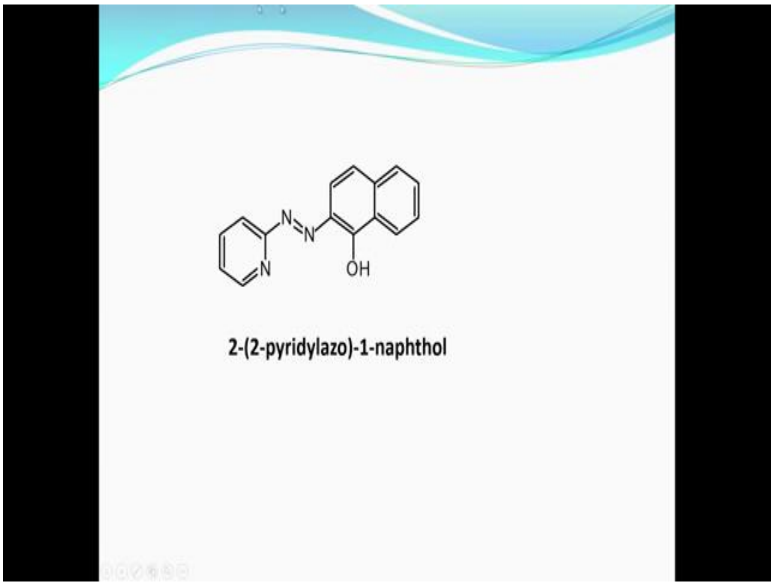

2-(2-pyridylazo)-1-naphthol

So, if we look at it this is the structure of the organic reagent, it is a ternary tri phenyl 3 rings, 3 aromatic rings fuse together with azo group that is N, N, N, and then there is one OH group both these nitrogen and OH groups are electron releasing groups and it 4 2 pyridyl azo naphthol, this is a 2 2 if I have some 3 4 if I have a OH group here then it is known as 4 2 pyridyl azo naphthol, and this reagent can be used for the determination of manganese.

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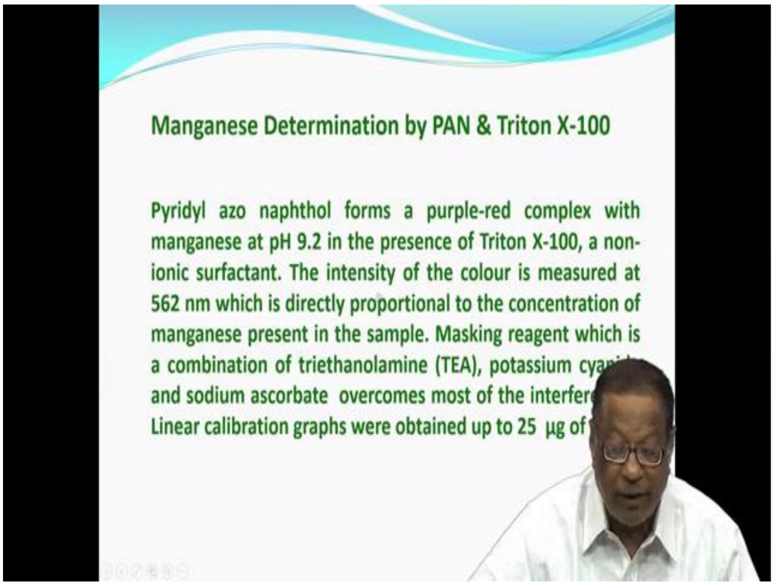

Manganese Determination by PAN & Triton X-100

Pyridyl azo naphthol forms a purple-red complex with manganese at pH 9.2 in the presence of Triton X-100, a non-ionic surfactant. The intensity of the colour is measured at 562 nm which is directly proportional to the concentration of manganese present in the sample. Masking reagent which is a combination of triethanolamine (TEA), potassium cya
and sodium ascorbate overcomes most of the interfer
Linear calibration graphs were obtained up to 25 µg of

So, this pyridyl azo naphthol it forms a purple red complex with manganese, the reaction occurs in alkaline Ph, that is one advantage very few metals can be normally determined in alkaline media, that is because most of the metals in the periodic table or whatever we come across in normal day to day life, they all precipitate as hydroxides and oxides, oxides and hydroxides in alkaline range. But in presence of triton X-100 most of these precipitates precipitation does not occur and manganese is no exception. So, manganese at pH 9.2 is still in the form of as an anion, as a magnate ion and if we form a complex with a 4 2 pyridyl azo naphthol and triton x 100, we the form the red complex and the intensity of the color is measured at 562 nanometers, 562 nanometer is usually the typical measurement for potassium permanganate.

So, this is also similar in composition, and the concentration is directly proportional to the absorbance and vice versa. A masking agent normally we use are not EDTA or CDTA, but the complexing agents which should be stable in alkaline medium. So, we have not much choice except try ethanol amine that is 3 e a, that is known as TEA and potassium cyanide is also a good complexing agent, and sodium ascorbate instead of ascorbic acid we use sodium ascorbate for the overcoming of the interferences. Usually linear calibration graphs are obtained with about 25 microgram of manganese.

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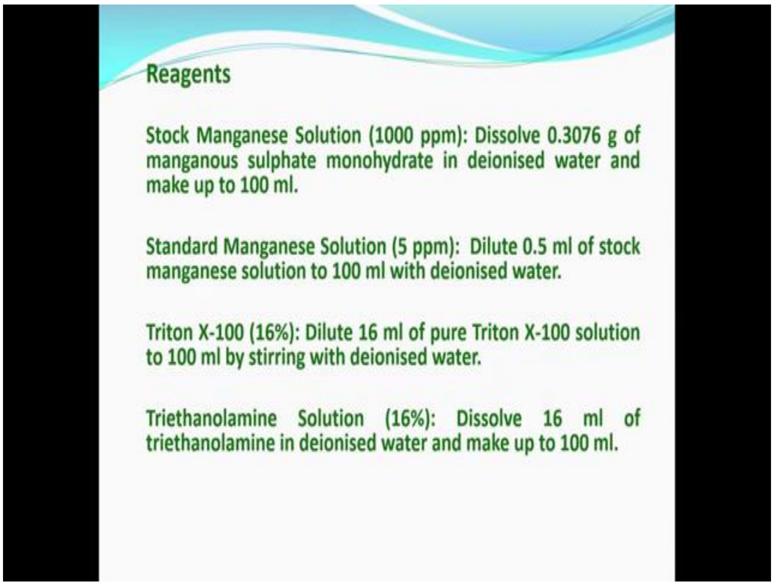

Reagents

Stock Manganese Solution (1000 ppm): Dissolve 0.3076 g of manganous sulphate monohydrate in deionised water and make up to 100 ml.

Standard Manganese Solution (5 ppm): Dilute 0.5 ml of stock manganese solution to 100 ml with deionised water.

Triton X-100 (16%): Dilute 16 ml of pure Triton X-100 solution to 100 ml by stirring with deionised water.

Triethanolamine Solution (16%): Dissolve 16 ml of triethanolamine in deionised water and make up to 100 ml.

So, with this information let us take a look at the reagents; reagent things are very simple that is we have to dissolve manganese sulphate as a monohydrate, and then we will have to dilute it to about 100 ml. The working standard should be 5 ppm that is about 0.5 ml we can take and dilute it to 100 ml with deionized water, triton X-100 is available across the shelf you have to prepare about 16 percent pure triton X-100 solution to we have to dilute it and with deionized water. Usually triton X-100 is a very thick viscous liquid. So, normally what we do is we try to prepare on a weight basis, you can either take 16 ml or you can weigh exactly in a beaker and dilute it to 100 ml, and triethanolamine is also fairly it is not so viscous as triton x 100, but we can prepare 16 ml of that triethanolamine in deionized water and use it as a complexing agent, we need to prepare a buffer because pH 9.2 is a very standard buffer of a ammonium chloride and ammonia.

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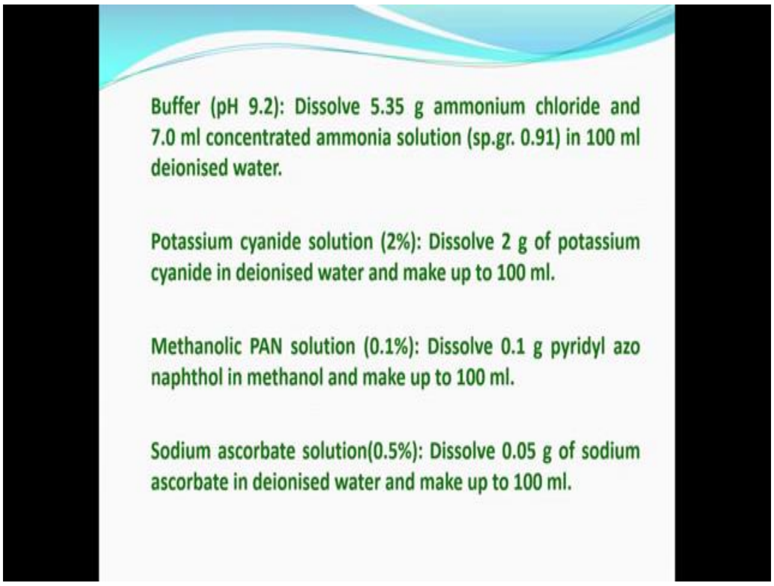

Buffer (pH 9.2): Dissolve 5.35 g ammonium chloride and 7.0 ml concentrated ammonia solution (sp.gr. 0.91) in 100 ml deionised water.

Potassium cyanide solution (2%): Dissolve 2 g of potassium cyanide in deionised water and make up to 100 ml.

Methanolic PAN solution (0.1%): Dissolve 0.1 g pyridyl azo naphthol in methanol and make up to 100 ml.

Sodium ascorbate solution(0.5%): Dissolve 0.05 g of sodium ascorbate in deionised water and make up to 100 ml.

So, this is very easily prepared by weigh dissolving 5.35 gram of ammonium chloride and 7 ml of concentrated ammonia, that is in about 100 ml of water (Refer Time: 20:08) potassium cyanide usually people do not like to use potassium cyanide as a chemical reagent in the laboratory because it is very dangerous to use, but sometimes it becomes necessary to use such chemicals as and when required that is the speciality and hazard of the laboratory also.

So, there is not much choice if we have to have deal with the complexing agents, potassium cyanide is one of the excellent complexing agent with us. Then we can go for methanolic solution, pan solution, pyridyl azo naphthol what we do is we dissolve 0.1

gram of pyridyl azo naphthol in methanol and make it upto 100 ml using methanol only; sodium ascorbate you can prepare in the acidic aqueous medium that is no problem.

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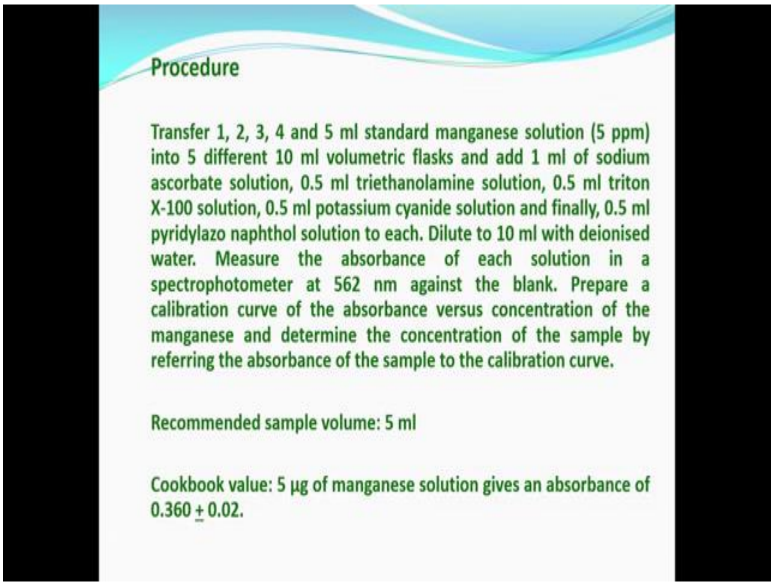

Procedure

Transfer 1, 2, 3, 4 and 5 ml standard manganese solution (5 ppm) into 5 different 10 ml volumetric flasks and add 1 ml of sodium ascorbate solution, 0.5 ml triethanolamine solution, 0.5 ml triton X-100 solution, 0.5 ml potassium cyanide solution and finally, 0.5 ml pyridylazo naphthol solution to each. Dilute to 10 ml with deionised water. Measure the absorbance of each solution in a spectrophotometer at 562 nm against the blank. Prepare a calibration curve of the absorbance versus concentration of the manganese and determine the concentration of the sample by referring the absorbance of the sample to the calibration curve.

Recommended sample volume: 5 ml

Cookbook value: 5 µg of manganese solution gives an absorbance of 0.360 ± 0.02.

And the procedure involves transfer of up to 5 ppm in a volumetric flask, you have to add sodium ascorbate to reduce the manganese. Manganese to manganic to manganous and 0.5 ml of tri ethanolamine and a triton X-100 and potassium cyanide and finally, you have to add 4 2 pyridyl azo naphthol solution to each and you have to dilute to 10 ml with deionized water.

So, you can measure the absorbance of each solution in the spectrophotometer again around 562 nanometer as I have already explained to it is the violet color that we are measuring; and we have to prepare a calibration curve the calibration curve is linear up to about 25 micrograms, and 25 microgram in 10 ml will give you approximately 2 absorbance of about 0.2. So, that is very high normally we do not determine any material up to two, but in this case especially why I put this up to 2 is because the concentrations very quite a very over a quite a large range especially in the determination of molybdenum. I am sorry manganese and even if the concentration is upto 25 ppm which is normally found in the soils as well as in some of the extreme effluent waters, you can straight away go for the determination without any dilution, that is the requirement and R square value is about 0.998.

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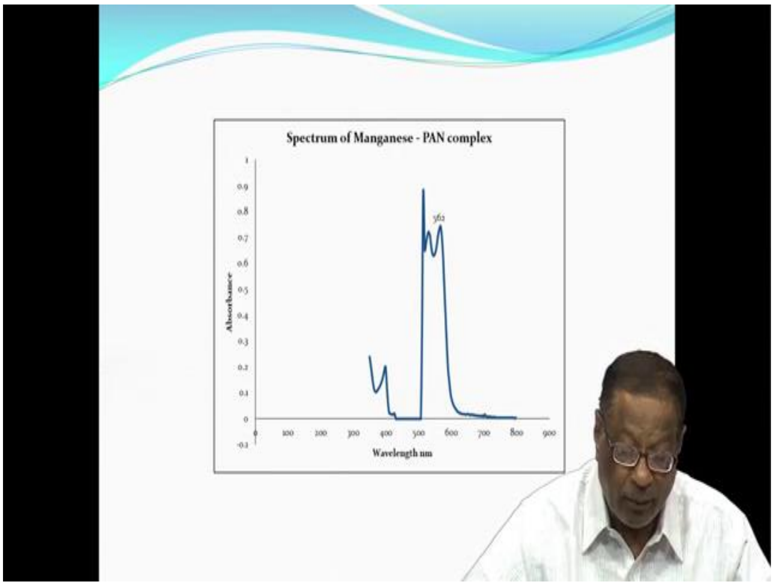

So, that is also very good basically and this is the spectrum of manganese pan complex, you can see that around 562 we have a peak here, and we can use other peaks, but they are not so specific. So, easily identified and there are shoulders etcetera, but this 562 is fairly readable fairly attainable in a spectrophotometer also, and the cook book value recommended sample volume is up to 5 ml, and cook book value gives you an absorbance of about 0.36 plus or minus 0 2 that is 0.038 2.034 using manganese in about 5 ml of the substance. Regarding the interference I would like to tell you that the interference from about 1000 ppm, I would like to report to you iodide, chloride, fluoride, sulphate etcetera nitric most of the anions phosphate, bromide, citrate ,tartrate triton X-100 of course, we are using it as a reagent and then SLS sodium, lauryl, sulphate all these things in 1000 ppm do not interfere and many metal ions cupric cobaltous nickelous manganese, magnesium, calcium, antimony, silver, aluminium, silver and molybdenum they do not interfere at 1000 ppm level.

Now, we have also looked at the interference from other elements that is vanadium, chromium, aluminium, mercury and arsenate; these ions cations and anions as well do not interfere up to 50 ppm that is 10 times value, and then equal volumes would be ferric and lead they do interfere to some extent, but not much because the even though ferric iron precipitates as a hydroxide, it is complexed before precipitation it is complexed with these tri ethanolamine, and then lead also is the meets the same fate whenever we use tri ethanolamine and then at 5 ppm equivalent levels we should not worry if chromium cadmium and zinc are there. In then EDTA also does not interfere if it is there up to 5 ppm. Now why I want to tell you EDTA in this case is because the EDTA has become a part of the our river waters, industrial waters, lake waters as well as municipal waters, because of the use extensive use of EDTA in most of the laundry materials.

So, with this introduction with this introduction, I would like to show you the calibration and then next we will discuss about cadmium in the drinking water.