Basic Environmental Engineering and Pollution Abatement

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Lecture 17

Sampling and Characterization – 2
(Water, Wastewater, Effluents)

Hello everyone, now we will discuss on the topic sampling and characterization part 2, in the previous class we have discussed that sampling is very important for the analysis of environmental parameters like say air, water and soil samples and we have discussed about the sampling methods for air.

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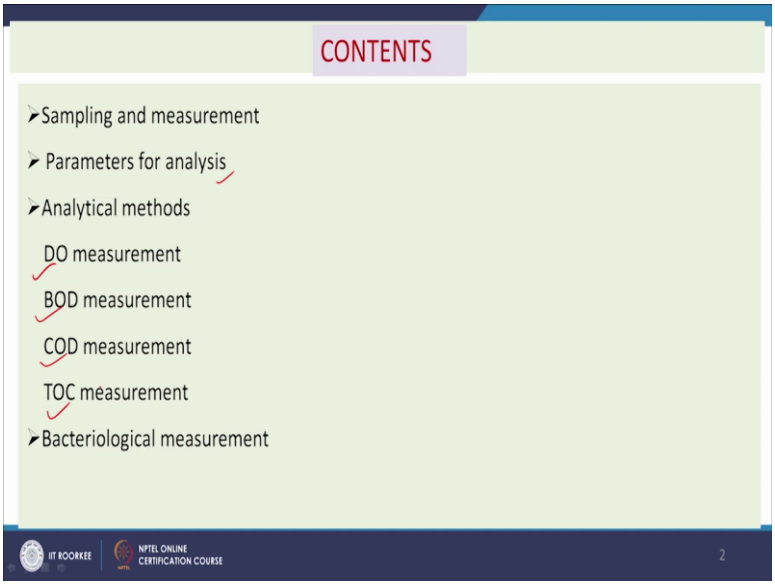

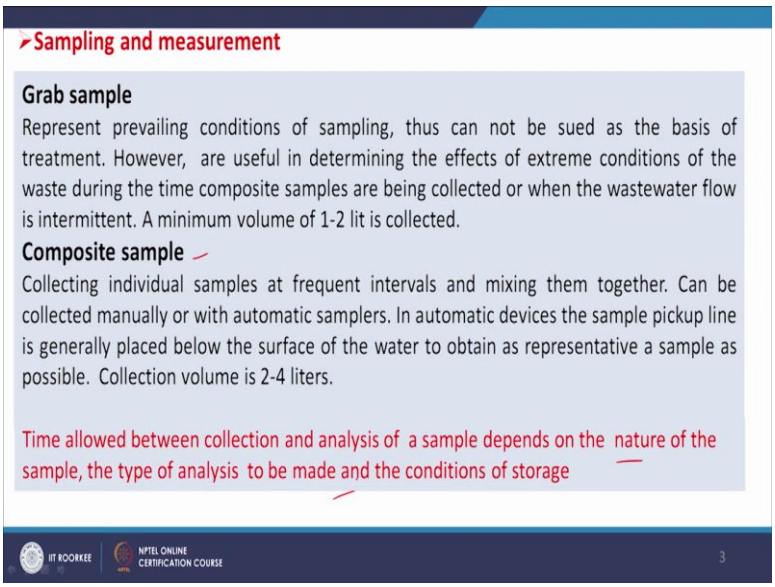

And in this class we will discuss sampling and measurement of water samples and parameters for analysis then different analytical methods which are used to measure different parameters that will be discussed, some of those like say DO measurement then BOD measurement, COD measurement, TOC measurement and bacteriological measurement. Like air we can also use the grab sampling and composite sampling, in case of water sampling we can use grab sampling and composite sampling method.

So grab sampling means within very small time duration will be collecting the water sample and composite sampling that indicates basically we will be collecting number of grab samples after certain interval of times and then we will be mixing it and get the mixer of it. Now we will see the grab sample represent prevailing conditions of sampling thus cannot be used as the basis of treatment however are useful in determining the effects of extreme conditions of the waste during the time composite samples are being collected or when the waste water flow is intermittent a minimum volume of 1-2 liter is collected.

And collecting individual samples at frequent intervals and mixing them together that is called composite sampling. Can be collected manually or with automatic samplers. In an automatic device the sample pickup line is generally placed below the surface of the water to obtain as representative a sample as possible, collection volume is 2 to 4 liters.

Now time allowed between collection and analysis of sample depends on the nature of the sample, the type of analysis to be made and conditions of storage. So we may get the sample then we have to get the quality parameters so different quality parameters we have to get it analyzed within certain time period that is the matter of questions and we will see.

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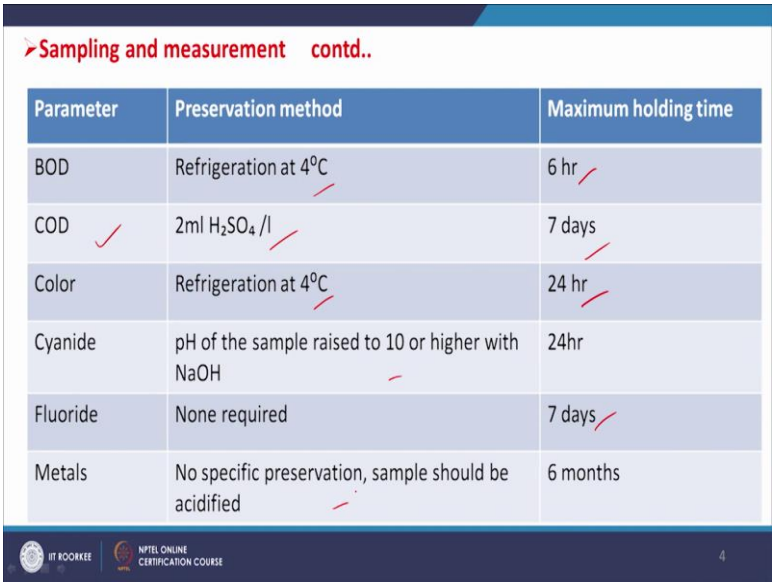

For BOD it can be stored at refrigeration at 4 ^{o}C and the holding time is maximum 6 hours, within 6 hours it is recommended to test the sample or analyze the sample for BOD. Similarly for COD within 7 days and the preservation method is 2 ml H_2SO_4 per liter and then color it can be refrigerated at 4 ^{o}C and 24 hour holding time. Cyanide pH of the sample raise to 10 or higher with NaOH and 24 hour holding time. Fluoride nothing is required but within 7 days we need to analyze and metals no specific preservation, sample should be acidified and within 6 months we need to analyze for the metals.

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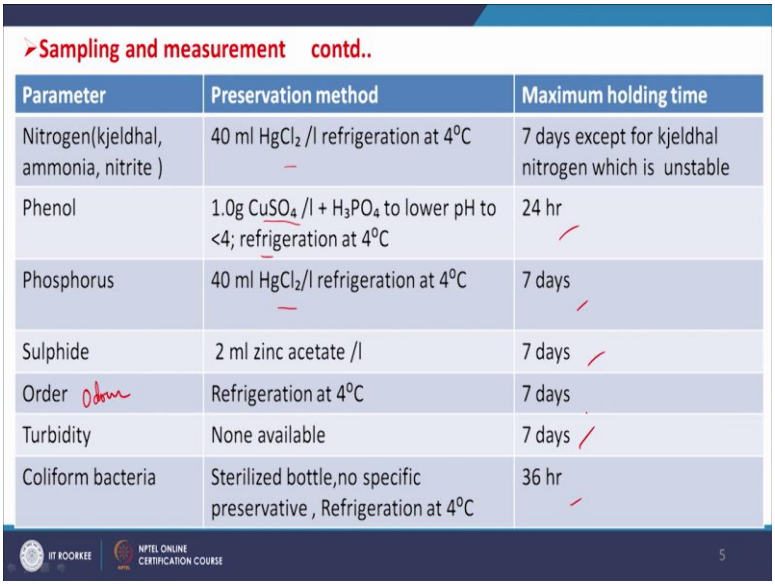

And for nitrogen kjeldhal, ammonia and nitrate this is 40 ml mercuric chloride per liter refrigeration at 4 ^{o}C and 7 days except for kjeldhal nitrogen which is unstable so phenol it is for 24 hour holding time and 1 gram $CuSO_4$ per liter plus H_3PO_4 to lower pH to less than 4 and refrigeration at 4 ^{o}C, similarly phosphorous we can use 40 ml $HgCl_2$ per liter refrigeration at 4 ^{o}C and 7 days holding period.

And sulphide 2 ml zinc acetate per liter and then 7 days holding period, odour refrigeration at 4 ^{o}C 7 days. Turbidity no preservation needed for 7 days holding period and coliform bacteria 37 hour holding period and sterilized bottle no specific preservative and refrigeration at 4 ^{o}C. So these are the different methods and holding period for the analysis of different types of parameters

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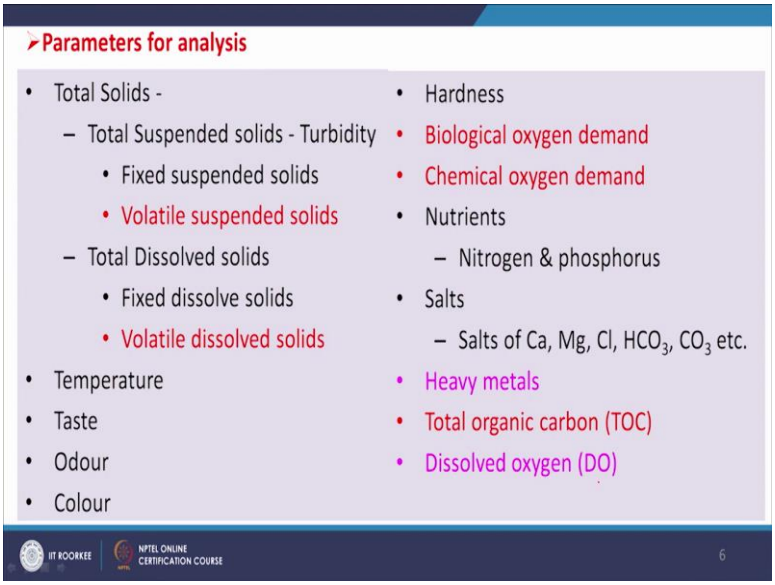

Now if we see the quality parameters these are mentioned here like say total solids, the total dissolved solid, total suspended solids, temperature, taste, odour and colour these are our physical properties and hardness, biological, chemical oxygen demand, nutrients and heavy metals, total organic carbon and dissolve oxygen these are other important properties those are chemical properties.

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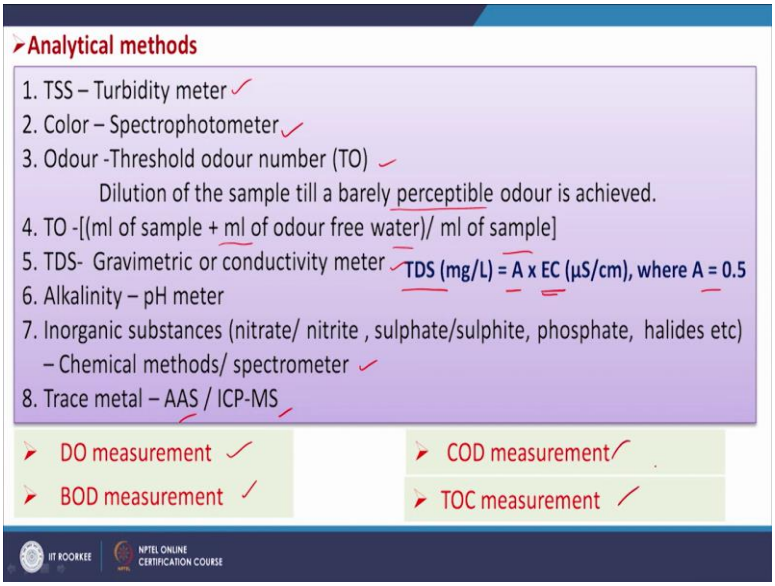

So we will be discussing how to measure these parameters, so turbidity meter is used to measure the TSS total suspended solid and to measure the color spectrophotometer is used and odour is determined on the basis of threshold odour number. This is certainly sensed by the human and that is the perception, the dilution of the sample till a barely perceptible odour is achieved, the sample is diluted until we get a perceptible odour minimum.

So threshold odour number that is ml of sample plus ml of odour free water divided by ml of sample. TDS we can measure by gravimetric or conductivity meter and as you have discussed that electrical conductivity is related with TDS by this expression.

TDS (mg/L) = A*EC (µs/cm)

where A is equal to 0.5 a constant and alkalinity you can analyze with the help of pH meter and inorganic substances like different types of cations and anions we can measure it in a lab, chemical test method or using spectrophotometer.

And trace metals may be analyzed by atomic absorption spectroscopy and ICP-MS inductively coupled plasma mass spectroscopy. And for the measurement of DO, BOD, COD and TOC different instrumental methods as well as chemical methods are used we will be discussing those.

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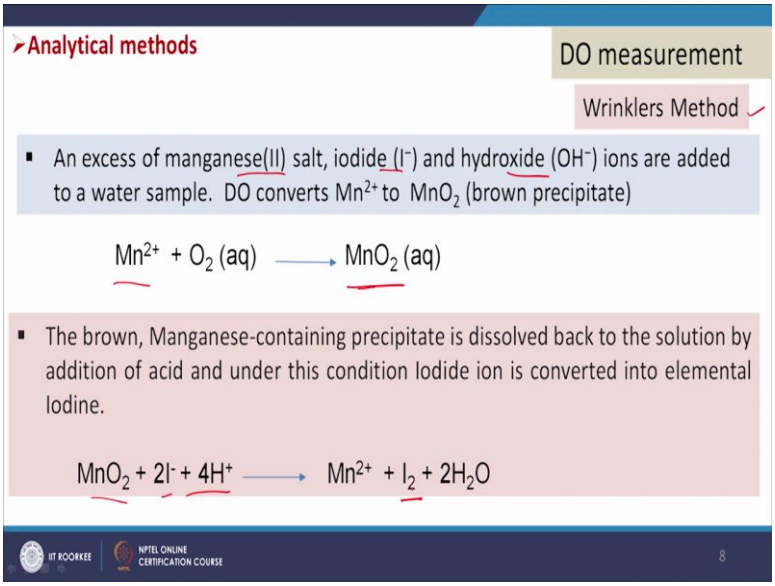

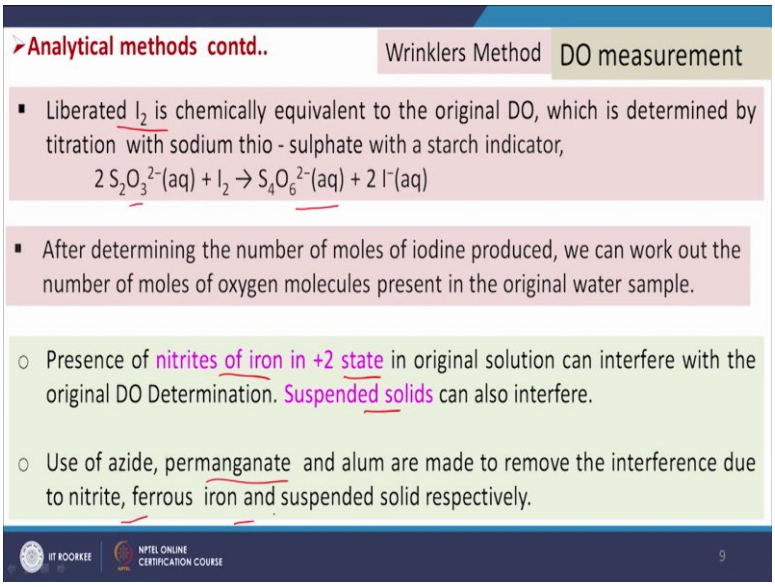

Now we will discuss the analysis of dissolve oxygen, so dissolve oxygen can be analyzed by chemical method as well as some instrumental method. So that Wrinklers method this is very old method is a chemical method that was used initially to measure the DO value. And the principle was that in the solution iodide manganese 2 salt and hydroxide these are added in excess and at higher pH

$Mn^{2+} + O_2$ (aq) → MnO_2

so that MnO2 is precipitated and that is dissolved further in presence of acid. So then when it is dissolved with acid then iodide is converted to iodine. Now this iodine is further titrated against the sodium thiosulphate and then this is the reaction so we can find out the end point

by using starch indicator. So if we know the how much iodine is liberated then you can guess how much oxygen was present because if we see the stoichiometry so here

$MnO_2 + 2I^- + 4H^+ \rightarrow Mn^{2+} + I_2 + 2H_2O$

So how much oxygen was used to convert this iodide to iodine that is equal, that means mole of iodine is equal to mole of oxygen. So after determining the number of moles of iodine produced we can work out the number of moles of oxygen molecules present in the original water sample. But in this case there may be some possibility of interferences like say nitrites of iron in plus 2 state in original solution can interfere with the original DO determination and suspended solids can also interfere and use of azide, permanganate and alum are made to remove the interference due to nitrite, ferrous iron and suspended solids respectively.

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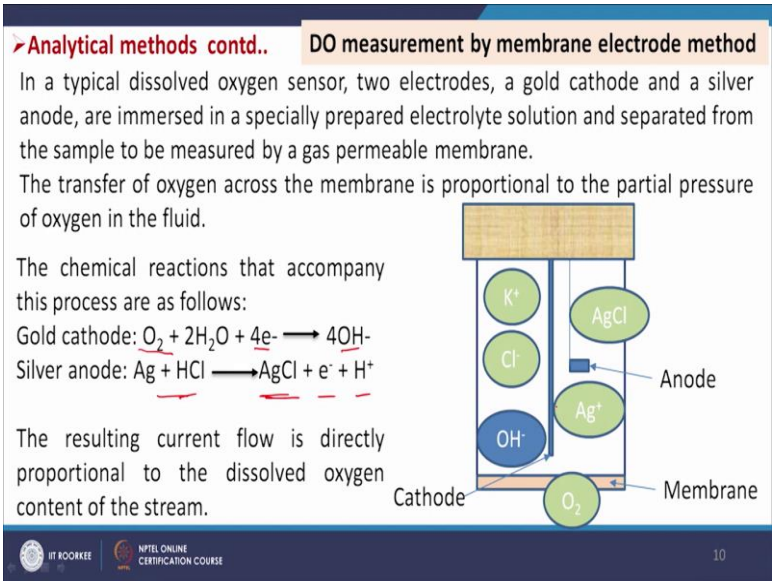

And for instrumental analysis, some DO analyzer is available. So in this case one electrode is used as shown here so inside this electrode we have one electrolytes that is AgCl and HCl, KCl and AgCl, and when the electrode is put into the water sample which we need to analyze so oxygen present in the water will diffuse through this membrane, this membrane oxygen can be diffused through it because it will be having higher pressure outside the this electrode.

And then when oxygen is coming here there will be some reaction inside say we have anode and cathode inside this so gold cathode and silver anode so silver anode when it is KCl we are using in acidic media so it will give us this type of reactions

$Ag + HCl \rightarrow AgCl + e^- + H^+$

so which e^- is generated here in the anode so when oxygen is coming to this electrolyte so that $O_2 + 2H_2O + 4\ e^- \rightarrow OH^-$

So if we connect these two anode and cathode will get one electricity through it and that electricity generation will be proportional to the oxygen which is being dissolved from water to this electrode or to the electrolyte. If we use the standard solution then by calibration we can measure the DO value in the water.

Now we will discuss BOD measurement so BOD we know that the biological oxygen demand so if we determine the DO at t = 0 and if we determine the DO of the sample after 5 days incubation at 20 ^oC or 3 days it to be incubation at 27 ^oC then the difference DO will be the DO consumed by the microorganism for the oxidations of the organic compounds present in the water. so knowing these two values or the difference in the DO values we can calculate the BOD value.

So now for this we collect the sample then we dilute it with some dilution solution and the incubation takes place and sometimes addition of micro microorganism is needed so that is called seeding. So, seeding is done with the dilution water and then after dilution the addition of dilution water and the sample in a proper ratio we go for incubation.

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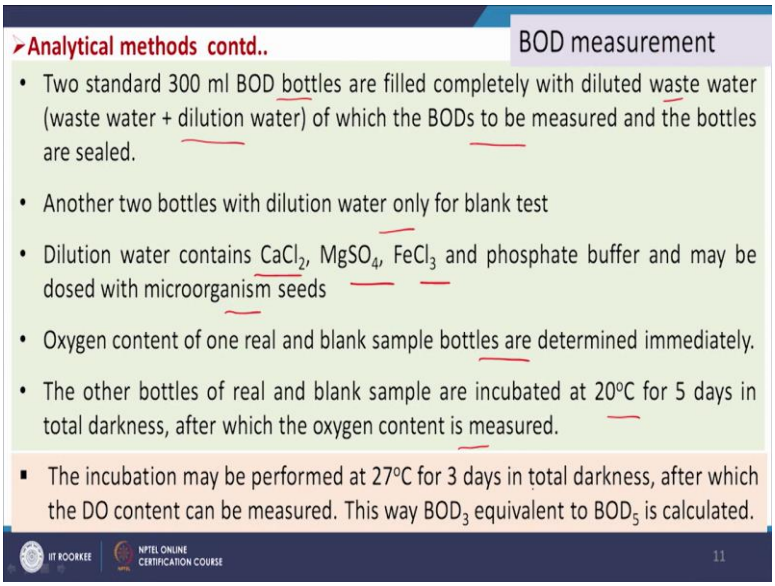

So we take two standard 300 ml BOD bottles and fill completely with diluted waste water that is (waste water + dilution water) of which the BOD_5 to be measured and the bottles are sealed. Another two bottles with dilution water only no sample is added. One is to determine the oxygen content at t equal to 0 on the day of collection and at t = 5 or = 3 day we will get the DO for another bottle. So two bottles for waste water plus dilution water will be getting, one bottle will be analyzed at t =o 0 and another bottle will be analyzed at t = 5 or 3 day and similarly for the bottles with only diluted water also will be tested at t = 0 and t = 5 or t = 3 respectively.

And this dilution water which we are adding that contains CaCl2, MgSO4, FeCl3 and phosphate buffer and may be dosed with microorganism seeds. oxygen content of one real and blank sample bottles are determined immediately. The other bottles of real and blank samples are incubated 25 ^oC for 5 days in total darkness, after which the oxygen content is measured. It can be done at 27 d ^oC for 3 days also.

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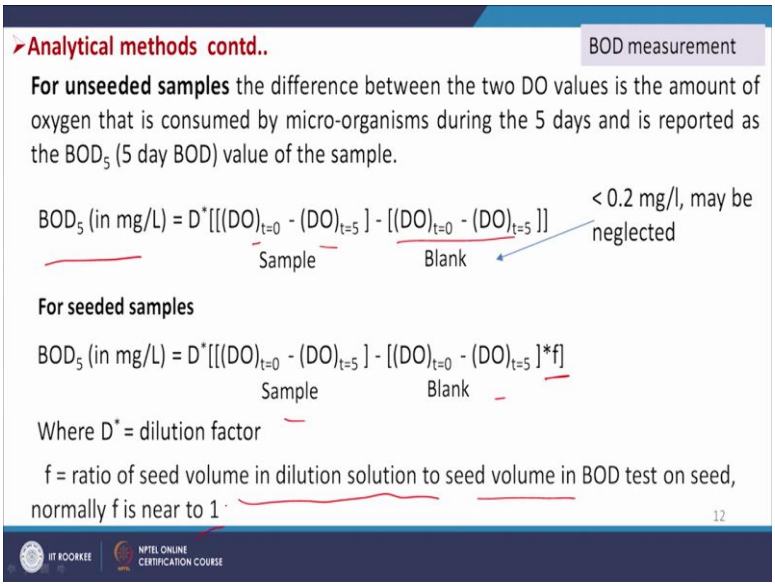

Then how can you calculate the BOD we can use this formula,

$$BOD_5\left(\frac{mg}{L}\right) = D * [[(DO)_{t=0} - (DO)_{t=5}]_{sample} - [(DO)_{t=0} - (DO)_{t=5}]_{Blank}]$$

so this term that is to correct the error due to the use of dilution order so normally this is very less than 0.2 mg/L and it is neglected. so you will see in many books

$$BOD_5\left(\frac{mg}{L}\right) = D * [(DO)_{t=0} - (DO)_{t=5}]_{sample}$$

Now if seeding is needed for seeded samples

$$BOD_5\left(\frac{mg}{L}\right) = D * [[(DO)_{t=0} - (DO)_{t=5}]_{sample} - [(DO)_{t=0} - (DO)_{t=5}]_{Blank}] * f$$

f is the ratio of seed volume in dilution solution to seed volume in BOD test on seed, normally f is near to 1.

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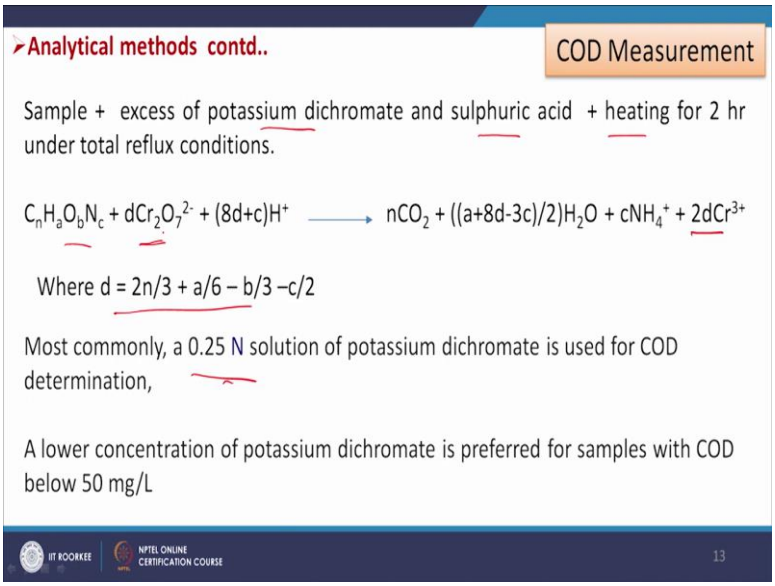

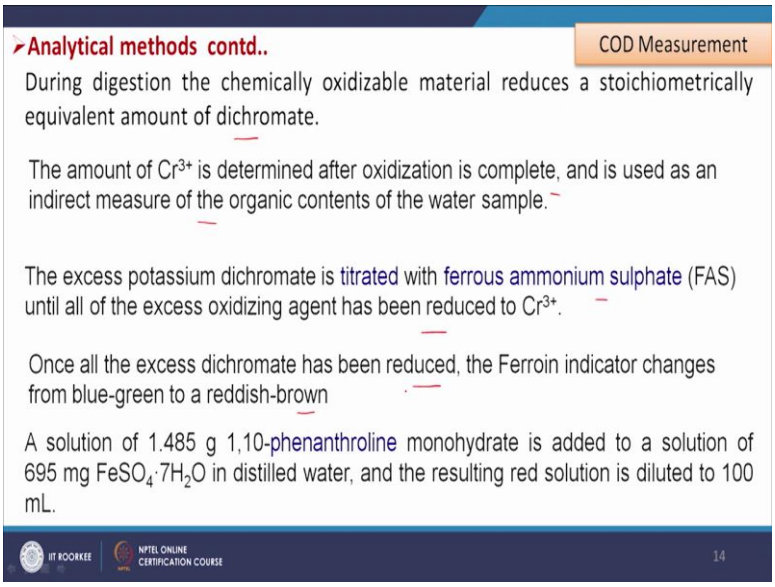

Now COD measurement, sample plus excess of potassium dichromate and sulfuric acid is heated for 2 hours under total reflux conditions. so that is called digestion of the sample with these chemicals and then what happens in this case, now this organic compound is oxidized and dichromate is reduced to chromium. So there is some empirical relationship as shown

here and these coefficients are correlated like this and most commonly 0.25 N solution of potassium dichromate is used for COD determination and excess amount of potassium dichromate is used.

And then after these conversions of this organic compound the Cr_2O_7 is remaining. So that is titrated against some chemical that is ferrous ammonium sulphate and during digestion the chemically oxidizable material reduces a stoichiometrically equivalent amount of dichromate. The amount of $Cr^{3+}$is determined after oxidation is complete and is used as an indirect measure of the organic content of the water sample.

The excess potassium dichromate is filtered, the excess potassium dichromate is titrated with ferrous ammonium sulphate until all of the excess oxidizing agent has been reduced to Cr^{3+}. Once all the excess dichromate has been reduced the Ferroin indicator changes from blue green to reddish brown. So when we are using the ferrous ammonium sulphate for the titration of excess Cr^{3+}so then we can find the end point by this color change of this indicator.

Now we know how much dichromate initially we added now we know how much dichromate is titrated against ferrous ammonium sulphate so balance the remaining one was used for the oxidation of the organic compounds and dichromate was reduced to Cr^{3+} and from that we will be able to determine the COD value.

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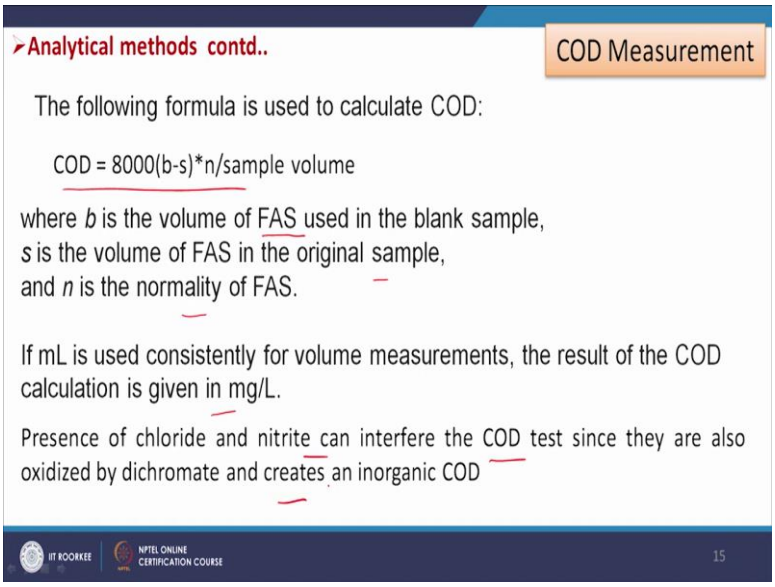

And COD value can be calculated by this expression that is

COD = 8000(b-s)*n/sample volume

where b is the volume of ferrous ammonium sulphate used in the blank sample, s is the volume of ferrous ammonium sulphate in the original sample and n is the normality of ferrous ammonium sulfate. If mL is used consistently for volume measurements the result of the COD calculations is given in mg/L. But presence of chloride and nitrite can interfere the COD test since they are also oxidized by dichromate and creates an inorganic COD.

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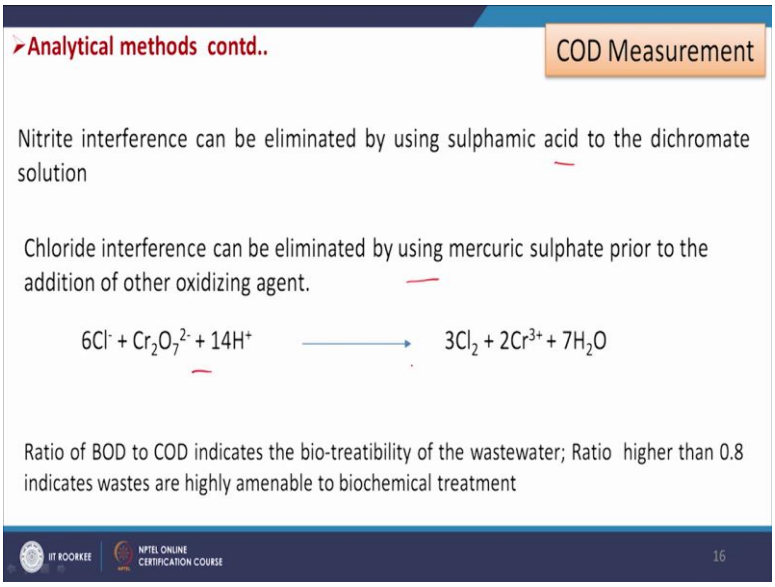

So nitrite interference can be eliminated by using sulphamic acid to the dichromate solution so chloride interference can be eliminated by using mercuric sulphate prior to the addition of other oxidizing agent so these are the reaction.

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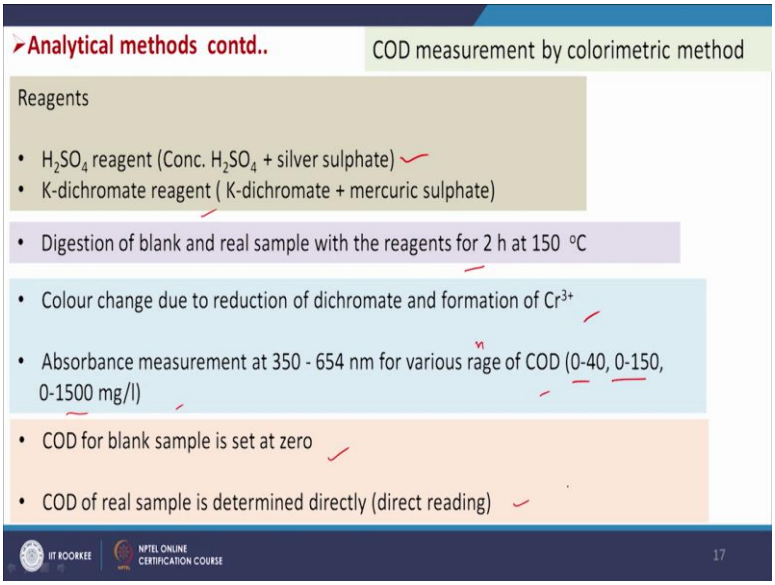

Now the reagents used for the COD measurement are H_2SO_4 then potassium dichromate and digestion of blank and real sample with the reagents for 2 hours at 150 °C, color change due to reductions of dichromate and formation of Cr^{3+} and then absorbance measurement at 350 to 654 nm for various range of COD that is 0 to 40, 0 to 150, 0 to 1500 mg/L, COD for blank sample is set at 0 and COD of the real sample is determined directly.

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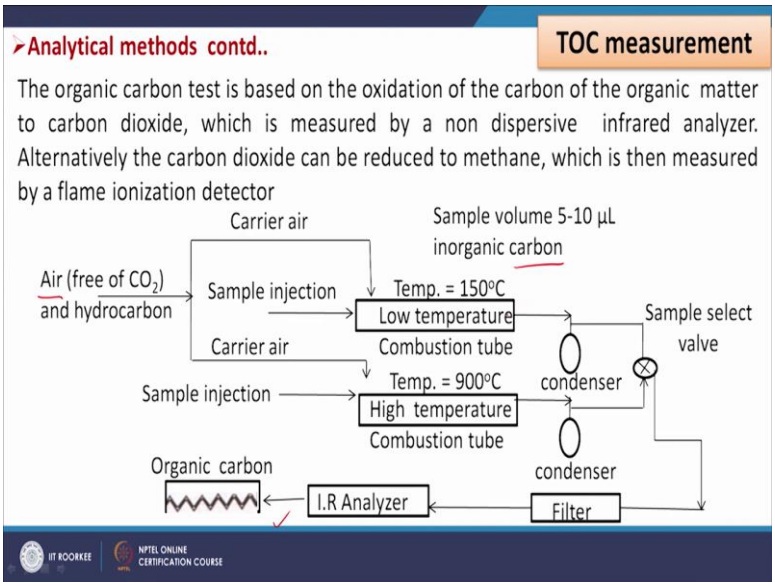

Now we will see total organic carbon determination, so for the determination of TOC we will be using carbon dioxide free air and we will be putting the sample here. So here we are air free from carbon dioxide and hydrocarbon then it is coming here and it is coming here we are putting sample. So sample at high temperature air and hydrocarbon so this will give us high temperature here we are putting the samples and then when we are getting the around 900 °C.

So then our organic compounds present in it that will be converted to carbon dioxide. Here also when it is coming so then but it is at low temperature, at low temperature also so will be getting the some carbon dioxide produced here so this will be for inorganic carbon so inorganic carbon will be converted to carbon dioxide so here at high temperature organic carbon will be converted to CO_2 along with the inorganic, both so when the carbon dioxide is coming here is produced so if we can sense it by IR analyzer.

So, then we can get how much CO_2 is produced and that is proportional to the concentration of the organic compound present in it. And this will give us total and this route will give us inorganic so the difference will give us the total organic carbon present in it.

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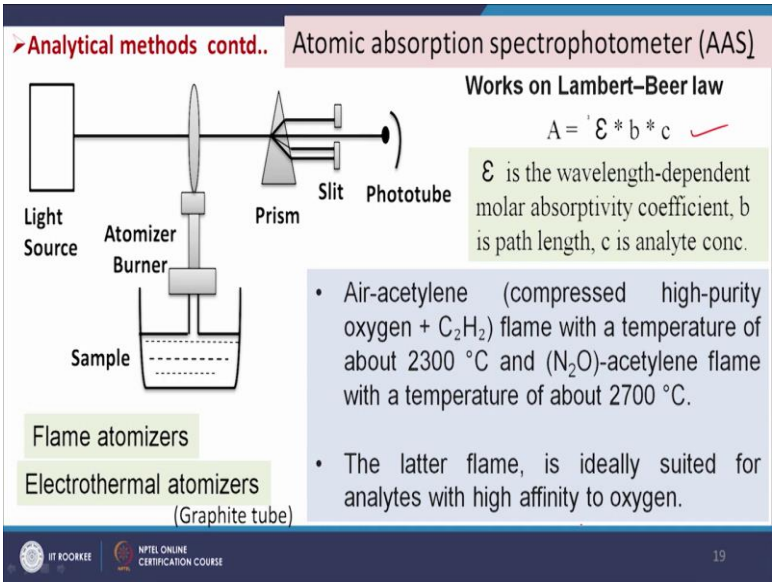

Next atomic absorption spectrophotometer, so atomic absorption spectrophotometer is used to measure the concentration of heavy metals at lower concentration in ppm level. If we want to measure in ppb level then ICP-MS will be more preferred. So in this case of atomic absorption spectroscopy the working principle is Lambert Beers law that is

$A = \varepsilon * b * c$

Where epsilon is the wavelength dependent molar absorptivity coefficient, b is path length c is analyte concentration.

And in this case we need one monochromatic light so then here we are having sample so it will be atomized so light will pass through it then it will be separated and the one prism will be used and then there will be some photo tube. so from the intensity we will be able to measure the concentration of the heavy metals present in it and different lenghts will be used for different heavy metals present in the sample.

And flame atomizers and electro thermal atomizers both are used sometime graphite tube are also used and air acetylene compressed high purity oxygen + C_2H_2 flame with a temperature of about 2300 ^oC and N_2O acetylene flame with a temperature of about 2700 ^oC. So how much temperature is needed that will depend upon the type of heavy metals and to raise this temperature these systems can be used and the latter flame is ideally suited for analyzed with high affinity to oxygen.

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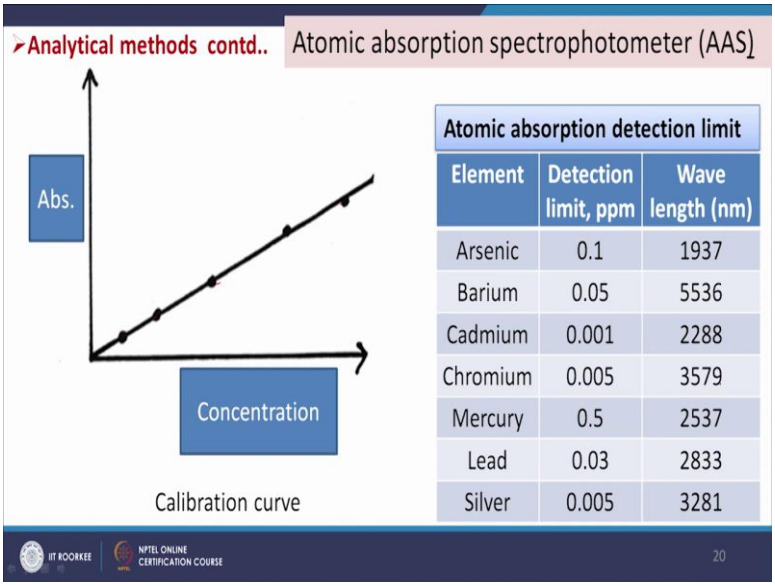

And this is a calibration graph so concentration versus absorbance so these are known concentration so then after knowing the absorbance of any unknown value we can get the value of concentration of it by using this formula for this graph. And some detection limits are given here for arsenic, barium, cadmium, chromium, mercury, lead, silver, etc. we see here all are in ppm level and not in ppb level and the corresponding wavelength is given so this so different lengths we have to use to generate the light of this wavelength.

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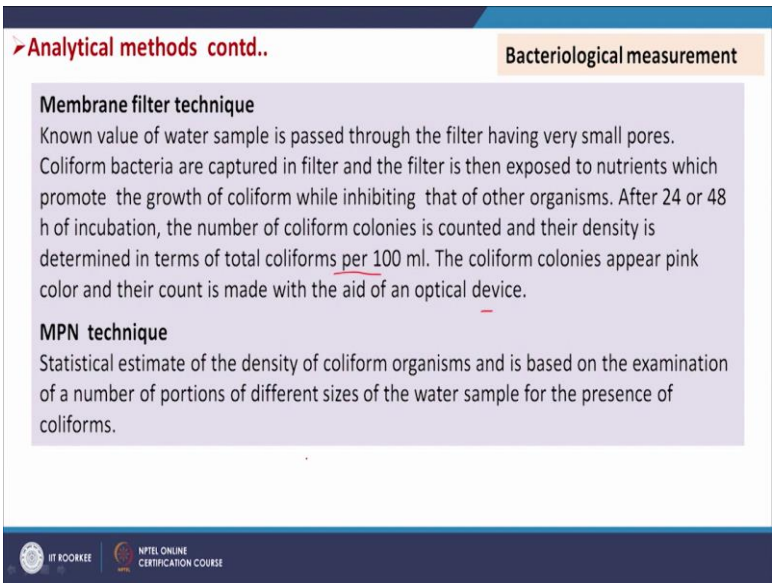

And now we will discuss the bacteriological measurement. So most probable number how many microbes are present in the water that we can determine by some methods that is

bacteriological measurement. So membrane filter technique, so we can filter the sample through a membrane and then we can the material which is available on the surface of the membrane that can be transferred into the broth and then it can be grown and the number of colony can be counted.

And known value of water sample is passed through the filter having very small pores. Coliform bacteria are captured in filter and the filter is then exposed to nutrients which promote the growth of coliform while inhibiting that of other organisms. After 24 or 48 hour of incubation the number of coliform colonies is counted and their density is determined in terms of total coliforms per 100 ml. The coliform colonies appear pink colour and their count is made with the aid of an optical device.

MPN most probable number techniques, so the statistical estimation of the density of coliform organisms and is based on the examination of a number of portions of different sizes of the water sample for the presence of coliforms.

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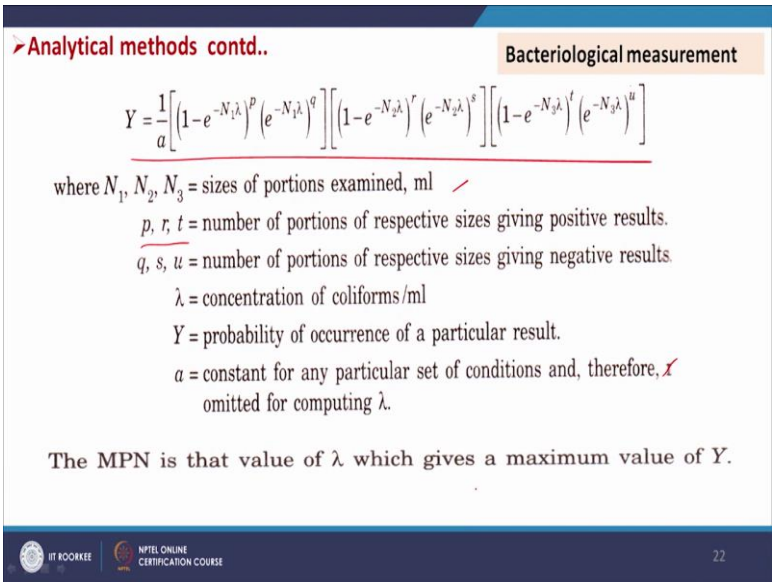

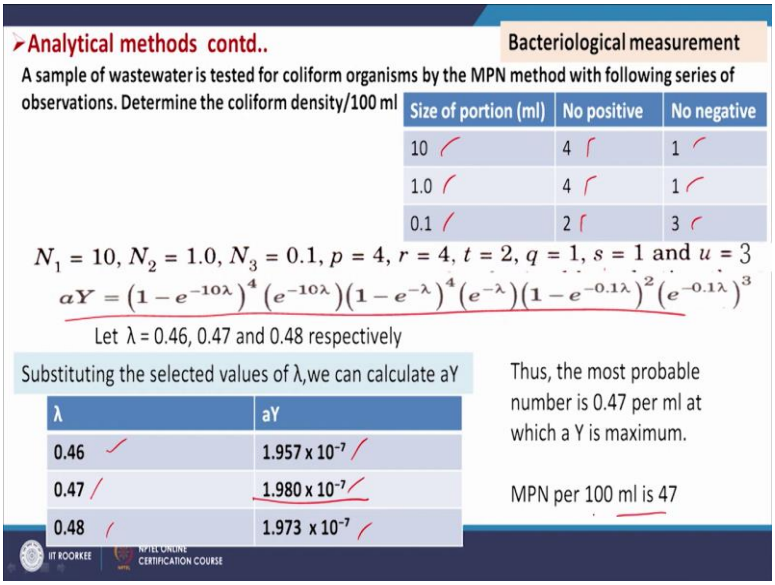

And this expression is used so here

$$Y = \frac{1}{a}\left[(1 - e^{-N1\lambda})^p (e^{-N1\lambda})^q\right]\left[(1 - e^{-N2\lambda})^r (e^{-N2\lambda})^s\right]\left[(1 - e^{-N3\lambda})^t (e^{-N3\lambda})^u\right]$$

Y is the probability of occurrence of a particular result and lambda is the concentration of coliforms per ml and N_1, N_2, N_3 are the size of the portions examined that is ml and p, r, t number of portions of representative sizes giving positive results and lambda and a is the constant for any particular set of conditions and therefore omitted for computing lambda, the MPN is that value of lambda which gives a maximum value of Y.

One some example if we take then it will very clear, so a sample of wastewater is tested for coliform organisms by MPN method with following series of observations determine the coliform density per 100 ml so size of portions is 10 ml, 1 ml and 0.1 ml and total 5 number of samples collected so 4 positive 1 negative for this case, for this case 4 positive 1 negative and for this case 2 positive 3 negative so in the previous expressions which we have we have to identify all the values of all these parameters so here N1 is equal to 10, N2 1 and N3 is equal to 0.1 and then p is equal to 4, r is equal to 4 and t equal to 2 and q equal to 1, s equal to 1 and u equal to 3.

And this was our formula, so in this formula let lambda value is 0.46, 0.47 and 0.48 so by trial and error you can check it and then out of these three examples we see if we calculate the aY value so aY value is giving us for different lambda value so 0.46 it is giving $1.957*10^{-7}$ then for 0.47 it is this one and 0.48 it is this one, so you see out of these three this value is higher so MPN per 100 ml is 47.

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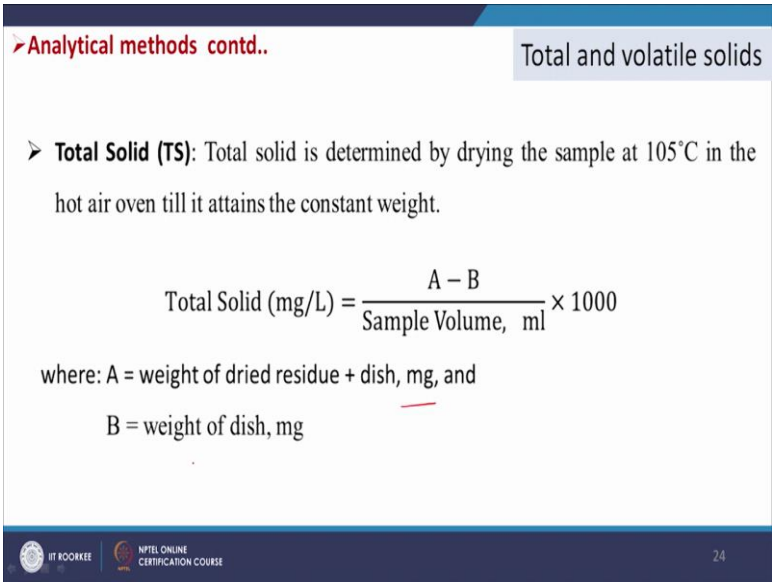

Now total and volatile solids, so total solid is determined by drying the sample at 105 ^{o}C in the hot air oven till it attains the constant weight.

$$\text{Total Solid } \left(\frac{\text{mg}}{\text{L}}\right) = \frac{\text{A} - \text{B}}{\text{sample volume (ml)}} * 1000$$

where A is the weight of dried residue + dish and B is the weight of the dish in mg.

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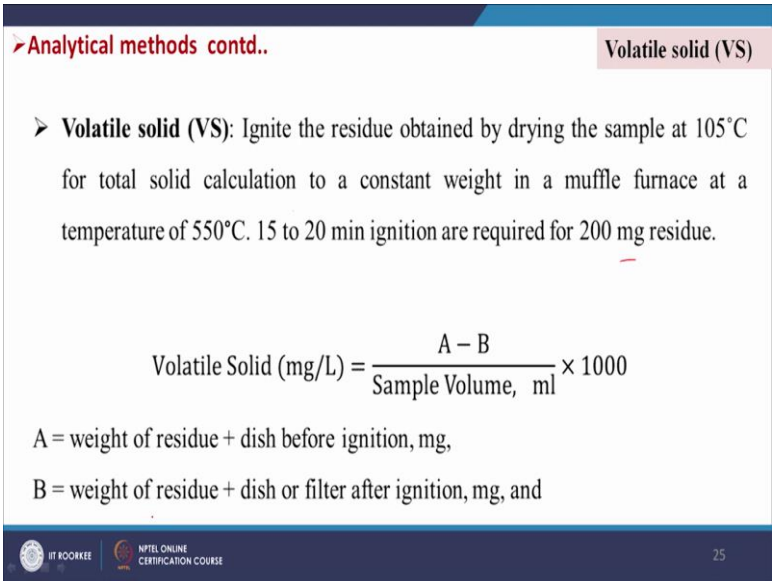

And volatile solid, so ignite the residue obtained by drying the sample at 105 ^{o}C for total solid calculation to a constant weight in a muffle furnace at a temperature of 550 ^{o}C. 15 to 20 minute ignition are required for 200 mg residue

$$\text{Volatile Solid } \left(\frac{\text{mg}}{\text{L}}\right) = \frac{\text{A} - \text{B}}{\text{sample volume (ml)}} * 1000$$

A is the weight of residue + dish before ignition and B weight of residue + dish or filter after ignition (mg). Up to this in this class, thank you very much for your patience.