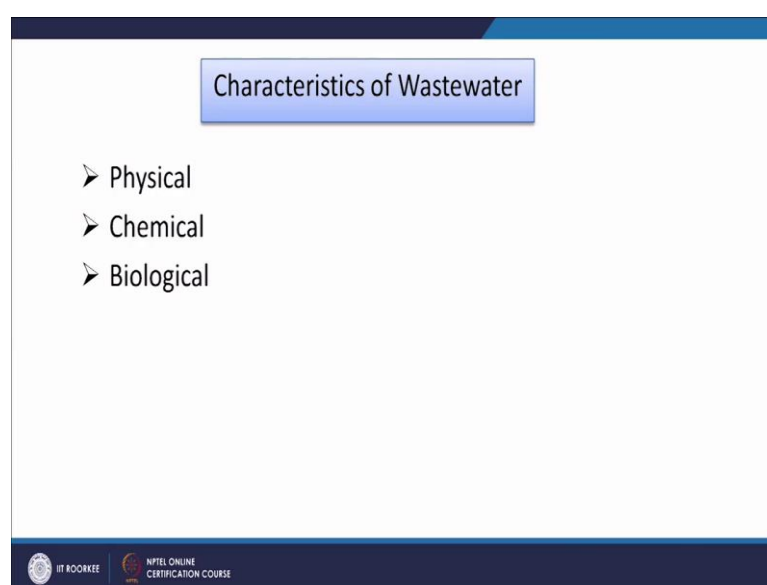


**Waste to energy conversion**  
**Dr. Prasenjit Mondal**  
**Department of Chemical Engineering**  
**Indian Institute of Technology, Roorkee**

**Lecture - 05**  
**Characterization of wastes – 3**

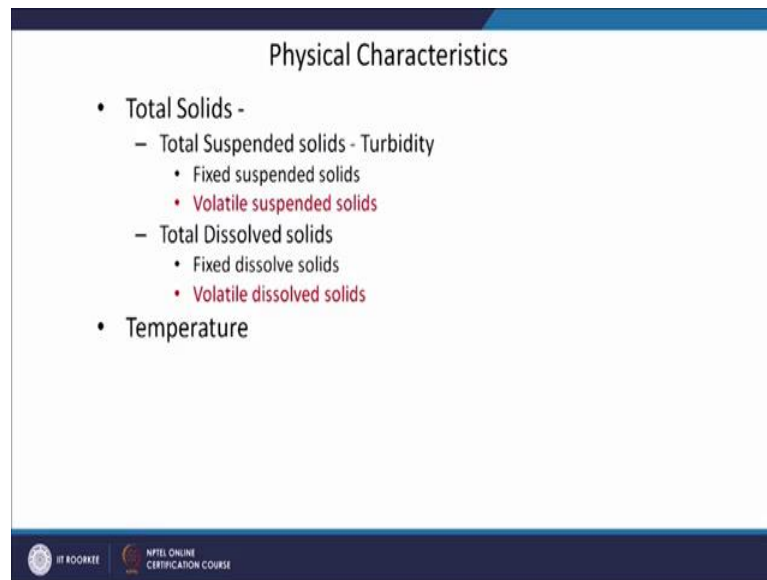
Hi friends. We will now start discussion on the third part of the module; Waste Characterization under the course Waste to Energy Conversion.

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In this part we will discuss on the characterization of waste water, as discussed earlier waste water have different properties or characteristics those can be characterized into 3 category that is physical, chemical and biological properties. Now we will discuss how we can get the values of these different properties or the characteristics.

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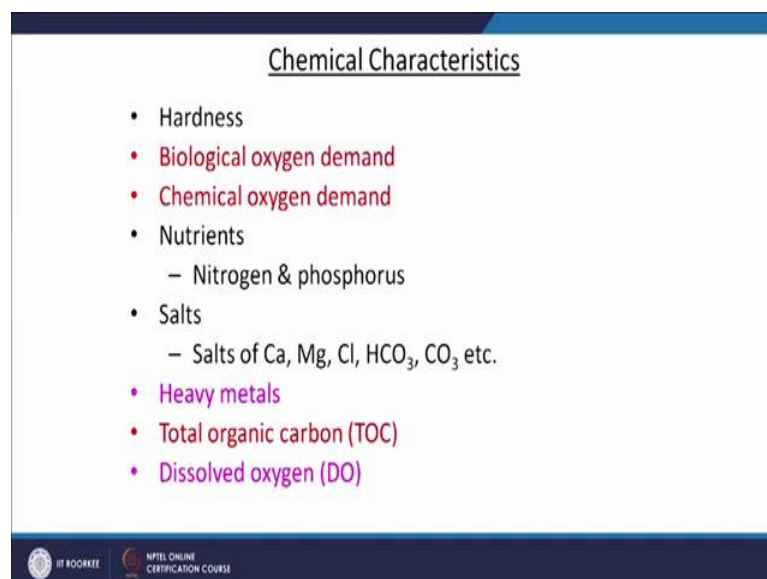
**Physical Characteristics**

- Total Solids -
  - Total Suspended solids - Turbidity
    - Fixed suspended solids
    - Volatile suspended solids
  - Total Dissolved solids
    - Fixed dissolve solids
    - Volatile dissolved solids
- Temperature

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Different physical properties of waste water include temperature, total solids, suspended solids, then dissolved solid, color, taste, odor, these total suspended solids that is TSS and dissolved solid that is total dissolved solid TDS, these may be of 2 types; one is fixed suspended solids and another is volatile suspended solids, but TSS and for TDS those are fixed dissolved solids and volatile dissolved solids these volatile dissolved solids is more important on energy production point of view.

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**Chemical Characteristics**

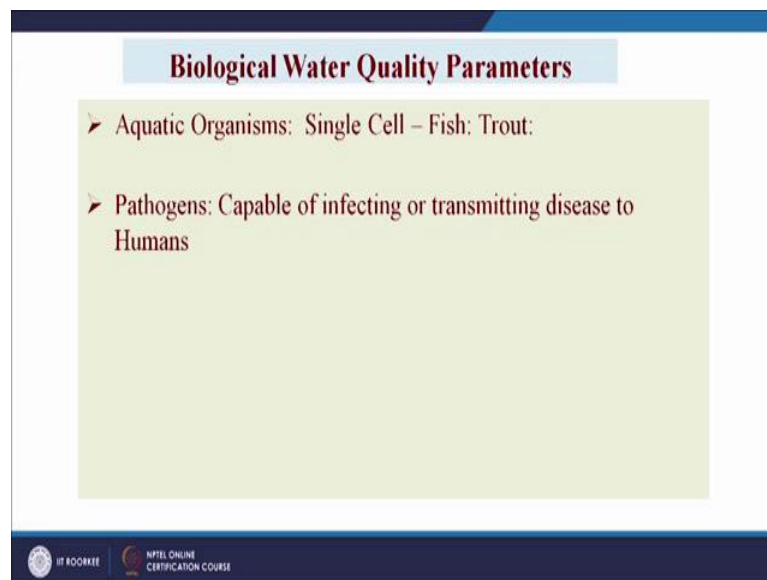
- Hardness
- Biological oxygen demand
- Chemical oxygen demand
- Nutrients
  - Nitrogen & phosphorus
- Salts
  - Salts of Ca, Mg, Cl, HCO<sub>3</sub>, CO<sub>3</sub> etc.
- Heavy metals
- Total organic carbon (TOC)
- Dissolved oxygen (DO)

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Along different chemical characteristics we will see the hardness biological oxygen demand; BOD, chemical oxygen demand; COD, nutrients, nitrogen and phosphorus present in waste water different salts and different ions, Cations and anions, heavy metals total organic carbon and dissolved oxygen.

So, out of these properties the biological oxygen demand chemical oxygen demand and the total organic carbon are very very important on energy production point of view and heavy metals and dissolved oxygen these are also play significant role because heavy metals influence; the growth of the microorganisms and dissolved oxygen is also required for the bacterial degradation.

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If we think about the biological quality parameters of waste water then it may include the aquatic plants animals present in it and like say single cell to fish trout and pathogens physically the microorganisms capable of infecting or transmitting disease to humans. So, these 2 are measured biological water quality parameter, but these are not so much important in terms of energy production. Now we see some important parameters and we will discuss the analytical methods or other methods through which we can give the value of these parameters.

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**Analytical methods**

1. TSS – Turbidity meter
2. Colour – Spectrophotometer
3. Odour -Threshold odour number (TO)  
Dilution of the sample till a barely perceptible odour is achieved.
4. TO -[(ml of sample + ml of odour free water)/ ml of sample]
5. TDS- Gravimetric or conductivity meter
6. Alkalinity – pH meter
7. Inorganic substances (nitrate/ nitrite , sulphate/sulphite, phosphate, halides etc) – Chemical methods/ spectrometer
8. Trace metal – AAS / ICP-MS

➤ DO measurement	➤ COD measurement
➤ BOD measurement	➤ TOC measurement

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So, here TSS that is total suspended solids of any waste water is measured indirectly by measuring the turbidity. So, turbidity meter is available using turbidity meter we will measure indirectly the total suspended solids and TDS total dissolved solids we can measure it through gravimetric method or conductivity meter. So, gravimetric analysis means we will apply heat. So, water will be vaporized. So, the residue will be on the container and we will get that weight difference and get the weight of the TDS present in the waste water sample now TDS may be of fixed TDS and volatile TDS.

So, once we are heating the waste water at 105 centigrade. So, that all the water is vaporized and the residual part is remaining and after constant weight. So, that is the total TDS and out of this total TDS, if we further apply heat say around 550 degree centigrade for certain times around 15 to 20 minutes see then we will get some difference of this weight because of the volatilizations of the TDS of which are volatiles in nature.

So, that weight loss is volatiles due to the volatiles and the remaining is for fixed TDS alkalinity we can measure it by pH meter and the color we can measure it by spectrophotometer then odor measurement test is done by its dilution and threshold number threshold odor number is one parameter which has been derived that is ml of sample plus ml of odor free water. So, we will be taking odor free water and we will also be mixing this odor free water with the sample water and we will test the odor of it and we will be diluting this until we can get a wearily perceptible odor. So, that is our

threshold limit and by definition TO is equal to ml of sample plus ml of odor free water divided by ml of sample.

Now, inorganic substances like say Cations and anions those can be measured by different chemical methods as well as analytical methods. So, spectrophotometer is used for this and for the measurement of the concentration of heavy metals atomic absorption spectroscopy and ICP-MS Inductively coupled plasma mass spectroscopy is used when very low concentration is required then we can go for ICP-MS otherwise AAS atomic absorption spectroscopy is a suitable one another parameters which are more important when we think about the energy production from waste water those are DO dissolve oxygen BOD biological oxygen demand COD chemical oxygen demand and TOC total organic carbon. So, we will be putting more emphasis on the measurement of these DO, BOD, COD, TOC and also the trace metals.

Now what is DO? Dissolve Oxygen. So, any waste water sample will be having some dissolve oxygen because air is diffused from air to the water through the surface of the water and always certain amount of oxygen is present as dissolve oxygen in the waste water the value of this DO for surface water at normal conditions it around nine to ten ppm, but it varies depending upon the conditions now our objective is to determine the concentration of dissolve oxygen.

So, we have to develop some methodology may be in through some chemical methods or may be using some instrument. So, the chemical methods which was first used for this determination of dissolve oxygen that was Winkler's method and in this method  $Mn^{2+}$  plus containing salts is added in certain amount of water in excess amount and potassium iodide is also added in alkaline medium, under this conditions  $Mn^{2+}$  present in the solutions is converted to  $MnO_2$  in aqueous and this  $MnO_2$  aqueous forms brown precipitate and here one mole of oxygen reacts with one mole of  $Mn^{2+}$  plus. Now on this  $MnO_2$  brown precipitate is further dissolved into solution by adding acid.

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DO measurement



Winklers Method

- An excess of manganese(II) salt, iodide ( $I^-$ ) and hydroxide ( $OH^-$ ) ions is added to a water sample. DO converts from  $Mn^{2+}$  to  $MnO_2$  (brown precipitate)

$$Mn^{2+} + O_2(aq) \longrightarrow MnO_2(aq)$$

- The brown, Manganese-containing precipitate is dissolved back to the solution by addition of acid and under this condition iodide ion is converted into elemental iodine.

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

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So, when this acid is added to dissolve the  $MnO_2$  in the solution then that  $Mn$ ,  $MnO_2$  reacts with iodide ions in presence of  $H^+$  and forms iodine now here one mole of iodine is produced from one mole of  $MnO_2$  and one mole of  $MnO_2$  is produced from one mole of oxygen. So, amount of iodine which is produced now in the solution is equivalent to the amount of oxygen in terms of moles present in the waste water or any water sample.


Now we have to quantify the iodine present in the solution and for this purpose it is titrated with sodium thiosulfate. So, sodium thiosulfate converts iodine to iodide and it is converted to tetrathionate. So, this when the iodine is present if we use starch indicator will get some blue coloration.


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Winklers Method

- Liberated  $I_2$  is chemically equivalent to the original DO, which is determined by titration with sodium thio - sulphate with a starch indicator,  
$$2 S_2O_3^{2-}(aq) + I_2 \rightarrow S_4O_6^{2-}(aq) + 2 I^-(aq)$$
- 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.

- Presence of **nitrites of iron in +2 state** in original solution can interfere with the original DO Determination. **Suspended solids** can also interfere.
- Use of azide, permanganate and alum are made to remove the interference due to nitrite, ferrous iron and suspended solid respectively.

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So, when the iodine concentration is reduced and it is converted to iodine at end point that color will change it will be colorless. So, we will get the end point and then from the end point calculation we will get the strength and volume of thiosulfate used and correspondingly iodine reacted with this thiosulfate we can calculate by this reaction and equivalent amount of oxygen is also present in the waste water. So, this is the method for the determination of DO through Winkler's method.

In this method there are some possibility of interferences like say presence of nitrides iron ferrous salt plus 2 state even suspended solids can interfere the on the concentration of D o. So, some correction is required that is we have to add some other chemicals like say some azide permanganate and alum are used to remove the interference due to nitride ferrous iron and suspended solids. So, this is the procedure for the determination of DO though Winkler's method. Nowadays with the advancement of the instrumentation some instruments like DO meter is available to directly measure the concentration of DO dissolve oxygen in the water or waste water sample.

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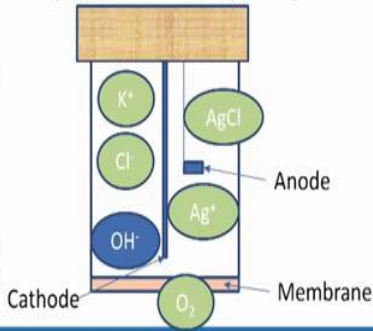
**DO measurement by membrane electrode method**

In a typical dissolved oxygen sensor, two electrodes, a gold cathode and a silver anode, are immersed in a specially prepared electrolyte solution and separated from the sample to be measured by a gas permeable membrane.

The transfer of oxygen across the membrane is proportional to the partial pressure of oxygen in the fluid.

The chemical reactions that accompany this process are as follows:  
Gold cathode:  $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$   
Silver anode:  $Ag + HCl \rightarrow AgCl + e^- + H^+$

The resulting current flow is directly proportional to the dissolved oxygen content of the stream.



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In this case one DO sensor is used in DO sensor a specific electrolyte is used that is made of KCL specific strength of KCL that is used in the electrode; in a cell. And then in this cell we have 2 electrodes one is anode and another is cathode the anode is made of silver and cathode is made of gold and this chamber is separated with the sample water or waste water through gas permeable membrane. So, now, oxygen which is dissolved in water sample that will pass through this permeable membrane and when KCL is used, so, silver of anode is converted to Ag plus and forms AgCL and emits electron. So, this electron which is emitted here by the anode that electron helps to react oxygen with H<sub>2</sub>O water molecules to form o h minus in the cathode cathodic part.

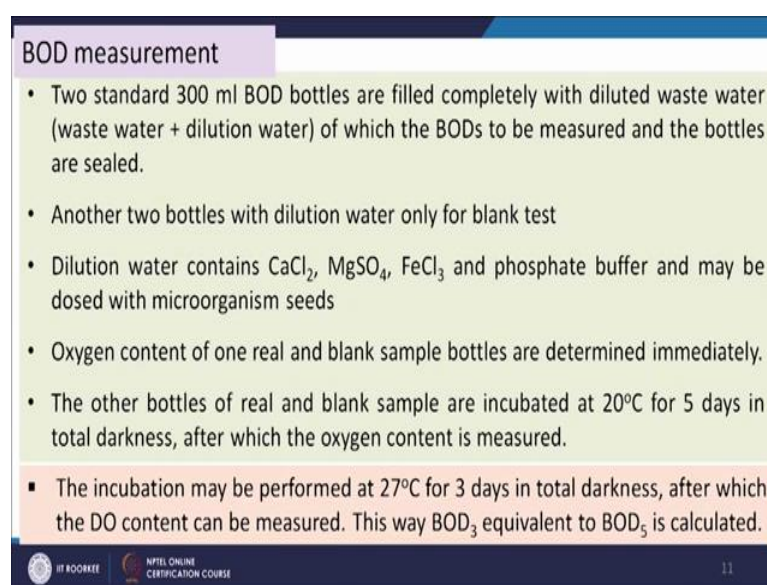
So, we will get one current and that current flow is directly proportional to oxygen concentration which is diffused or oxygen which is diffused through the membrane or in short the concentration of dissolve oxygen in the water. So, directly we can get the dissolved concentration of the waste water using this DO probe next important property is BOD that is biological oxygen demand. And we have discussed earlier that BOD is nothing, but the amount of oxygen required for a waste water sample for the degradation of organic compounds present in it by the micro or microorganisms present in it.

So, for this purpose obviously we need to determine the dissolve oxygen or DO value at initial stage and DO value after certain stage. So, differentiating the value of DO will be

give us the oxygen reduced due to the oxidations of the organic compounds; that means, that will be proportional to the organic compounds present in it.

Now how to do? So, for doing, we have to take 2 BOD bottles and 2 BOD bottles said around 3 hundred ml BOD bottles we will put sample water plus dilution water and make 300 ml volume 2 BOD bottles and DO content of one bottle will be tested immediately and DO a dissolve oxygen content of another bottle will be tested after 5 days incubation and incubations will be done at 20 degree centigrade in a dark place in total darkness.

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**BOD measurement**

- Two standard 300 ml BOD bottles are filled completely with diluted waste water (waste water + dilution water) of which the BODs to be measured and the bottles are sealed.
- Another two bottles with dilution water only for blank test
- Dilution water contains  $\text{CaCl}_2$ ,  $\text{MgSO}_4$ ,  $\text{FeCl}_3$  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 sample are incubated at 20°C for 5 days in total darkness, after which the oxygen content is measured.
- The incubation may be performed at 27°C for 3 days in total darkness, after which the DO content can be measured. This way  $\text{BOD}_3$  equivalent to  $\text{BOD}_5$  is calculated.

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This is dilution water is required to reduce the concentration of the organics present in the waste water if it is in higher extent and the ratio of waste water and dilution water will vary depending upon the initial concentrations of the waste water that is solid organic solid concentration or BOD value in the waste water.

this dilution water contains calcium carbonate magnesium sulfate ferric chloride and phosphate buffer 2 blank test are also done in this to blank test another 2-300 ml BOD bottles are used and filled with dilution water only no waste water this is done because to remove the errors because the dilution water may have some organics theoretically and it may have consumed some oxygen, to reduce that the blank test are done. So, out of these 2 blank test the DO of one test is measured on DT equal to 0 for the same day and another is for T equal to 5 on the 5 days. These 5 days incubation at 20 degree centigrade can be replaced by incubation for 3 days at 27 degree centigrade. So, BOD in this case

we can get 3 D BOD or BOD 3 and the first case we get BOD 5 or a 5 D BOD, but it has been proved that under this 2 conditions almost BOD 3 and BOD 5 values become similar.

One thing is done if some specific organics are present in waste water the specific microorganisms may be added. So, some seeding of microorganisms is also necessary in some cases for the determination of BOD 5 or BOD 3 and when we are carrying the Seeds the formula for calculation BOD 5 changes slightly here we see how it changes.

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

Sample                      Blank

30ml waste water + 270 ml dilution water = 300 ml

300ml - 5ml Seeding Dilution = 300 ml

270 ml Dilution + 30 ml w. water = 300 ml

$D = \frac{300}{30} = 10$

So, for unseeded samples the BOD 5 can be calculated as BOD 5 is equal to D that is dilution factor BOD 5 is equal to D dilution factor into DO dissolve oxygen at T equal to 0ed it minus dissolve oxygen T equal to 5D it for sample minus DO T equal to 0 minus DO T equal to 5 for blank for blank D equal to D is the dilution factor. So, for example, for example, say we have taken thirty ml of waste water thirty ml of waste water waste water plus 270 ml of dilution water. So, it will give us 300 volume 300 ml.

Now out of this 300, 330 ml, we had now the volume is 300. So, dilution factor dilution is equal to 300 by 30 that is equal to 10 times. So, that way we calculate the D, now D into DO at T equal to 0 and at T equal to 5 per sample minus DO for T equal to 0 and DO for T equal to 5 for blank. Now these values DO for blank sample at T equal to 0 and T equal to 5 is not much it is normally less than 0 point 2 mg per liter. So, in many cases this is ignored and directly BOD 5 is calculated by this formula, but when seed seeding is

done means microbes are added externally in that case the formula changes to some extent this is similar only here we have to multiply by some f some factor we have to multiply it by some F.

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**For unseeded samples** the difference between the two DO values is the amount of oxygen that is consumed by micro-organisms during the 5 days and is reported as the BOD<sub>5</sub> (5 day BOD) value of the sample.

$$\text{BOD}_5 \text{ (in mg/L)} = D^* \left[ \underbrace{[(\text{DO})_{t=0} - (\text{DO})_{t=5}]}_{\text{Sample}} - \underbrace{[(\text{DO})_{t=0} - (\text{DO})_{t=5}]}_{\text{Blank}} \right]$$

< 0.2 mg/l, may be neglected

**For seeded samples**

$$\text{BOD}_5 \text{ (in mg/L)} = D^* \left[ \underbrace{[(\text{DO})_{t=0} - (\text{DO})_{t=5}]}_{\text{Sample}} - \underbrace{[(\text{DO})_{t=0} - (\text{DO})_{t=5}]}_{\text{Blank}} * f \right]$$

Where D\* = dilution factor

f = 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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So, this f is equal to what f is the ratio of seed volume in dilution solution to seed volume in BOD test on seed normally it is around one. So, in this case say said in 270. So, we can consider that the seed volume in dilution water say out of 300 ml, we may have 5 ml seeds. So, 270 ml we may have 5 or we can say here we are considering 5 ml we are adding. So, it is in 300 ml per dilution or say for the real sample we are adding 270 ml dilution water plus 30 ml of waste water; waste water. So, here we are having seed is equal to 5 into 270 divided by 300 which is present in 300 ml of this. So, that is in that way this way we can calculate the f value the ratio of it, but f value is normally near to one that is why directly we can put this formula putting f particularly when dilution is very high.

Now, we will discuss on COD measurement. So, COD is chemical oxygen demand. So, for the measurement of COD, we have to oxidize the organic compounds present in waste water by chemical means and potassium dichromate is normally used for the oxidation of the organic compounds present in the waste water. So, that potassium dicarbonate is reduced to chromium 3 as for the reactions as shown here. So, this is

organic; organic compound is converted to chromium 3 plus and CO<sub>2</sub> and H<sub>2</sub>O and NH<sub>4</sub><sup>+</sup> plus now if we take 2 samples one is waste water and another is blank distilled water.

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**COD Measurement**



Sample + excess of potassium dichromate and sulphuric acid + heating for 2 hr under total reflux conditions.

$$C_nH_aO_bN_c + dCr_2O_7^{2-} + (8d+c)H^+ \longrightarrow nCO_2 + ((a+8d-3c)/2)H_2O + cNH_4^+ + 2dCr^{3+}$$

Where  $d = 2n/3 + a/6 - b/3 - c/2$

Most commonly, a 0.25 N solution of potassium dichromate is used for COD determination,

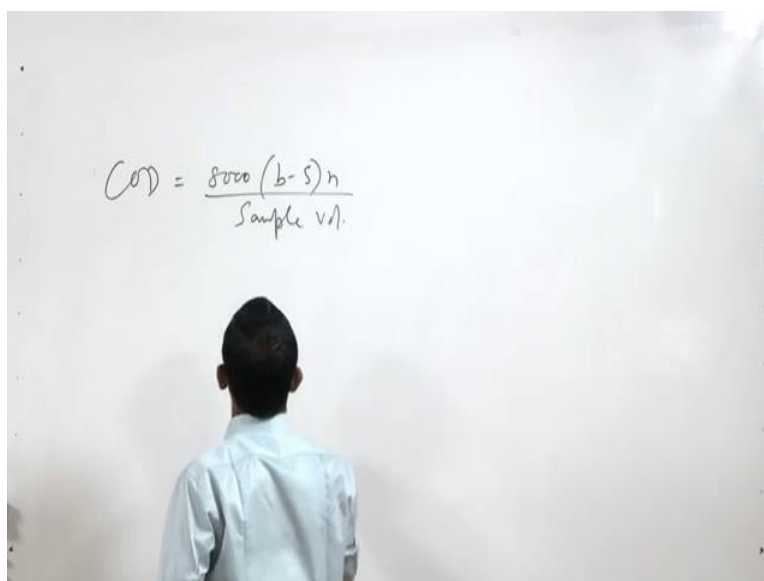
A lower concentration of potassium dichromate is preferred for samples with COD below 50 mg/L



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So, distilled water having will have no organic compounds, but the waste water will be having. So, when we will be using dicarbonate in acid media and we will allow the 2 samples for digestions that is 2 hour heating under total reflux conditions. So, some of the dichromate will be reduced in the real water sample, but in blank that will not be reduced.

Then we will be following some titration method to know the remaining concentration of the potassium dichromate and that is done by using ferrous ammonium sulfate and there will be some end point and from the end point will be calculating the amount of ferrous ammonium sulfate consumed and ferrous ammonium sulfate consumed will be proportional to remaining potassium dichromate. So, that way we can calculate for the blank total dichromate and for the real estate for sample the remaining dichromate. So, by differentiating these two, we can get the dichromate which is consumed by the organic compounds further oxidation and we can get the value of COD.

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Here the formula which is used to calculate COD is equal to 8,000 into b minus s into n divided by volume of sample volume; sample volume, what is b? B is the volume of; it is used in blank sample and s is the volume of ferrous ammonium sulfate used in case of real sample. So, b is more than s and n is the normality of the f s. So, if we put all those things in ml then the cod value will be in mg per liter in this case also the presence of chloride and nitrate nitride can interfere cod test since they are also oxidized and contribute some inorganic cod chlorine and nitride.

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The following formula is used to calculate COD:

$$COD = 8000(b-s)*n/\text{sample volume}$$

where *b* is the volume of FAS used in the blank sample,  
*s* is the volume of FAS in the original sample,  
and *n* is the normality of FAS.

If mL is used consistently for volume measurements, the result of the COD calculation is given in mg/L.

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, nitride interference can be eliminated by using sulphamic acid and to reduce the chloride interference mercurus sulfate is used.

Now, with the development of the instrumentation again in this case also using some colorimetric method directly cod value can be calculated or determined what happens in this case the chromium 3 plus which is produced during oxidation process that is proportional to the organic compound present or oxidized during this reaction. So, during this process the conversion of dichromate to chromate the change of the solution change takes place and for blank and for real sample different color we get and now for c f 3 plus the color intensity is proportional to the concentration of Cr 3 plus.

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**COD measurement by colorimetric method**

**Reagents**

- $\text{H}_2\text{SO}_4$  reagent (Concn.  $\text{H}_2\text{SO}_4$  + silver sulphate)
- K-dichromate reagent ( K-dichromate + mercuric sulphate)

• Digestion of blank and real sample with the reagents for 2 h at 150 °C

• Colour change due to reduction of dichromate and formation of  $\text{Cr}^{3+}$

• Absorbance measurement at 350 - 654 nm for various rage of COD (0-40, 0-150, 0-1500 mg/l)

• COD for blank sample is set at zero

• COD of real sample is determined directly (direct reading)

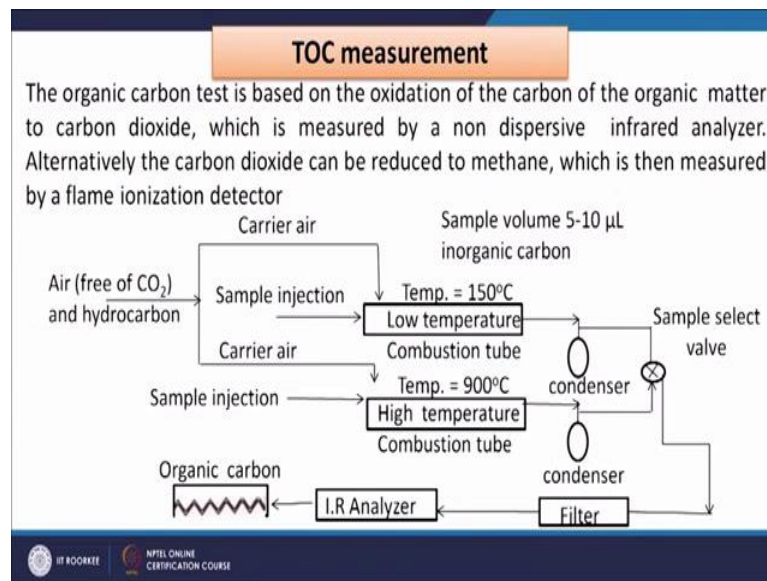
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So, if we use a light of certain absorbance which is applicable for Cr 3 plus then the absorbance value will give us the indication of the oxygen used or the organic compound present and there is some calculations and some softwares are available in the machines that convert these absorbents to cod and directly gives us cod value for blank test this is put 0 and for real sample this is determined directly.

Next we will see the TOC; total organic carbon measurement. So, total organic carbon organic carbon present in the solution if we apply heat then those will be converted to  $\text{CO}_2$ . So, if we use carbon dioxide free air and hydrocarbons and this burn or combustion takes place and very small amount of sample is injected then C present in it will be converted to  $\text{CO}_2$ . So, if the temperature is less then inorganic C is converted to  $\text{CO}_2$ ,

but if temperature is high then organic carbon is converted to CO<sub>2</sub> then that CO<sub>2</sub> after condensing the gas means the H<sub>2</sub>O will be removed and then only this free CO<sub>2</sub> will be going through the off gas and that CO<sub>2</sub> concentration can be used by using non dispersive infrared analyzer or that CO<sub>2</sub> can be converted to methane and that methane concentration can be measured and indirectly TOC can be determined.

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So, that way when we will be using only 150 degree centigrade temperature then we will get inorganic TOC and when we will be using nine hundred centigrade we will be getting both by difference we will get the organic TOC. So, these are the very important parameters for waste water on energy point of view that is DO BOD cod and TOC.

So, we have discussed and we have come to know how we can get the values of these characteristics of waste water.

Thank you very much.