

## Lab - 5

### 1.1 Dissolved Oxygen (DO)

#### Standardization of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> Solution

Potassium bi-iodate (KH(IO<sub>3</sub>)<sub>2</sub>) is first reduced to an equivalent amount of iodine by the addition of KI. This iodine is then quantified by titration with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> as described in experiment 5A.

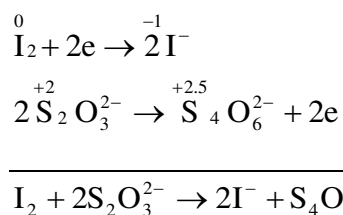
*Note: Write the relevant equations for the above reactions.*

#### Procedure:

- Accurately prepare a 0.0021 M KH (IO<sub>3</sub>)<sub>2</sub> solution. Label, "**Standard KH (IO<sub>3</sub>)<sub>2</sub> Solution**". (This solution will be available in the laboratory).
- To 80 mL of distilled water add 1 mL of concentrated H<sub>2</sub>SO<sub>4</sub>, 10 mL of
- KH (IO<sub>3</sub>)<sub>2</sub> and approximately 1 g of KI.
- Titrate with 0.025 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> until the color is almost discharged.
- Add 1 mL of starch indicator and titrate until the blue color is discharged. Note the volume of titrant required.
- Based on the volume of titrant required, calculate the actual strength of the Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution.
- Using the above strength of the Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution, calculate the strength of the iodine solution used in experiment 5A.

#### Titration of Iodine with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>

Iodine may be reduced to I<sup>-</sup> when titrated with sodium thiosulfate. The relevant equations are as follows:



Starch is used as an indicator. Starch combines with iodine to give a dark blue colour. When thio-sulphate is added to this solution, it extracts iodine from the iodine-starch complex and reduces it to iodide. Once all iodine is thus extracted, the blue colour of the solution is discharged, signifying the end-point of titration.

#### Procedure:

- Prepare an iodine solution by adding 10 g of iodine to a 150 mL solution containing 10 g of potassium iodide. Let stand overnight. Decant 85 mL and dilute to 1000 mL. Label, "**Standard Iodine Solution**". (This solution will be available in the laboratory).
- To 25 g of soluble starch, add 500 mL of boiling distilled water. Stir and let settle overnight. Add 0.6 g of salicylic acid to the supernatant and store as, "Starch Indicator Solution". (This solution will be available in the laboratory).

- Prepare a 0.025 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution. (This solution will be available in the laboratory).
- Titrate 25 mL of the iodine solution with the thiosulfate solution until the yellow colour is almost discharged.
- Add 1 mL of starch indicator and titrate until the blue colour is discharged. Note the volume of titrant required.

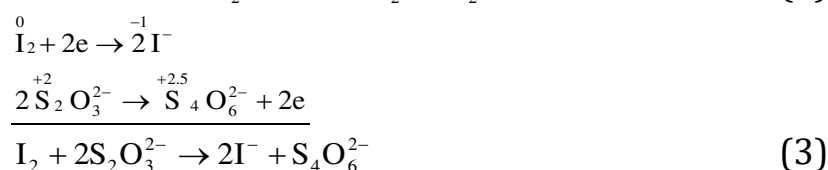
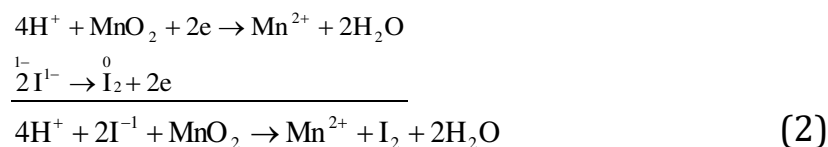
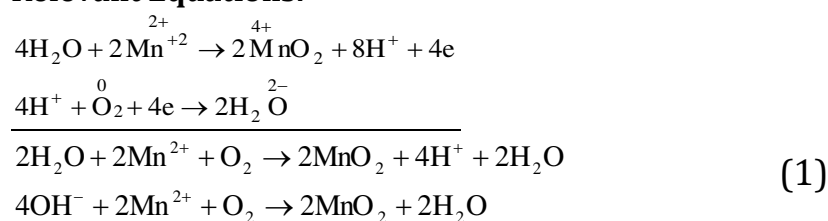
### Dissolved Oxygen Determination:

Dissolved Oxygen (DO) concentration in natural waters is of great importance. Reduction of DO values to less than 4 mg/L results in difficulties and even death for aquatic animals, i.e., fish. The normal DO level of a healthy surface water body ranges from 8-10 mg/L, while the value for groundwater may be as low as 1-2 mg/L. Low DO values may indicate organic pollution and/or presence of reduced species in the water bodies, resulting in DO depletion of the water. DO is generally determined in the laboratory by the **Azide Modification Method**.

### Theory:

- Dissolved oxygen in the sample is converted to an equivalent amount of manganese dioxide (MnO<sub>2</sub>) precipitate by addition of manganous sulphate (see Equation 1 below).
- Precipitated manganese dioxide (MnO<sub>2</sub>) is converted to an equivalent amount of iodine by addition of excess potassium iodide in acidic media (see Equation 2 below).
- Iodine is quantified by titration with sodium thiosulfate in the presence of starch indicator (see Equation 3 below).
- Based on iodine quantification, the dissolved oxygen concentration in the original sample may be calculated.

### Relevant Equations:



### Procedure for Dissolved Oxygen Determination:

- Dissolve **48 g MnSO<sub>4</sub>·4H<sub>2</sub>O** or **40 g of MnSO<sub>4</sub>·2H<sub>2</sub>O** or **36.4 g of MnSO<sub>4</sub>·H<sub>2</sub>O** in distilled water, filter and dilute to 100 mL. Label the

bottle, "**Manganous Sulfate Solution for DO Determination**". (*This solution will be available in the lab*).

- Dissolve **50 g of NaOH** and **15 g KI** in distilled water, and dilute to 100 mL. Add **1 g of NaN<sub>3</sub>** in **4 mL** of distilled water. Mix together. Label the bottle, "**Alkali-Azide-Iodide Reagent for DO Determination of Saturated or Less than Saturated Samples**." (*This reagent solution will be available in the lab*).
- Collect two samples each of "direct" sample and "overhead tank" water in 300 mL BOD bottles.
- To a sample collected in a 300 mL BOD bottle, add **1 mL of MnSO<sub>4</sub> solution**, followed by **1 mL of the alkali-iodide-azide** reagent. When the precipitate has settled sufficiently, add 1 mL of concentrated H<sub>2</sub>SO<sub>4</sub> to the supernatant. Close the bottle and mix until the dissolution of precipitate is complete. **Titrate 200 mL of this sample** with **0.025 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>** solution for iodine quantification adding 1 mL starch Indicator.
- Find the dissolved oxygen concentration (expressed in mg/L O<sub>2</sub>) for the "**direct**" **sample** samples, and samples from the **overhead tank**.

## 1.2 Biochemical Oxygen Demand (BOD)

The five-day biochemical oxygen demand (BOD<sub>5</sub>) at 20°C is the most widely used parameter for quantifying biodegradable organic pollution, applied to both wastewater and surface waters. This determination involves the measurement of the dissolved oxygen used by microorganisms in the biochemical oxidation of organic matter. Biochemical oxidation is a slow process and theoretically takes an infinite time to go to completion. Within a 20-day period, the oxidation is about 95-99 percent complete, and in the 5-day period used for the BOD test, oxidation is 60-70 percent complete.

Thus a sample having biodegradable organic matter, i.e., domestic wastewaters and surface water bodies polluted with wastewaters would have substantial BOD<sub>5</sub>. Also, a sample having more organic pollution should exhibit a higher BOD<sub>5</sub> value.

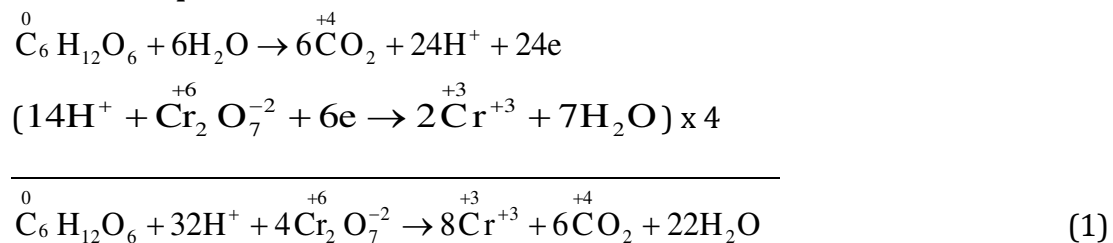
### Estimation of BOD in Water

- Saturate overhead tank water with oxygen by bubbling air through it by using a compressor. Measure dissolved oxygen (DO) concentration in this water. It should be at least 8 mg/L. This is known as **dilution water**.
- Prepare a blank sample (using 300 mL of dilution water only) in a BOD bottle. Incubate for 5 days at 20°C. The DO of the dilution water should not be much different from the initial value. Call this value DO<sub>B</sub>.
- Prepare three samples by adding 5 mL of the wastewater in the BOD bottle, and making up to 300 mL with dilution water. Incubate for 5 days at 20°C. Measure DO in each sample after 5 days. Call this value DO<sub>i</sub>.
- Derive the expression for BOD<sub>5</sub> based on these DO values and extent of dilution of the wastewater sample.

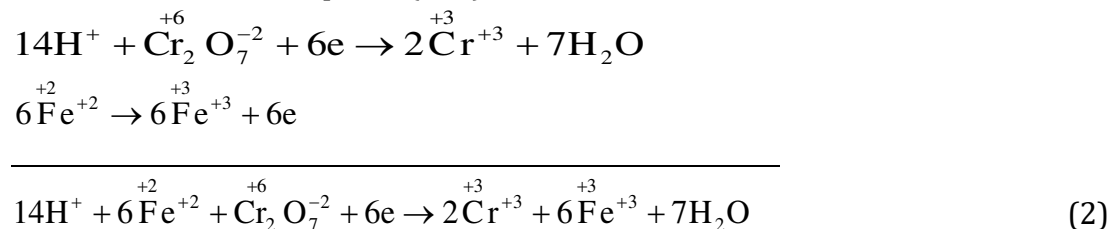
### Understanding About Organic Matter and Oxygen Demand in Water

The chemical oxygen demand (COD) is a surrogate parameter for organic carbon content of a sample. The COD value represents the amount of oxygen that will be required to completely oxidize all organic matter in the sample to CO<sub>2</sub>. As an example, let us discuss the COD of glucose solution, which is determined by completely oxidizing glucose by boiling with a known (but excess) amount of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> as the oxidizing agent under acidic conditions.

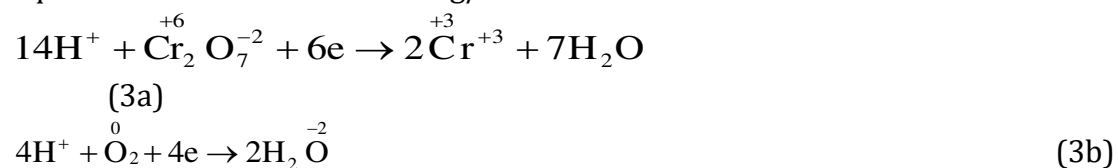
#### Relevant Equations:



The excess K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> remaining in the solution is quantified by titration with ferrous ammonium sulphate (FAS) as follows:



The amount of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> consumed is then expressed in terms of oxygen equivalents and hence COD in mg/L.



### 1.3 Chemical Oxygen Demand (COD)

- Determination of COD is based on the fact that a boiling mixture of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and sulfuric acids (*Similar to Equation 1*) oxidizes most organic molecules to inorganic carbon (+4 oxidation state).
- Thus for COD determination, unknown organic samples are refluxed/digested/boiled in strongly acidic solution with a **known excess volume** of potassium dichromate solution of known strength.
- During this procedure, organic molecules in the sample consume a part of the dichromate (*as in Equation 1*) as they get oxidized to inorganic carbon, while the rest remains un-reacted in the refluxed solution.
- The amount of this excess or un-reacted dichromate remaining after refluxing is determined by titration with a FAS solution of known strength (*as in Equation 2*).

- Thus the amount of dichromate solution consumed by organic matter in the sample can be determined.
- Based on this value, the COD of the solution may be determined (*by comparing Equations 3a and 3b*).

## Estimation of Chemical Oxygen Demand (COD) in Water

### Standardization of FAS solution

- Dilute 10 mL of standard  $K_2Cr_2O_7$  solution (0.0417 M) to about 100 mL.
- Add 30 mL of concentrated  $H_2SO_4$  and cool.
- Add 2-3 drops of ferroin indicator.
- Titrate with 0.1 M (approximately) FAS solution. Prepare the FAS solution by diluting 39.2 gm  $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$  in distilled water at 20 ml concentrated  $H_2SO_4$  cool and dilute to 1000 ml.
- During titration, the colour of the solution changes gradually from orange to green due to reduction of  $Cr_2O_7^{2-}$  to  $Cr^{3+}$  by  $Fe^{2+}$ .
- Then suddenly, the colour of the solution changes from green to red. This is due to exhaustion of  $K_2Cr_2O_7$  in solution, and consequent combination of added  $Fe^{2+}$  with ferroin indicator, resulting in the red coloured complex formation.
- This change in colour signifies the end point of titration.  
Molarity can be calculated as =  
(Vol. of 0.0417M  $K_2Cr_2O_7$  solution titrated, mL/Vol. of FAS used in titration, mL)\* 0.25
- This titration must be done in duplicate.

### Chemical Oxygen Demand by Closed Reflux Method

- Each group will prepare three COD tubes.
- Place 2.5 mL of distilled water in tube 1 and 2.5 mL of wastewater sample in tube nos. 2 and 3.
- Add 1.5 mL of the 0.0167 M **digestion solution**, which is prepared by adding 4.913 gm  $K_2Cr_2O_7$  in 500 mL distilled water with 167 mL concentrated  $H_2SO_4$  and 33.3 gm  $HgSO_4$ . Cool and make up to 1L .
- Prepare **COD acid**: Add  $Ag_2SO_4$  reagent to concentrated  $H_2SO_4$  at the rate of 5.5 gm  $Ag_2SO_4$ /kg  $H_2SO_4$ , let Stand for 1-2 days to dissolve  $Ag_2SO_4$ .
- Add 3.5 mL of COD acid reagent down the inside of each tube, so that an acid layer is formed below the sample-digestion solution layer. Tightly cap the tubes, and mix by inverting each tube several times.
- Heat all three tubes in a block digester for 1 hour.
- Cool to room temperature. Transfer the contents of each tube to a conical flask for titration. Add water if required.
- Titrate  $K_2Cr_2O_7$  in tube 1 with 0.10 M FAS solution using 1 to 2 drops of ferroin indicator. Let this reading be A. Let the corresponding amount of  $K_2Cr_2O_7$  be  $A_1$  moles.

- Titrate excess  $K_2Cr_2O_7$  in tubes 2 and 3 in a similar manner. Let the average of these readings be B. Let the corresponding amount of  $K_2Cr_2O_7$  be  $B_1$  moles.
- Then the amount of  $K_2Cr_2O_7$  consumed by organic matter in the tubes is  $(A_1 - B_1)$  moles.
- Now, based on comparison between equations 3a and 3b, figure out what would have been the number of moles of  $O_2$  consumed (*i.e., corresponding to  $(A_1 - B_1)$  moles of  $K_2Cr_2O_7$* ) if  $O_2$  was used as the oxidizing agent instead of  $K_2Cr_2O_7$ . Report the number of moles of  $O_2$  consumed as mg/L of  $O_2$  that would be consumed by the original wastewater. This is the required COD value.

**COD in mg/L as  $O_2$  = (volume of FAS consumed for blank - volume of FAS consumed for sample) \* Molarity of FAS \* 8000 / volume of sample**

Solve the following problems, which must be attached with the laboratory report.

1. 425 mg of potassium hydrogen phthalate (KHP) is dissolved in 1000 mL of water. Find the theoretical oxygen demand of this solution. Formula of KHP is  $HOOC\overset{+1}{C}\overset{-2}{C}\overset{-2}{C}\overset{+4}{C}\overset{-1}{C}H_4\overset{+1}{C}\overset{+4}{C}\overset{-2}{C}\overset{-2}{C}\overset{+1}{C}OOK$ .
2. Propionitrile has the general formula  $\overset{-2}{C}H_3\overset{-2}{C}H_2\overset{+2}{C}\overset{-3}{N}$ . Assume that it is completely oxidized by dichromate in the COD test.
  - a) Write a balanced equation for reaction of propionitrile with dichromate. Assume that the nitrogen end-product of the reaction is  $NH_3$  (since ammonia is not oxidized to nitrate during refluxing).
  - b) What is the COD of a 50 mg/L solution of propionitrile.
  - c) Add 10 mL of a 500 mg/L solution of propionitrile to a COD flask. Also add 10 mL of 0.1 M  $K_2Cr_2O_7$  plus other necessary reagents. Dilute to 50 mL. What is the molarity of the  $K_2Cr_2O_7$  solution in the COD flask after refluxing is completed. Assume 100 % oxidation of  $CH_3CH_2CN$ .
3. Calculate the theoretical oxygen demand of the following compounds:
  - (i). 100 mg/L solution of phenol ( $C_6H_5OH$ ). (the average oxidation state of C in phenol is  $-2/3$ )
  - (ii). 10 mg/L solution of  $Fe^{2+}$ . Assume  $Fe(OH)_3$  (s) is the end product.

## Lab Exercise - 5

### 5A: Estimation of DO in Water

1. Calculate the amount of Dissolved Oxygen (ppm O<sub>2</sub>) using the following data: **(10 Marks)**
  - Sample volume (mL) = 226
  - Burette Reading, initial (mL) = 3.787
  - Burette Reading, final (mL) = 18.25
  - Volume of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> dispensed (mL) = 14.4 mL
  - Average molar concentration of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (mol/L) = 0.02178
  - Moles of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> dispensed (mol) =
  - Moles of I<sub>3</sub><sup>-</sup> reduced by S (mol) =
  - Moles of O<sub>2</sub> (mol) =
  - Mass of O<sub>2</sub> (mg) =
  - Dissolved oxygen, ppm O<sub>2</sub> (mg/L) =

Round off your final answer to three decimal places.

2. During a titration for the determination of Dissolved Oxygen in water sample, 25mL of water sample consumed 23.8 mL of 0.0248 M thiosulphate solution. Calculate the moles the thiosulphate consumed. What would be the moles of oxygen? **(10 Marks)**
3. If  $1.58 \times 10^{-3}$  moles of O<sub>2</sub> present in 100 mL of sample, calculate the amount of dissolved oxygen present in ppm (mg/L) units. (Atomic Weigh of Oxygen = 16) **(10 Marks)**

### 5B: Understanding Biochemical Oxygen Demand (BOD) in Water

1. What use is made of the BOD test in water pollution control? **(5 Marks)**
2. What factors affect the rate of biological oxidation in the BOD test? **(5 Marks)**

### 5C: Estimation of BOD in Water

1. Compute ultimate BOD and oxygen consumption rate constant using the following data for a stream receiving treated effluent. **(10 Marks)**

Time (days)	BOD exerted at time t (Y <sub>t</sub> )
2	11
4	18
6	22
8	24
10	26

2. To determine BOD of a sample, three dilutions of the samples are made (BOD bottle volume = 300 mL). In the BOD dilution water (without sample), initial DO = 9.5 mg/L (blank). All samples are incubated at 20°C for 5 days. Look at the following data and calculate 5-day BOD value of the sample at 15°C? **(10 Marks)**

$$t\text{-day BOD} = [\text{DO}_t - \text{DO}_0] / (P) \quad (1)$$

where P = Dilution factor = 300mL / (sample volume in mL)

Bottle no.	Wastewater sample (mL)	Initial DO (mg/L) (DO <sub>0</sub> )	DO at 5-day (mL) (DO <sub>5</sub> )
1	20	8.9	1.5
2	10	9.1	2.5
3	5	9.2	5.8
4	2	9.2	7.5

3. In determining the BOD<sub>5</sub> of a sample, an analyst added 2, 5 and 10 mL of sample to three different 300 mL BOD bottles and filled them with seed and dilution water. The analyst also prepared three blank bottles with the same seed and dilution water and incubated the set at 20°C for 5 days. Dissolved oxygen (DO) measurements were made on the samples before and after with the following results.

Sample size in bottle (mL)	Initial DO (mg/L)	Final DO (mg/L)
2	8.1	5.6
5	8.0	1.7
10	8.1	0.0
Blank average	8.2	8.0

What is BOD<sub>5</sub> for the sample?

**(10 Marks)**

## 5D Estimation of Chemical Oxygen Demand (COD) in Water

- 25 mL of sewage water when treated with 50 mL of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution, the residual K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> required 18 mL of 0.25 N FAS solution. Under similar conditions, for blank titration, 30mL of FAS solution is consumed. Calculate the COD of wastewater. **(10 Marks)**
- 50 mL of an industrial effluent has consumed 11.5mL of 0.4N K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution for complete oxidation. Calculate COD of the industrial effluent. **(10 Marks)**



3. The chemical oxygen demand (COD) test is used to characterize the amount of  $O_2$  that the dissolved organic matter in a wastewater could theoretically consume. In a COD test, dichromate ( $Cr_2O_7^{2-}$ ) is mixed with organic matter and allowed to react to form  $CO_2$  and  $Cr^{3+}$ . The Dissolved Oxygen is necessary to mineralize the dissolved organic carbon. **(10 Marks)**

- a. Write the full redox chemical equation for the COD test using perchloroethylene ( $Cl_2C=CCl_2$ ) as the organic matter.
- b. What is the change in the oxidation state of carbon atoms in perchloroethylene?  
What is the change in the oxidation state of the chromium atoms?
- c. If 2 mM of dichromate are consumed in the reaction with perchloroethylene, how much perchloroethene is present?
- d. How much  $O_2$  would be consumed to oxidize this amount of perchloroethene?