

# ENGINEERING CHEMISTRY, 15ECHB102 - UNIT 3 - CHAPTER 8: EVIRONMENTAL CHEMISTRY

# WATER

Water is a colourless and odourless substance found all over the Earth. Water is made up of billions of molecules. Water on our planet flows as liquid in rivers, streams and oceans; is solid as ice at the North and South Poles; and is gas (vapour) in the atmosphere. Water is also underground and inside plants and animals.

# SOURCES AND ILL EFFECTS OF WATER POLLUTANTS

## [1] FLUORIDE:

#### Sources:

- Traces of fluorides are present in many water; higher concentrations are often associated with underground sources.
- In seawater, a total fluoride concentration of 1.3 mg/litre has been reported.
- In areas rich in fluoride-containing minerals, well water may contain up to about mg of fluoride per litre.
- Fluorides may also enter a river as a result of industrial discharge.
- In groundwater, fluoride concentrations vary with the type of rock the water flows through but do not usually exceed 10 mg/litre.

#### Ill Effects:

- Low concentrations provide protection against dental caries, especially in children.
- However, fluoride can also have an adverse effect on tooth enamel and may give rise to mild dental fluorosis at drinking-water concentrations between 0.9 and 1.2 mg/litre;
- In general, dental fluorosis does not occur in temperate areas at concentrations below 1.5–2 mg of fluoride per litre of drinking-water.
- In warmer areas, because of the greater amounts of water consumed, dental fluorosis can occur at lower concentrations in the drinking-water.
- It is possible that in areas where fluoride intake via routes other than drinking water (e.g., air, food) is elevated, dental fluorosis will develop at concentrations in drinkingwater below 1.5 mg/litre.
- Elevated fluoride intakes can also have more serious effects on skeletal tissues.
   Skeletal fluorosis may be observed when drinking-water contains 3–6 mg of fluoride per litre.
- Crippling skeletal fluorosis usually develops only where drinking-water contains over 10 mg of fluoride per litre.



# ENGINEERING CHEMISTRY, 15ECHB102 - UNIT 3 - CHAPTER 8: EVIRONMENTAL CHEMISTRY

## [2] NITRATE:

# Sources:

- Sources of nitrogen and nitrates may include runoff or seepage from fertilized agricultural lands, municipal and industrial waste water, refuse dumps, animal feedlots, septic tanks and private sewage disposal systems, urban drainage and decaying plant debris.
- The largest anthropogenic sources are septic tanks, application of nitrogen-rich fertilizers to turf grass and agricultural processes.
- High levels of nitrate in well water often result from improper well construction, well location, over use of chemical fertilizers or improper disposal of human and animal waste.
- Drinking water with levels of nitrate at or below 10 mg/L is considered safe for everyone.

# Ill Effects:

- High enough concentrations of nitrate in drinking water can result in a temporary blood disorder in infants called "Methemoglobinemia", commonly called "Blue baby syndrome."
- In severe, untreated cases, brain damage and eventually death can result from suffocation due to lack of oxygen.
- Misuse or excessive use of any medicine or product containing nitrates, whether unintentionally or intentionally, can lead to poisoning.
- Poisoning can result from swallowing, inhaling or even skin contact.
- People have been poisoned after drinking nitrate-contaminated rural well water.
- In addition to threats of cancer, nitrate exposure in drinking water can cause a number of health problems such as: high-blood pressure, blood poisoning, thyroid disorders and even severe cyanosis.



ENGINEERING CHEMISTRY, 15ECHB102 - UNIT 3 - CHAPTER 8: EVIRONMENTAL CHEMISTRY

# DETERMINATION OF TOTAL HARDNESS OF WATER USING Na<sub>2</sub>EDTA BY COMPLEXOMETRIC TITRATION

<u>Aim</u>: To estimate the Total Hardness present in the supplied sample of water using Na<sub>2</sub>EDTA by complexometric titration.

Apparatus: Burette, pipette, conical flask, volumetric flask, beakers, funnel and glass-rod.

<u>Chemicals</u>: Disodium salt of ethylene diamine tetra acetic acid crystals, Eriochrome black-T indicator and Buffer solution (Mixture of NH<sub>4</sub>Cl and NH<sub>4</sub>OH).

#### Theory:

**Hardness** is that characteristic property of water, which prevents lather formation with soap solution. There are two types of hardness, viz., temporary and permanent hardness.

**Temporary hardness** of water is due to the presence of soluble salts of bicarbonates of calcium and magnesium in water that can be removed merely by boiling. Boiling of water converts the bicarbonates of soluble salts present in the water into insoluble carbonates and hydroxides of metal ions, which can be removed by filtration.

$$Ca(HCO_3)_2 \rightarrow CaCO_3 \downarrow + H_2O + CO_2$$
  
 $Mg(HCO_3)_2 \rightarrow Mg(OH)_2 \downarrow + 2CO_2$ 

**Permanent hardness** of water is due to the presence of soluble salts of chlorides, sulphates and nitrates of Ca and Mg which cannot be removed by boiling the water. Hence permanent hardness is due to the presence of these salts.

Total hardness of water is the algebraic sum of temporary and permanent hardness and it is expressed in terms of CaCO<sub>3</sub> equivalent hardness in ppm. or mg./lit., because

- The amount of Ca is maximum in the earth's crust compared to any other hardness producing substances.
- Its molecular weight is 100, which makes mathematical calculations easier.
- It is most insoluble salt, thus can be easily precipitated.

Total hardness of water permissible in potable water is 200 ppm. Water samples having Total hardness greater than 250 ppm causes scale deposits in plumbing, boilers and leads to corrosion.

The hardness of water is determined by using Std. disodium salt of EDTA solution and EBT indicator.



# ENGINEERING CHEMISTRY, 15ECHB102 - UNIT 3 - CHAPTER 8: EVIRONMENTAL CHEMISTRY

# **Procedure:**

# • Preparation of Standard Na2EDTA solution:

Dissolve the supplied disodium salt of EDTA ('W'g.) in a 250ml clean beaker by adding four test tubes of warm distilled water. Transfer this solution to 250ml volumetric flask. Wash the beaker 2-3 times with distilled water thoroughly and transfer the same in to the volumetric flask. Dilute up to the mark of the volumetric flask using distilled water. Shake the flask well to make the solution homogeneous. Rinse and fill the burette with the prepared std. disodium salt of EDTA solution.

Weight of disodium salt of EDTA = 'W' g.

Molecular weight of disodium salt of EDTA = 372.24Molarity of disodium salt of EDTA =  $\frac{W \times 4}{372.24}$  = 'x' M.

# • Titration:

Pipette out 50 ml of the supplied hard water sample into a clean conical flask. Add about 5ml of buffer solution, 2-3 drops of EBT indicator and titrate against std. disodium salt of EDTA solution until a sharp colour changes from wine red to purple to clear blue. Note down the burette reading and perform another 2 sets of titrations for accuracy.

| B.R. → B.L. ↓ | I ml. | II ml. | III ml. | Mean BR  |
|---------------|-------|--------|---------|----------|
| Final level   |       |        |         |          |
| Initial level |       |        |         | ' V ' ml |
| Difference    |       |        |         |          |

Calculate the amount of total hardness present in the supplied sample of hard water in terms of calcium carbonate equivalent hardness, in ppm, using the standard conversion factor.



## ENGINEERING CHEMISTRY, 15ECHB102 - UNIT 3 - CHAPTER 8: EVIRONMENTAL CHEMISTRY

# Reactions:

$$(Ca^{2+}, Mg^{2+}) + EBT \rightarrow [Ca-EBT, Mg-EBT]$$
Blue Less stable, wine-red

$$(Ca^{2+}, Mg^{2+}) + 2Na_2EDTA \rightarrow [Mg-EDTA, Ca-EDTA]^{-2} + 4Na^{+}$$
Colourless Stable, colourless

$$(Ca^{2+}, Mg^{2+}) + EBT \rightarrow [Ca-EBT, Mg-EBT] + 2Na_2EDTA \rightarrow [Mg-EDTA, Ca-EDTA]^{-2} + 4Na^+ + EBT$$
Blue Less stable, wine-red Stable, colourless Blue

# Calculation:

The given Conversion Factor is:

1000 ml of 1M Na<sub>2</sub>EDTA solution ≡ 100 g. of CaCO<sub>3</sub> equivalent hardness.

Now, 'V' ml of 'x' M Na<sub>2</sub>EDTA solution 
$$\equiv 0.1 \text{ x 'x' x 'V'} = \text{'y'} \text{ g. of CaCO}_3$$
.

i.e., 50 ml of hard water sample contains = 'y' g. of CaCO<sub>3</sub> equivalent hardness.

Therefore, 1000ml of hard water sample 
$$\equiv$$
 'y' x 1000 = 'z' g./lit. of CaCO<sub>3</sub>

Hence, Total Hardness of water in terms of CaCO<sub>3</sub>, in ppm. = 'z' x 1000 mg/lit. = 'H' ppm.

# Result:

Total Hardness of Water in terms of CaCO<sub>3</sub> equivalent hardness = 'H' ppm.

# NOTE:

- Molecular weight of CaCO<sub>3</sub> = 100
- Equivalent weight of CaCO<sub>3</sub> = 50
- Molecular weight of Ca(HCO<sub>3</sub>)<sub>2</sub> = 162
- Molecular weight of Mg(HCO<sub>3</sub>)<sub>2</sub> = 146
- Molecular weight of CaCl<sub>2</sub> = 111
- Molecular weight of MgCl<sub>2</sub> = 95
- Molecular weight of CaSO<sub>4</sub> = 136
- Molecular weight of MgSO<sub>4</sub> = 120



ENGINEERING CHEMISTRY, 15ECHB102 - UNIT 3 - CHAPTER 8: EVIRONMENTAL CHEMISTRY

# NUMERICAL PROBLEMS ON TOTAL HARDNESS

 Calculate the temporary and permanent hardness of water sample which contains 16.2 mg/lit of Ca(HCO<sub>3</sub>)<sub>2</sub>, 29.2 mg/lit of Mg(HCO<sub>3</sub>)<sub>2</sub>, 33.3 mg/lit of CaCl<sub>2</sub>, 18.0 mg/lit of MgSO<sub>4</sub>, and 55.0 mg/lit of NaCl.

## Given:

- Mass of Ca(HCO<sub>3</sub>)<sub>2</sub> = 16.2 mg/lit
- Mass of Mg(HCO<sub>3</sub>)<sub>2</sub> = 29.2 mg/lit
- Mass of CaCl<sub>2</sub> = 33.3 mg/lit
- Mass of MgSO<sub>4</sub> = 18.0 mg/lit
- Mass of NaCl = 55.0 mg/lit

#### Solution:

- ❖ CaCO3 equivalent = <u>Mass of hardness producing salt X Molecular weight of CaCO3</u> Molecular weight of harness producing salt
  - CaCO<sub>3</sub> equivalent of 16.2 mg/lit of Ca(HCO<sub>3</sub>)<sub>2</sub> = (16.2 X 100) / 162 = 10 ppm.
  - CaCO<sub>3</sub> equivalent of 29.2 mg/lit of Mg(HCO<sub>3</sub>)<sub>2</sub> = (29.2 X 100) / 146 = 20 ppm.
  - CaCO<sub>3</sub> equivalent of 33.3 mg/lit of CaCl<sub>2</sub> = (33.3 X 100) / 111 = 30 ppm.
  - CaCO<sub>3</sub> equivalent of 18.0 mg/lit of MgSO<sub>4</sub> = (18. X 100) / 120 = 15 ppm.
  - NaCl does not impart hardness.
- Temporary hardness is due to the presence of Ca(HCO<sub>3</sub>)<sub>2</sub> and Mg(HCO<sub>3</sub>)<sub>2</sub>.
- Permanent hardness is due to the presence of CaCl<sub>2</sub> and MgSO<sub>4</sub>.
- ❖ Total Hardness = Temporary Hardness + Permanent Hardness
  - Temporary Hardness = 10 + 20 = 30 ppm
  - Permanent Hardness = 30 + 15 = 45 ppm
  - Total Hardness = 30 + 45 = 75 ppm.



## ENGINEERING CHEMISTRY, 15ECHB102 - UNIT 3 - CHAPTER 8: EVIRONMENTAL CHEMISTRY

 50ml of water sample requires 10ml of 0.01N EDTA when titrated using buffer solution whose pH is 10 to attain the end point. Calculate the total hardness of water sample in terms of ppm equivalent of CaCO<sub>3</sub> per lit.

## Given:

- Volume of water sample = V<sub>1</sub> = 50ml
- Normality of water sample in terms of hardness = N<sub>1</sub>
- Volume of EDTA = V<sub>2</sub> = 10ml
- Normality of EDTA = N<sub>2</sub> = 0.01N

### Solution:

- $V_1 X N_1 = V_2 X N_2$
- Therefore,  $N_1 = V_2 \times N_2 / V_1 = (10 \times 0.01) / 50 = 0.002N$ .
- ❖ Total Hardness water sample = (Normality of water sample in terms of hardness X Equivalent weight of CaCO<sub>3</sub> X 1000 ppm.)
- Total Hardness = 0.002 X 50 X 1000 ppm
- **❖** Total Hardness = 100 ppm.

#### Additional Problems:

- Calculate the temporary, permanent and total hardness of water sample which contains 32.4 mg/liter of Ca(HCO<sub>3</sub>)<sub>2</sub>, 14.6 mg/liter of Mg(HCO<sub>3</sub>)<sub>2</sub>, 22.2 mg/liter of CaCl<sub>2</sub> and 24.0 mg/liter of MgSO<sub>4</sub>.
- 25 ml of water sample requires 15ml of 0.02N EDTA when titrated using buffer solution whose pH is 10 to attain the end point. Calculate the total hardness of water sample in terms of ppm equivalent of CaCO<sub>3</sub> per lit.



ENGINEERING CHEMISTRY, 15ECHB102 - UNIT 3 - CHAPTER 8: EVIRONMENTAL CHEMISTRY

# BIOLOGICAL OXYGEN DEMAND

BOD is defined as the number of milligrams of Dissolved Oxygen required for the oxidation of biologically oxidizable impurities present in 1000 ml of waste water under aerobic conditions at 20 °C over a period of 5 days.

# Determination of BOD by Winkler's method

Aim: To estimate the amount of Biological Oxygen Demand present in the supplied sewage sample by Winkler's method.

Apparatus: 300 ml BOD bottle, Burette, 10 ml pipettes, 100 ml measuring cylinder, 250 ml volumetric flask, beakers, conical flasks and funnel.

<u>Chemicals:</u> Manganese sulphate, alkaline potassium iodide, sodium thiosulphate, sulphuric acid and starch indicator.

#### Theory:

Dissolved oxygen is used as an indicator for the health of a water body. Aquatic animals need dissolved oxygen (DO) to live.

Winkler's Method is a technique used to measure Dissolved Oxygen (DO) in freshwater systems. The amount of dissolved oxygen available in waste water is determined before and after 5 days of incubation by Iodometric titration.

Biodegradable load (CHONS) +  $O_2$   $\longrightarrow$   $CO_2$  +  $H_2O$  +  $NO^{3-}$  +  $SO_4^{2-}$ 

#### Principle:

The DO in water oxidizes KI solution to liberate equivalent quantity of iodine, which is then titrated against std. Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution using starch as an indicator.

# **Procedure:**

A definite known volume ('A' ml) of sewage sample is diluted to a known volume ('B' ml) with fresh water. Equal quantities of diluted sewage samples are taken in two BOD Bottles.

# • Blank Titration:

**Dissolved Oxygen (D1)** in **BOD Bottle-1** is determined immediately as given below. To the Bottle-1 sample, add with the help of pipette, 5ml of MnSO<sub>4</sub> and 5ml of alkaline KI reagents. Stopper the bottle immediately and shake well by inverting the bottle 3 to 4 times and allow it stand for 5 minutes. The brown precipitate of basic manganic oxide, MnO(OH)<sub>2</sub> gets settles down.



#### ENGINEERING CHEMISTRY, 15ECHB102 - UNIT 3 - CHAPTER 8: EVIRONMENTAL CHEMISTRY

Now, add one test tube of dil. H<sub>2</sub>SO<sub>4</sub>, insert the stopper and shake well till the precipitate is completely dissolved. The **reaction mixture** acquires **brownish yellow colour** due to the **liberation of iodine**.

Take 100 ml of the above reaction mixture into a conical flask and titrate against Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution until the reaction mixture becomes pale yellow colour, then add 1ml of freshly prepared starch solution. The reaction mixture turns into deep blue colour due formation of less stable starch-iodide complex. Continue the titration till the colour disappears. Note down the burette reading and perform another 2 sets of for accuracy.

| B.R. →        |       |        |         |                       |
|---------------|-------|--------|---------|-----------------------|
| в.г. ↓        | I ml. | II ml. | III ml. | Mean BR               |
| Final level   |       |        |         |                       |
| Initial level |       |        |         | ' V <sub>1</sub> ' ml |
| Difference    |       |        |         |                       |

# • Sample Titration:

The BOD **Bottle-2** is incubated for 5 days under aerobic conditions at 20 °C. After 5 days of incubation, the unconsumed **Dissolved Oxygen (D2)** in BOD **Bottle-2** is determined as described above in blank titration.

| B.R. →        | I ml. | II ml. | III ml. | Mean BR   |
|---------------|-------|--------|---------|-----------|
| Final level   |       |        |         |           |
| Initial level |       |        |         | ' V2 ' ml |
| Difference    |       |        |         |           |



# ENGINEERING CHEMISTRY, 15ECHB102 - UNIT 3 - CHAPTER 8: EVIRONMENTAL CHEMISTRY

# Reactions:

- MnSO<sub>4</sub> + 2NaOH + ½ O<sub>2</sub> → MnO(OH)<sub>2</sub>↓ (or) MnO<sub>2</sub> H<sub>2</sub>O↓ + Na<sub>2</sub>SO<sub>4</sub> Basic manganic oxide
- MnO(OH)<sub>2</sub> + H<sub>2</sub>SO4 → MnSO<sub>4</sub> + 2H2O + [O]
   Basic manganic oxide
- $2KI + H_2SO4 + [O] \rightarrow K_2SO_4 + H2O + I_2$ Iodine (brownish yellow colour)
- I<sub>2</sub> + Starch → [Starch- Iodide]
   Colourless Unstable blue coloured complex
- I<sub>2</sub> + Starch + 2Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> → Na<sub>2</sub>S<sub>4</sub>O<sub>6</sub> + 2NaI
   Disappearance of blue colour (end point)

# Calculation:

Volume of sewage sample before dilution =  $\mathbf{A}$  ml

Volume of sewage sample after dilution  $= \mathbf{B} \text{ ml}$ .

Volume of reaction mixture (sewage sample) used for both blank and sample titration = 'Vs' ml

Volume of  $Na_2S_2O_3$  consumed for blank titration in **Bottle-1** =  $V_1$  ml

Volume of  $Na_2S_2O_3$  consumed for sample titration in **Bottle-2** =  $V_2$  ml

Normality of  $Na_2S_2O_3$  solution =  $N_1$ 

Normality of reaction mixture (sewage sample) in **Bottle-1** =  $N_{DO1}$ 

Normality of reaction mixture (sewage sample) in **Bottle-2** =  $N_{DO2}$ 



#### ENGINEERING CHEMISTRY, 15ECHB102 - UNIT 3 - CHAPTER 8: EVIRONMENTAL CHEMISTRY

# Dissolved Oxygen – D1 in Bottle-1:

 $V_s N_{DO1} = V_1 N_1$ 

 $N_{DO1} = V_1 N_1 / V_s$ 

Dissolved Oxygen in Bottle-1 = D1 = Normality of reaction mixture (sewage sample) in Bottle-1 x Equivalent weight of Oxygen x 1000 ppm

 $D1 = N_{DO1} \times 8 \times 1000 \text{ ppm}.$ 

# Dissolved Oxygen – D2 in Bottle-2:

 $V_s N_{DO2} = V_2 N_1$ 

 $N_{DO2} = V_2 N_1 / V_s$ 

Dissolved Oxygen in Bottle-2 = **D2** = Normality of reaction mixture (sewage sample) in Bottle-2 x Equivalent weight of Oxygen x 1000 ppm

 $D2 = N_{DO2} \times 8 \times 1000 \text{ ppm}.$ 

# Biological Oxygen Demand (BOD):

$$BOD = \underbrace{(D1 - D2) \times B}_{A} \quad ppm.$$

# NUMERICAL PROBLEMS ON BOD

#### Lesson Plan - Q.No. 7:

25ml of waste water was diluted to 500ml and equal volumes are filled in two BOD bottles. In the blank titration 100ml of diluted waste water when titrated immediately required 6.1ml of 0.02N thiosulphate solution. 100ml of the incubated sample after 5 days required 3.6ml of 0.02N thiosulphate solution. Calculate BOD of the waste water.

#### Given:

Volume of sewage sample before dilution = A = 25ml

Volume of sewage sample after dilution =  $\mathbf{B} = 500 \text{ml}$ 

Volume of reaction mixture (sewage) used for both blank and sample titration =  ${}^{\circ}V_{s}{}^{\circ} = 100$ ml

Volume of  $Na_2S_2O_3$  consumed for blank titration in **Bottle-1** =  $V_1$  = 6.1ml

Volume of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> consumed for sample titration in **Bottle-2** =  $V_2$  = 3.6 ml

Normality of  $Na_2S_2O_3$  solution =  $N_1 = 0.02N$ 

Normality of reaction mixture (sewage sample) in **Bottle-1** =  $N_{DO1}$ 

Normality of reaction mixture (sewage sample) in Bottle-2 =  $N_{DO2}$ 



#### ENGINEERING CHEMISTRY, 15ECHB102 - UNIT 3 - CHAPTER 8: EVIRONMENTAL CHEMISTRY

#### Dissolved Oxygen – D1 in Bottle-1:

 $V_s N_{DO1} = V_1 N_1$ 

$$N_{DO1} = V_1 N_1 / V_s = (6.1 \times 0.02) / 100 = 0.00122N$$

Dissolved Oxygen in Bottle-1 = D1 = Normality of reaction mixture (sewage sample) in Bottle-1 x Equivalent weight of Oxygen x 1000 ppm

$$D1 = N_{DO1} X 8 X 1000 = 9.76 ppm$$

# **❖** Dissolved Oxygen – D2 in Bottle-2:

 $V_s N_{DO2} = V_2 N_1$ 

$$N_{DO2} = V_2 N_1 / V_s = (3.6 \times 0.02) / 100 = 0.00072N$$

Dissolved Oxygen in Bottle-2 = **D2** = Normality of reaction mixture (sewage sample) in Bottle-2 x Equivalent weight of Oxygen x 1000 ppm

$$D2 = N_{DO2} X 8 X 1000 = 5.76 ppm$$

# ❖ Biological Oxygen Demand (BOD):

**BOD** = (D1 – D2) X B ppm. = 
$$((9.76 - 5.76) \times 500) / 25 \text{ ppm}$$

> Biological Oxygen Demand = 80 ppm.

#### Additional Problem:

30 ml of waste water was diluted to 600 ml and equal volumes are filled in two BOD bottles.
 In the blank titration 100 ml of diluted waste water when titrated immediately required 10 ml of 0.05 N thiosulphate solution. 100 ml of the incubated sample after 5 days required 6 ml of 0.05 N thiosulphate solution. Calculate BOD of the waste water.



ENGINEERING CHEMISTRY, 15ECHB102 - UNIT 3 - CHAPTER 8: EVIRONMENTAL CHEMISTRY

# CHEMICAL OXYGEN DEMAND

COD is defined as the number of milligrams of Oxygen required for the oxidation of both biologically and chemically oxidizable impurities present in 1000 ml of waste water using strong oxidizing agent like K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>.

# **Determination of COD by Redox reaction**

<u>Aim:</u> To estimate the amount of <u>Chemical Oxygen Demand</u> present in the supplied sewage sample by redox reaction.

Apparatus: Round bottom flask, water condenser, Burette, pipette, conical flasks and funnel.

<u>Chemicals:</u> Potassium dichromate, 1:1 sulphuric acid, mercuric sulphate, silver sulphate and ferrous ammonium sulphate (FAS) and ferroin indicator.

#### Theory:

Chemical Oxygen Demand represents the total amount of oxygen required to oxidize all oxidizable impurities present in a sample of sewage wastes. COD is always greater than BOD since in COD measurement, both biodegradable and non-biodegradable load are completely oxidized. The difference in COD and BOD is equivalent to the quantity of biologically resistant organic matter.

COD is a satisfactory quantitative method for measuring total organic load. It is preferable to BOD as the results are reliable. COD is a rapidly measurable parameter and needs 2 hours for completion.

# Procedure:

#### • Sample Titration:

A definite known volume ('Vs' ml) of sewage sample was pipetted out into a round bottom flask. A definite known excess of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> was pipetted out into the same round bottom flask. To the reaction mixture, one test tube of 1:1 H<sub>2</sub>SO<sub>4</sub> containing HgSO<sub>4</sub> and Ag<sub>2</sub>SO<sub>4</sub> was added (HgSO<sub>4</sub> prevents Cl<sup>-</sup> ion interference and Ag<sub>2</sub>SO<sub>4</sub> catalyzes the oxidation of organic compounds). The round bottom flask was fitted with a water condenser and the reaction mixture was refluxed for 2 hours.

The above reaction mixture was cooled and transferred into a conical flask. Now, 4-5 drops of ferroin indicator was added and the reaction mixture turns into bluegreen colour. The reaction mixture was titrated against ferrous ammonium sulphate taken in the burette until a sharp colour changes from blue-green to red-brown. Note down the burette reading ('A' ml).



#### ENGINEERING CHEMISTRY, 15ECHB102 - UNIT 3 - CHAPTER 8: EVIRONMENTAL CHEMISTRY

| Burette Level | Burette Reading |
|---------------|-----------------|
| Final level   |                 |
| Initial level |                 |
| Difference    | 'A' ml          |

# Blank Titration:

Same volume of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> was pipetted out into a conical flask. To this, one test tube of 1:1 H<sub>2</sub>SO<sub>4</sub> containing HgSO<sub>4</sub> and Ag<sub>2</sub>SO<sub>4</sub> and 4-5 drops of ferroin indicator were added and the reaction mixture turns into blue-green colour. This reaction mixture was titrated against ferrous ammonium sulphate taken in the burette until a sharp colour changes from blue-green to red-brown. Note down the burette reading ('B' ml).

| Burette Level | Burette Reading |
|---------------|-----------------|
| Final level   |                 |
| Initial level |                 |
| Difference    | 'B' ml          |

#### Calculation:

Volume of sewage sample taken =  ${}^{\circ}V_{s}{}^{\circ}$  ml

Normality of reaction mixture (sewage sample) in terms of  $COD = N_{COD}$ 

Volume of FAS consumed in sample titration =  $\mathbf{A}$  ml.

Volume of FAS consumed in blank titration =  $\mathbf{B}$  ml.

Volume of  $K_2Cr_2O_7$  consumed in satisfying COD in terms of FAS solution = (B-A) ml

Normality of FAS solution =  $N_{FAS}$ 

# ENGINEERING CHEMISTRY, 15ECHB102 - UNIT 3 - CHAPTER 8: EVIRONMENTAL CHEMISTRY

#### Chemical Oxygen Demand (COD):

 $V_s N_{COD} = (B-A) N_{FAS}$ 

 $N_{COD} = (B-A) N_{FAS} / V_s$ 

Chemical Oxygen Demand of sewage sample = **COD** = Normality of reaction mixture (sewage sample) in terms of COD x Equivalent weight of Oxygen x 1000 ppm

 $COD = N_{COD} \times 8 \times 1000 \text{ ppm}.$ 

# NUMERICAL PROBLEMS ON COD

20ml of sewage sample for COD is reacted with 25ml of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and the un-reacted K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> requires 9.0ml of N/4 FAS solution. Under similar conditions, in blank titration, 15.0ml of FAS is used up. Calculate the COD of the sewage sample.

# Given:

- Volume of sewage sample taken = 'Vs' = 20ml
- Normality of reaction mixture (sewage sample) in terms of COD = N<sub>COD</sub>
- Volume of FAS consumed in sample titration = A = 9.0 ml
- Volume of FAS consumed in blank titration = B = 15.0 ml.
- Volume of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> consumed in satisfying COD in terms of FAS solution = (B-A) ml
- Normality of FAS solution = N<sub>FAS</sub> = N/4 = 0.25 N

#### Solution:

# Chemical Oxygen Demand (COD):

 $V_s N_{COD} = (B-A) N_{FAS}$ 

$$N_{COD} = (B-A) N_{FAS} / V_s = ((15.0 - 9.0) \times 0.25) / 20 = 0.075 N.$$

Chemical Oxygen Demand of sewage sample = **COD** = Normality of reaction mixture (sewage sample) in terms of COD x Equivalent weight of Oxygen x 1000 ppm

 $COD = N_{COD} \times 8 \times 1000 \text{ ppm.}$ 

Therefore,  $COD = 0.075 \times 8 \times 1000 \text{ ppm}$ .

# ❖ Chemical Oxygen Demand = 600 ppm



## ENGINEERING CHEMISTRY, 15ECHB102 - UNIT 3 - CHAPTER 8: EVIRONMENTAL CHEMISTRY

 In COD experiment, 50ml of an effluent sample required 10ml of 0.2N K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution for oxidation. Calculate the COD of sewage sample.

#### Given:

- Volume of effluent sample = 'V<sub>s</sub>' = 50ml
- Normality of reaction mixture (effluent sample) in terms of COD = Ncop
- Volume of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution = V<sub>1</sub> = 10 ml.
- Normality of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution = N<sub>1</sub> = 0.2N

#### Solution:

- $\bullet$   $V_s N_{COD} = V_1 X N_1$
- $\bullet$  N<sub>COD</sub> =  $(V_1 \times N_1) / V_s$
- $\bullet$  N<sub>COD</sub> =  $(10 \times 0.2) / 50 \text{ N}$ 
  - ❖ Normality of reaction mixture in terms of COD = Ncop = 0.04N
- Chemical Oxygen Demand of effluent sample = COD = (Normality of reaction mixture in terms of COD x Equivalent weight of Oxygen x 1000) ppm

$$COD = N_{COD} \times 8 \times 1000 \text{ ppm.}$$

Therefore,  $COD = 0.04 \times 8 \times 1000 \text{ ppm}$ .

Chemical Oxygen Demand = 320 ppm.

## Additional Problems:

- 30 ml of sewage sample for COD is reacted with 50 ml of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and the un-reacted K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> requires 14 ml of 0.5N FAS solution. Under similar conditions, in blank titration, 20 ml of FAS is used up. Calculate the COD of the sewage sample.
- In COD experiment, 30 ml of an effluent sample required 9.8 ml of 0.01 N K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution for oxidation. Calculate the COD of sewage sample.