Environmental Quality & Pollution Monitoring Techniques

# Water Quality Parameters

## Examination of Water: Chemical Oxygen Demand (COD)

- What ?
- Why ?
- How ?

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## Water Quality Parameters – Chemical Oxygen Demand (COD)

- The chemical oxygen demand (COD) is a surrogate parameter for chemically oxidizable substances, mostly due to organic carbon content in the sample.
- Expressed as equivalent of Oxygen.
- The COD value represents the amount of oxygen that will be required to completely oxidize all organic matter in the sample to $CO_2$.
- However, Oxygen is NOT used for oxidation, instead other strong oxidising agents and conditions are used for oxidation. $K_2Cr_2O_7$ is used as the most preferred oxidizing agent under acidic conditions.

## Water Quality Parameters – Chemical Oxygen Demand (COD)

- Several Strong Oxidizing Agents:
  - Chlorine ($Cl_2$)
  - Ozone ($O_3$)
  - Potassium per magnate ($KMnO_4$)
  - Potassium dichromate ($K_2Cr_2O_7$)
- $K_2Cr_2O_7$ is used as the most preferred oxidizing agent under acidic conditions.

## Water Quality Parameters – Chemical Oxygen Demand (COD)

### Oxidation of Glucose using Potassium Dichromate

$$\overset{0}{C}_6H_{12}O_6 + 6H_2O \rightarrow 6\overset{+4}{C}O_2 + 24H^+ + 24e$$

$$(14H^+ + \overset{+6}{Cr}_2O_7^{-2} + 6e \rightarrow 2\overset{+3}{Cr}^{+3} + 7H_2O) \times 4$$

$$\overset{0}{C}_6H_{12}O_6 + 32H^+ + 4\overset{+6}{Cr}_2O_7^{-2} \rightarrow 8\overset{+3}{Cr}^{+3} + 6\overset{+4}{C}O_2 + 22H_2O \quad (1)$$

## Water Quality Parameters – Chemical Oxygen Demand (COD)

The excess $K_2Cr_2O_7$ remaining in the solution is quantified by titration with ferrous ammonium sulphate (FAS) as follows:

$$14H^{+} + \overset{+6}{Cr_2}\,O_7^{-2} + 6e \rightarrow 2\overset{+3}{Cr}^{+3} + 7H_2O$$

$$6\overset{+2}{Fe}^{+2} \rightarrow 6\overset{+3}{Fe}^{+3} + 6e$$

$$14H^{+} + 6\overset{+2}{Fe}^{+2} + \overset{+6}{Cr_2}\,O_7^{-2} + 6e \rightarrow 2\overset{+3}{Cr}^{+3} + 6\overset{+3}{Fe}^{+3} + 7H_2O \qquad (2)$$

## Water Quality Parameters – Chemical Oxygen Demand (COD)

The amount of $K_2Cr_2O_7$ consumed is then expressed in terms of oxygen equivalents and hence COD in mg/L.

$$14H^{+} + \overset{+6}{Cr_2}\,O_7^{-2} + 6e \rightarrow 2\overset{+3}{Cr}^{+3} + 7H_2O \qquad (3a)$$

$$4H^{+} + \overset{0}{O_2} + 4e \rightarrow 2H_2\overset{-2}{O} \qquad (3b)$$

## Water Quality Parameters – Chemical Oxygen Demand (COD)

### Theory of COD Determination of an unknown sample

- Determination of COD is based on the fact that a boiling mixture of $K_2Cr_2O_7$ and sulfuric acids *(Similar to Equation 1)* oxidizes most organic molecules to inorganic carbon (+4 oxidation state).
- 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.

## Water Quality Parameters – Chemical Oxygen Demand (COD)

### Theory of COD Determination of an unknown sample

- 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).
- The amount of dichromate solution consumed by oxidizable 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).

## Water Quality Parameters – Chemical Oxygen Demand (COD)

### 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 dissolving 39.2 gm $Fe(NH_4)_2(SO_4)_2.6H_2O$ in approximately 100-200 mL of distilled water added with 20 ml concentrated $H_2SO_4$. Cool and dilute to 1000 ml.
- During titration, the color of the solution changes gradually from orange to green due to reduction of $Cr_2O_7^{2-}$ by $Fe^{2+}$.

## Water Quality Parameters – Chemical Oxygen Demand (COD)

- 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.

## Water Quality Parameters – Chemical Oxygen Demand (COD)

### Chemical Oxygen Demand by Closed Reflux Method

- Place 2.5 mL of distilled water in a COD Tube and 2.5 mL of wastewater sample in an another COD Tube.
- 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 inside of each COD 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 COD Tubes in a block digester for 2 hour.
- Cool to room temperature. Transfer the contents of each tube to a conical flask for titration. Add water if required.

## Water Quality Parameters – Chemical Oxygen Demand (COD)

- Titrate $K_2Cr_2O_7$ in COD Tube having distilled water 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 COD Tubes having sample in a similar manner. Let the reading 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**