

Water Quality Parameters

Examination of Water: Chemical Oxygen Demand (COD)

- What ?
- Why ?
- How ?



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Water Quality Parameters – Chemical Oxygen Demand (COD)

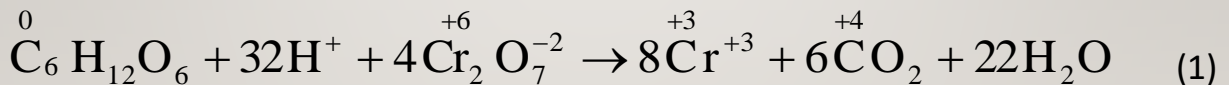
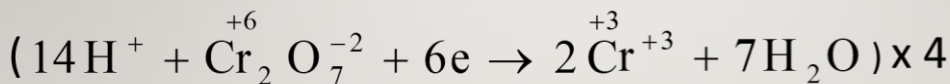
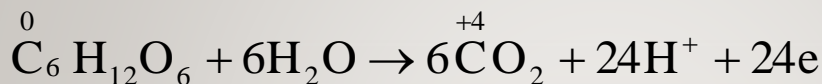
- The chemical oxygen demand (COD) is a surrogate parameter for chemically oxidizable substances, mostly due to organic carbon content in the sample.
- Expressed as equivalent of Oxygen.
- The COD value represents the amount of oxygen that will be required to completely oxidize all organic matter in the sample to CO_2 .
- However, Oxygen is NOT used for oxidation, instead other strong oxidising agents and conditions are used for oxidation. $\text{K}_2\text{Cr}_2\text{O}_7$ is used as the most preferred oxidizing agent under acidic conditions.

Water Quality Parameters – Chemical Oxygen Demand (COD)

- Several Strong Oxidizing Agents:
 - Chlorine (Cl₂)
 - Ozone (O₃)
 - Potassium permanganate (KMnO₄)
 - Potassium dichromate (K₂Cr₂O₇)
- K₂Cr₂O₇ is used as the most preferred oxidizing agent under acidic conditions.

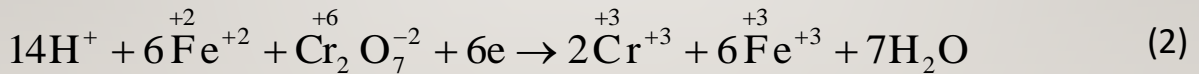
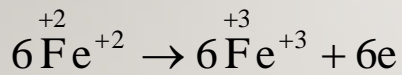
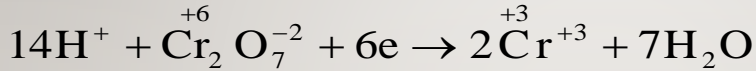
Water Quality Parameters – Chemical Oxygen Demand (COD)

Oxidation of Glucose using Potassium Dichromate



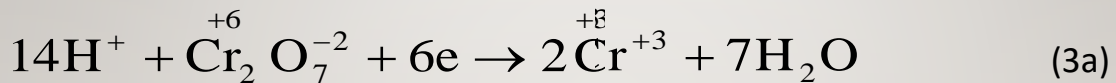
Water Quality Parameters – Chemical Oxygen Demand (COD) →

The excess $\text{K}_2\text{Cr}_2\text{O}_7$ remaining in the solution is quantified by titration with ferrous ammonium sulphate (FAS) as follows:



Water Quality Parameters – Chemical Oxygen Demand (COD) →

The amount of $\text{K}_2\text{Cr}_2\text{O}_7$ consumed is then expressed in terms of oxygen equivalents and hence COD in mg/L.



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 $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ 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