# Estimation of Chemical Oxygen Demand (COD)

## Introduction:

The chemical oxygen demand (COD) is used as a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. For samples from a specific source, COD can be related emphirically to BOD, organic carbon or organic matter. The dichromate reflux method is preferred over procedures using other oxidants because of superior oxidizing capacity.

## Interference and Limitations:

1. Volatile straight chain aliphatic compounds are not oxidized to appreciable content. This interference is overcome by adding silver sulphate as a catalyst, which oxidizes these compounds more efficiently.
2. The difficult is caused by presence of halides can be overcome largely but not completely by complexing with mercuric sulphate. (1 g $HgSO_4$ for 50 ml of Sample)
3. Nitrite in water rarely exceeds 1 or 2 mg/l, the interference is considered insignificant and usually ignored.

## Sampling and Sample Storage:

Preferably collect samples in glass bottles. Test unstable sample without delay. If delay before analysis is unavoidable, preserve sample by acidification to pH ≤ 2.0.

## Open Reflux Method:

## Principle:

A sample is refluxed with a measured amount of potassium dichromate and concentration $H_2SO_4$. After digestion, the remaining unreduced amount of $K_2Cr_2O_7$ is measured and the oxidizable organic matter is calculated in terms of oxygen equivalent.

## Reagents:

### 1. Standard $K_2Cr_2O_7$ (0.0417 M):

Dissolve 12.259 g $K_2Cr_2O_7$ previously dried at $103^0$C for 2 hrs in distilled water and dilute to 1000 ml

### 2. Ferrion Indicator:

Dissolve 1.485 g 1, 10–phenonthroline monohydrate and 695 mg $FeSO_4.7H_2O$ in distilled water and dilute to 100 ml.

### 3. Standard Ferrous Ammonium Sulphate (FAS - 0.25 M):

Dissolve 98 g of FAS in distilled water. Add 20 ml conc. $H_2SO_4$, cool and dilute to 1000 ml.

**Standardization of FAS:**

Dilute 10 ml standard $K_2Cr_2O_7$ to about 100 ml. Add 30 ml conc. $H_2SO_4$ and cool. Titrate against FAS using ferroin indicator.

### 4. Silver Sulphate:

Add $Ag_2SO_4$ crystals or powder to conc. $H_2SO_4$ at the rate of 5.5 g $Ag_2SO_4$ per Kg of $H_2SO_4$. Let it stand for 1-2 days to dissolve $Ag_2SO_4$.

### 5. Mercuric Sulphate:

Crystals or powder.

### 6. Conc. $H_2SO_4$

### Procedure:

1. Take 50 ml sample in a 500 ml refluxing flask.
2. Add 1 g $HgSO_4$ and several glass beads and slowly add 5 ml conc. $H_2SO_4$ to dissolve $HgSO_4$.
3. Add 25 ml 0.0417 M $K_2Cr_2O_7$ solution and mix.
4. Attach flask to condenser and turn on cooling water.
5. Add remaining $H_2SO_4$ (70 ml), continue swirling and mixing, while adding.
6. Reflux the mixture for 2 hrs.
7. Remove the flask and cool the mixture to room temperature.
8. Dilute the sample to double quantity and titrate with standard FAS using ferroin indicator.

### End point:

Sharp colour change from blue green to reddish brown. Run the blank with distilled water.

### Calculation:

$$\text{COD as mg. } O_2 \text{ /L} = \frac{(A-B) \times M \times 8000}{\text{ml of sample}}$$

Where, A = ml of FAS rundown for blank

B = ml of FAS rundown for sample

M = molarity of FAS

## Procedure for Microwave Digester Method:

1. Take 20 ml of sample
2. Add 10 ml of potassium dichromate
3. Add 30 ml of conc. $H_2SO_4$
4. Add a pinch of $Ag_2SO_4$
5. Keep it for digestion
6. Connect the condenser and keep the cooling water on
7. Press “List”, “control” appears
8. Press “List”, “System” appears
9. Press “List”, “Program 0” appears
10. Press “Start”. Digestion time is 10 min
11. After 10 min, “End” appears and green light glows
12. Cool the digested mixture to room temperature
13. Dilute the sample with 90 ml distilled water and titrate with standard FAS using ferroin indicator
14. End point is sharp colour change from blue green to reddish brown

Run the blank with distilled water

## Result: