CHEMICAL OXYGEN DEMAND (COD)

TITLE

Determination of amount of Chemical Oxygen Demand (COD) in water.

THEORY

Chemical Oxygen Demand (COD)

The Chemical Oxygen Demand, or COD, is a measurement of the amount of material that can be oxidized (combined with oxygen) in the presence of a strong chemical oxidizing agent. Since the COD test can be performed rapidly, it is often used as a rough approximation of the water's BOD, even though the COD test measures some additional organic matter (such as cellulose) which is not normally oxidized by biological action. As with the BOD test, the COD test is reported as mg/Lit of oxygen used. The table below shows the normal range of COD found in various kinds of domestic wastewater. Keep in mind that the addition of industrial waste can cause these values to vary widely. Biochemical oxygen demand is a measure of the quantity of oxygen used by microorganisms (e.g. aerobic bacteria) in the oxidation of organic matter.

METHODS OF DETERMINATION OF COD

1. Open Reflux Titrimetric Method

Principle

In this method known amount of strong oxidizing agent is being added. Then reaction takes place to form CO_2 and H_2O. Then remaining amount of oxidizing agent is being determined by titration. The amount of oxidizing agent to be added depends upon the COD of sample which can roughly be known by knowing the source of sample.

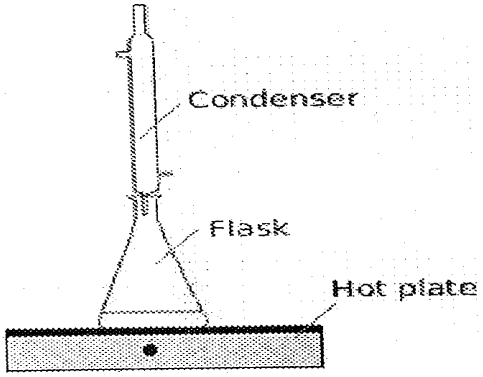
Equipment:

Caution: The presence of minute traces of organic matter on the equipment will cause large errors in the test results. So clean all equipment thoroughly before using.

- Erlenmeyer flask
- Small beaker
- Titration apparatus:
  - 25 or 50 mL burette, graduated in 0.1 mL

- burette support
- 100 mL graduated cylinder
- rubber-tipped stirring rod, or magnetic stirrer and stir bar
- white porcelain evaporating dish, 4.5 inches in diameter

- Reflux apparatus:



  - 500 or 250 mL Erlenmeyer flasks with ground glass 24/40 neck
  - 300 mm jacket Liebig, West, or equivalent condenser with 24/40 ground-glass joint
  - hot plate with sufficient power to produce at least 1.4 W /cm^2 of heating surface
- Blender
- Pipets
- Glass beads
- Fume hood

Reagents

- Standard potassium dichromate solution, 0.25N or O.025N
- Sulfuric acid reagent containing silver sulfate catalyst
- Standard ferrous ammonium sulfate titrant
- Ferroin indicator solution
- Mercuric sulfate crystals
- Sulfamic acid
- Concentrated sulfuric acid
- Distilled water

Theory of Titration

The COD analysis, by the dichromate method, is more commonly used to control and

continuously monitor wastewater treatment systems, The COD of an effluent is usually higher than the BOD_5 since the number of compounds that can be chemically oxidized is greater than those that can be degraded biologically, It is also common to make a correlation of BOD_5 versus COD and then use the analysis of COD as a rapid means of estimating the BOD_5 of a wastewater. This may be convenient since only about three hours are needed for a COD determination while a BOD_5 takes at least 5 days. However, this procedure can be used only for specific situations where there is low variability in the composition of a wastewater, and the results of a system cannot be used reliably in other cases.

The method of COD which uses dichromate as oxidant is carried out by heating under total reflux a wastewater sample of known volume in an excess of potassium dichromate ($K_2Cr_2O_7$) in presence of sulphuric Acid (H_2SO_4) for a fixed period (usually two hours) in presence of silver sulphate (Ag_2SO_4) as catalyst. The organic matter present is oxidized and, as a result, the dichromate ion (orange colour) is consumed and replaced by the chromic ion (green colour):

$$\mathbf{Cr_2O_7^{-2} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O}$$

The COD is calculated by titrating the excess of dichromate or by spectrophotometrically measuring the Cr^{+3} ions at 606 nm. Another possibility is to measure the excess dichromate spectrophotometrically at 440 nm. Titration requires more work but is considered more precise.

The presence of silver sulphate as catalyst is needed for complete oxidation of aliphatic carbon compounds. The standard method implies cooling of the sample after the two hour digestion period, adding a few drops of indicator (ferroin) solution and titrating the excess dichromate with a solution of ferrous ammonium sulphate of known concentration, until the colour changes from brilliant green to reddish brown. The titration reaction corresponds to the oxidation of the ferrous ammonium sulphate by the dichromate:

$$\mathbf{Cr_2O_7^{-2} + 14H^+ + 6Fe^{+2} \longrightarrow 2Cr^{3+} + 6Fe^{+3} + 7H_2O}$$

The change in colour corresponds to the formation of the complex ferrous ion phenanthroline which occurs when all the dichromate ion has been reduced to Cr^{3+}.

$$\mathbf{(Fe(C_{12}H_8N_2)_3)^{3+} + e \longrightarrow (Fe(C_{12}H_8N_2)_3)^{2+}}$$

Ferric Phenanthroline	Ferrous Phenanthroline
(Green Blue)	(Reddish Brown)

Interferences

A common interference factor in the COD test is the presence of chlorides. If seawater is used at some point in the processing or salt brines are used for some "curing" operations, chlorides will most probably appear in the wastewater causing interference while they are oxidized by the dichromate:

$$\mathbf{Cl^- + Cr_2O_7^{2-} + 14H^+ \longrightarrow 3Cl_2 + 2Cr^{3+} + 7H_2O}$$

This interference causes erroneously high values of COD which can be prevented by the addition of mercuric sulphate ($HgSO_4$) which reacts to form mercuric chloride and precipitates:

$$\mathbf{Hg^{2+} + 2Cl^- \longrightarrow HgCl_2}$$

Procedure:

1) Place 50ml sample in 500ml refluxing flask (for samples with COD>900mg/L use a smaller sample diluted to 50ml).
2) Add 1g $HgSO_4$ and several glass beeds.
3) Add slowly 5ml H_2SO_4 reagent while mixing to dissolve $HgSO_4$
4) Cool while mixing to avoid the loss of volatile materials.
5) Add 25 ml 0.25N $K_2\ Cr_2O_7$ solution and mix.
6) Attach the flask to the condenser and turn on cooling water.
7) Add remaing H_2SO_4 (70ml) through open end of the condenser continue mixing while adding H_2SO_4.
8) Reflux the mixture for 2 hrs and cool to room temperature, after diluting the mixture to about twice its volume with distilled water.
9) Titrate excess of $K_2\ Cr_2O_7$ with Ferrous ammonium sulfate using 2,3 drops of ferrion indicator. The end point will be from blue green to reddish brown.
10) Reflux and titrate in the same manner a blank containing the reagents and the voume of the distilled water will be equal to that of sample.

OBSERVATIONS AND CALCULATIONS (COD)

Sr. No.	Description of Sample	Volume of titrant used for sample	Volume of titrant used for blank	COD
		ml	ml	mg/litre
1				
2				

COD, mg/L = (A - B) x N x 8,000 / (Volume of Sample, mL)

Where:

A = mL of titrant used for Blank

B = mL of titrant used for Sample

N = normality of ferrous ammonium sulfate (FAS) = 0.25N

8000 = Equivalent Wt. of Oxygen x 1000

Comments:

Questions:

1) Compare BOD and COD.

2) Why COD values are always higher then BOD values?

3) Write the applications of COD data to environmental Engineering?

4) Write the NEQS for COD.

5) What would be the role of Ag_2SO_4 in COD determination?