Table of Contents

Experiment No. 1

Determination of amount of DO in water

To determine the amount of Dissolved Oxygen (DO) in water

Dissolved oxygen:

The dissolved oxygen (DO) is oxygen that is dissolved in water. The oxygen dissolves by diffusion from the surrounding air; aeration of water that has tumbled over falls and rapids; and as a waste product of photosynthesis. A simplified formula is given below:

Photosynthesis (in the presence of light and chlorophyll):

Carbon dioxide + Water ⟶ Oxygen + Carbon-rich foods

$(CO_2) + (H_2O) \longrightarrow (O_2) + (C_6H_{12}O_6)$

Fish and aquatic animals cannot split oxygen from water (H2O) or other oxygen-containing compounds. Only green plants and some bacteria can do that through photosynthesis and similar processes. Virtually all the oxygen we breathe is manufactured by green plants. A total of three-fourths of the earth's oxygen supply is produced by phytoplankton in the oceans.

- ⇒ Fish, invertebrates, plants, and aerobic bacteria all require oxygen for respiration.
- ⇒ Much of the dissolved oxygen in water comes from the atmosphere. After dissolving at the surface, oxygen is distributed by current and turbulence. Algae and rooted aquatic plants also deliver oxygen to water through photosynthesis.
- ⇒ The main factor contributing to changes in dissolved oxygen levels is the build-up of organic wastes. Decay of organic wastes consumes oxygen and is often concentrated in summer, when aquatic animals require more oxygen to support higher metabolisms.
- ⇒ Depletions in dissolved oxygen can cause major shifts in the kinds of aquatic organisms found in water bodies.
- ⇒ Temperature, pressure, and salinity affect the dissolved oxygen capacity of water. The ratio of the dissolved oxygen content (ppm) to the potential capacity (ppm) gives the percent saturation, which is an indicator of water quality.

Methods of determination of DO in water:

Following are the methods used for the determination of dissolved oxygen in water.

- ⇒ Winkler method
- ⇒ Azide modification of Winkler method
- ⇒ Rideal Stewart method
- ⇒ DO-meters

(1) Winkler Method

Its principle is that oxygen oxidizes manganese (Mn^{+2}) to higher oxidation state then this higher oxidation state manganese converts iodide ion (I^{-1}) to iodine I2 and amount of free iodide librated is equivalent to DO.

$$Mn^{+2} + 2OH^{-1} \longrightarrow Mn(OH)_2$$

$$Mn(OH)_2 + 1/2O_2 \longrightarrow MnO_2 + H_2O$$

$$MnO_2 + 2I^{-1} + 4H^{+1} \longrightarrow Mn^{+2} + I_2 + H_2O$$

Then by titration with $S2O3^{-2}$, thiosulphate ion (thiosulphate ion comes from sodium thiosulphate), iodine can be calculated.

$$2S_2O_3^{-1} + I_2 \longrightarrow S_4O_6^{-2} + 2I^{-1}$$

If we use 0.025 N $_{Na2S2O3}$ then 1ml of titrant = 1mg of DO

(2) Azide modification of Winkler Method

If nitrites $NO2^{-1}$ will present in water, they will change the results because they convert iodide ions to iodine before performance of experiment. To remove $NO2^{-1}$ sodium azides are added.

Procedure:

1. Take BOD bottle (300 ml volume)
2. Fill the bottle with water sample.
3. Add 1 ml $MnSO_4$ solution to it and mix uniformly with the help of pipette.
4. Add 1ml alkali azide iodide solution. On addition, if white ppts. are formed, then there is no DO in water. Formation of Reddish brown ppts. Indicates the presence of DO.
5. If Reddish brown ppts are formed, stopper the bottle and shake it upside down for 20 times and allow the ppts. To settle down for about 2 inches.
6. Add 1 ml Concentrated H_2SO_4 and again shake for about 8 times.
7. Take 200 ml of this water sample in a titration flask and titrate it with 0.025 N $Na_2S_2O_3$ till the appearance of light yellow color.
8. Then add 1 ml starch solution. The color of solution becomes blue on this addition.
9. Again titrate it with 0.025N $Na_2S_2O_3$ till the disappearance of blue color.
10. Note the volume of titrant used.

ml of titrant used = DO in mg/liter

The above formula is applicable if we use 200ml of water sample solution and 0.025N $Na_2S_2O_3$. General formula is given by

$$DO\ (mg/L) = \frac{\text{mean volume of titrant used x N x 8000}}{\text{F x volume of sample in ml}}$$

Where,

$$F = \frac{\text{volume of BOD bottle} - \text{volume of reagents used}}{\text{volume of BOD bottle}}$$

Observations & Calculations:

Dissolved oxygen:

N= 0.025N , F = (300-3)/300 = 0.99

Sample#1:

As the sample was not tuned brown after adding three regents. So,

DO = 0 mg / liter

Sample#2:

Volume of titrant ($Na_2S_2O_3$):

Sample Volume	***Initial reading***	***Final Reading***	***Volume of $Na_2S_2O_3$***
(ml)	**(ml)**	**(ml)**	**(ml)**
100	2.20	8.90	3.70
100	8.70	12.60	3.70
100	12.60	16.50	3.90
		Sum	*11.30*

So,

Dissolved Oxygen (DO):

DO = (11.30 x 0.025 x 8000) / (0.99 x 300) = **7.609 mg/l**

Sample#3:

Volume of titrant ($Na_2S_2O_3$):

Sample Volume	***Initial reading***	***Final Reading***	***Volume of $Na_2S_2O_3$***
(ml)	**(ml)**	**(ml)**	**(ml)**
100	17	20.80	4.00
100	20.80	24.70	3.90
100	16.90	20.90	4.00
		Sum	*11.90*

So,

Dissolved Oxygen (DO):

DO = (11.90 x 0.025 x 8000) / (0.99 x 300) = **8.02 mg/l**

Comments:

⇒ From the results it is clear that both samples are of almost same type or we can say from same source.

⇒ The values obtained indicate that water has sufficient amount of oxygen for species.

Questions:

1. ***What are the factors upon which solubility of oxygen depends?***

It depends upon following parameters:

⇒ Effect of pressure change: The practical effect is that the amount of oxygen at an interface of air and water decreases as the pressure of air is decreased.

⇒ Effect of temperature change: At constant pressure, the volume of specific weight of air changes in direct ratio to the absolute temperature (K). The concentration of oxygen at the air-water interface increases by decreasing air temperature.

⇒ Effect of dissolved materials: Dissolved materials in water reduces solubility of oxygen if interact with air to decrease attractive molecular forces between water and oxygen.

2. Why starch is added when light yellow colour appears?

The titration is titrating iodine from yellow to clear color. As yellow color change is very hard so to see it we add starch which turns blue in the presence of iodine. Once all the iodine has been titrated out, the starch goes clear. Change of color from blue to clear is easy to see than yellow to clear.

3. Write the significance of this test in Environmental Engineering.

This test is use to determine

⇒ The health or cleanliness of lake or stream.

⇒ Amount and type of biomass a fresh water system can support.

⇒ Amount of deposition occurring in a lake.

4. What type of titration is involved in above test?

Titrations are based on a redox reaction between an oxidizing agent and a reducing agent. The oxidizing agent (resp. reducing agent) is added to the burette, which was rinsed with the same oxidizing agent. The reducing agent (resp. reducing agent) is added the conical flask, which had been rinsed with distilled water. Like in an acid-base titration, the standard solution is often the one in the conical flask, and the solution whose concentration is to be determined is the one in the burette. The procedure for carrying out redox titrations is similar to that required for carrying out acid-base titrations.

5. What is azide modification?

The Azide modification of the Winkler method is the standard test for dissolved oxygen. It uses a burette and 0.025N sodium thiosulfate. The standard APHA regents in solution form also are available. In the analysis, manganous ion reacts with the dissolved oxygen present in the alkaline solution to form a manganese (IV) oxide hydroxide flocculent. Azide is added at this time suppress interference from any nitrite present which would react with the iodide. The solution is then acidified and the manganese (IV) floc is reduced by iodide to produce free iodine as 13- in proportion to the oxygen concentration. The liberated iodine is then titrated to the starch-iodide end point.

Experiment No. 2

Determination of amount of BOD in sewage

To determine the amount of Biochemical Oxygen Demand (BOD) in domestic waste water

Biochemical Oxygen Demand (BOD):

The amount of oxygen required by the bacteria while stabilizing decomposable organic matter under aerobic conditions. Decomposable\w means that organic matter can serve as food for the bacteria and energy is derived from its oxidation.

- ⇒ Biochemical oxygen demand is a measure of the quantity of oxygen used by microorganisms (e.g., aerobic bacteria) in the oxidation of organic matter.
- ⇒ Natural sources of organic matter include plant decay and leaf fall. However, plant growth and decay may be unnaturally accelerated when nutrients and sunlight are overly abundant due to human influence.
- ⇒ Urban runoff carries pet wastes from streets and sidewalks; nutrients from lawn fertilizers; leaves, grass clippings, and paper from residential areas, which increase oxygen demand.

Oxygen consumed in the decomposition process robs other aquatic organisms of the oxygen they need to live. Organisms that are more tolerant of lower dissolved oxygen levels may replace a diversity of more sensitive organisms.

BOD Level (in ppm)	Water Quality
1 – 2	Very Good-not much organic waste present
3 – 5	Moderately clean
6 – 9	Somewhat polluted
10+	Very polluted

Importance of BOD Test in Environmental Engineering:

The BOD test is used to determine the relative oxygen requirements of wastewaters, effluents, and polluted waters. This test measures the oxygen utilized during a specified incubation period for the biochemical degradation of organic material. It is also used to determine treatment plant efficiency.

Determination of BOD

Principle:

The method consists of filling with sample, to overflowing, an airtight bottle of the specified size and incubating it at the specified temperature for 5 days. Dissolved oxygen is measured initially and after incubation, and the BOD is computed from the difference between initial and final DO. Because the initial DO is determined shortly after the dilution is made, all oxygen uptake occurring after this measurement is included in the BOD measurement.

Sampling and Storage:

Sample for BOD analysis may degrade significantly during storage between collection and analysis, resulting in low BOD values. Minimize reduction of BOD by analyzing sample promptly or by cooling it to near-freezing temperature during storage. However, even at low temperature, keep holding time to a minimum. Warm chilled samples to 20 ± 3°C before analysis.

Apparatus:

⇒ Incubation bottles: Use glass bottles having 60 mL or greater capacity (300mL bottles having ground-glass stopper and a flared mouth are preferred).

⇒ Air incubator or water bath, thermo-statistically controlled at 20 ± 1°C. Exclude all light to prevent possibility of photosynthetic production of DO.

Reagents:

Prepare reagents in advance but discard if there is any sign of precipitation or biological growth in the stock bottles.

⇒ Phosphate buffer solution: Dissolve 8.5 g KH_2PO_4, 21.75 g K_2HPO_4, 33.4 g

⇒ $Na_2HPO_4.7H_2O$, and 1.7 g NH_4Cl in about 500 mL distilled water and dilute to 1 Lit. The pH should be 7.2 without further adjustment. Alternatively dissolve 42.5 g KH_2PO_4 or 54.3 g K_2HPO_4 in about 700 mL distilled water. Adjust pH to 7.2 with 30% NaOH and dilute to I Lit.

⇒ Magnesium sulfate solution: Dissolve 22.5 g $MgSO_4.7H_20$ in distilled water and dilute to 1 L.

⇒ Calcium chloride solution: Dissolve 27.5 $CaCl_2$ in distilled water and dilute to

⇒ 1 L.

⇒ Ferric Chloride solution: Dissolve 0.25 g $FeCl_3.6H_2O$ in distilled water and dilute to 1 L.

⇒ Acid and alkali solution, 1N, for neutralization of caustic or acidic waste samples. 1) Acid-Slowly and while stirring, add 28 mL cone. Sulfuric acid to distilled Water. Dilute to 1 L. 2) Alkali-Dissolve 40 g sodium hydroxide in distilled water. Dilute to 1 L.

⇒ Sodium sulfate solution: Dissolve 1.575 g Na_2SO_3 in 1000 mL distilled water. This solution is not stable; prepare daily.

⇒ Nitrification inhibitor: 2-chloro-6-(trichloromethyl) pyridine (if nitrification inhibition desired).

⇒ Glucose-glutamic acid solution: Dry reagent-grade glucose and reagent-grade glutamic acid at 103°C for 1 h. Add 150 mg glucose and 150 mg glutamic acid to distilled water and dilute to 1 L. Prepare fresh immediately before use.

⇒ Ammonium chloride solution: Dissolve 1.15 g NH_4Cl in about 500 mL distilled water, adjust pH to 7.2 with NaOH solution and dilute to 1 L. Solution contains 0.3 mg N mL^{-1}

⇒ Dilution water: Use dematerialized, distilled, tap, or natural water for making sample dilutions

Procedure (without seeding):

- ✓ First of all it is important to know the amount of samples to be used for test. For this purpose the source of sample is to be recorded which will indicate the approximate value of BOD5 for the sample.
  - ⇒ Domestic sewage BOD5 =100-500mg/L
  - ⇒ Effluent from treatment plant= 20-80mg/L
  - ⇒ River water = 2-4mg/L
- ✓ Take 9 BOD bottles note their numbers and arrange them in 3 groups.
- ✓ Fill each bottle half with dilution media ensuring that no air gets mixed with the media while fill in as in DO test.
- ✓ Add 2ml sample in each of the three bottles marked as first group; 5 ml in each bottle pf 2nd group and 10ml in each bottle of the 3rd group.
- ✓ Fill the bottle completely with dilution media and place the stopper such that no air bubbles are trapped.
- ✓ Now take one bottle from each set and estimate its DO. This will be DO initial or DO 0 days.
- ✓ For comparison prepare two more bottles with blank dilutions media (without sewage sample) and find the DO from one bottle.
- ✓ Place the rest of the six bottles with sewage samples and one bottle for blank in the incubator at 20°C.
- ✓ After 5 days find out DO in all bottles.
- ✓ That value of oxygen depletion should be considered correct which gives an oxygen depletion of at least 2 mg/L. and which have at least 0.5 mg/L DO after 5 days of incubation.
- ✓ Calculate BOD5 at 20°C.

$$\text{BOD (mg/L)} = \frac{\text{DO depletion } \left(\frac{\text{mg}}{\text{L}}\right) \text{x } 300}{\text{volume of sample in ml}}$$

Observations and Calculations:

1) At zero days:

Bottle#	*Sample added (ml)*	*Volume of sample (ml)*	*Volume of Na2S2O3*	*DO (mg/L)*	*Mean DO (mg/L)*
A1	1	300	9.7	6.47	6.47
A2	3	300	9.8	6.53	6.53
A3	5	300	9.6	6.40	6.40
Blank1	Blank	300	10.2	6.80	6.80

2) After five days:

Bottle#	Sample added (ml)	Volume of sample (ml)	Volume of Na2S2O3	DO (mg/L)	Mean DO (mg/L)
B1	1	300	7.2	4.80	4.83
C1	1	300	7.3	4.87	
B2	3	300	6.9	4.60	4.67
C2	3	300	7.1	4.73	
B3	5	300	6.5	4.33	4.30
C3	5	300	6.4	4.27	
Blank2	Blank	300	10.1	6.73	6.73

3) DO depletion:

Bottle#	Sample added (ml)	DO at Zero days (mg/L)	DO at 5 days (mg/L)	DO Depleted (mg/L)	BOD5 (mg/L)
A1, B1, C1	1	6.47	4.83	1.64	491.00
A2, B2, C2	3	6.53	4.67	1.86	186.00
A3, B3, C3	5	6.40	4.3	2.10	126.00
Blank 1,2	Blank	6.8	6.78	0.02	

Mean (BOD)5 = 268 Mg/L

Comments:

- ✓ The DO depleted obtained is in a sequence as it should be more in case of 5ml, and least for 1ml sample solution. So our experimentation is right.
- ✓ The resulted value of $(BOD)_5$ is within the range of 1-600 mg/L. So our results are also within this range i.e. 268 mg/L.
- ✓ BOD_5 for A1,B1,C1 is maximum among all value because of less sample added (1 ml) and that the value of A3,B3,C3 is minimum due to more amount of sample added in it and that value to A2,B2,B3 is intermediate among the group due to intermediate amount of sample added.

Questions:

1. Define BOD.

B.O.D. is the amount of dissolved oxygen needed by aerobic biological organisms in a body of water to break down organic material present in a given water sample at certain temperature over a specific time period. It is also defined as the measure of quantity of oxygen used by microorganisms (eg, aerobic bacteria) in the oxidation of organic matter. The term also refers to a chemical procedure for determining this amount. It is measured in mg/L.

2. Why natural water and tap water cannot be used for preparing dilution media in the BOD test.

Natural water may already contain organic matter, bacteria or salts which can affect the efficiency of bacteria. Natural water often contains and tap water often contains a substantial amount of organic matter that is released intermittently and is undetectable with a conductivity water purity gauge. Also, the large surface to volume ratio that exists in the columns because of the resins beads encourages bacterial growth in the column. A much trouble with BOD is caused by excessive organic matter in the water used to prepare BOD dilution media. It can also happen that the prepared BOD dilution water itself had an oxygen demand in excess of the dissolved oxygen present in it, resulting in total depletion of in all incubated sample. It is required to have a near zero oxygen demand in the dilution water.

3. What is the role of nitrifying bacteria in BOD test?

Any ammonia present in a waste stream may also be oxidized by nitrifying bacteria in a process called nitrification. Nitrification also demands oxygen, which is referred to as nitrogenous BOD (NBOD). A general equation for the overall nitrification process is shown below.

ammonia + oxygen + carbon dioxide + nitrifying bacteria

=

nitrate + water + new cells + energy

Nitrifying bacteria grow slowly, more slowly than the microorganisms that oxidize organic matter, and it normally takes from 6 to 10 days before they start to consume oxygen. So for that reason 5 days are selected so that nitrification bacteria cannot interfere in our results. If a significant number of nitrifying bacteria are present in the wastewater, they might exert sufficient oxygen demand to introduce error even into the measurement of organic matter using the BOD_5 test. In these cases, the wastewater sample being tested should be pretreated with an agent that suppresses nitrifying bacteria, and the results of the BOD test should be reported as CBOD (carbonaceous BOD).

4. What is the history of BOD test?

The Royal Commission on River Pollution, which was established in 1865 and the formation of the Royal Commission on Sewage Disposal in 1898 led to the selection in 1908 of BOD_5 as the definitive test for organic pollution of rivers. Five days was chosen as an appropriate test period because this is supposedly the longest time that river water takes to travel from source to estuary in the U.K.. In its sixth report the Royal Commission recommended that the standard set should be 15 parts by weight per million of water. However in the Ninth report the commission had revised the recommended standard:

"An effluent taking up 2-0 parts dissolved oxygen per 100,000 would be found by a simple calculation to require dilution with at least 8 volumes of river water taking up 0.2 parts if the resulting mixture was not to take up more than 0.4 parts. Our experience indicated that in a large majority of cases the volume of river water would exceed 8 times the volume of effluent, and that the figure of 2-0 parts dissolved oxygen per 100,000, which had been shown to be practicable, would be a safe figure to adopt for the purposes of a general standard, taken in conjunction with the condition that the effluent should not contain more than 3-0 parts per 100,000 of suspended

solids. This was the cornerstone 20:30 (BOD: Suspended Solids) + full nitrification standard which was used as a yardstick in the U.K. up to the 1970s for sewage works effluent quality.

The United States includes BOD effluent limitations in its secondary treatment regulations. Secondary sewage treatment is generally expected to remove 85 percent of the BOD measured in sewage and produce effluent BOD concentrations with a 30-day average of less than 30 mg/L and a 7-day average of less than 45 mg/L. The regulations also describe "treatment equivalent to secondary treatment" as removing 65 percent of the BOD and producing effluent BOD concentrations with a 30-day average less than 45 mg/L and a 7-day average less than 65 mg/L.

5. What is seeding?

Some samples do not contain sufficient bacteria to oxidize any organic matter that is present. Many industrial and trade wastes are of this type. Also many sewerage treatment plants chlorinate their final effluent so that it is essentially sterilize and thus impossible to test directly for BOD. In order to test such samples, it is necessary to seed the prepared BOD dilution water. This is done by adding a small amount of water containing sufficient amount of bacteria population to the dilution water that is used to prepare the sample.

Seeding provides microorganisms to oxidize organic matter. It is not required for municipal wastes, biological treated effluents and surface water samples. The sources of seed can be settled sewage or soil culture etc.

Experiment No. 3

Determination of amount of COD in water

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

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:

- ✓ 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

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.

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)

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

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:

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

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

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

Ferric Phenanthroline (Green Blue) → Ferrous Phenanthroline (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:

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

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:

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

Procedure:

- ✓ Place 50ml sample in 500ml refluxing flask (for samples with COD>900mg/L use a smaller sample diluted to 50ml).
- ✓ Add 1g $HgSO_4$ and several glass beeds.
- ✓ Add slowly 5ml H_2SO_4 reagent while mixing to dissolve $HgSO_4$
- ✓ Cool while mixing to avoid the loss of volatile materials.
- ✓ Add 25 ml 0.25N $K_2Cr_2O_7$ solution and mix.
- ✓ Attach the flask to the condenser and turn on cooling water.
- ✓ Add reaming H_2SO_4 (70ml) through open end of the condenser continue mixing while adding H_2SO_4.
- ✓ Reflux the mixture for 2 hrs and cool to room temperature, after diluting the mixture to about twice its volume with distilled water.
- ✓ 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.
- ✓ Reflux and titrate in the same manner a blank containing the reagents and the volume of the distilled water will be equal to that of sample.

Observations and Calculations:

Sr. No.	*Description of Sample*	*Volume of titrant used for sample*	*Volume of titrant used for blank*	*COD*
		ml	*ml*	*ml*
1	Sample 1	21.7	14.7	280
2	Sample 2	21.8	14.7	284

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)

$\Rightarrow$ N = 0.25N 8000 = Equivalent Wt. of Oxygen x 1000

Comments:

- Chemical Oxygen Demand is a vital test for assessing the quality of effluents and waste waters prior to discharge. The Chemical Oxygen Demand (COD) test predicts the oxygen requirement of the effluent and is used for monitoring and control of discharges, and for assessing treatment plant performance.
- According to the National Environmental Quality Standards (NEQS) of august 2000 the value of COD should less 150 mg/l at 40^{O}C. Our test sample has 281 mg/l which shows that it is not safe to discharge n the river.

Questions:

1. Compare BOD and COD.

BOD	COD
1. The amount of oxygen required by the bacteria while stabilizing decomposable organic matter under aerobic conditions. 2. It is done by using bacteria. 3. BOD is less than COD. 4. It is time consuming (5 Days)	1. It is measurement of the amount of material that can be oxidized (combined with oxygen) in the presence of a strong chemical oxidizing agent. 2. This process requires $K_2Cr_2O_7$ 3. COD is greater than BOD. 4. It requires 2 to 3 hours.
COD / BOD = 1.5	

2. Why COD values are always higher than BOD values?

Because BOD is the oxygen required only for biodegradable organics but whereas COD includes both biodegradable and non-biodegradable that is the reason why COD is larger than BOD.

3. Write the NEQS for COD.

National Environmental Quality Standards for Municipal and Liquid Industrial Effluents (mg/L, Unless Otherwise Defined)

S.No	Parameter	Existing Standards	Revised Standards		
			Into Inland Water	Into Sewage Treatment[5]	Into Sea[6]
1.	Temperature or Temperature increase	40°C	=<3 °C	=< 3 ° C	=<3 °C
2.	pH value	6-10 pH	6 - 9	6 - 9	6 - 9
3.	5-days Biochemical Oxygen Demand (BOD_5) at 20°C[1]	80 mg/l.	80	250	80**
4	Chemical Oxygen Demand (COD)[1]	150 mg/l.	150	400	400
5.	Total suspended solids	150 mg/l.	200	400	200
6.	Total dissolved solids	3500 mg/l.	3500	3500	3500
7.	Grease and oil	10 mg/l.	10	10	10
8.	Phenolic compounds (as phenol)	0.1 mg/l.	0.1	0.3	0.3
9.	Chloride (as Cl)	1000 mg/l.	1000	1000	SC
10.	Fluoride (as F)	20 mg/l.	10	10	10
11.	Cyanide (as CN) total	2 mg/l.	1.0	1.0	1.0
12.	An-ionic detergents[2] (as MBAS)	20 mg/l.	20	20	20
13.	Sulphate (SO_4)	600 mg/l.	600	1000	SC
14.	Sulphide (S)	1.0 mg/l.	1.0	1.0	1.0
15.	Ammonia (NH_3)	40 mg/l.	40	40	40
16.	Pesticides, herbicides, fungicides and insecticides[3]	0.15 mg/l.	0.15	0.15	0.15

4. ***Write the applications of COD data to environmental Engineering?***

In environmental engineering, COD test is commonly used to indirectly measured measure the amount of organic compound in water. Most application of COD determines the amount of organic pollutants found in surface water, making COD a useful measure of water quality.

COD applications:

- ✓ Municipal applications
- ✓ Fast estimation of BOD
- ✓ Process control
- ✓ Influent /effluent for removal
- ✓ Discharge Permits
- ✓ Steam condensate
- ✓ Cooling water

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

The presence of silver sulphate as catalyst is needed for complete oxidation of aliphatic carbon compounds. $AgSO_4$ catalyst is used for oxidation of low molecular weight fatty acids.

Experiment No. 4

Determination of amount of Nitrogen in water

To determine the amount of nitrogen* (Kjeldhal Nitrogen) *in given water sample

General Theory:

All nitrogen present in the organic compounds may be considered as organic nitrogen. This includes amino acids, amines, amides, nitroderivatives and no of other organic compounds. In waters and waste water the form of nitrogen of greatest intrest are organic –N and ammonia-N, nitrates and nitrites. Organic nitrogen is defined functionally as organically bound nitrogen in tri negative state. In wastewaters organic-N include such natural materials like proteins, peptides, nucleic acids, urea and numerous synthetic organic materials. Organic nitrogen and ammonia can be determined together and have been referred as kjeldhal nitrogen.

Principle:

In the presence of H_2SO_4, $K_2 S0_4$ and $CuSO_4$, Ammonia nitrogen of many organic materials is converted to ammonium sulfate. Free ammonia and ammonia nitrogen also are converted to ammonium sulfate. During sample digestion a cupric ammonia complex is formed. After this mercury ammonia complex in the digestion has been decomposed by sodium thiosulfate, the ammonia is distilled from an alkaline layer and absorbed in boric acid.

Basic Steps involved:

1. Digestion
2. Distillation
3. Titration.

Titration theory:

The organic nitrogen is converted to ammonia nitrogen during the digestion. Boric acid is an excellent buffer. It combines with ammonia in the distillate to form ammonia and borate ions.

$$NH_3 + H_3BO_3 \longrightarrow NH_4^+ + H_2BO_3$$

The ammonia then is measured by back titration with strong acid such as sulfuric acid. Actually the acid measures the amount of boric ion present in the solution as follows.

$$H_2BO_3^- + H^+ \longrightarrow H_3BO_3$$

Reagents:

1. Digestion reagent (dissolve 134g K_2SO_4 and 7.3g $CuSO_4$ in about 800ml water carefully add 134ml Conc. H_2SO_4. Cool to room temperature, dilute to 1 lit with water. Mix well keeps at temp 20^0C to prevent vaporization).
2. Phenolphthalein indicator
3. Sodium hydroxide
4. Mixed indicator solution
5. Indicating boric acid solution
6. Standard sulfuric acid titrant.
7. Hydroxide thiosulfate reagent.

Procedure:

(a) Digestion

1. Take 280ml of sample in a kjeldhal flask.
2. Add few glass beads to it then add 50ml digestion reagent
3. Mix, heat and continue boiling until solution remains 25-50ml.
4. Cool it and add distilled water to it to make the volume 300ml.
5. Add 0.5 ml phenolphthalein indicator.
6. Add 50 ml thiosulfate hydroxide reagent solution.
7. If pink colour does not appears then add more 50ml thiosulfate hydroxide reagent solution.

(b) Distillation

1. In collect the distillate in a flask containing boric acid solution.
2. Collect 200ml distillate into 50ml boric acid solution.

(c) Titration

1. Titrate it against 0.02N H_2SO_4 solution until colour changes from purple to green.
2. Carry the blank titration, following all steps of procedure.

Calculations:

Total Nitrogen (mg/L) = $\frac{(A-B)^{*}280}{ml\ of\ Sample}$

Where,

A = volume of H_2SO_4 used for sample = 148 ml

B = Volume of H_2SO_4 used for blank = 0.5 ml

So,

$$\textbf{\textit{Total nitrogen (mg/L)}} = \frac{(148-0.5)^{*}280}{140} = \textbf{\textit{295 mg/L}}$$

Comments:

⇒ According to the NEQS of August 2000, there is no information about the total organic nitrates in the water requires for the safe disposal of waste water. It gives only the limitations for NH_3 in the waste water which is 40 mg/l.

⇒ The extra nitrogen present in the sample is too much then this is removed in the treatment plants using nitrification and de-nitrification processes.

Questions:

1. ***What is Kjeldhal nitrogen?***

Nitrogen attached to the organic compounds and Ammonia (NH_3) and ammonium ion (NH^{+1}) is called Kjeldhal nitrogen.

2. ***What is blue baby disease?***

Blue baby syndrome is characterized by reduced ability of the blood to carry oxygen because of reduced levels of normal hemoglobin. It is uncommon. Infants are most often affected, and may seem healthy, but show signs of blueness around the mouth, hands, and feet, its scientific name “Methaemoglobinemia”. These children may also have trouble breathing as well as vomiting and diarrhea. In extreme cases, there is marked lethargy, an

increase in the production of saliva, loss of consciousness and seizures. Some cases may be fatal. In the body nitrates are converted to nitrites. The nitrites react with hemoglobin in the red blood cells to form methaemoglobin, affecting the blood's ability to carry enough oxygen to the cells of the body. One of the most common causes is nitrate in drinking water. It is most important in bottle fed infants and water from wells in rural areas is of special concern. Controlling nitrate levels in drinking water sources to below around 50mg/litre is an effective preventive measure.

3. ***How ammonia nitrogen can be determined?***

Ammonia nitrogen can be determined using:

a. By micrometric method
b. By colorimetric method
c. By ion selective electrod method

Titrimetric procedure for the determination of ammonia nitrogen can be used only for samples which have been treated by the preliminary distillation into boric acid absorbing solution. In this procedure, the ammonium concentration of the boric acid solution is titrated with a strong acid titrant to the pale lavender end-point of methyl red-methylene blue indicator.

4. ***Why hydroxide thiosulphate reagent is added in above experiment?***

Hydroxide thiosulphate reagent is required to remove the residual chlorine from the solution before distillation. During sample digestion cupric-ammonium complex is formed. When this complex is formed then digestion is decomposed by sodium thiosulphate. For this purpose 0.025M Sodium tetraborate—Dissolve 5 g anhydrous sodium tetraborate (Na2B4O7) or 9.5 g sodium tetraborate decahydrate (Na2B4O7C10H2O) in reagent water and dilute to 1 L is added.

5. ***Write the significance of nitrogen test in Environmental Engineering.***

The significance is as follows:

Amount of nitrogen shows the quality of water. Excess amount is very dangers for health so test is necessary to determine the amount of nitrogen.

Nitrogen is an essential nutrient that is required for plants and animals for the formation of amino acids. It cannot be used by the plants in molecular form. One of such forms is ammonia

$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$

The toxicity to ammonia is primarily attributable to an un ionized from NH_3 as opposed to the ionized from NH_4^+. In general, more NH_3 and more toxicity exists at higher pH. So nitrogen in the soil etc is determined by this test. A good fertilizer is that which have proper amount of nitrogen. So this amount is determined by this test.