Indian Institute of Technology Delhi
Department of Civil Engineering
CEL212 Environmental Engineering
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Laboratory Experiment 6: Dissolved Oxygen (DO)

Objective: Determine DO content of a given sample

Background:

Dissolved oxygen (DO) levels in environmental water depend on the physiochemical and biochemical activities in water body and it is an important useful in pollution and waste treatment process control. Two methods are commonly used to determine DO concentration: (1) The iodometric method which is a titration-based method and depends on oxidizing property of DO and (2) The membrane electrode procedure, which works based on the rate of diffusion of molecular oxygen across a membrane.

In the Iodometric method, divalent manganese solution is added to the solution, followed by addition of strong alkali in a glass-stopper bottle. DO rapidly oxidize an equivalent amount of the dispersed divalent manganese hydroxide precipitates to hydroxides of higher valence states. In the presence of iodide ions in an acidic solution, the oxidized manganese reverts to the divalent state, with the liberation of iodine equivalent of the original DO content. The iodine is then titrated with a stranded solution of thiosulfate. The titration end point can be detected visually with a starch indicator. Some oxidizing and reducing agents present in solution can interfere with the iodometric method. Oxidizing agents liberate iodine from iodides (positive interference) and some reducing agents reduce iodine to iodide (negative interference). Also, organic matter present in solution can be oxidized partially in the presence of oxidized manganese precipitate, thus causing negative errors. Thus some modification of procedure is required.

Standardization of thiosulfate solution

$2Na_2S_2O_3.5H_2O+I_2 \Leftrightarrow Na_2S_4O_6 +2NaI+10H_2O$ (1a)

$2S_2O_3^{2-}+I_2 \Leftrightarrow S_4O_6^{2-}+2I^-$ (1b)

$Cr_2O_7^{2-}+6I^-+14H^+ \Leftrightarrow 2Cr^{3+}+3I_2+7H_2O$ (1c)

$2IO_3^-+10I^-+12H^+ \Leftrightarrow 6I_2+6H_2O$ (1d)

The Winkler Method for DO Determination

If no oxygen is present, a pure white precipitate is formed when MnSO4 and alkali-iodide reagent (NaOH+KI) are added to the sample.

$Mn^{2+} + 2OH^- \rightarrow Mn(OH)_2$ (white precipitate) (2a)

If sample has some oxygen, Mn2+ is oxidized to Mn4+ and precipitates brown hydrated oxide.

$Mn^{2+} + 2OH^- +0.5O_2 \rightarrow MnO_2$ (brown hydrated precipitate) + H_2O (2b)

The oxidation of Mn2+ to MnO2 is called fixation of the oxygen, occurs slowly at low temperature.

$Mn(OH)_2 +0.5O_2 \rightarrow MnO_2 +H_2O$ (2c)

After shaking the sample for a time sufficient to allow all oxygen to react, the floc is allowed to settle so to leave 5 cm of clear liquid below the stopper; then sulfuric acid is added. Under the low pH conditions, MnO2 oxidizes to produce I_2. I2 is insoluble in water and forms complex is excess iodide ion is present in solution, thus preventing escape of iodine ions from solution.

$MnO_2 + 2I^- + 4H^+ \rightarrow Mn^{2+} + I_2 + 2H_2O$ (2d)

$I_2 + I^- \Leftrightarrow I_3^-$ (2e)

Now the sample is ready for titration with thiosufate solution.

The Azide Modification with the Winkler Method for DO Determination

This modification is used because of presence of nitrite ions. This occurs in effluents from wastewater treatment plants employing biological processes, in river water and in incubated BOD samples. It does not oxidize Mn2+ but doses oxidize I^- to I2 under acidic conditions. When the reduced form of nitrite (N2O2) is oxidized by oxygen, it is converted to NO_2^- again, establishing the cycle again that can result in erroneous results, far in excess of amounts that would be expected.

$2NO_2^- + 2I^- + 4H^+ \rightarrow I_2 + N_2O_2 + 2H_2O$ (3a)

$N_2O_2 + 0.5O_2 + H_2O \rightarrow 2NO_2^- + 2H^+$ (3b)

When interference from nitrites is present, it is impossible to obtain a permanent end point. As soon as the blue color of the starch indicator has been discharged, the nitrites formed by the reaction (3b) reacts with more iodide ions to produce I_2 and the blue color of the starch indicator will return. The nitrite interference is easily overcome with use of sodium azide (NaN_3), which is incorporated in the alkali-KI reagent. When sulfuric acid is added, following reactions happen:

$NaN_3 + H^+ \rightarrow HN_3 + Na^+$ (3c)

$HN_3 + NO_2^- + H^+ \rightarrow N_2 + N_2O + H_2O$ (3d)

Lab Procedure

Method: The Azide Modification (For nitrite-N < 0.05 mg/L and Ferrous iron<1 mg/L)

The azide modification is used to minimize the effect of interfering materials. It removes interference caused by nitrite which is most commonly found interference in biologically treated effluents and in incubated BOD samples.

Collection of Samples for DO Determination

Samplers are designed to ensure that air cannot enter into the sample. Most samplers are designed to retain 3-4 times the volume of samples which is required for analysis purposes. As oxygen values change with time due to any biological activity, it is important to fix it in field immediately after collection. This is done using reagents using in DO test and then the titration is done in laboratory. This method gives low results for samples with high iodine demand and in this case it is better to preserve sample using 0.7 mL concentrated sulfuric acid and 0.02 g sodium azide. When this is doe it is necessary to add 3 mL of alkali-iodide reagent rather than the usual 2 mL because of the extra acid the sample contains. Better results are also obtained if the sample is fixed and stored in the dark and on the ice until the analyses are conducted. The final titration should not be delayed more than 6 hours.

Reagents:

1. Manganese sulfate solution: Dissolve 480 g $MnSO_4.4H_2O$, 400 g $MnSO_4.2H_2O$ or 364 g $MnSO_4.H_2O$ in distilled water, filter, and dilute to 1L. The $MnSO_4$ solution should not give a color with starch when added to an acidified potassium iodide (KI) solution.
2. Alkali-iodide-azide reagent
3. Sulfuric acid: One mL is equivalent to ~ 3mL alkali-iodide-azide reagent.
4. Starch solution: Dissolve 2 g laboratory-grade soluble starch and 0.2 g salicyclic acid as preservative in 100 mL hot distilled water.
5. Standard sodium thiosulfate titrant: Dissolve 6.205 g $Na_2S_2O_3 .5H_2O$ in distiller water and add 1.5 mL 6N NaOH or 0.4 g solid NaOH and dilute to 1000 mL. Standardize with bi-iodate solution.
6. Standard potassium bi-iodate solution (0.0021M): Dissolve 812.4 mg $KH(IO_3)$ in distilled water and dilute to 1000 mL.
7. Standardization: Dissolve e ~ 2 g KI, free from iodate in an Erlenmeyer flask with 100 to 150 mL distilled water; add 1 mL 6N H_2SO_4 or a few drops of conc. H_2SO_4 and 20.00 mL standard bi-iodate solution. Dilute to 200 mL and titrate librated iodine with thiosulfate titrant, adding starch toward end of titration, when a pale straw color is reached. When the solution is of equal, 20.00 mL 0.025M $Na_2S_2O_3$ should be required. If not, adjust the $Na_2S_2O_3$ solution to 0.025M.

Apparatus: Incubation bottle 300mL volume; Air compressor

Steps:

1. Make dilution water by adding 2mL/L of following reagents in distilled water:
    a. Phosphate buffer solution
    b. Magnesium sulfate solution
    c. Calcium chloride solution
    d. Ferric chloride solution
    e. Sodium Sulfite solution
2. Take 300 mL sample in BOD bottle. Prepare two sets of this sample. Keep one set for DO analysis for day 0 (i.e., Sample0Day) and another sample in BOD incubator for 5 days at 20°C (Sample5Day) (*this is how 5-day BOD experiment is done).* **Here you will prepare duplicate samples and analyze at Day 0 (i.e., Sample0Day_A and Sample0Day_B).**
3. For a given sample bottle, add 1 mL of alkali azide and then 1 mL manganous sulfate solution. Shake well the bottle and keep it open for 5 minutes to settle the precipitate. Add 2 mL concentrated H_2SO_4 and place the cap on the bottle. Shake well the bottle till all the precipitate is dissolved.
4. Take 203 mL of sample in conical flask and titrate with standard sodium thiosulfate solution (0.025N) till the colour changes from dark yellow to light yellow. Then add few drops of starch indicator and continue to titrate till the color of the solution becomes either colorless or changes to its original sample colour. Note down volume of 0.025N sodium thiosulfate consumed.
5. Calculate DO value of the sample. ***Remember that in 200 mL sample, 1 mL of sodium thiosulfate of 0.025N equals to 1 mg/L dissolved oxygen***:
    =>Dissolved oxygen (DO) (in mg/L) = mL of sodium thiosulfate (0.025N) consumed.

Notes: Dilution of Sample

1. 0.1, 0.5, and 1% for strong waste water
2. 1.0, 2.5, and 5% for raw and settled sewage
3. 5.0, 12.5 and 25% for oxidized effluent
4. 25, 50 and 100% for polluted river water

Questions

Q1. What precautions do you need to take during DO measurement in raw wastewater sample? Hint: This sample can have both oxidizing and reducing agents.

Reference Materials:

AWWA, WEF, APHA, 1998, Standard Methods for the Examination of Water and Wastewater (Method: 4500-O. C. Azide Modification)

Sawyer, C.N., McCarty, P.L., and Parkin, G.F. 2000. *Chemistry for Environmental Engineering* 4th Edition. Tata McGraw-Hill Publishing Company Limited.

++++++++Additional Question (Not for Submission)+++++++

QA1. Compute ultimate BOD and oxygen consumption rate constant using the following data for a stream receiving treated effluent.

Time (days)	BOD exerted at time t (Y_t)
2	11
4	18
6	22
8	24
10	26

Q2. To determine BOD of a sample, three dilutions of the samples are made (BOD bottle volume=300mL). In the BOD dilution water (without sample), initial DO=0 (blank). All samples are incubated at 20°C for 5 days. Look at the following data and calculate 5-day BOD value of the sample at 15°C?

$$\textbf{t-day BOD} = [DO_t - DO_0]/(P) \quad (1)$$

where P= Dilution factor = 300mL/(sample volume in mL)

Bottle no.	Wastewater sample (mL)	Initial DO (mg/L) (DO_0)	DO at 5-day (mL) (DO_5)
1	20	8.9	1.5
2	10	9.1	2.5
3	5	9.2	5.8
4	2	9.2	7.5