Chap. 1 Dissolved Oxygen (DO)

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Contents

- Water pollution
- Dissolved Oxygen (DO)

Definition

Water pollution refers to the addition of foreign substances (pollutants) to a water source.

These impurities have a detrimental effect on water quality, and can be harmful to living organisms and aquatic life.

Pollution can be introduced to water from both point sources and non-point sources.

- Point sources: man-made industrial waste and domestic sewage
- Non-point sources: natural sources (soil erosion and silt-bearing runoff)

1.1. General consideration

- All living organism are dependent upon oxygen
  - To maintain metabolic processes – producing energy for growth and reproduction

- All the gases of the atmosphere are soluble in water to some degree
  - Both nitrogen and oxygen are classified as poorly soluble
  - They do not react with water chemically
  - Solubility is directly proportional to their partial pressures (Henry's law)

- The solubility of both nitrogen and oxygen varies greatly with the temperature over the range of interest for natural water
  - Fig 1.1 shows solubility curves for the two gases in distilled or low-solid-content water in equilibrium with air at 760mm Hg (1atm) pressure
  - The solubility is less in saline waters

1.1 General consideration

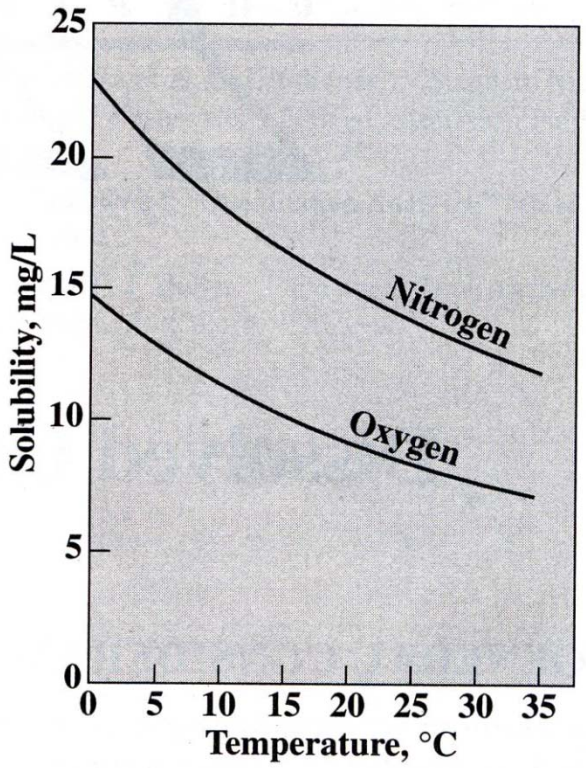


Figure 1.1 Solubility of oxygen and nitrogen
In distilled water saturated with air at 1 atm.

- More nitrogen than oxygen dissolves in water under partial-pressure conditions
- At saturation, the dissolved gases contain about 38% oxygen on a molar basis
  - Twice as much oxygen as in the normal atmosphere
- The solubility of atmospheric oxygen in fresh water
  - 0 °C 14.6 mg/L
  - 35 °C 7 mg/L
- Oxygen is poor soluble gas
  - The atmospheric pressure
  - At any given temperature

1.1 General consideration

- Rate of biological oxidation increase with temperature, and oxygen demand increases accordingly, high-temperature conditions
  - Dissolved oxygen is least soluble, can be of concern
- During the summer months when temperatures are high and solubility of oxygen at a minimum
  - Dissolved-oxygen levels of about 8 mg/L as being the maximum available under critical conditions
- In aerobic biological treatment processes, the limited solubility of oxygen is of great importance
  - It governs the rate at which oxygen will be absorbed by the medium and therefore the cost of aeration

1.1 General consideration

- The solubility of oxygen is less in salt-containing water than it is clean water (Table 1.1)
  - The chloride content of seawater : approximately 19,000 mg/L

Table 1.1 Solubility of dissolved oxygen in water in equilibrium with dry air at 1 atm and containing 20.9 % oxygen

Temperature, °C	Chloride concentration, mg/L				
	0	5000	10,000	15,000	20,000
0	14.6	13.8	13.0	12.1	11.3
1	14.2	13.4	12.6	11.8	11.0
2	13.8	13.1	12.3	11.5	10.8
3	13.5	12.7	12.0	11.2	10.5
4	13.1	12.4	11.7	11.0	10.3
5	12.8	12.1	11.4	10.7	10.0
6	12.5	11.8	11.1	10.5	9.8
7	12.2	11.5	10.9	10.2	9.6
8	11.9	11.2	10.6	10.0	9.4
9	11.6	11.0	10.4	9.8	9.2
10	11.3	10.7	10.1	9.6	9.0
11	11.1	10.5	9.9	9.4	8.8
12	10.8	10.3	9.7	9.2	8.6
13	10.6	10.1	9.5	9.0	8.5
14	10.4	9.9	9.3	8.8	8.3
15	10.2	9.7	9.1	8.6	8.1
16	10.0	9.5	9.0	8.5	8.0
17	9.7	9.3	8.8	8.3	7.8
18	9.5	9.1	8.6	8.2	7.7
19	9.4	8.9	8.5	8.0	7.6
20	9.2	8.7	8.3	7.9	7.4
21	9.0	8.6	8.1	7.7	7.3
22	8.8	8.4	8.0	7.6	7.1
23	8.7	8.3	7.9	7.4	7.0
24	8.5	8.1	7.7	7.3	6.9
25	8.4	8.0	7.6	7.2	6.7
26	8.2	7.8	7.4	7.0	6.6
27	8.1	7.7	7.3	6.9	6.5
28	7.9	7.5	7.1	6.8	6.4
29	7.8	7.4	7.0	6.6	6.3
30	7.6	7.3	6.9	6.5	6.1

*After G. C. Whipple and M. C. Whipple, Solubility of Oxygen in Sea Water, *J. Amer. Chem. Soc.*, **33:** 362 (1911).

1.2. Environmental significance of dissolved oxygen

- In liquid wastes, dissolved oxygen is the factor that determines whether the biological changes are brought about by aerobic or by anaerobic organisms
  - Free oxygen for oxidation of organic and inorganic matter → producing innocuous end product
  - Reduction of certain inorganic salts such as sulfate → obnoxious end product

- Both types of organisms are ubiquitous in nature
  - Aerobic organisms (aerobic condition) have to be maintained

- Dissolved oxygen measurements are vital for maintaining aerobic conditions
  - In natural waters that receive pollutional matter
  - To purify domestic and industrial wastewaters

1.2. Environmental significance of dissolved oxygen

- Determinations of dissolved oxygen serve as the basis of the BOD test
  - The most important factor to evaluate the pollutional strength of domestic and industrial wastes

- All aerobic treatment processes depend upon the presence of dissolved oxygen, and tests for it are indispensable
  - Controlling the rate of aeration → adequate amounts of air for maintaining aerobic conditions
  - To prevent excessive use of air and energy

1.3. Collection of samples for determination of dissolved oxygen

- In most case of interest, the dissolved oxygen level will be below saturation, and exposure to the air will lead to erroneous

- A special sample device: “Standard method”
  - Contact with air cannot be avoid during the sampling

- If space is available to allow the bottles to overflow, a sample of water that is representative of the mixture being sampled can be obtained

- Most samplers are designed to provide an overflow of two of three times the bottle volume to ensure collection of representative samples

- As oxygen readily penetrates most rubber and plastic tubing, great caution is required in their use for sampling

1.3. Collection of samples for determination of dissolved oxygen

- Since oxygen values may change radically with time because of biological activity, it is customary to “fix” the samples immediately after collection
- The usual procedure is to treat the sample with the conventional reagents used in the dissolved-oxygen test and then perform the titration when the samples
- This procedure will give low results for sample with a high iodine demand
  - Addition of 0.7mL concentrated H_2SO_4 and 0.02g sodium azide
  - The final titration may be delayed up to 6h
- “Fixed” samples are stored in the dark and on ice

수질오염공정시험법 (용존산소)

윙클러-아지드화나트륨 변법

1.1 측정원리

황간망간과 알칼리성 요도드칼륨용액을 넣을 때 생기는 수산화제일망간이 시료중의 용존산소에 의하여 산화되어 수산화제이망간으로 되고, 황산 산성에서 용존산소량에 대응하는 요오드를 유리한다. 유리된 요오드를 티오황산나트륨으로 적정하여 용존산소의 양을 정량하는 방법이다.

이 방법은 아질산염 5 ㎎/ℓ 이하, 제일철염 1.0 ㎎/ℓ 이하에서 방해를 받지 않으며, 하천수, 하수 및 공장폐수에 적용한다. 정량범위는 0.1 ㎎/ℓ 이상이다.

1.2 시료의 전처리

-생략-

수질오염공정시험법 (용존산소)

윙클러-아지드화나트륨 변법

1.3 시험방법

시료를 가득 채운 300 ㎖ 용존산소측정병(또는 BOD병, 그림 1)에 황산망간용액 1 ㎖와 알칼리성 요오드화 칼륨-아지드화나트륨 용액 1 ㎖를 넣고 기포가 남지 않게 조심하여 마개를 닫고 수회 병을 회전하면서 섞는다.

시료가 해수이거나 알칼리성에서 산화되기 쉬운 유기물을 함유하는 폐수의 경우에는 2 분간 병을 회전하여 섞는다.

2 분간 이상 정치시키고 위의 맑은 액에 미세한 침전이 남아 있으면 다시 회전시켜 혼화한 다음 정치하여 완전히 침전시킨다.

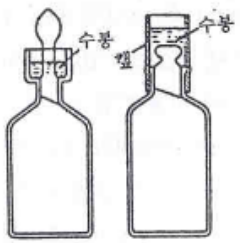


그림 1. 용존산소 측정병(용량 300㎖)

수질오염공정시험법 (용존산소)

윙클러-아지드화나트륨 변법

1.3 시험방법

100 ㎖이상의 맑은층이 생기면 마개를 열고 황산 2.0 ㎖를 병목으로부터 넣는다.

마개를 다시 닫고 갈색의 침전물이 완전히 용해할 때까지 병을 회전시킨다.

용존산소측정병의 용액 200 ㎖를 정확히 취하여 황색이 될 때까지 0.025N - 티오황산나트륨액으로 적정한 다음, 전분용액 1 ㎖를 넣고 액의 청색이 무색이 될 때까지 적정한다.

윙클러-아지드화나트륨 변법 시험방법 정리

시료 300mL

↓

황산망간+알카리성 요오드화칼륨 아지트화나트륨 용액 혼합 (각 1mL)

↓

2분간 정치 (침전물 존재여부확인)

↓

황산 2mL 주입후, 갈색침전물 용해시까지 회전

↓

용액 200mL 취하여 황색될때까지 적정

↓

전분용액 1mL 넣고, 액이 청색에서 무색까지 적정

1.4. Standard reagent for measuring dissolved oxygen

Selection of 0.025N Thiosulfate Solution

- The eqiuvalent weight of oxygen : 8g
- The normality of most titrating agents used in water and wastewater analysis
  - 1mL is equivalent to 1.0mg of measured material
  - N/8 (0.125N) of thiosulfate should be used
- Standard practice to use 200mL samples for titration (1/5 L)
  - 1L samples : 0.125N = 200mL sample : **0.025N**

1.5. Methods of determining dissolved oxygen

The Winkler Method

The unmodified Winkler method is subject to interference from a great many substances. Certain oxidizing agents such as nitrite and Fe^{3+} are capable of oxidizing I^- to I_2 and produce results that are too high. Reducing agents such as Fe^{2+}, SO_3^{2-}, S^{2-}, and polythionate, reduce I_2 to I^- and produce results that are too low. The unmodified Winkler method is applicable only to relatively pure waters.

The reactions involved in the Winkler procedure are as follows:

$$Mn^{2+} + 2OH^- \rightarrow Mn(OH)_2(s) \qquad \text{(white precipitate)} \qquad (22.4)$$

If no oxygen is present, a pure white precipitate of $Mn(OH)_2(s)$ forms when $MnSO_4$ and the alkali-iodide reagent (NaOH + KI) are added to the sample. If oxygen is present in the sample, then some of the Mn(II) is oxidized to Mn(IV) and precipitates as a brown hydrated oxide. The reaction is usually represented as follows:

$$Mn^{2+} + 2OH^- + \tfrac{1}{2}O_2 \rightarrow MnO_2(s) + H_2O \qquad (22.5)$$

or

$$Mn(OH)_2 + \tfrac{1}{2}O_2 \rightarrow MnO_2(s) + H_2O \qquad (22.6)$$

The oxidation of Mn(II) to $MnO_2(s)$, sometimes called fixation of the oxygen, occurs slowly, particularly at low temperatures. Furthermore, it is necessary to move the flocculated material throughout the solution to enable all the oxygen to react. Vigorous shaking of the samples for at least 20 seconds is needed. In the case of brackish or seawaters, much longer contact times are required.

After shaking the samples for a time sufficient to allow all oxygen to react, the floc is allowed to settle so as to leave at least 5 cm of clear liquid below the stopper;

1.5. Methods of determining dissolved oxygen

The Winkler Method

then sulfuric acid is added. Under the low pH conditions that result, the MnO_2 oxidizes I^- to produce I_2.

$$MnO_2(s) + 2I^- + 4H^+ \rightarrow Mn^{2+} + I_2 + 2H_2O \qquad (22.7)$$

I_2 is rather insoluble in water, but forms a complex with the excess iodide present to reversibly form the more soluble tri-iodate, thus preventing escape of I_2 from solution:

$$I_2 + I^- \rightleftharpoons I_3^- \qquad (22.8)$$

The sample should be stoppered and shaken for at least 10 seconds to allow the reaction to go to completion and to distribute the iodine uniformly throughout the sample.

The sample is now ready for titration with 0.025 N thiosulfate. The use of 0.025 N thiosulfate is based upon the premise that a 200-mL sample will be used for titration. In adding the reagents used for the Winkler test, a certain amount of dilution of the sample occurs; therefore, it is necessary to take a sample somewhat greater than 200 mL for the titration. When 300-mL bottles are used in the test, 1 mL of $MnSO_4$ and 1 mL of alkali-KI solutions are used. These are added in such a manner as to displace approximately 2 mL of sample from the bottle, and a correction should be made. When the 2 mL of acid is added, none of the oxidized floc is displaced; thus, no correction need be made for its addition. To correct for the addition of the first two reagents, 201 mL of the treated sample is taken for titration.

Titration of a sample of a size equivalent to 200 mL of the original sample with 0.025 N thiosulfate solution yields results in milliliters, which can be interpreted directly in terms of milligrams per liter of dissolved oxygen.

Summary of the Winkler Method

$$Mn^{2+} + 2OH^- \rightarrow Mn(OH)_2(s)$$

If no oxygen is present: white precipitate

1 $$Mn^{2+} + 2OH^- + \tfrac{1}{2}O_2 \rightarrow MnO_2(s) + H_2O$$

$$Mn(OH)_2 + \tfrac{1}{2}O_2 \rightarrow MnO_2(s) + H_2O$$

If oxygen is present: Brown precipitate

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

Brown precipitate is removed from solution

$$I_2 + I^- \rightleftharpoons I_3^-$$

3 $$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$

Titration with thiosulfate

1.5. Methods of determining dissolved oxygen

The azide modification of the Winkler Method

The nitrite ion is one of the most frequent interferences encountered in the dissolved-oxygen determination. It occurs principally in effluents from wastewater treatment plants employing biological processes, in river waters, and in incubated BOD samples. It does not oxidize Mn^{2+} but does oxidize I^- to I_2 under acid conditions. It is particularly troublesome because its reduced form, N_2O_2, is oxidized by oxygen, which enters the sample during the titration procedure and is converted to NO_2^- again, establishing a cyclic reaction that can lead to erroneously high results, far in excess of amounts that would be expected. The reactions involved may be represented as follows:

$$2NO_2^- + 2I^- + 4H^+ \rightarrow I_2 + N_2O_2 + 2H_2O \qquad (22.9)$$

and

$$N_2O_2 + \tfrac{1}{2}O_2 + H_2O \rightarrow 2NO_2^- + 2H^+ \qquad (22.10)$$

When interference from nitrite 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 nitrite formed by the reaction in Eq. (22.10) will react with more I^- to produce I_2 and the blue color of the starch indicator will return.

Nitrite interference may be easily overcome by the use of sodium azide (NaN_3). It is most convenient to incorporate the azide in the alkali-KI reagent. When sulfuric acid is added, the following reactions occur and the NO_2^- is destroyed.

$$NaN_3 + H^+ \rightarrow HN_3 + Na^+ \qquad (22.11)$$

$$HN_3 + NO_2^- + H^+ \rightarrow N_2 + N_2O + H_2O \qquad (22.12)$$

By this procedure, nitrite interference is eliminated and the method of determination retains the simplicity of the original Winkler procedure.

1. Dissolved Oxygen (DO)

Summary of the Azide Modification of the Winkler Method

$$2NO_2^- + 2I^- + 4H^+ \rightarrow I_2 + N_2O_2 + 2H_2O$$
$$N_2O_2 + \tfrac{1}{2}O_2 + H_2O \rightarrow 2NO_2^- + 2H^+$$

Nitrite Interferences

$$NaN_3 + H^+ \rightarrow HN_3 + Na^+$$
$$HN_3 + NO_2^- + H^+ \rightarrow N_2 + N_2O + H_2O$$

Nitrite is destroyed

$$Mn^{2+} + 2OH^- \rightarrow Mn(OH)_2(s)$$

If no oxygen is present: white precipitate

1

$$Mn^{2+} + 2OH^- + \tfrac{1}{2}O_2 \rightarrow MnO_2(s) + H_2O$$
$$Mn(OH)_2 + \tfrac{1}{2}O_2 \rightarrow MnO_2(s) + H_2O$$

If oxygen is present: Brown precipitate

2

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

Brown precipitate is removed from solution

$$I_2 + I^- \rightleftharpoons I_3^-$$

3

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

Titration with thiosulfate

1. Dissolved Oxygen (DO)

윙클러-아지드화나트륨 변법

시료 300mL

황산망간+알카리성 요오드화칼륨 아지트화나트륨 용액 혼합 (각 1mL)

$$2NO_2^- + 2I^- + 4H^+ \rightarrow I_2 + N_2O_2 + 2H_2O$$
$$N_2O_2 + \tfrac{1}{2}O_2 + H_2O \rightarrow 2NO_2^- + 2H^+$$

$$NaN_3 + H^+ \rightarrow HN_3 + Na^+$$
$$HN_3 + NO_2^- + H^+ \rightarrow N_2 + N_2O + H_2O$$

2분간 정치 (침전물 존재여부확인)

$$Mn^{2+} + 2OH^- \rightarrow Mn(OH)_2(s)$$

황산 2mL 주입후, 갈색침전물 용해시까지 회전

$$Mn^{2+} + 2OH^- + \tfrac{1}{2}O_2 \rightarrow MnO_2(s) + H_2O$$
$$Mn(OH)_2 + \tfrac{1}{2}O_2 \rightarrow MnO_2(s) + H_2O$$

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

용액 200mL 취하여 황색될때까지 적정

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

전분용액 1mL 넣고, 액이 청색에서 무색까지 적정

Thank you !!!