Dissolved Oxygen

~ All living organisms are dependent upon oxygen.

~ All the gases of the atmosphere are soluble in water to some degree

~ Henry's Law O_2, N_2, poorly soluble

~ 14.6 mg/L at 0℃

~ 7 mg/L at 35℃ under 1atm of pressure

~ Temp & Pressure dependent

~ Most of the critical conditions related to dissolved oxygen deficiency occur during the summer months (high temp, low DO)

~ 8 mg/L as being the maximum available under critical conditions

[Cl^-] in seawater 19,000mg/L (Table 21-1)

~ less soluble in saline waters

~ less soluble in polluted waters.

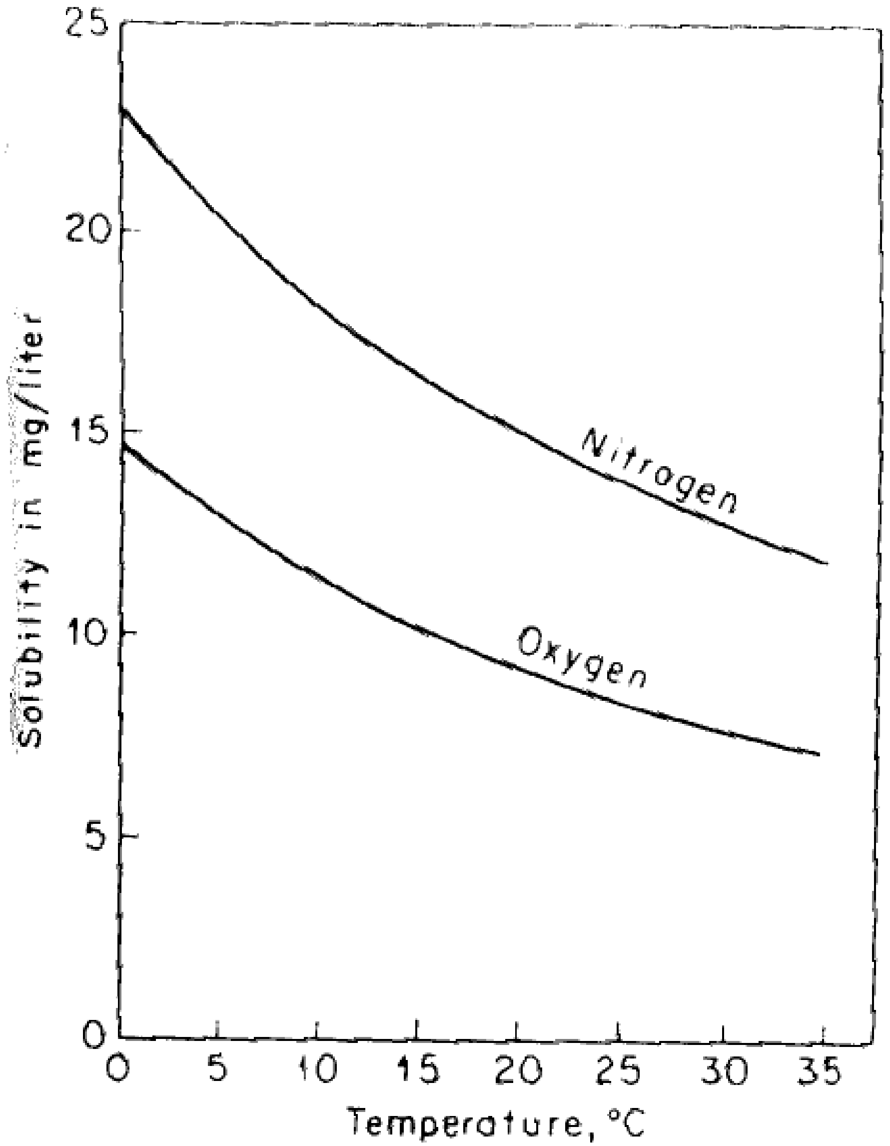


FIGURE 21-1
Solubility of oxygen and nitrogen in distilled water saturated with air at 760 mm Hg.

TABLE 21-1

Solubility of dissolved oxygen in water in equilibrium with dry air at 760 mm Hg and containing 20.9 percent 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)

$$K_H = \frac{P_i}{C_w} \quad (\text{atm}\cdot\text{L mol}^{-1})$$

$$K_{H'} = \frac{C_a}{C_w} (\text{mol La}^{-1}/\text{ mol Lw}^{-1})$$

$$K_{H'} = \frac{K_H}{RT} \quad (P_i = \left(\frac{n_i}{V}\right)RT)$$

$$\frac{K_H}{RT} = \frac{C_a}{C_w}$$

$$K_H = \frac{0.2atm}{\left(\frac{9.2}{32}\right)\times 10^{-3}\frac{mol}{L}} = 696 \text{ atm L mol}^{-1}$$

Environmental Significance of Dissolved Oxygen

~ dissolved oxygen is the factor that determines whether the biological changes are brought about by aerobic or by anaerobic organisms

~ anaerobic organisms → oxidation products are very often obnoxious

~ dissolved oxygen measurements are vital for maintaining aerobic conditions

~ water quality management

~ serve of the basis of the BOD test

~ aerobic treatment processes

~ oxygen is a significant factor in the corrosion of iron and steel

Collection of samples for determination of Dissolved Oxygen

~ any exposure to the air → erroneous results

~ a special sampling device

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

~ because of biological activity, it is customary to fix the samples immediately after the collection.

~ 0.7mL Conc H_2SO_4
0.02 g sodium azide N_aN_3 (biocide)
3mL KI

~ Stored in the dark and on ice

Section of Methods

(1) Iodometric Methods

positive errors ~ NO_2^-, Fe^{3+}

negative errors ~ Fe^{2+}

organic matter ➔ negative errors

(2) Azide modification – removes interferences caused by nitrite ~ O_2^-

(3) Permanganate modification Fe^{2+}

(4) Flocculation modification -SS

Choice of std Reagent for Measuring Dissolved Oxygen

~ depend upon reactions that release an amount of iodine equivalent to the amount of oxygen

~ titration by sodium thiosulfate such as reducing

$Na_2S_2O_3$ reagent

reducing agent

~ starch-iodine complex (blue color) ➔ colorless (iodide ion)

Choice of stdand reagent for measuring Dissolved Oxygen

(0.025N) $Na_2S_2O_3$

Selection of (N/40) thiosulfate solution

Equivalent Weight of oxygen is 8 ➔ $\frac{N}{8}$

Sample volumes 200 mL ➔ $\frac{N}{8} \times \frac{1}{5} = \frac{N}{40}$

* the normality of most titrating agents used in water and wastewater is adjusted so that each milliliter is equivalent to 1.0 mg of the measured material.

1 mg O_2 ➔ 1.25×10^{-4} eq

$NV = N'V'$

$\therefore$ if sample size is 200 mL ➔ $\frac{N}{40}$

$$\left(1.25 \times 10^{-4}\right) eq = \frac{1.0}{8}$$

Preparation and standardization of N/40 thiosulfate

reducing agent

$Na_2S_2O_3 \cdot 5H_2O$ ~ because of water hydration it cannot be dried to a compound of definite composition

~ it is necessary to prepare solutions that are slightly stronger than desired and to standardize them against a primary std.

The equivalent weight of $Na_2S_2O_3$ cannot be calculated from its formula

$2Na_2S_2O_3 \cdot 5H_2O + I_2 \rightarrow Na_2S_4O_6 + 2NaI + 10\ H_2O$

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

~ each molecule of thiosulfate supplies one electron

is equivalent to one atom of iodine

~ EW of sodium thiosulfate is equal to the Molecular weight

Methods of Determining Dissolved Oxygen

Originally, heating sample → analyze gas

cumbersome and time-consuming

The winkler method

NO_2^-, Fe^{3+} (oxidizing compound) I^- to I_2

positive interference

Fe^{2+}, SO_3^{2-}, S^{2-} (reducing compound) are capable of reducing I_2 to I^-

negative interference

Methods of Determining Dissolved Oxygen

In the absence of oxygen

① $Mn^{2+} + 2OH^{-} \rightarrow \underline{Mn(OH)_2}$ (white precipitate)

when $MnSO_4$ and (NaOH + KI) are added to the sample,
if no oxygen is present

if oxygen is present

In the presence of oxygen

② $Mn^{2+} + 2OH^{-} + \frac{1}{2}O_2 \rightarrow \underline{MnO_2} + H_2O$

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

brown hydrated oxide

the oxidation of Mn(II) to MnO_2 ~ fixation of the oxygen

~ occurs slowly, particularly at low temp

~ vigorous shaking for at least 20sec is needed

Then sulfuric acid is added (2mL)

낮은 pH에서 MnO_2가 I^-를 I_2로 전환!!!

③ $MnO_2 + 2I^- + 4H^+ \rightarrow Mn^{2+} + I_2 + 2H_2O$

④ $I_2 + I^- \rightleftarrows I_3^-$

tri-iodate preventing escape of I_2 from the solution

the sample should be stoppered shaken for at least 10 sec to allow reaction to go to completion.

~ the sample is now ready for titration with N/40 thiosulfate

$Mn^{2+} + 2OH^{-} + \frac{1}{2} O_2 \rightarrow MnO_2 + H_2O$

$MnO_2 + 2 I^{-} + 4 H^{+} \rightarrow Mn_2+ + I_2 + 2 H_2O$

$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_2O_6 + 2 NaI + 10 H_2O$

Dissolved Oxygen Membrane Electrodes

DO 전극법

~ in situe measurements

~ analaytical principles; diffusion currents through membrane is linearly proportional to the concentration of dissolved oxygen (polarographic principle)

~ calibration by the winkler method is required

~ sufficient movement of the sample by the electrode

~ equipped with a thermistor

~~ dissolved oxygen profiles of reservoirs and streams, and BOD test

~ an excellent methods for DO analysis in polluted waters,

~ highly colored waters, and strong waste effluents

Dissolved Oxygen Membrane Electrodes

5.6 The Effect of Oxygen-Demanding Water on River

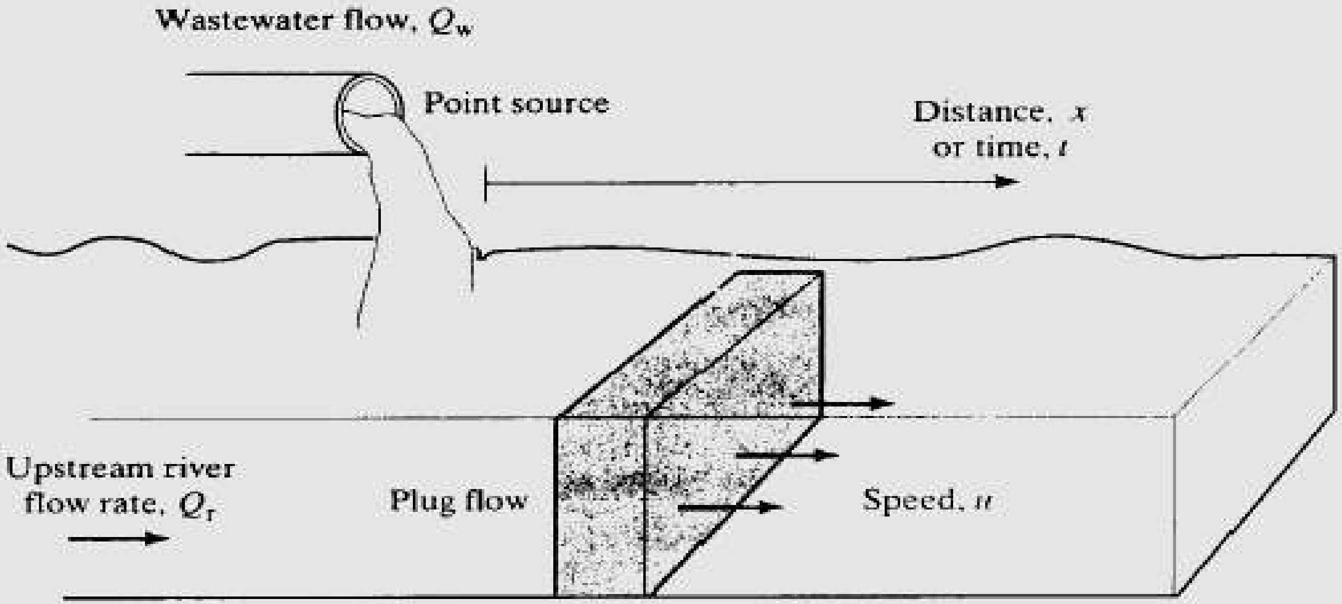


FIGURE 5.14 The point-source, plug flow model for dissolved-oxygen calculations.

Rate of deoxygenation $= k_d L_t$

k_d ***= the deoxygenation rate constant (day***$^{-1}$***)***

L_t ***= the BOD remaining t (days) after the wastes enter the river (mg/L)***

The Oxygen sag curve

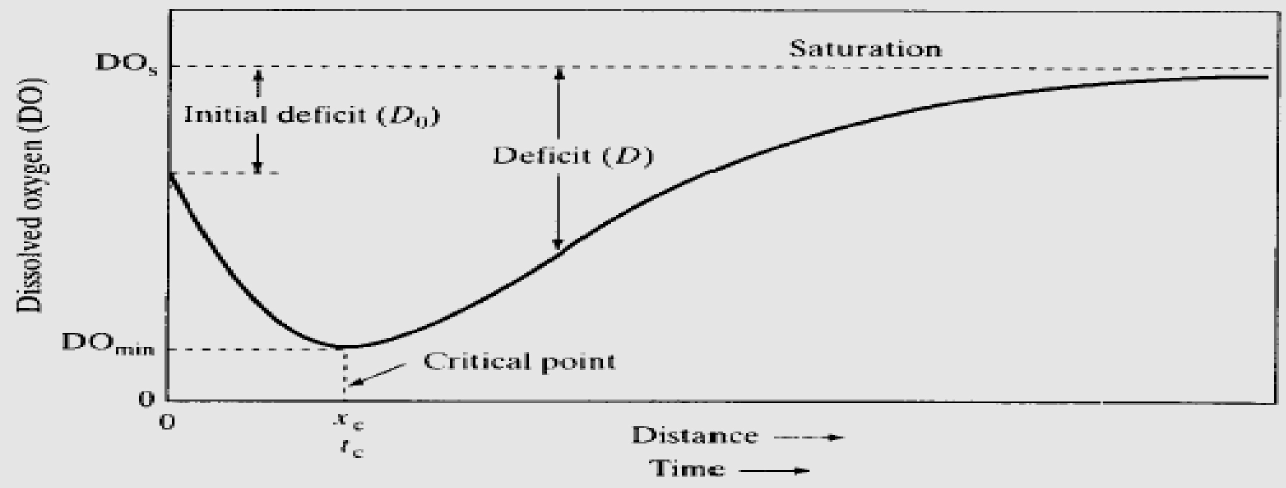


FIGURE 5.15 Streeter-Phelps oxygen sag curve.

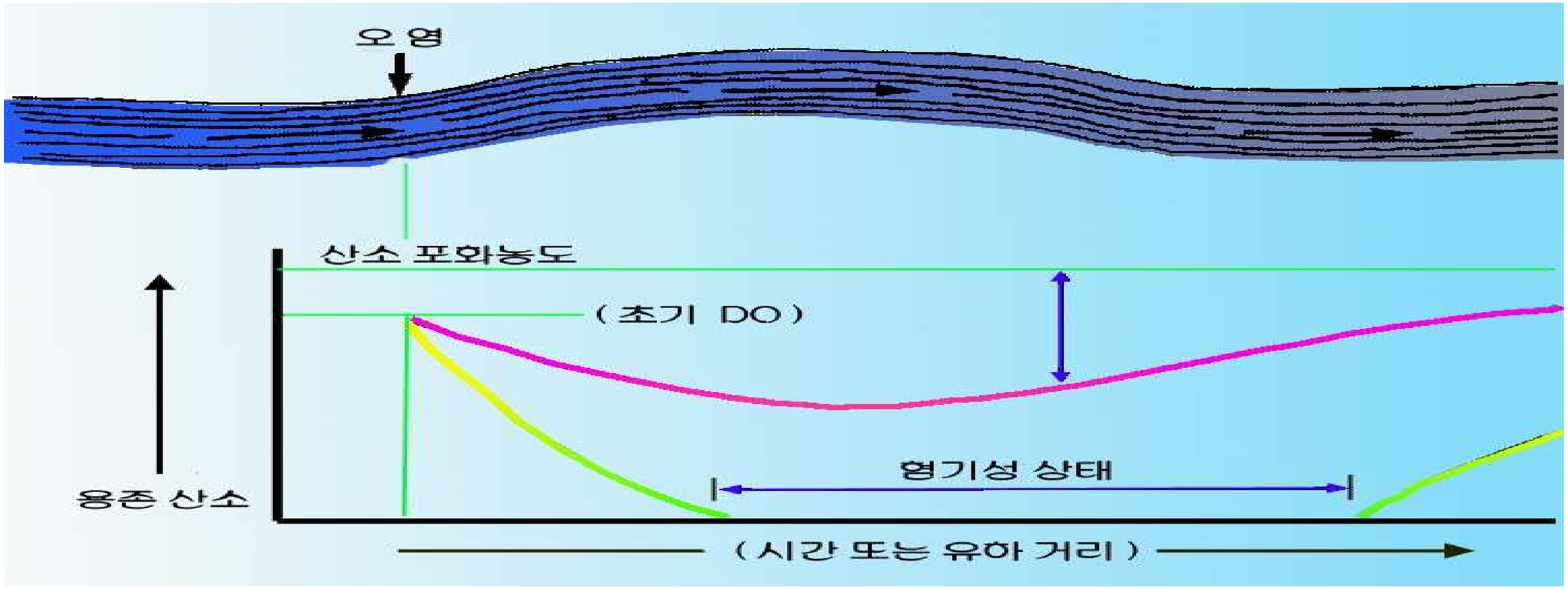
$$\frac{dD}{dt} = k_d L_0 e^{-k_d t} - k_r D$$

$$D = \frac{k_d L_0}{k_r - k_d}(e^{-k_d t} - e^{-k_r t}) + D_0 e^{-k_r t}$$

$$DO = DO_S - [\frac{k_d L_0}{k_r - k_d}(e^{-k_d t} - e^{-k_r t}) + D_0 e^{-k_r t}]$$

Streeter-Phelps oxygen sag equation

Dissolved Oxygen (DO)



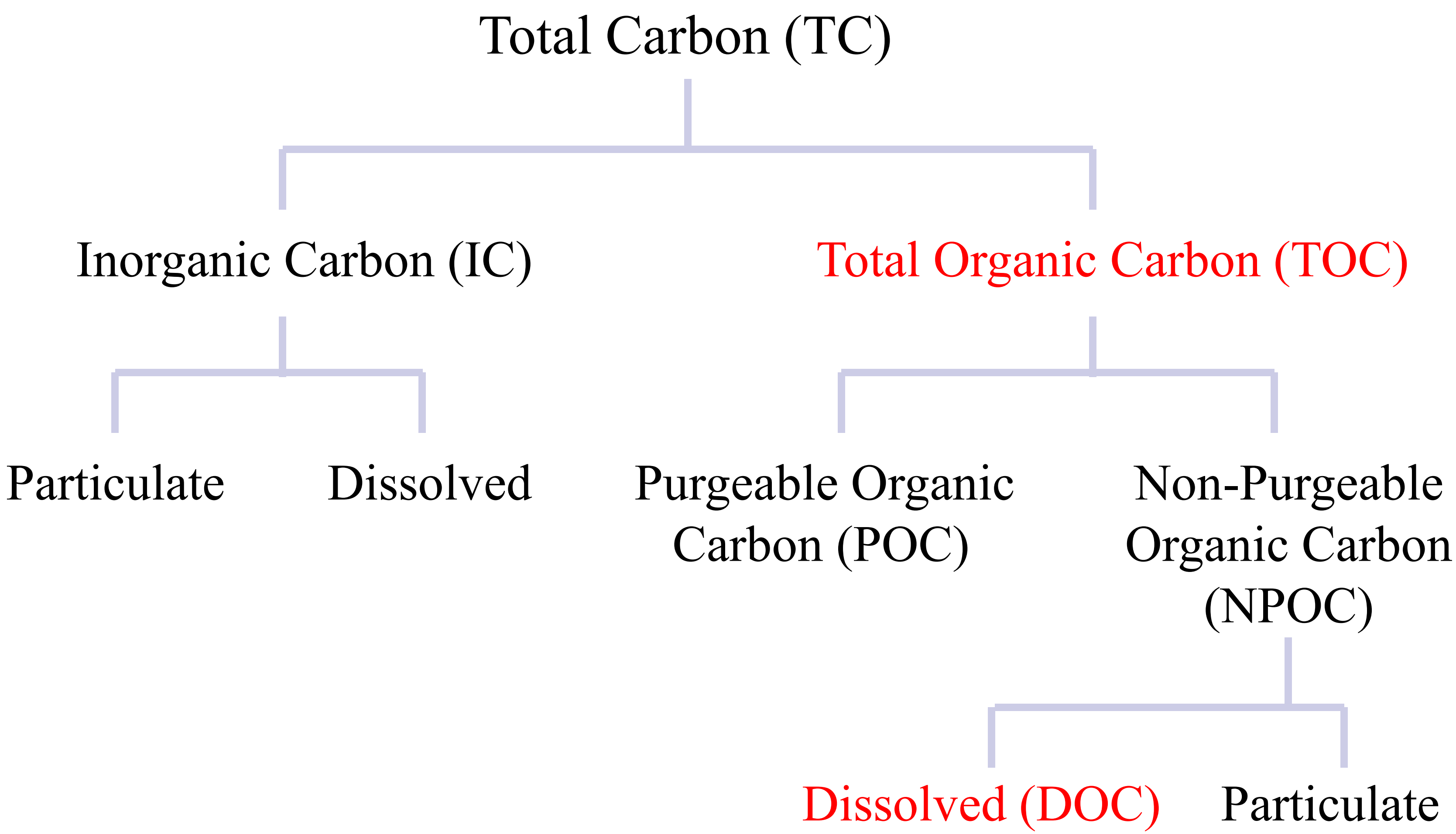
Total Organic Carbon

- 유기물을 최종 단계까지 산화시켜 CO_2의 형태로 바꾼 후 CO_2의 양을 측정
- mg C/L
- 유기물 함량이 작은 경우에도 사용 가능
- 고가장비가 필요; BOD, COD 보다 유리한 면이 많아 점차 사용 증대

Typical Levels of Carbon in Water

Type of Water	TOC (mg/L)	IC (mg/L)
Ground Water	<1	<10
Surface Water	<10	ca. 200
Process Water (high purity)	0.05	<0.05
Municipal wastewater	>10	ca.25
Seawater	<1	ca.25
Drinking Water	<5	ca.50

Flow Chart



TOC = TC - IC (difference)

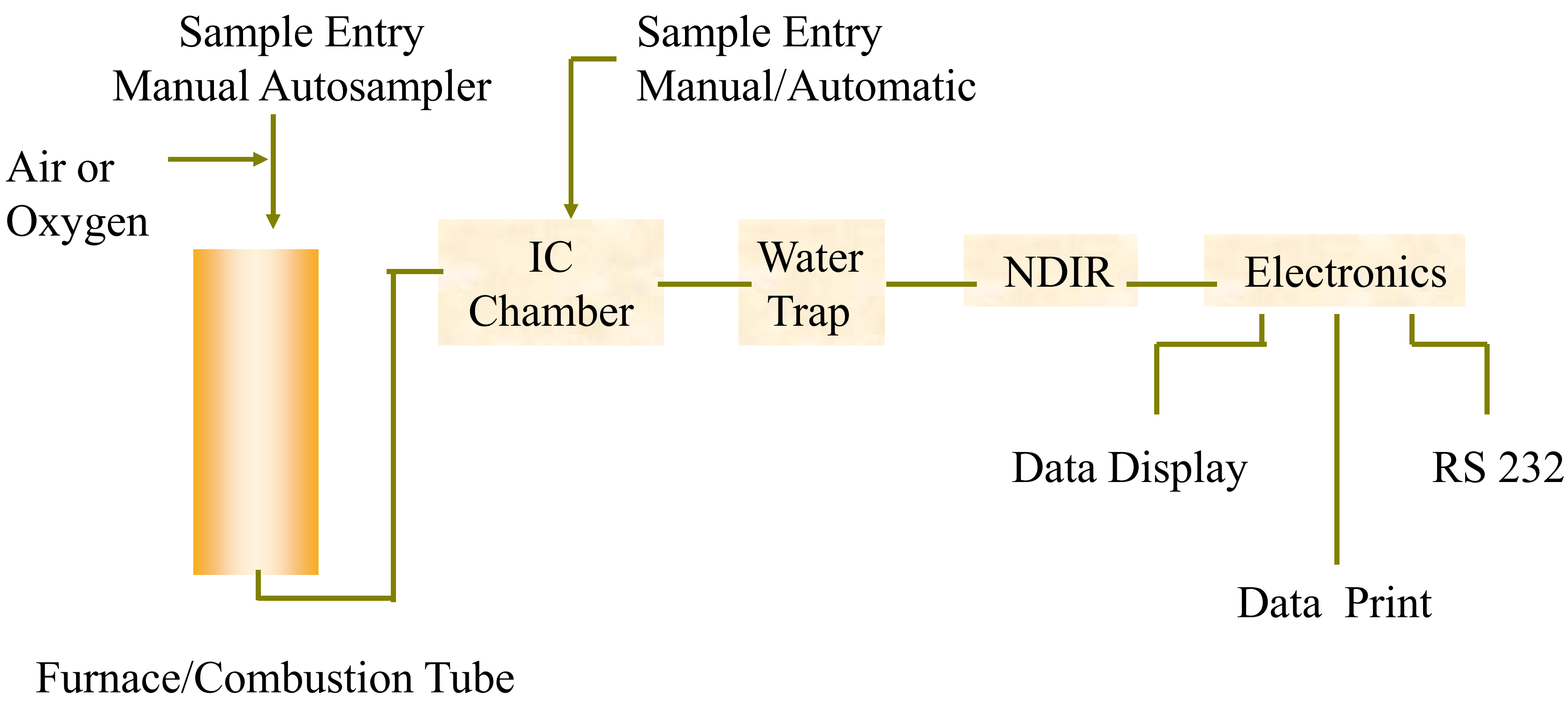
TOC Applications

- Environmental Testing
  - Ground Water
  - Surface Water
- Waste Water Contamination
- Solids and Sludges
- Drinking Water Quality
- Process Fluids
- High Purity Water
- Sea Water
- Pharmaceutical Grade Water

TOC Oxidation Methods

Combustion:	Catalyst 680 - 900ºC	CO2
Photo-oxidation:	UV H^+	CO_2
Thermo-chemical:	95ºC S_2O_8	CO_2
Photo-chemical: (UV-Persulfate)	UV S_2O_8	CO_2

Combustion, High Temperature Oxidation



Mechanisms of UV–Persulfate Oxidation

Main Oxidants

$SO_4^{-}\cdot$

$\cdot OH$

$$S_2O_8^{2-} + h\nu \rightarrow 2SO_4^{-}\cdot$$

$$H_2O + h\nu \rightarrow H\cdot + \cdot OH$$

$$SO_4^{-}\cdot + H_2O \rightarrow SO_4^{2-} + \cdot OH + H^+$$

Excitation of Organics

$$R + h\nu \rightarrow R^*$$

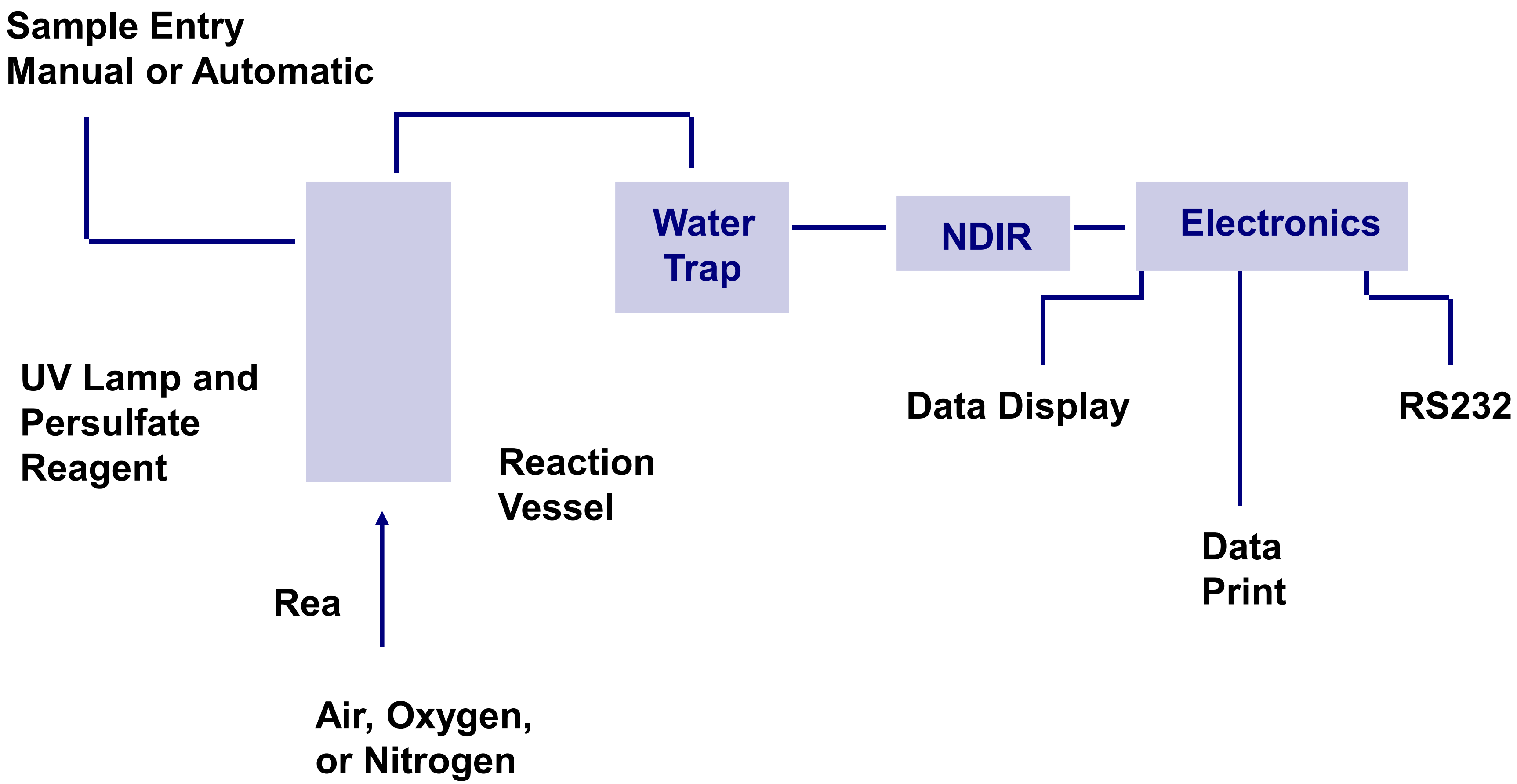
Oxidation of Organics

$$R + SO_4^{-}\cdot + H_2O \rightarrow n\,CO_2 + \ldots\ldots$$

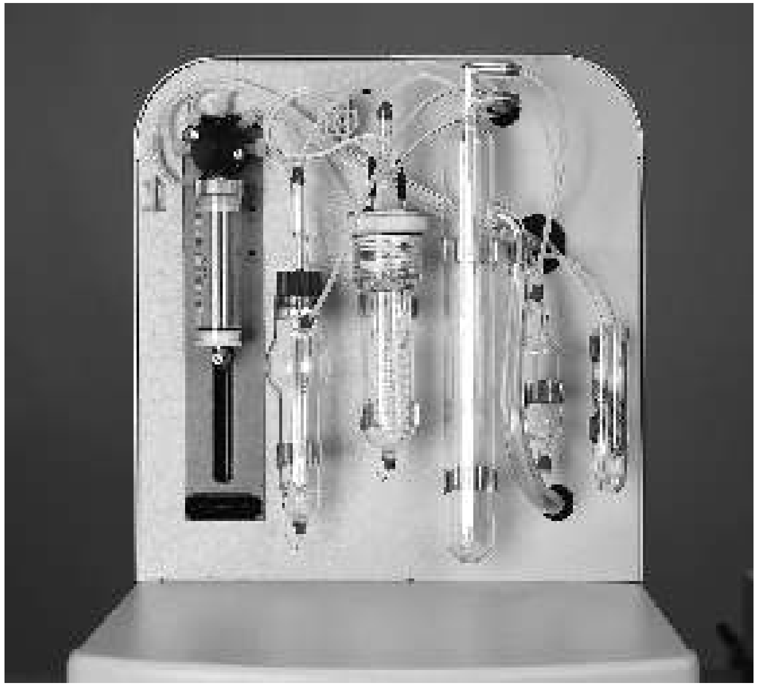
Interference

$$SO_4^{-}\cdot + Cl^{-} \rightarrow SO_4^{2-} + Cl\cdot$$

UV/Persulfate



Phoenix 8000 – The UV Persulfate TOC Analyzer



- Automated Sample Volume Injection
  - No sample loops or pump tubing needed
  - Programmed dilutions
- UV Reactor

The UV Persulfate TOC – CO2 selective membrane

Oxidation Reactor

The instrument oxidizes organic compounds to CO_2 using the chemical oxidizing agent ammonium persulfate, and UV radiation. The oxidation reactor is a spiral quartz tube wrapped around an UV lamp. The lamp emits light at 184 and 254 nanometers, resulting in the formation of powerful chemical oxidizing agents from the photolysis of water and persulfate:

$$H_2O + hn\ (184\ nm) \dashrightarrow OH\cdot + H\cdot \qquad (1)$$

$$S_2O_8^{-2} + hn\ (254\ nm) \dashrightarrow 2\ SO_4^{\cdot -} \qquad (2)$$

$$SO_4^{\cdot -} + H_2O \dashrightarrow HSO_4^{-} + OH\cdot \qquad (3)$$

Hydroxyl radical (OH·) will completely oxidize organic compounds to form carbon dioxide:

$$\text{Organic Compounds} + OH\cdot \rightarrow \rightarrow \rightarrow CO_2 + H_2O \qquad (4)$$

When low levels of organic compounds (< 1 ppm) are present in the sample, complete oxidation can usually be achieved by hydroxyl radicals produced from the photolysis of water, without the addition of persulfate.

The lifetime of the UV lamp is 6 months of operation and a warning message will indicate when it is time to replace the lamp.

CO_2 Sensors

Two membrane-based conductometric CO_2 sensors are used in the instrument. Each CO_2 sensor consists of a deionized (DI) water source, a membrane module, and a conductivity and temperature measurement cell. The IC sensor measures the concentration of CO_2 in the sample (without oxidation). The TC sensor measures the combined concentration of CO_2 initially in the sample and CO_2-produced by the oxidation of organic compounds.

SIEVERS®

TOTAL ORGANIC CARBON ANALYZER

MODEL 800/810/820

OPERATION and MAINTENANCE MANUAL

Minimum Versions Required:

TOC Firmware Versions 3.14 (CAS) with
Autosampler PC Software Versions 3.14(PRA) or
TOC Firmware Versions 3.14 (CMS) or
TOC Firmware Versions 2.10 (CTB) *Turbo* or
TOC Firmware Version 2.10 (CBI)

DLM 30007-03 Rev. 01

(303) 444-2009 (phone)
(303) 444-9543 (fax)
1-800-255-6964 (toll free)

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6060 Spine Road
Boulder, CO 80301 USA

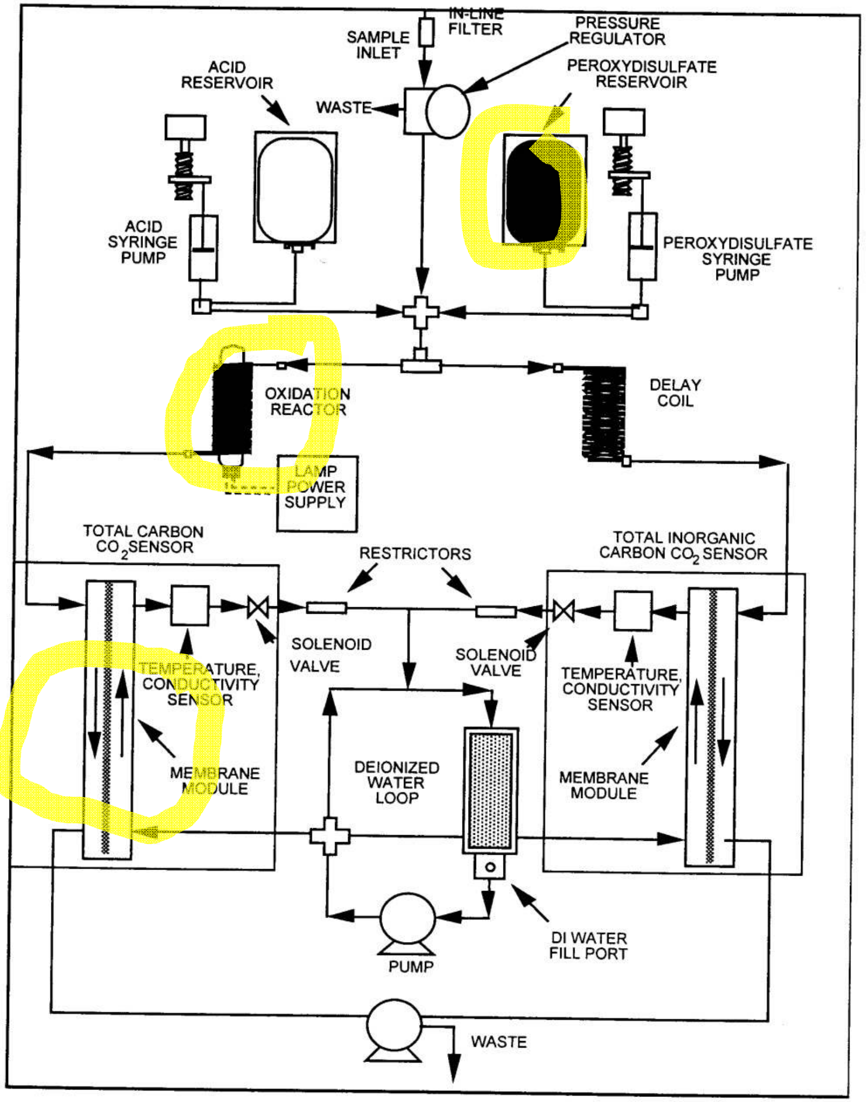

FIGURE 3-1: *Schematic of Model 800 TOC Instrument*

A brief description of the major components of the instrument follows.