Dissolved Oxygen

The measure of the amount of gaseous oxygen dissolved in a solution.

Oxygen

Oxygen is one of the fundamental resources required by life forms on Earth.

Aquatic ecosystems have a wide assortment of life forms.

Oxygen is also required for some natural chemical decays.

What do YOU know about oxygen?

1. Oxygen is a gas at room temperature.
2. Oxygen is a diatomic molecule – O_2.
3. Oxygen is soluble in water.
4. Oxygen is clear and colorless.
5. Oxygen has no smell.
6. Oxygen is highly reactive.

Aqueous oxygen

Solubility is limited.

- In pure water, solubility is a function of temperature.
- As temperature increases…
  - …solubility decreases.
- As the atmospheric pressure increases…
  - …solubility increases.

What if it isn't "pure" water?

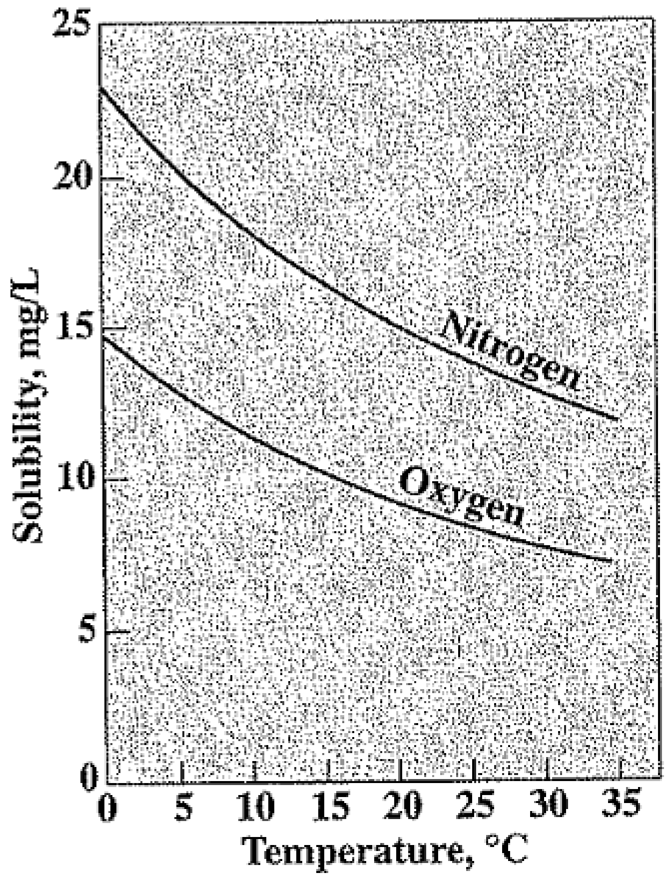


Figure 22.1
Solubility of oxygen and nitrogen in distilled water saturated with air at 1 atm.

Aqueous oxygen

The solubility of all molecules is affected by the presence of other molecules.

Some things increase solubility, most things decrease the solubility.

The solubility of oxygen is less in salt-containing water than it is pure water.

Table 22.1 | Solubility of dissolved oxygen in water in equilibrium with dry air at 1 atm 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

β– a measure of impurity

Normal solubility of oxygen in pure water at 1 atm and 25° C is 8 mg/L.

This is a modest value – oxygen is considered to be a poorly soluble gas in water!

Impure water will typically have a value less than 8 mg/L

β– a measure of impurity

The ratio between the actual solubility and the theoretical solubility is β:

$$\beta = \frac{\text{actual mg/L } O_2}{\text{theoretical mg/L } O_2}$$

The smaller β is, the more "impure" the water is.

Solubility is about equilibrium

Keep in mind that "solubility" is an equilibrium value representing the MAXIMUM amount that can be dissolved.

Equilibrium is not achieved instantaneously – it takes time for oxygen to be absorbed (or desorbed) from water.

Rate of oxgyen absorption

Solubility is 8 mg/L, but if you boil water (decrease the solubility), there is less oxygen in the water. If you then cool it down, it takes some time for the oxygen in the atmosphere to dissolve to the MAX (solubility).

The solution may be unsaturated for a time.

It’s the fish tank

That’s why fish tanks have bubblers in them. It is an attempt to increase the rate at which the oxygen dissolves to keep it saturated.

It’s also why wastewater treatment facilities have aeration devices.

The α that goes with the β

There is a corresponding value to represent the rate of oxygen absorption of water systems:

$$\alpha = \frac{\text{actual rate of } O_2 \text{ absorption (mg/L s)}}{\text{theoretical rate (mg/L s)}}$$

The α that goes with the β

In pure water,

$\alpha = 1$

$\beta = 1$

In "impure" water,

$1 > \alpha > 0.4$ (heavily polluted waters)

$1 > \beta > 0.8$ (heavily polluted waters)

The Double-Edged Sword

Dirty water has less oxygen than clean water - β

It is slower for dirty water to dissolve oxygen – α

The very waters that need the most oxygen have the least!

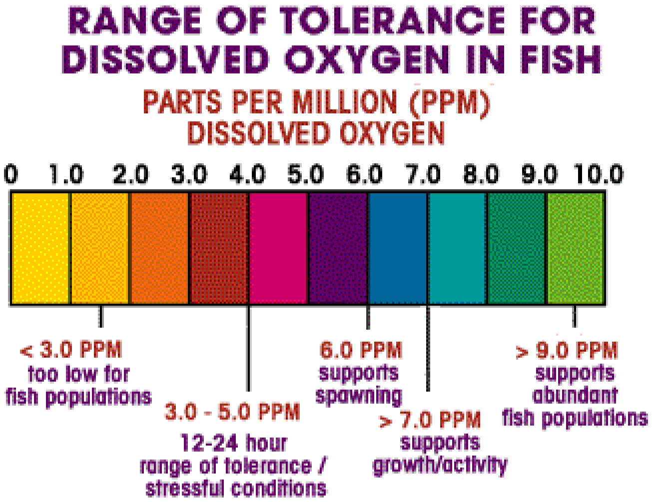
Environmental Significance of DO

* In streams, it is desirable to maintain conditions favorable to fish and other aquatic microorganisms
* Drinking water should be rich in DO for good taste.
* Higher values of DO may cause corrosion of iron and steel.
* Algae growth in water may release oxygen during photosynthesis.
* In liquid wastes DO is the factor that determines whether the biological changes are brought about by aerobic or anaerobic microorganisms.
  * Aerobic→ innocuous end products
  * Anaerobic→ obnoxius

Sewage depletes oxygen

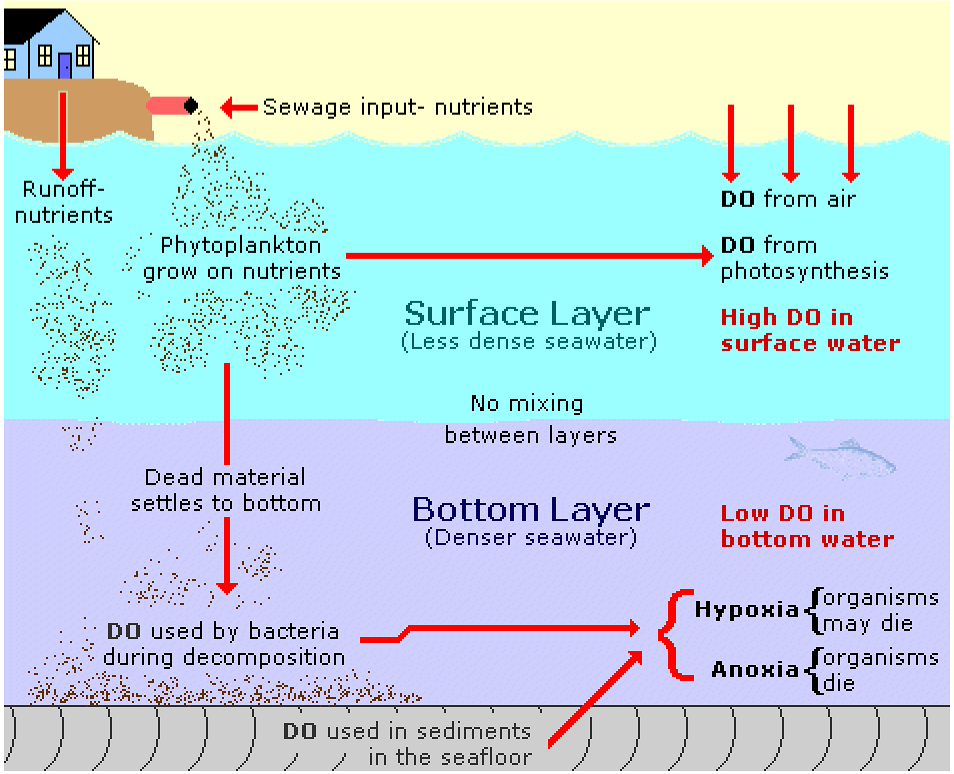
* Decomposition of the organic material uses up the oxygen

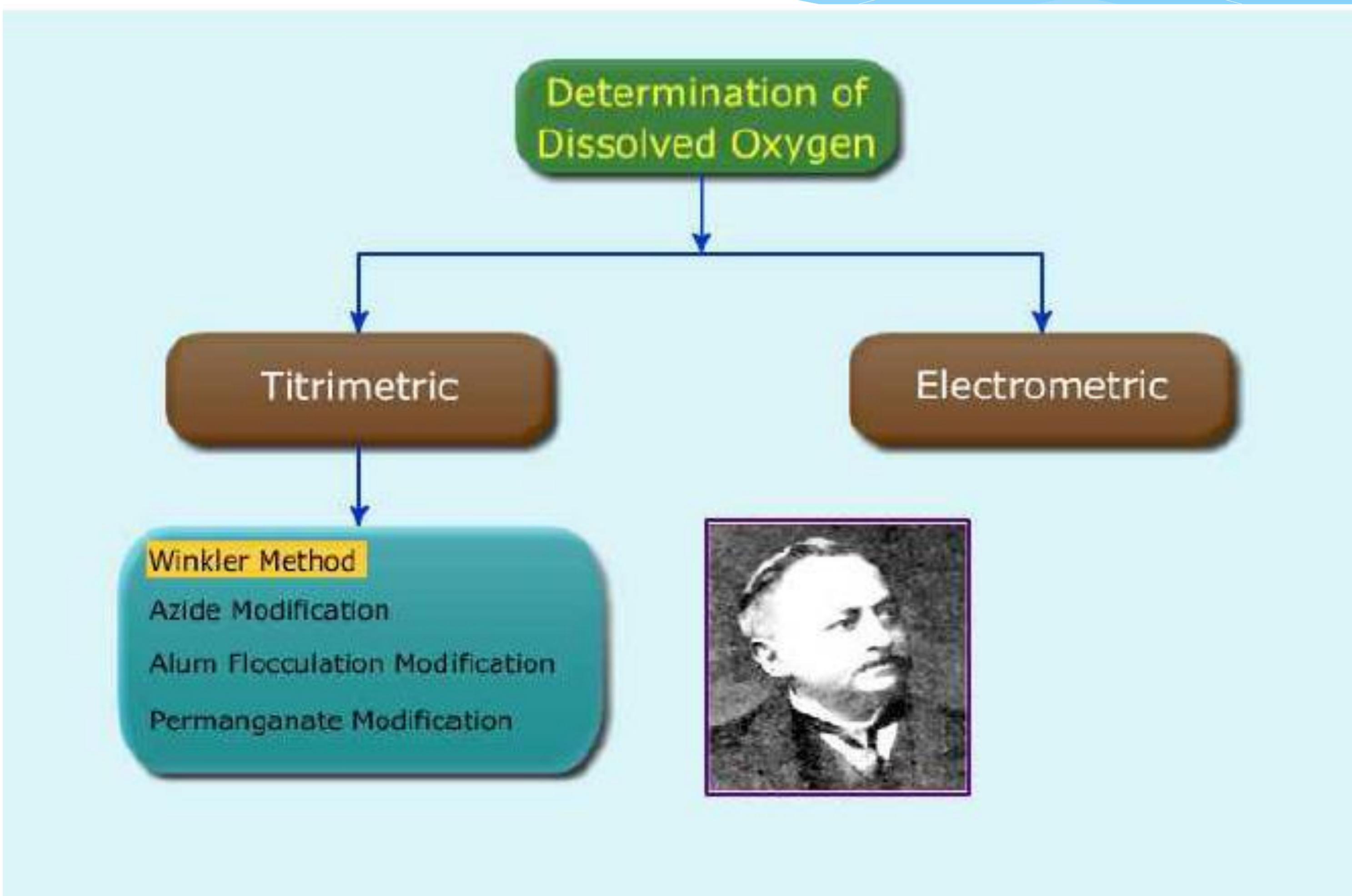
Fish need dissolved Oxygen to survive



Eutrophication

* Algae on surface, block light to lower plants




Determination of Dissolved Oxygen
Titrimetric
Electrometric
Winkler Method
Azide Modification
Alum Flocculation Modification
Permanganate Modification

Determining oxygen content

The challenges:

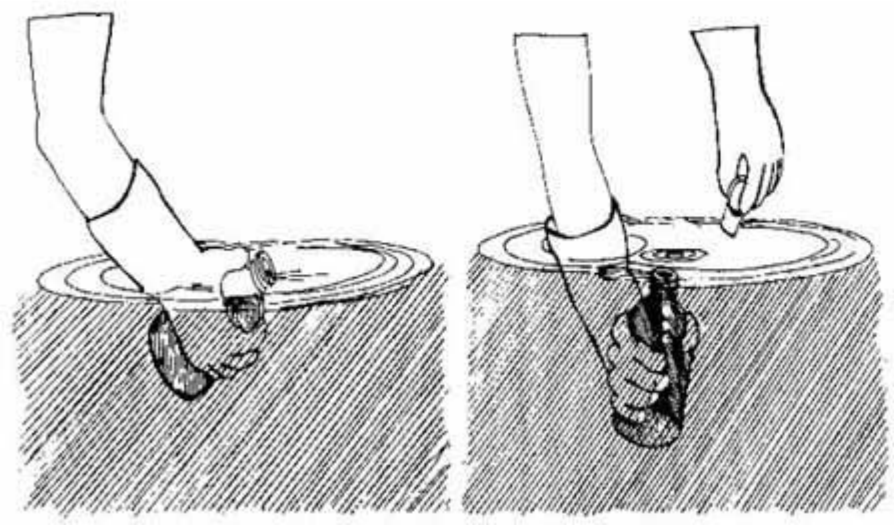
1. Oxygen can be lost to or gained from the air after collection. (usually gained)
2. Titration of the oxygen will force additional oxygen to dissolve.

Collection of water samples

Special sample collection devices must be used that seal with no air.

The simplest collection device is a glass bottle with an air tight cap.

Bottle needs to be overfilled then capped.



Taking a water sample for DO analysis

Point the bottle downstream and fill gradually. Cap underwater when full.

Source: http://water.epa.gov/type/rsl/monitoring/vms52.cfm

“Fixing” the oxygen content

Immediately after collection, sometimes before reaching the lab, the oxygen content of the samples is “fixed” by conversion to another material that is later titrated in the lab.

Even after fixing, you need to minimize biological activity in the samples

How do you minimize biological activity?

Ice – if you aren't warm blooded, you always slow down in the cold.

Dark – many water species are photosynthetic and can't do anything in the dark.

Poison – add enough chemicals in the fixing process to kill a lot of the normal biological species in the water sample.

Methods of analysis

The Winkler Method

- the most famous method
- usually most accurate for relatively pure waters, prone to errors due to inteference from things like Fe^{2+}, SO_3^{2-}, Fe^{3+}

The Winkler Fixing

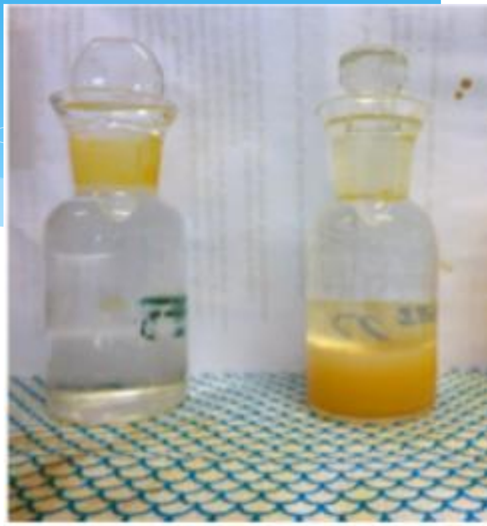
Addition of Mn^{2+} and an alkali-iodide (OH^- and I^- mixture) fixes the oxygen.

If there is no oxygen present:

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

And a white solid is observed.

The Winkler Fixing – 1st step



If there is oxygen present:

$Mn^{2+} + 2\ OH^{-} + ½\ O_2 \longrightarrow MnO_{2\ (s)} + H_2O$

This reaction can also be written as:

$2\ Mn^{2+} + 4\ OH^{-} + O_2 \longrightarrow 2\ MnO_{2\ (s)} + 2\ H_2O$

or

$Mn(OH)_2 + ½\ O_2 \longrightarrow MnO_{2\ (s)} + H_2O$

The Winkler Fixing – 1st step

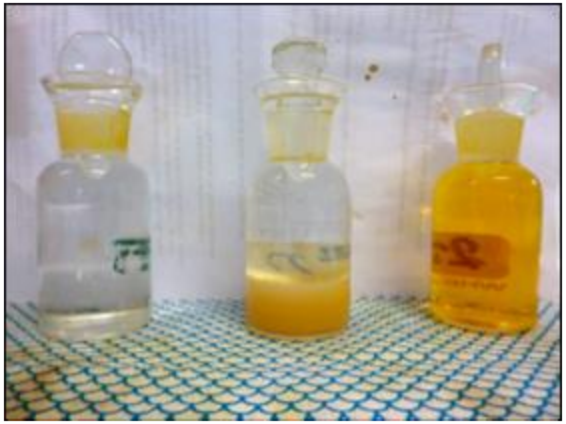
$$Mn^{2+} + 2\ OH^{-} + \frac{1}{2}\ O_2 \longrightarrow MnO_{2\ (s)} + H_2O$$

The first step converts the dissolved oxygen to MnO_2 solid.

The Winkler Fixing – 2nd step

Sulfuric acid is added. This neutralizes the OH^- and allows the MnO_2 to oxidize the iodide:

$$MnO_{2\,(s)} + 2\,I^- + 4\,H^+ \longrightarrow Mn^{2+} + I_2 + 2\,H_2O$$



Analyzing the oxygen content

Once it is "fixed" – converted to I_2 – we can analyze the amount of I_2 present and, therefore, the amount of oxygen originally present.

How would you analyze the I_2 present?

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

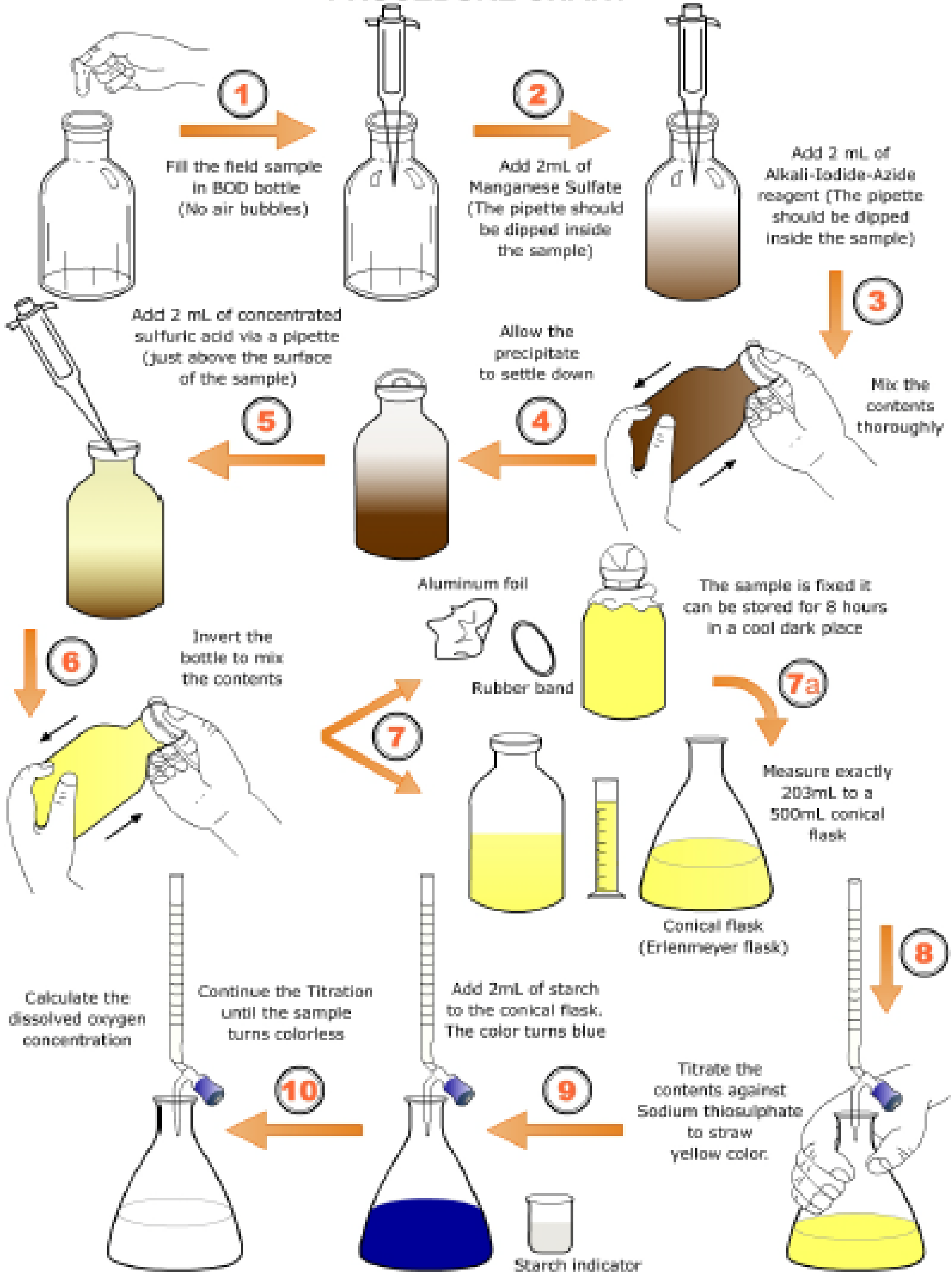
So, there are 3 reactions:

$Mn^{2+} + 2\ OH^- + \frac{1}{2}\ O_2 \longrightarrow MnO_{2\ (s)} + H_2O$

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

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

PROCEDURE CHART



A sample problem:

250.0 mL of waste water is collected and fixed using the Winkler method. Titration of the sample yields a starch-iodide endpoint after addition of 12.72 mL of a standardized 0.0187 M sodium thiosulfate solution. What is the oxygen content of the wastewater expressed in mg/L?

Where would you start?

Where would you start?

Moles!

12.72 mL $Na_2S_2O_3$ * 0.0187 M $Na_2S_2O_3$ =

0.2379 mmol $Na_2S_2O_3$

So, there are 3 reactions:

$Mn^{2+} + 2\ OH^{-} + ½\ O_2 \longrightarrow MnO_{2\ (s)} + H_2O$

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

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

Where would you start?

$$0.2379 \text{ mmol } S_2O_3^{2-} * \frac{1 \text{ mol } I_2}{2 \text{ mol } S_2O_3^{2-}} * \frac{1 \text{ mol } MnO_2}{1 \text{ mol } I_2}$$

$$= 0.1189 \text{ mmol } MnO_2 * \frac{½ \text{ mol } O_2}{1 \text{ mol } MnO_2} =$$

0.05947 mmol O_2

Finishing…

$$\frac{0.05947 \text{ mmol } O_2}{250.0 \text{ mL}} = 2.379 \times 10^{-4} \text{ M } O_2$$

$$= \frac{2.379 \times 10^{-4} \text{ moles } O_2}{1 \text{ L waste water}} * \frac{32.0 \text{ g } O_2}{1 \text{ mol } O_2} * \frac{1000 \text{ mg}}{1 \text{ g}} =$$

$$= 7.61 \text{ mg/L}$$

Calculation of DO

* Equivalent weight of oxygen is 8 g.
* Normality of most titrants in water analysis is selected so that 1 ml=1 mg of measured material
* In this case N/8 (0.125 N) thiosulfate can be chosen, however, this solution would be too concentrated to get accurate results.
* Sample size=200 ml
* So, N/8/5=N/40 (0.025N)

Calculation

$$D.O.\ mg\ l^{-1} = \frac{(8 X 1000 X N)}{V}\ X\ v$$

Where:-

V= volume of sample

v= volume of titrant used (ml)

N= normality of the titrant

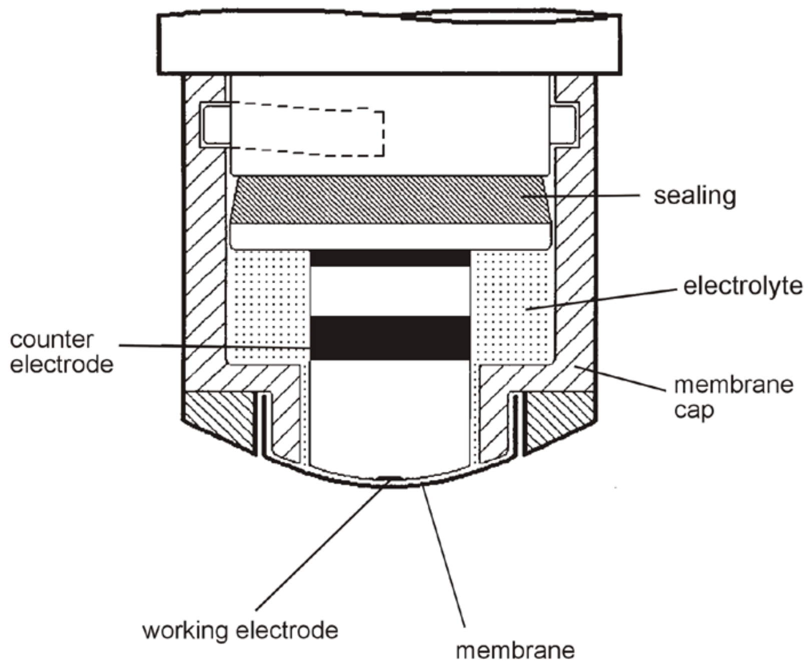
Result. Express D.O. in mg l^{1}

mg/L D.O. =

$$\frac{\text{mL of Titrant} \times \text{Normality of Titrant} \times 8 \times 1000}{\text{mL of Sample}}$$

$$\frac{0.025\ N \times 8 \times 1000}{200} = 1$$

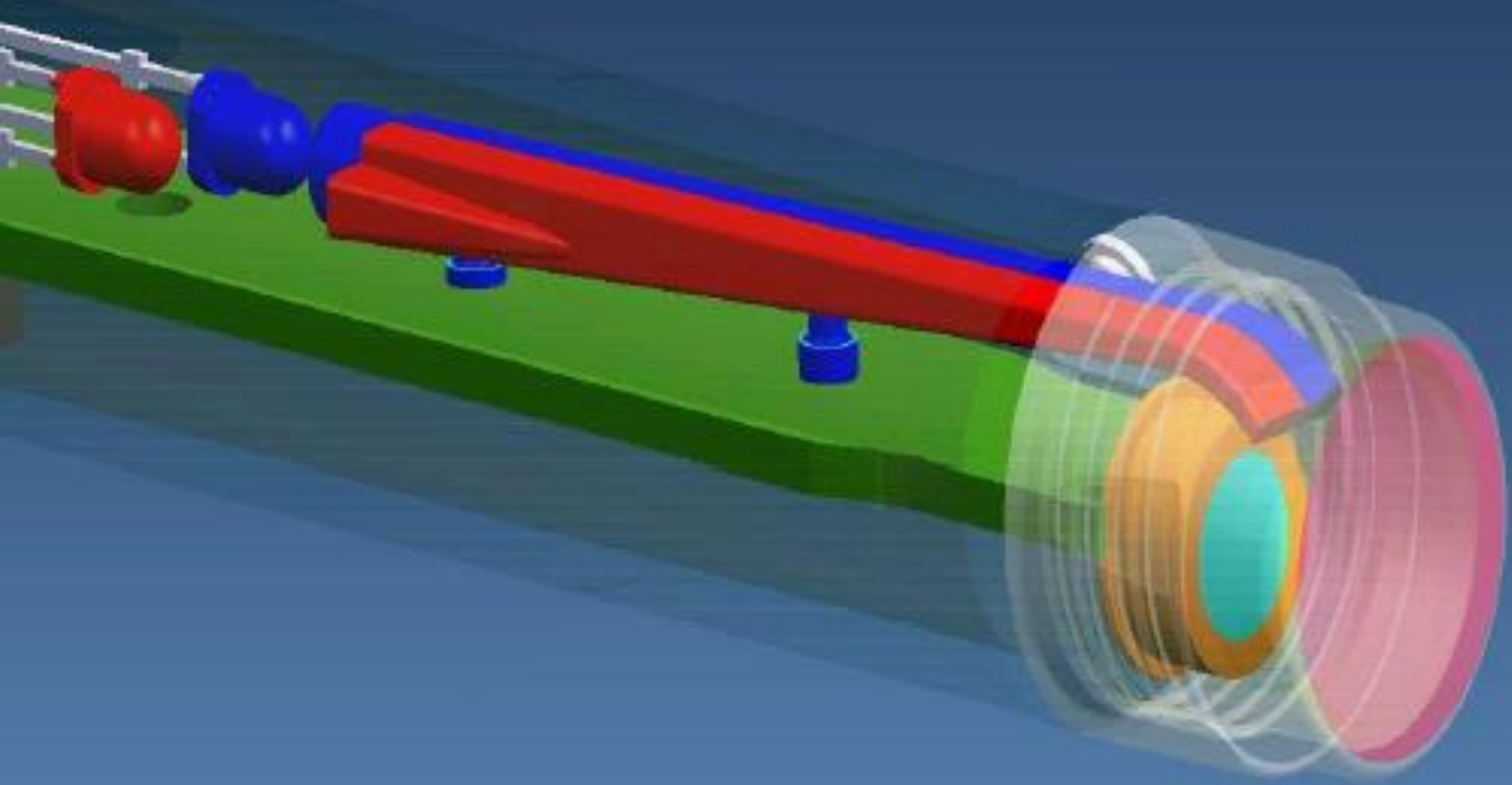
Dissolved Oxygen Sensor



* Oxygen molecules diffuse through the membrane based on the partial pressure of oxygen.
* ORP Reaction
  * Oxygen is reduced to hydroxide ions (OH-) at the gold cathode.
  * Silver is oxidized to silver bromide (M-4) or silver chloride (M-4HD) at the silver anode
* The current flow is directly proportional to the concentration of Dissolved Oxygen in solution

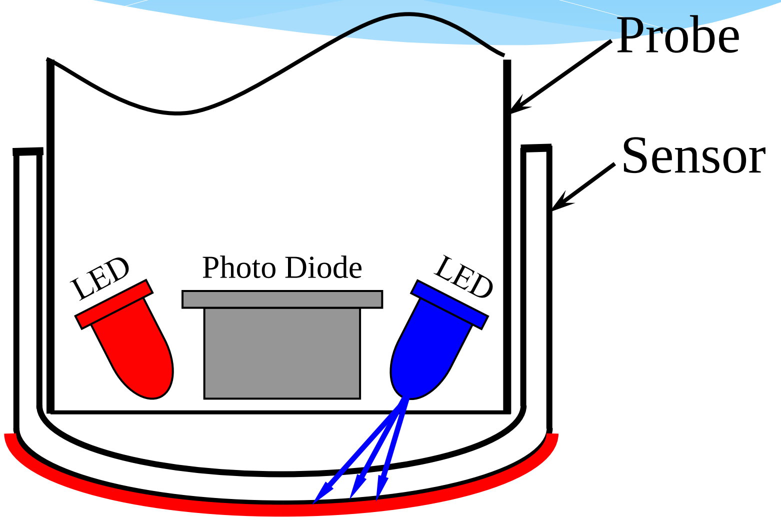
Luminescence D.O. Probe

Luminescence D.O. Probe



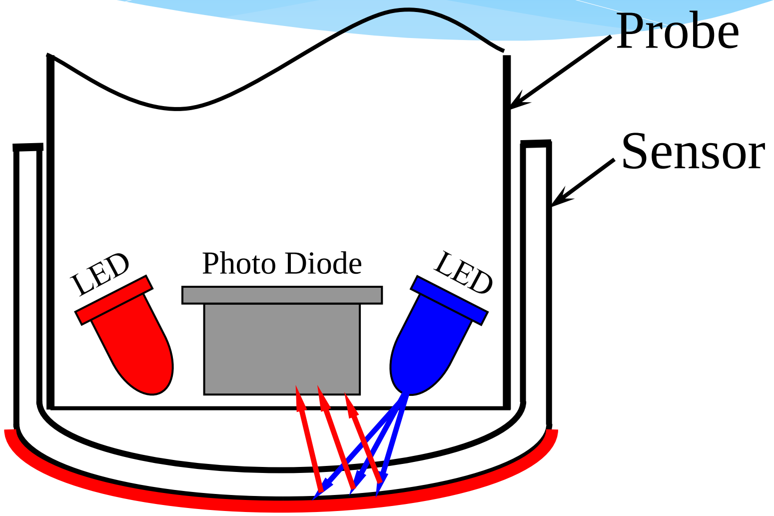
How Does LDO Work?

* A sensor is coated with a luminescent material.
* Blue light from an LED strikes the luminescent chemical on the sensor.
* The luminescent chemical instantly becomes excited.



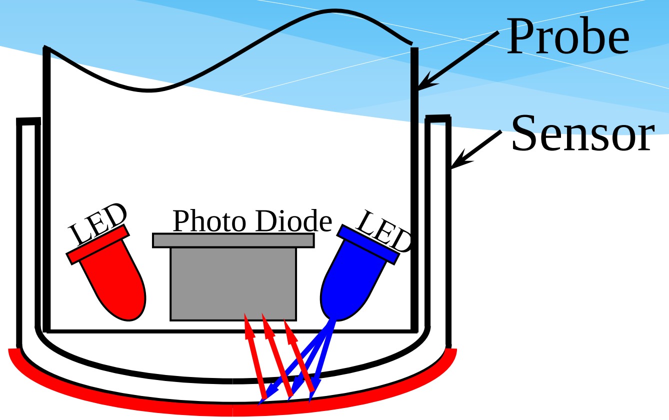
How Does LDO Work?

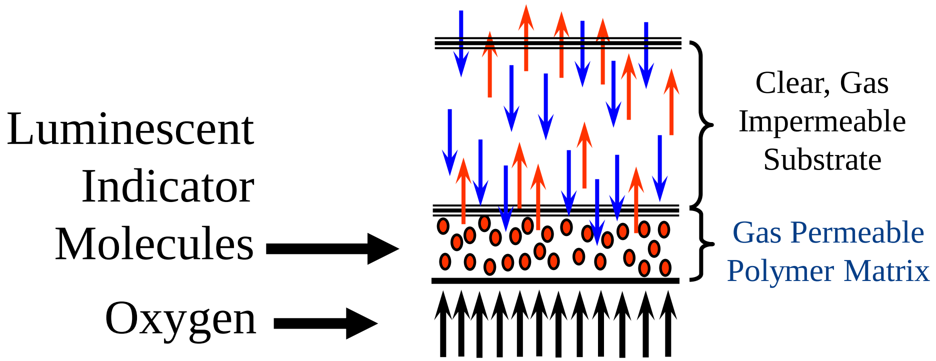
- **As the excited chemical relaxes, it releases red light.**
- The red light is detected by a photo diode.
- The time it takes for the chemical to return to a relaxed state is measured



How Does LDO Work?

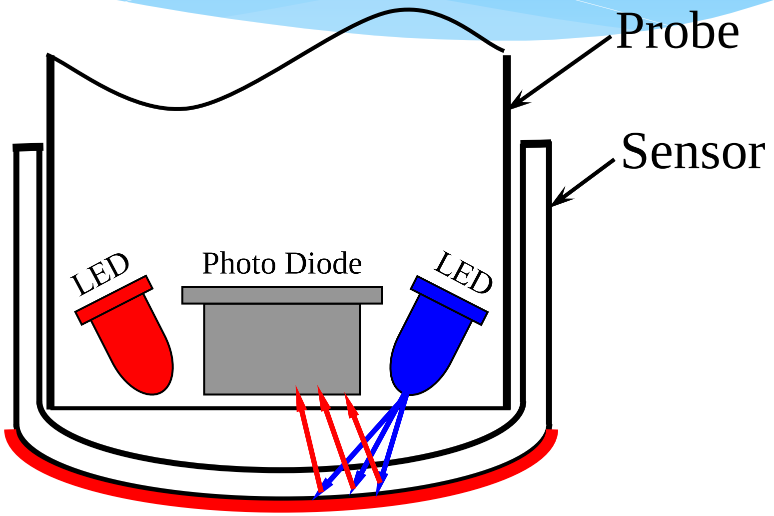
- When oxygen contacts the luminescent chemical, the intensity of the red light decreases
- The amount of time it takes for the material to relax is reduced





How Does LDO Work?

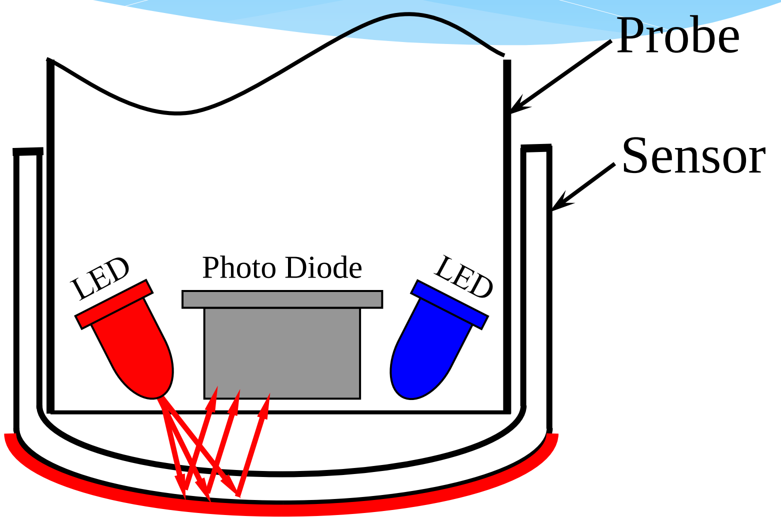
- **The intensity of the red light is <u>not</u> what's being measured.**
- **What's being measured is the time it takes after excitation for red light to be given off.**
  - **Lifetime of luminescence**



How Does LDO Work?

* **A red LED is also present in the probe.**

* **Between flashes of the blue LED, a red LED of known intensity, is flashed on the sensor.**
    * The red LED acts as an internal standard (or reference) for a comparison to the red light given off by the luminescent chemical.



Why is this a Big Deal?

Reduced Maintenance

No membrane to replace

- No more stretching of Teflon and worrying about air bubbles
- No more punctured membranes

No electrolyte to foul or poison

- No H_2S poisoning of the electrolyte

No anode or cathode

- No cleaning of anodes
- No more coating of electrodes