Dissolved Oxygen Testing Tips

Oxygen is critical to the survival of aquatic plants and animals, and a shortage of dissolved oxygen is not only a sign of pollution, it is harmful to the fish. Some aquatic species are more sensitive to oxygen depletion than others, but some general guidelines to consider when analyzing test results are:

5-6 ppm: Sufficient for most species

<3 ppm: Stressful to most aquatic species

<2 ppm: Fatal to most species

Because of its importance to the fish's survival, aquaculturists, or "fish farmers," and aquarists use the dissolved oxygen test as a primary indicator of their system's ability to support healthy fish.

Where Does The Oxygen Come From?

The oxygen found in water comes from many sources, but the largest source is oxygen absorbed from the atmosphere. Wave action and splashing allows more oxygen to be absorbed into the water. A second major source of oxygen is aquatic plants, including algae; during photosynthesis plants remove carbon dioxide from the water and replace it with oxygen.

Absorption:

Oxygen is continuously moving between the water and surrounding air. The direction and speed of this movement is dependent upon the amount of contact between the air and water. A tumbling mountain stream or windswept, wave covered lake, where more of the water's surface is exposed to the air, will absorb more oxygen from the atmosphere than a calm, smooth body of water. This is the idea behind aerators; by creating bubbles and waves the surface area is increased and more oxygen can enter the water.

Photosynthesis:

In the leaves of plants one of the most important chemical processes on Earth is constantly occurring-photosynthesis. During daylight, plants constantly take carbon dioxide from the air, and, in the presence of water, convert it to oxygen and carbohydrates, which are used to produce additional plant material. Since photosynthesis requires light, plants do not photosynthesize at night, so no oxygen is produced. Chemically, the photosynthesis reaction can be written as:

$Light + nCO_2 + nH_2O \rightarrow (CH_2O)n + nO_2$

Light + Carbon Dioxide + Water → Carbohydrate + Oxygen

Where Does The Oxygen Go?

Once in the water, oxygen is used by the aquatic life. Fish and other aquatic animals need oxygen to breathe or respire. Oxygen is also consumed by bacteria to decay, or decompose, dead plants and animals.

Respiration:

All animals, whether on land or underwater, need oxygen to respire, and grow and survive. Plants and animals respire throughout the night and day, consuming oxygen and producing carbon dioxide, which is then used by plants during photosynthesis.

Decomposition:

All plant and animal waste eventually decomposes, whether it is from living animals or dead plants and animals. In the decomposition process, bacteria use oxygen to oxidize, or chemically alter, the material to break it down to its component parts. Some aquatic systems may undergo extreme amounts of oxidation, leaving no oxygen for the living organisms, which eventually leave or suffocate.

Other Factors:

The oxygen level of a water system is not only dependent on production and consumption. Many other factors work together to determine the potential oxygen level, including:

- Salty vs. fresh water: Fresh water can hold more oxygen than salt water.
- Temperature: Cold water can hold more oxygen than warm water.
- Atmospheric pressure (Altitude): The greater the atmospheric pressure the more oxygen the water will hold.

Testing Dissolved Oxygen:

Dissolved oxygen is often tested using the Azide modification of the Winkler method. When testing dissolved oxygen it is critical not to introduce additional oxygen into the sample. Many people avoid this problem by filling the sample bottle all the way and allowing the water to overflow for one minute before capping.

The first step in a DO titration is the addition of Manganous Sulfate Solution (4167) and Alkaline Potassium Iodide Azide Solution (7166). These reagents react to form a white precipitate, or floc, of manganous hydroxide, $Mn(OH)_2$. Chemically, this reaction can be written as:

Next page...

$MnSO_4 + 2KOH \rightarrow Mn(OH)_2 + K_2SO_4$

Light + Carbon Dioxide + Water → Manganous Hydroxide + Potassium Sulfate

Immediately upon formation of the precipitate, the oxygen in the water oxidizes an equivalent amount of the manganous hydroxide to brown-colored manganic hydroxide. For every molecule of oxygen in the water, four molecules of manganous hydroxide is converted to manganic hydroxide. Chemically, this reaction can be written as:

$4Mn(OH)_2 + O_2 + 2H_2O \rightarrow 4Mn(OH)_3$

Manganous Hydroxide + Oxygen + Water → Manganic Hydroxide

After the brown precipitate is formed, a strong acid, such as Sulfamic Acid Powder (6286) or Sulfuric Acid, 1:1 (6141) is added to the sample. The acid converts the manganic hydroxide to manganic sulfate. At this point the sample is considered "fixed" and concern for additional oxygen being introduced into the sample is reduced. Chemically, this reaction can be written as:

$2Mn(OH)_3 + 3H_2SO_4 \rightarrow Mn2(SO_4)_3 + 6H2O$

Manganic Hydroxide + Sulfuric Acid → Manganic Sulfate + Water

Simultaneously, iodine from the potassium iodide in the Alkaline Potassium Iodide Azide Solution is oxidized by manganic sulfate, releasing free iodine into the water. Since the manganic sulfate for this reaction comes from the reaction between the manganous hydroxide and oxygen, the amount of iodine released is directly proportional to the amount of oxygen present in the original sample. The release of free iodine is indicated by the sample turning a yellow-brown color. Chemically, this reaction can be written as:

$Mn_2(SO_4)_3 + {}_2KI \rightarrow 2MnSO_4 + K_2SO_4 + I_2$

Manganic Sulfate + Potassium Iodide → Manganous Sulfate + Potassium Sulfate + Iodine

The final stage in the Winkler titration is the addition of sodium thiosulfate. The sodium thiosulfate reacts with the free iodine to produce sodium iodide. When all the iodine has been converted the sample changes from yellow-brown to colorless. Often a starch indicator is added to enhance the final endpoint. Chemically, this reaction can be written as:

$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$

Sodium Thiosulfate + Iodine → Sodium Tetrathionate + Sodium Iodide

7414 and 5860 Dissolved Oxygen Kit Testing Tips:

Fixing Dissolved Oxygen Samples:

- "Fix" dissolved oxygen samples in the field as soon as collected. Biological activity in the sample and exposure to air can quickly change the dissolved oxygen level in the sample bottle.
- Fixed samples may be stored for up to 8 hours before titration, if refrigerated and kept in the dark.
- Some of the sample will overflow as chemicals are added during the "fixing" steps, but sufficient amounts of the oxygen-reacting chemicals WILL fall to the bottom of the bottle. The overflow assures that when the sample bottle is closed again, no air will be trapped inside. An air bubble in the sample bottle may introduce additional oxygen during the mixing step, producing false, high readings.

Floc/Precipitate During Fixing of Samples:

- Mix for the full amount of time specified and allow the "floc" to settle according to the instructions. Impatience may result in an incomplete reaction and produce false, low readings. Salt water may take longer to settle.
- After addition of the acid, reagent and precipitate may take up to 20-30 minutes to dissolve. The more dissolved oxygen present, the longer it will take to dissolve. Low readings may result if not enough time is allowed for sample to completely dissolve.

What Is Faint Yellow?:

The titration is actually titrating iodine, from yellow to clear. Since the yellow to clear change is very hard to see we add starch, which turns blue in the presence of iodine. Once all the iodine has been titrated out the starch goes clear. The blue to clear is much easier to see than yellow to clear. The reason that we titrate some of the iodine out (titrate to faint yellow) before adding starch is two-fold:

1. The starch stays dark blue right up until it goes clear, unlike most titrations where the color gradually moves toward the endpoint. Therefore, it is easy to become complacent during the titration and add an excess amount of titrant (overshooting the endpoint), thinking that you are far from the endpoint because the color is not changing.
2. Also starch can be partially decomposed by a large amount of iodine. Therefore, the starch should not be added until the bulk of the iodine has been reduced (titrated out).

So, for both of these reasons, the sample should be titrated to a faint yellow (the exact shade does not matter) before adding the starch.

NOTE: Prior to adding the starch indicator, be sure to carefully remove the titrator and cap. Leave the titrator plunger in it's exact position within the titrator barrel, add the 8 drops of starch and then finish the titration.