Environmental Dissolved Oxygen Testing: CHEMetrics Test Kits vs. Winkler Titration

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Significance of Dissolved Oxygen in Aquatic Environments

Measuring the concentration of dissolved oxygen (DO) in natural waters is vital in assessing the overall health of aquatic environments. While every ecosystem is different, water bodies need approximately 6 – 10 mg/L (ppm) DO to support aquatic life. Low dissolved oxygen concentration is a strong indicator that sources of pollution are negatively impacting water quality. Often, low levels of DO can be traced to non-point sources such as stormwater runoff. Typical contaminants stemming from runoff are petroleum hydrocarbons and excess fertilizer which supplies plant nutrients that create algae blooms. As the algae decompose the oxygen in the water is consumed causing hypoxia (low levels of DO) or anoxia (complete absence of DO). In a healthy water environment, oxygen can be replenished in the water naturally through the atmosphere and photosynthesis by aquatic plants. Flowing water such as streams and rivers will have greater levels of DO due to natural aeration of the water caused by agitation.

Oxygen solubility in water is dependent upon temperature, atmospheric pressure, and salinity of the water. When assessing the dissolved oxygen concentration in a body of water, it is important to consider all of these factors. Oxygen solubility is often expressed in terms of percent (%) air saturation. Air saturation tables provide theoretical values of dissolved oxygen at 100% air saturation at various temperatures and air pressures.

Testing for Dissolved Oxygen in the Field

Various types of dissolved oxygen measurement equipment are commercially available that utilize galvanic, polarographic, and optical sensors. These probes are reliable but require calibration and maintenance which may not always be cost effective for certain kinds of project specific monitoring requirements.

Test kits are a lower cost option than probes but may require multiple steps to obtain test results. Many test kits on the market today utilize an older method called the Winkler Titration. CHEMetrics offers test kits that employ the simpler but equally reliable indigo carmine method. A comparison study was conducted between CHEMetrics K-7513 Vacu-vials® and K-7512 CHEMets® test kits (indigo carmine method) and LaMotte's 5860-01 test kit (Winkler Titration).

What is the Winkler Titration?

The Winkler Test, also referred to as the Winkler Titration or the Iodometric Method, was created by Lajos Winkler in 1888 while working on his dissertation at Budapest University. The method is broken down into a few steps that can be altered with slightly different chemicals. The first step is the fixation of oxygen in the sample. For the LaMotte 5860-01 kit, manganous sulfate, $MnSO_4$, and an alkaline potassium iodide azide solution are added to the sample. This creates a white precipitate of manganous hydroxide, $Mn(OH)_2$. Once the precipitate is formed, oxygen in the water oxidizes an equivalent amount of $Mn(OH)_2$ to a brown precipitate called manganic hydroxide, $Mn(OH)_3$. A strong acid, commonly sulfuric acid, is added to acidify the solution. The acid converts the $Mn(OH)_3$ to manganic sulfate, $Mn_2(SO_4)_3$. After this step, because the oxygen within the sample is "fixed," additional atmospheric oxygen being introduced to the sample is unlikely to interfere with the test result. The manganic sulfate oxidizes potassium iodide to form iodine. The amount of iodine released is proportional to the amount of oxygen present in the sample. The release of iodine changes the color of the sample to a yellow-brown color. The final step is to determine the amount of iodine in the sample by titrating with sodium thiosulfate ($Na_2S_2O_3$). When the iodine has been completely converted into sodium iodide (NaI) the solution will turn colorless. It is not uncommon for an indicator to be added to make the final endpoint easier to determine.

The LaMotte 5860-01 test kit utilizes the Winkler method for Dissolved Oxygen analysis.

What is the Indigo Carmine Method?

CHEMetrics K-7512 CHEMets (visual) and K-7513 Vacu-vials (instrumental) dissolved oxygen test kits are based on the Indigo Carmine Method and self-filling ampoule technology. The indigo carmine method utilizes the reduced (or leuco) form of the indigo carmine dye which is yellow. When this form of indigo carmine reacts with oxygen, it changes from a yellow green to a blue color. The intensity of the blue color is directly proportional to the concentration of dissolved oxygen in the water sample.

CHEMetrics K-7512 visual test kit utilizes indigo carmine method for Dissolved Oxygen analysis.

The indigo carmine reagent is packaged inside CHEMetrics glass ampoules sealed under vacuum. The analyst snaps the ampoule tip in the water sample prompting sample to be drawn into the ampoule. When the ampoule is inverted, the bubble mixes the reagent with the sample. After a 2-minute color development time, K-7512 CHEMets ampoules are read in a color comparator where the intensity of the blue color developed in the test ampoule is visually compared against color standards representing DO concentrations ranging from 1 – 12 mg/L (ppm). Likewise, K-7513 Vacu-vials ampoules can be read in spectrophotometer at 485 nm in absorbance mode. CHEMetrics provides a calibration equation to convert absorbance to ppm DO. Alternatively, K-7513 Vacu-vials ampoules can be read in CHEMetrics pre-calibrated photometers that display direct ppm DO test results ranging from 2 – 15 ppm.

CHEMetrics K-7513 Is an instrumental version of the indigo carmine method for Dissolved Oxygen analysis.

Unlike the Winkler method, the CHEMetrics indigo carmine test procedure is simple, fast and does not require measuring and adding multiple reagents to the sample to complete the required chemical reactions. Therefore, the test can easily be performed immediately at the time of sample collection, minimizing the opportunity for atmospheric oxygen to enter the sample. Furthermore, the K-7512 and K-7513 test kits are not susceptible to interferences from temperature, salinity, or dissolved gases like sulfide. The ease of this method makes it especially convenient for environmental water analysis.

Comparing Performance of Winkler and Indigo Carmine Dissolved Oxygen Test Kits

A protocol was designed to compare test results generated by the two methods. Oxygen in nitrogen gas standards representing two levels of oxygen were bubbled into a 2-liter separatory funnel containing deionized water. The concentration of dissolved oxygen was determined from the application of Henry's Law, the barometric pressure, and water temperature. The sampling bottle provided with the LaMotte's 5860-01 was filled with sample from the separatory funnel. This sampling technique was found to be a more reliable procedure in a lab setting than the submerged bottle method suggested by the LaMotte kit instructions. Once the LaMotte bottle was filled, the LaMotte test procedure was followed. Both the K-7512 CHEMets and the K-7513 Vacu-vials ampoules were snapped while the sample continually flowed into a beaker. A Hach DR 2800 spectrophotometer was used to measure K-7513 absorbance values. An I-2002 CHEMetrics Single Analyte Meter (SAM) was used for a second set of instrumental readings. Two DO concentrations were evaluated, 4.0 and 10.7 ppm.

The results of the testing are displayed below.

CHEMetrics vs. Winkler test results

Theoretical DO concentration, ppm	K-7513 result with spectrophotometer	Error relative to theoertical, ppm	K-7513 result with I-2002 SAM photometer	Error relative to theoertical, ppm	K-7512 result	Error relative to theoretical, ppm	LaMotte Winkler result	Error relative to theoretical, ppm
4.0	4.4	0.4	4.3	0.3	4.5	0.5	4.4	0.4
	4.5	0.5	4.3	0.3				
	4.6	0.6	4.6	0.6				
4.0	4.5	0.5	4.4	0.4	4.5	0.5	4.2	0.2
	4.5	0.5	4.3	0.3	4.5	0.5		
	4.5	0.5	4.4	0.4				
10.7	10.6	-0.1	10.9	0.2	11	0.3	9.6	-1.1
	10.7	0.0	10.8	0.1	11	0.3		
	10.3	-0.4	10.5	-0.2	11	0.3		
10.7	10.4	-0.3	10.6	-0.1	11	0.3	9.8	-0.9
	10.5	-0.2	10.9	0.2	11	0.3		
	10.7	0.0	10.9	0.0	11	0.3		

Results

Test results agreed favorably among the LaMotte and CHEMetrics instrumental and visual test kits. At 4.0 ppm DO, less than 1 ppm error was observed with both the Winkler and the indigo carmine methods. At 10.7 ppm DO, both methods performed similarly with errors ranging between -1.1 and 0.3 ppm DO. K-7513 test results were consistent between the spectrophotometer and I-2002 SAM photometer.

Conclusion

Measuring dissolved oxygen is critical to understanding the health of aquatic environments. There are many ways to analyze dissolved oxygen, such as probes and test kits. Many test kits offer the Winkler titration method which is labor intensive and complicated, requiring addition of multiple chemicals. CHEMetrics offers an indigo carmine method packaged in our self-filling ampoules to create a simplified testing procedure. It can be used to obtain accurate results with fewer steps and less chemical handling than with the Winkler method. The ease of use and portability of the CHEMetrics test kits and I-2002 SAM photometer make them perfect for testing in the field. To purchase CHEMetrics test kits or find more technical information about the K-7512 and K-7513 test kits please visit https://www.chemetrics.com/product-category/test-kits/oxygen-dissolved/

References

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3. LaMotte Dissolved Oxygen Water Quality Test Kit Instruction Manual Code 5860-01.