In-Situ® Optical RDO® Methods for Dissolved Oxygen Measurements Outperform Traditional Methods

Cristina Windsor, Product Marketing Manager, In-Situ Inc.
cwindsor@in-situ.com
Ashley Steinbach, Chemist, In-Situ Inc.
asteinbach@in-situ.com
Amy Lockwood, Technical Writer, In-Situ Inc.
alockwood@in-situ.com
Robert J. Mooney

ABSTRACT
Three methods are generally used to measure dissolved oxygen (DO) in surface waters: Winkler titration, membrane-covered electrochemical sensors (polarographic or galvanic cell), and luminescent-based sensors. Optical (luminescent) technology for measuring DO levels in water has quickly become a well-accepted method due to many advantages over membrane-based sensors, and its close correlation to Winkler titrations (Figure 3). Laboratory, process, and long-term field applications can all benefit from the optical DO method, which offers improved accuracy and reduces operating costs.

TECHNOLOGY BACKGROUND

EPA-approved, optical Rugged Dissolved Oxygen (RDO) methods are quickly becoming the most convenient and widely accepted methods for determining DO, biochemical oxygen demand (BOD), and carbonaceous biochemical oxygen demand (CBOD). The standard Winkler titration has always presented drawbacks for the determination of dissolved oxygen in an ambient setting. Titrations are difficult to perform accurately in changing environmental conditions and cannot be used for continuous monitoring due to the laborious nature of the method.

The development of electrochemical sensors offered several benefits over the Winkler method. With electrochemical sensors, DO monitoring became a valuable *in-situ* measurement. However, electrochemical sensors have inherent drawbacks. The polarographic or Clark-cell sensor requires a constant current to be applied to the sensor, which increases power consumption. Like all electrochemical sensors, extensive maintenance is required to ensure accurate results. In addition, the reaction consumes oxygen, so constant sample flow must be provided.

Electrochemical sensor technology is quickly being replaced by optical technology, which allows the user to acquire stable, accurate results and significantly reduce maintenance. Optical technology has been tested in the field for over a decade and has gained widespread acceptance by both regulatory and environmental monitoring communities. In-Situ Inc.'s first optical DO sensor became commercially available in 2004. In-Situ Inc. and its subsidiary, TauTheta Instruments LLC, have further pioneered the development of commercial luminescent-based DO sensors for environmental monitoring.

Optical DO sensors rely on lifetime-based luminescent technology to accurately measure DO levels *in-situ*. When the oxygen-specific lumiphore is excited by a blue light, lumiphore molecules embedded in the sensing element emit red light (see Figures 1 and 2). Oxygen molecules quench the excited lumiphore molecules and prevent the emission of red light. This process is called "dynamic luminescence quenching." Determination of DO concentration by luminescence quenching has a linear response over a broad range of concentrations and offers a high degree of accuracy and stability.

Optical sensors are especially accurate below 2 ppm—a range in which most membrane sensors routinely give poor results. When monitoring anoxia in open bodies of water, achieving accurate readings below 2 ppm allows researchers to reliably characterize nutrient-related hypoxic zones. Data is especially accurate in anoxic conditions with accuracy in normal environmental DO ranges as good or better than traditional membrane sensors.

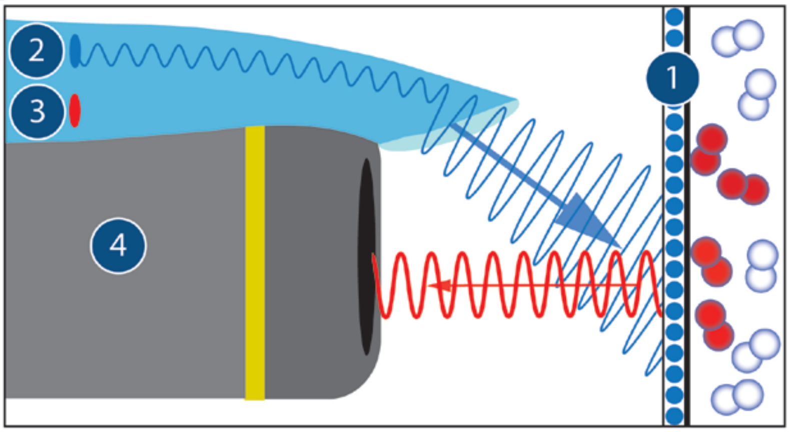

Figure 1: The RDO® Sensor eliminates the use of membranes, filling solution, and hazardous chemicals. The sensor includes lumiphore molecules (1) embedded in a sensing element, blue LED (2), red LED (3), and photodiode (4).

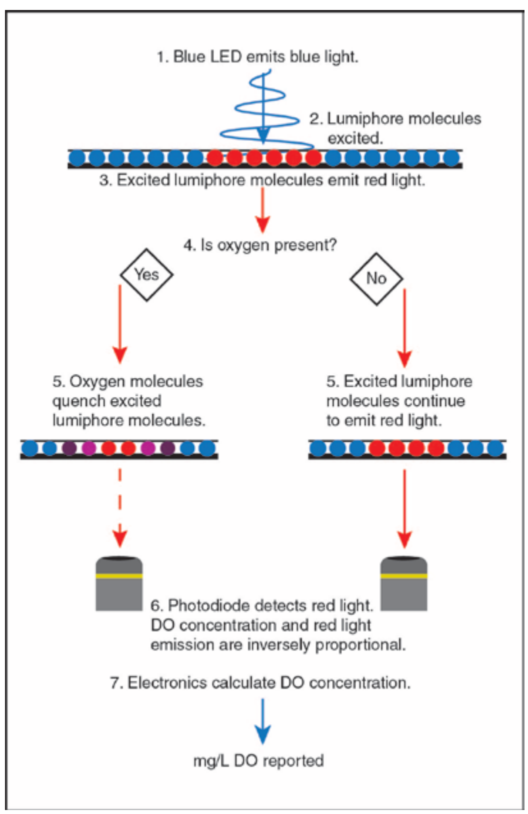

Figure 2: Lumiphore excitation process

PERFORMANCE TESTING

In-Situ® RDO Sensors were compared to traditional Clark-cell sensors across three performance matrices in internal laboratory testing. Test protocols were designed to measure accuracy, flow dependence, temperature, response times, and sensor precision in saturated and anoxic conditions. Three 50-gallon water baths with internal temperature control were allowed to stabilize to saturated DO conditions. Water bath temperatures were set to 4° C, 20° C, and 45°C and allowed to stabilize. In-Situ TROLL® 9500 Water Quality Instruments with RDO Sensors and Clark-cell sensors were completely submerged in the bath. Sample tubes were secured internally to the bath to allow for Winkler sample removal while preventing disruption of the bath.

TROLL® 9500 Water Quality Instruments with RDO® and Clark-cell sensors logged data at 15-minute intervals. Once bath conditions stabilized, duplicate Winkler samples were taken at 15-minute intervals. Winkler titrations were performed according to *Standard Methods for the Examination of Water and Wastewater (4500-O, Method C, Azide modification, pp. 4-131 to 4-133)*. The TROLL 9500 Instruments were sequentially moved from bath to bath at 30-minute intervals. Performance data from internal testing is shown in Figures 3 through 8.

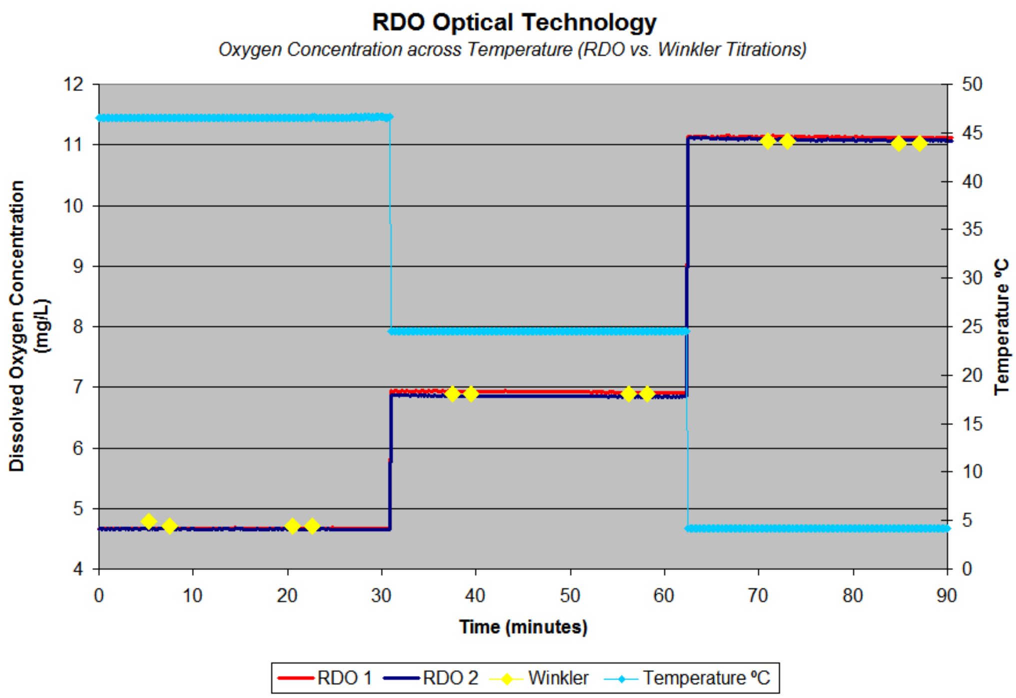

Figure 3: Results obtained by using the optical RDO Sensor correlate well to the Winkler titration method.

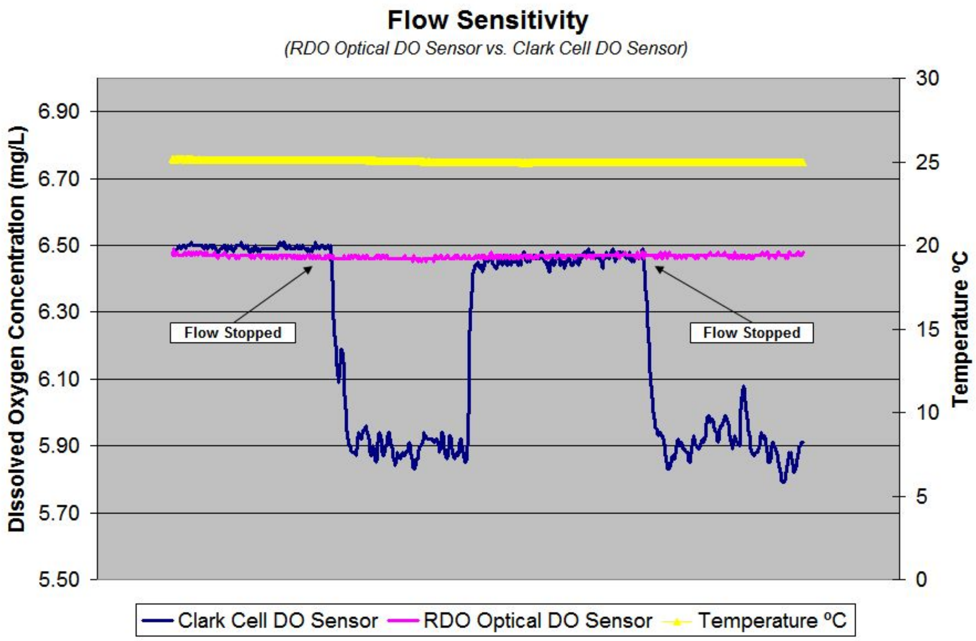

Figure 4: The Clark-cell DO sensor is highly dependent on sample flow because it consumes oxygen as part of the electrochemical reaction. The RDO® Sensor does not consume oxygen and does not require sample flow or stirring. The RDO Sensor provides accurate, stable readings throughout the test.

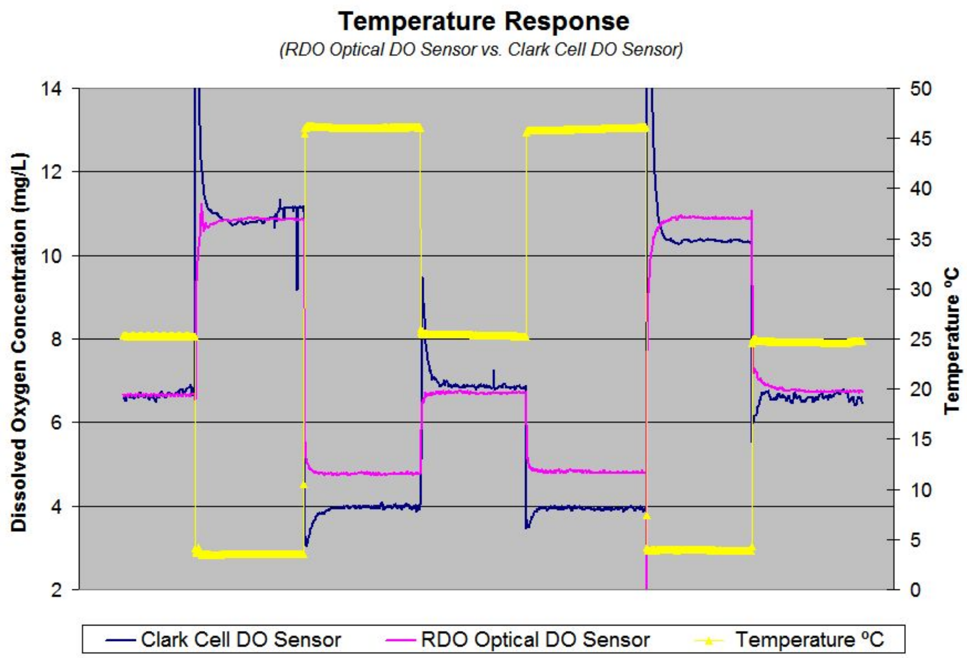

Figure 5: The Clark-cell DO sensor is sensitive to extreme temperature changes – stabilization takes nearly 3 minutes. The RDO Sensor responds quickly – stabilization typically occurs in less than 1 minute.

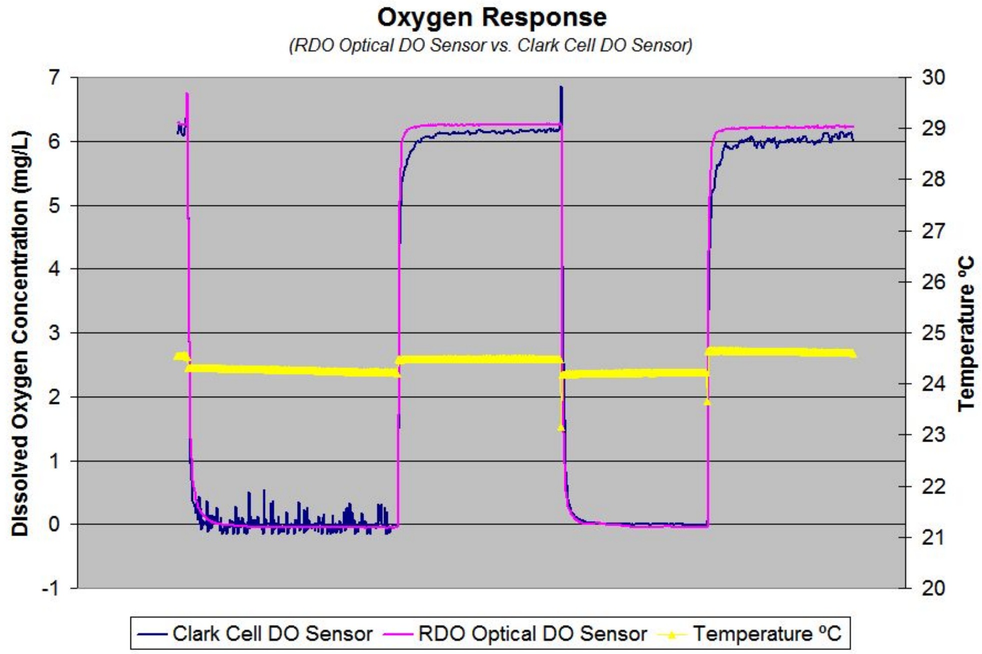

Figure 6: When oxygen levels change dramatically, the RDO® Sensor responds much faster than the Clark-cell DO sensor. T95 up: Clark-cell = 3:01 minutes; RDO Sensor = 35 seconds. T95 down: Clark-cell = 1:23 minutes; RDO Sensor = 15 seconds.

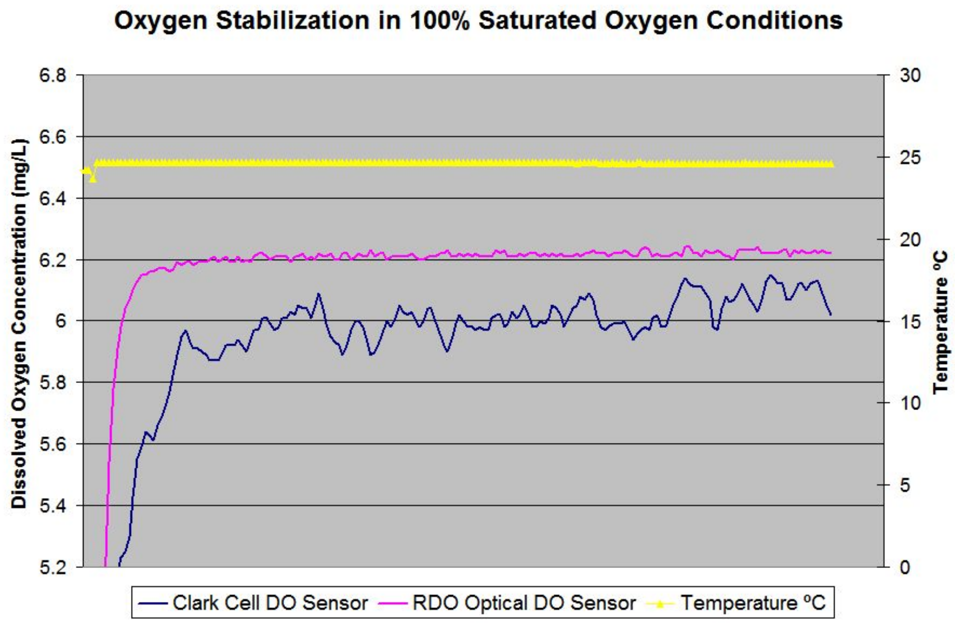

Figure 7: When comparing measurement stability at 100% oxygen saturation, the Clark-cell DO sensor exhibits noisy behavior, while the RDO Sensor shows a very stable response.

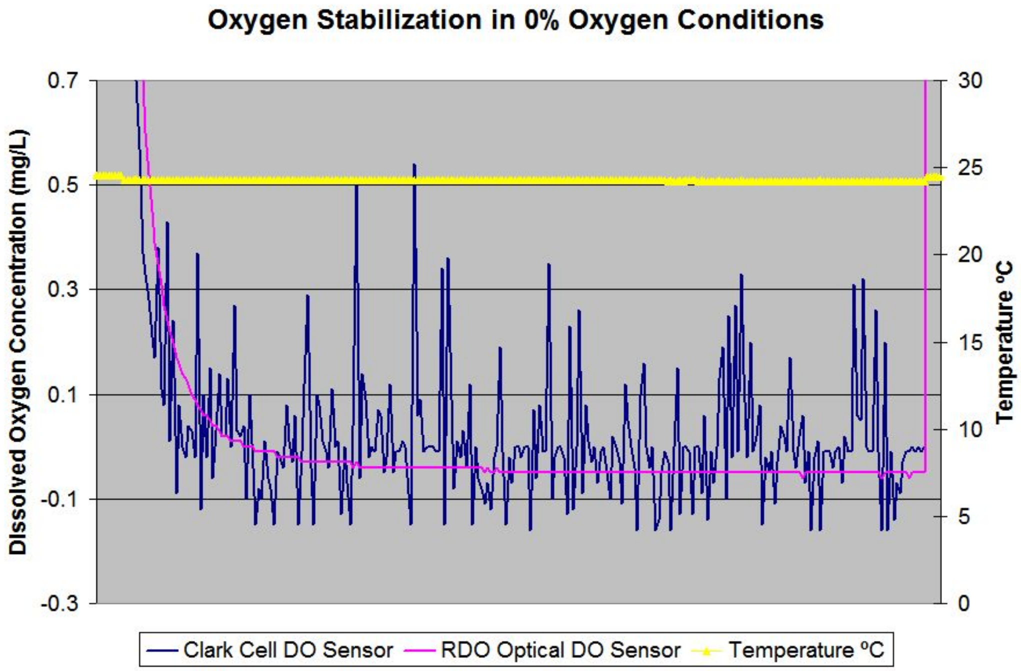

Figure 8: When comparing measurement stability at 0% oxygen conditions, the Clark-cell DO sensor does not stabilize in low DO conditions, while the RDO® Sensor remains stable in low DO conditions.

CONCLUSIONS

The In-Situ® Optical RDO® Sensor exhibits superior performance over traditional membrane-style DO sensors in several areas, including: stability, sensitivity, speed of response, accuracy in low DO conditions, and minimal maintenance requirements.

- Results demonstrated excellent correlation between the RDO Sensor and the Winkler titration method (Figure 3).
- Oxygen is not consumed as part of an electrochemical reaction, and optical sensors do not require sample flow or stirring for accurate readings (Figure 4).
- RDO Sensors respond faster than membrane-based sensors to changing temperature and DO (Figures 5 and 6).
- Readings are stable (Figures 7 and 8) and drift is minimal over long-term deployments.
- Durable sensing element offers a longer operational life than an oxygen-permeable membrane.
- Maintenance and calibration requirements are drastically reduced, minimizing site visits and operational costs.
- Material costs are reduced. Clark-cell sensors require frequent replacement of membranes and filling solution. The RDO Cap is replaced annually.
- In-Situ RDO methods are EPA-approved and can be used by all regulated entities and laboratories in all sample matrices.

For more information on In-Situ Inc.'s RDO methods, visit http://www.in-situ.com/RDO_EPA_Approval.