Firmware Update Improves Accuracy of aquaMeasure Dissolved Oxygen Sensors

Effective February 12, 2021, Version 3 firmware will be available for all aquaMeasure Dissolved Oxygen (DO) sensors. In addition to firmware upgrades performed by Innovasea during unit repair, customers will be able to upgrade their units in the field using the aquaMeasure app. The main objective of this firmware is to improve DO measurement accuracy. This firmware changes many aspects of the DO measurement including the specification, how DO is calculated and the definition of percent DO saturation. This white paper explains some of the technical details.

Change in DO Specification

The previous specification for the Innovasea aquaMeasure DO sensor was +/- 2% DO saturation. Each sensor was verified prior to shipping, by placing the sensor in water-saturated air and confirming the unit read within +/-2 % DO saturation of the actual condition (approximately 100% DO saturation depending on the temperature and atmospheric pressure).

Through continuous improvement initiatives, we discovered that the aquaMeasure DO sensors were reporting errors greater than 2% DO saturation, especially in the mid-range DO levels (50% to 70%). Working with Dalhousie CERC Ocean Science Laboratory and other experts in the field, Innovasea took a sample of sensors and ran them through a full sweep of DO and temperature conditions across the operating range of the sensor. It was found that the +/- 2% specification was not representative of the sensor's performance across the entire operating range.

Innovasea is updating the specification of the DO sensor to more accurately reflect how the sensor performs in the typical operating ranges our customers use. The specification is applicable to all sensors running the new Version 3 firmware which incorporates many of the improvements discussed in this paper.

As of February 12, 2021, the specification is changing to +/- 5% DO within the operating range of 0% to 120% DO and 5 to 25 degrees Celsius.

DO Measurement Improvements

The Innovasea aquaMeasure DO sensor measures the emitted light for fluorophores within the DO optical patch. The phase of this light, as well as the temperature of the environment, is then used to calculate the partial pressure of oxygen – and by extension DO. The previous model used to calculate oxygen is a version of the Uchida Modified Stern-Volmer equation (Uchida, 2008), which is used to relate the quenching effect that oxygen has on the fluorophores to the amount of oxygen acting on the patch.

The original aquaMeasure model was a simplified version of the Uchida Modified Stern-Volmer equation. This model had fewer coefficients and while it proved accurate for early prototypes, later patch groups had significant error when curve fitting to calibration data. This curve-fitting error resulted in aquaMeasures reporting higher values for mid-range DO levels (50% to 70%) and lower values for very high range DO levels (above 120%).

Innovasea reviewed the scientific literature and found a more complex version of the Uchida Modified Stern-Volmer equation with more coefficients that are better able to capture the

behavior of the DO optical patch. As shown in the plot below, the curve fitting of the new model is more accurate than the original:

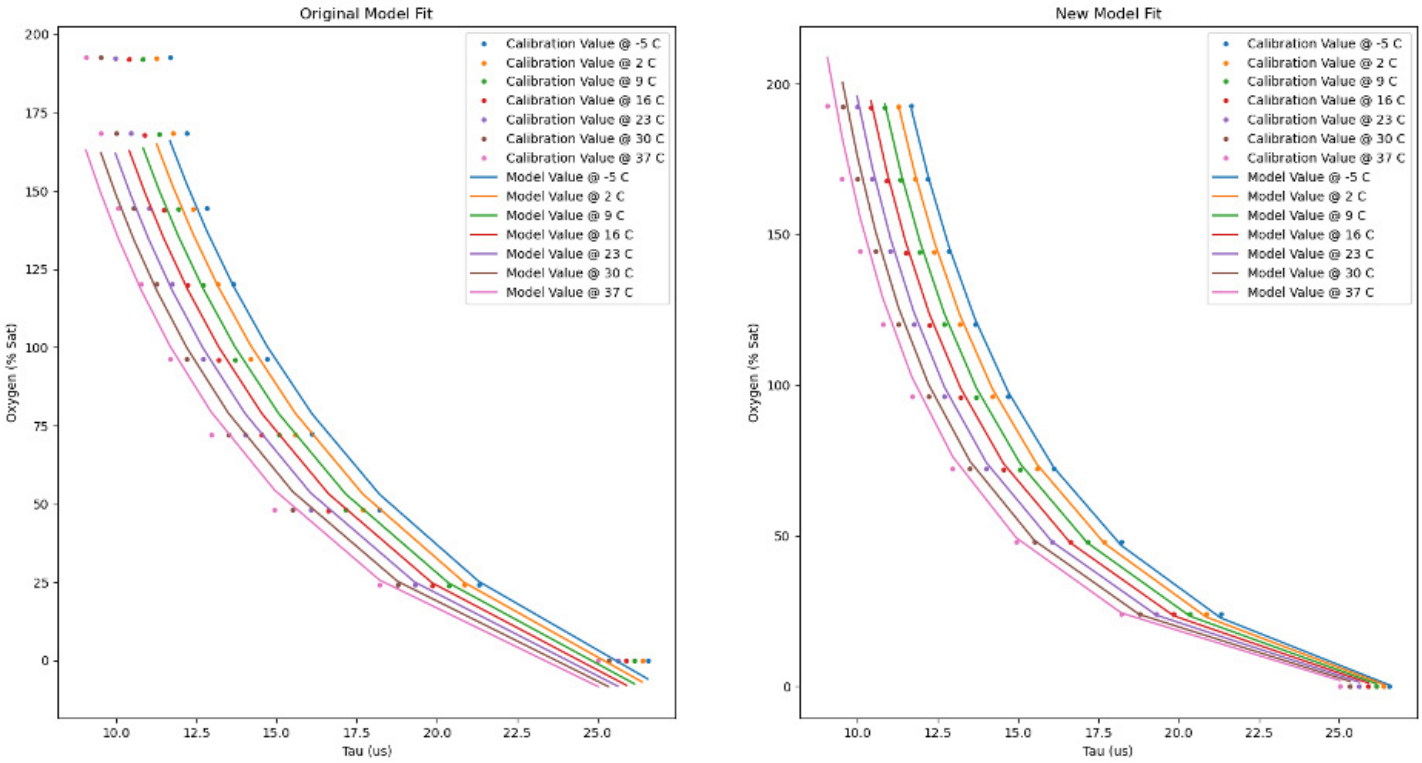

Figure 1: Comparison of Original and New Stern-Volmer Models

In-house and third-party testing have confirmed that the new DO model results in improved accuracy across the operating range of the sensor.

Moving forward, Innovasea is committing to improved quality assurance for the new model. For every order of patches we receive, the curve fit of the new model will be verified to ensure the patch behavior is fully captured.

aquaMeasure DO sensors will begin using the new model after upgrading to Version 3 firmware. For optimal results, we recommend users calibrate the device after upgrading, however, the sensor will continue to operate using old calibration data if a new calibration is not complete.

Changes to % DO Saturation

Percent DO saturation is a common unit for expressing the amount of oxygen in a body of water. It is defined as the ratio between the amount of oxygen measured in a sample and the amount of oxygen in a reference sample (with the same temperature and salinity), that is in equilibrium with the atmosphere:

$$\%DO = \frac{pO_2}{pO_{2,air}} = \frac{c_{O2}}{c^*_{O2}}$$

Where:

- %DO is percent DO saturation,
- pO_2 is the measured partial pressure of oxygen,
- $pO_{2,}$air is the partial pressure of oxygen in air,
- c_{O2} is the measured concentration of oxygen and
- c^*_{O2} is the concentration of oxygen of the sample if it were in equilibrium with the air.

Since the aquaMeasure DO is an optical probe, it measures the partial pressure of oxygen rather than the concentration. Therefore, the percent DO saturation calculation depends on the definition of $pO_{2,air}$. The aquaMeasure DO cannot measure the atmospheric pressure so it assumes standard pressure of 1013.25 hPa (10 hPa = 1 kPa). All percent DO saturation measurements are therefore referenced to standard pressure.

Originally, aquaMeasures definedp$O_{2,air}$ as the following:

$$pO_{2,air} = \chi O_2(p_{air}) = \chi O_2(1013.25\ \text{hPa})$$

Where:

- χO_2 is the mixing ratio of oxygen in the air (0.209) and
- p_{air} is the atmospheric pressure (assumed to be 1013.25 hPa).

While this is a common definition among DO sensors, the problem is that it assumes the air is dry. Any amount of water vapor pressure will reduce the amount of oxygen in the air. Since aquaMeasures are designed to work in maritime environments, it is more accurate to assume the air is 100% humid rather than 0%.

While reviewing scientific literature, the document "Recommendations on the Conversion Between Oxygen Quantities for Bio-Argo Floats and Other Autonomous Sensor Platforms" (SCOR WG 142) came to Innovasea's attention. The document acts as a set of recommendations for converting between units when dealing with dissolved oxygen. Innovasea decided to re-define its definition for $pO_{2,air}$ to be in accordance with SCOR WG 142 (Bittig, 2016):

$$pO_{2,air} = \chi O_2(p_{air} - pH_2O) = \chi O_2(1013.25\ hPa - pH_2O)$$

Where:

- pH_2O is the water vapor pressure, calculated from the condition's temperature and salinity.

Starting with Version 3 firmware, aquaMeasures will report percent DO saturation using the new definition of $pO_{2,air}$. This means the DO saturation value will be water vapor compensated.

If you prefer using the old definition of percent DO saturation or want to change a fixed calculation value such as atmospheric pressure or salinity, aquaMeasure sensors can be configured to do so. Please contact Innovasea Customer Success for help with this request.

Calibration Aging Effect

A new feature included with Version 3 firmware is the ability to track in the aquaMeasure app, how long it has been since a unit has been calibrated. Both single point calibrations (ambient condition only) and full calibrations (zero condition and ambient condition) are tracked in the app.

Long term testing has shown that sensors will become less accurate over time due to the DO optical patch drifting. It is an expected phenomenon for an optical based fluorophore system. As the fluorophores are exposed to more light, bleaching occurs over time and the patch emits less light as a result. While our patch manufacturer takes special steps to reduce the effect of patch drift, it is something that should be expected in all optical DO sensors.

Based on data collected from our sensors, Innovasea recommends performing a single point calibration every year and a full calibration every 2 years. This prevents the patch drift from introducing large amounts of error into the DO measurement.

Single point calibrations can be easily completed using the aquaMeasure app, which walks users through the procedure. See the User Manual for more details on how to get started. For full calibrations, units can be returned to Innovasea or calibrated by customers with special equipment. Contact Innovasea Customer Success to determine which is the best option for you.

Note: If a sensor is operating outside the recommended calibration timeframe, it will continue to function and provide data. The user should use that data with caution, as the patch drift may be introducing larger than expected error into the DO measurement.

Innovasea is beginning additional testing to help quantify this patch drift and determine what factors influence it. Expect additional information and updated recommendations in the future.

Continuing to Improve

Innovasea is committed to improving our dissolved oxygen sensors to provide the most accurate measurement possible. We are continuously running tests, working with our suppliers and investigating theories to provide top of the line DO measurements. This is the first step in a series moving toward a more accurate sensor and we hope to have more good news to share in the future.

Bibliography

Bittig, H. &.-J. (2016). SCOR WG 142: Quality Control Procedures for Oxygen and Other Biogeochemical Sensors on Floats and Gliders. Recommendations on the conversion between oxygen quantities for Bio-Argo floats and other autonomous sensor platforms.

Uchida, H. &. (2008). In Situ Calibration of Optode-Based Oxygen Sensors. Journal of Atmospheric and Oceanic Technology, 25. 10.1175.