

Optical Dissolved Oxygen Measurement in Power and Boiler Applications

Introduction

Dissolved oxygen (DO) is one of the key parameters that must be monitored and controlled in power and boiler applications to effectively minimize corrosion due to oxidation. Numerous guidelines exist from standards bodies on different chemistry methods that can be applied to effectively manage oxygen levels. Fossil fuel application chemistries, including all-volatile treatments (AVT) for both reducing and oxidizing (AVT(R) & AVT(O)), along with oxygenated treatment (OT) allow strict control of oxygen levels to minimize corrosion¹.

The use of Luminescent Dissolved Oxygen (LDO) sensors for the measurement of oxygen is now accepted by ASTM². With thousands of units in use globally, LDO measurement has been rapidly adopted by users in many industries. Optical measurement started with the measurement of relatively high oxygen levels, with measurements of ppm level samples now widely accepted and used in process. Technology advances resulted in ppb measurement systems; however, accurate and consistent measurement at levels below 10 ppb was limited due to the accuracy and detection limits. Since 2009, accurate measurement at levels below 1 ppb has now been made possible.

With the optical process for the measurement of dissolved oxygen, a measurement method has been developed that eliminates the process-related disadvantages of traditional electrochemical (amperometric) measurement methods, for example the progressive wear of the anodes due to the oxidation process and the decrease in electrolyte density.

Trends in Energy Management

Over the past decade a few of trends have started to gain pace within the industry, driving a change in instrumentation requirements for operations managers and plant chemists:

- ∞ Maintenance and operations budget cuts have resulted in fewer plant personnel. This in turn has forced plant personnel to optimize even further their daily work and reduce their maintenance and calibration workload. Accompanied by the switch to inline/in-process rather than lab measurements, this puts additional time pressure on personnel.
- ∞ As the cost of building new power and boiler systems spirals upwards, many operators now look to plant life extensions as a solution to bridge gaps in production capacity at a lower investment premium. Construction cost increases are compounded by fears over the cost of new carbon capture systems often demanded on new plants. Clearly, plant extensions are only possible if the heart of the system, the water-steam circuit, can be managed well and maintained.

These trends have changed the requirements in these applications. Starting from these trends, this article analyzes the options for oxygen measurements that are precise, reliable, stable, and above all require low to zero maintenance.

Principle of Measurement

LDO sensors, such as the K1100 and 3100, consist of:

- ∞ A sensor layer with the luminophore applied on a transparent carrier material
- ∞ The sensor body with a blue LED, a photodiode as a receiving unit and an additional red LED used as a reference light source.

The blue LED sends out a light pulse which passes through a transparent carrier material and hits the luminophore in the sensor layer (see Figure 1). Part of the radiant energy is transferred to the luminophore as a result. The electrons in the luminophore move from an energetic basic state to a higher energy level. This level is exited after a very short stay and a red light is emitted.

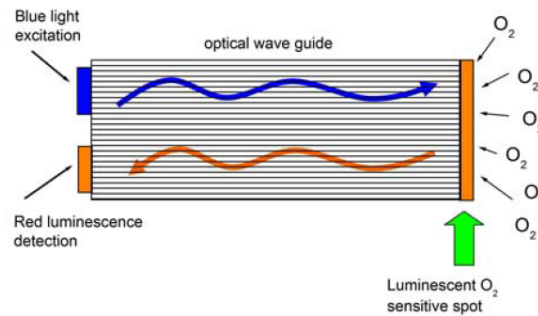


Figure 1: Basic representation of luminescent dissolved oxygen measurement system.

If oxygen molecules are in contact with the luminophore, they are in a position to take up the energy from the electrons (which are in the higher energy level) and enable their transition into the base level without emitting radiation (red light). This phenomenon is called quenching (see Figure 2). With an increasing oxygen concentration, this leads to a significant reduction in the emitted radiation intensity of the red light. The quenching also reduces the period the energy spends in the incited level, which leads to electrons leaving the higher energy level again faster. Both the life span and the intensity of the red emitted radiation are reduced by the presence of oxygen molecules.

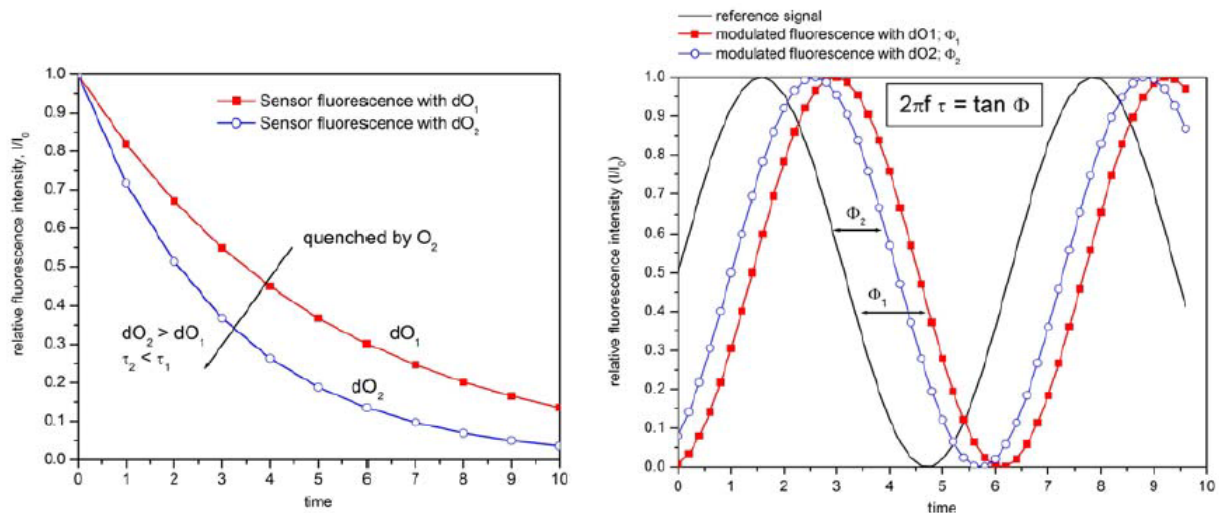


Figure 2: Phase shift of luminescence vs. oxygen concentration.

The light pulse sent out by the blue LED at point in time $t=0$ hits the luminophore, which emits red light immediately afterwards. The maximum intensity and the decay time of the red radiation depend on the ambient oxygen concentration. The decay time T is defined here as the period between incitement and the red radiation returning to one times the maximum intensity. To determine the oxygen concentration, the lifespan, T , of the red radiation is evaluated.

A constant alignment of the sensor occurs with the help of the red LED fitted in the probe. Before each measurement, this sends out a light beam of a known radiation characteristic. Changes in the measurement system are hence detected without any time delay.

System Calibration

Amperometric oxygen sensors generally require a two-point calibration—the zero point and the slope (via standards calibration sample). Optical oxygen sensors require a single-point zero-calibration. The single point calibration is used to set the zero; this is where the optical signal varies the most, hence an accurate setup is essential if accurate measurement below 1 ppb is required.

The big advantage of optical calibration is that no chemicals are required. The sensor can be calibrated using a pure oxygen-free gas such as nitrogen or carbon-dioxide with no other liquids required for cleaning due to the sensor being electrolyte-free. The only reliable calibration method remains to expose the sensor to a known reference sample to adjust the zero-point. The use of a quality-50 gas as a reference zero value is recommended, giving 99.999% purity, which helps ensure accuracy at sub-ppb measurement levels.

Figure 3 shows the maintenance, calibration, stabilization, and response time of an optical sensor compared to an amperometric sensor. It shows that the maintenance and stabilization time of an optical sensor is 82% less than that of a typical amperometric sensor. Combined with the fact that maintenance is required three times less often than an amperometric sensor, the operator workload can be reduced by 95%. Such time and cost savings become significant within a plant with a multitude of oxygen sensors. This also demonstrates that optical sensor response time post-calibration, from air to reach 4 ppb, is 79% faster than that of a typical amperometric sensor—resulting in more system uptime and much lower operator intervention.

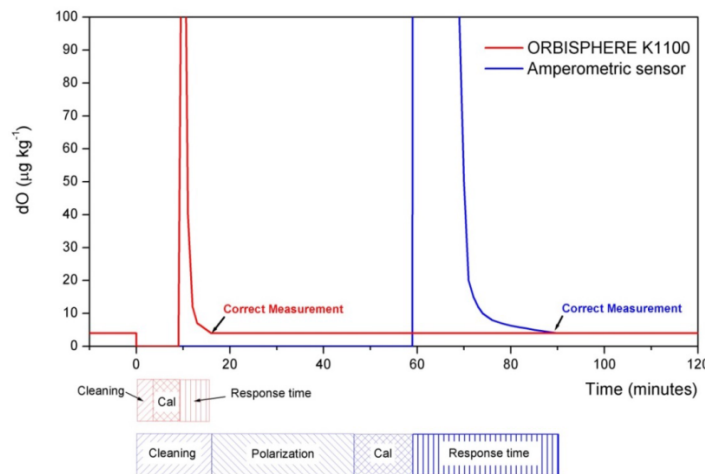


Figure 3: Maintenance, calibration, and stabilization timeline for an optical vs. an amperometric sensor.

Comparative Tests and Installation

Many different tests have been performed in industrial environments globally to demonstrate the significant benefits that can be achieved by using optical oxygen sensors when compared with amperometric sensors. Applications operating with AVT water chemistries typically require lower level, hence more accurate, oxygen measurement than those running OT water chemistries. The oxygen levels commonly encountered within fossil applications have been discussed in prior papers by Dooley and

Shields³. Given such varying concentrations and water chemistries, a clear understanding of the factors impacting system performance is essential.

Stability

While some amperometric sensors can measure with an accuracy of 0.1 ppb, this is balanced with a few drawbacks:

- ∞ Stability or drift between maintenance interventions
- ∞ Effort and costs associated with minimizing errors due to drift through more regular calibration and sensor maintenance.

For this reason, it is essential to consider the oxygen levels to be measured along with the constraints of time and the confidence to be placed in a system.

Sensor drift is the major cause of concern for plant operators and can result in excessive calibration and maintenance. The stability of a system directly impacts the confidence placed in it over time—a system that drifts significantly will never be trusted as the source of information in process control. With a number of systems publishing a drift of $\pm 5\%$ ⁴ and up to ± 2 ppb per week in the measured valuesⁱⁱⁱ, this leads to frequent operator intervention for calibration and a lack of trust in the system. Such drift of up to ± 2 ppb per week in applications below 5 ppm is not acceptable for many operators.

System Performance Under the Influence of Flow Variations

Within any power or boiler application, the performance of any sampling system plays a role in the accuracy of most analytical systems. When flow is reduced below recommended levels, this can impact the accuracy of the measurement systems. Figure 4 shows how the performance of the Orbisphere K1100 optical sensor is independent of flow when compared with an amperometric sensor.

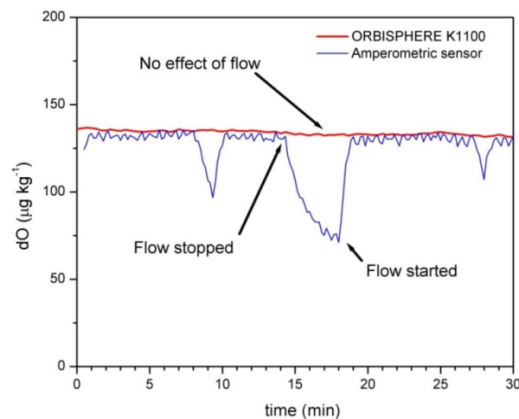


Figure 4: Comparison of an amperometric sensor with the Orbisphere K1100 experiencing variations in flow.

The optical system requires only enough flow to provide a fresh sample, while amperometric sensors have a range and minimal flow levels below which measurement errors could be encountered. For example, a flowrate that is 30% lower than a recommended minimum would likely result in an error of up to 10%.

Summary

The measurement and control of the dissolved oxygen at power and boiler applications has never been

as critical as it is today. While the number of qualified service engineers has been continually reduced and continues to be reduced further, economic pressure on operators to keep the capital equipment in operation for as long as possible grows. As a result, the labor time available to the personnel for servicing the measurement technology becomes an increasingly critical factor.

With respect to its stability, the K1100 optical sensor has proven that it far exceeds the amperometric sensors with a calibration interval of 12 months without an interim intervention. Flow fluctuations common in these applications have no negative influence on the accuracy of optical oxygen measurements. This is a decisive advantage, as conventional amperometric sensors often tend toward results that are too low due to their attrition measurement in the case of flow fluctuations. This occurs in particular at very low flow speeds.

The response time of the K1100, following successful calibration and return to operation upon reaching an oxygen concentration of 4 ppb, was approximately 79% faster than that of the fastest amperometric sensor. The calibration and maintenance effort is lower by up to 95%.

In general, the K1100 offers all users cost-efficient and exact oxygen measurements. With a proven repeatability of ± 0.1 ppb and the possibility of measuring for a time period of 12 months without additional service intervals, calibration or personnel intervention, the K1100 LDO sets new standards in oxygen measurements within power and boiler applications.

¹ Dooley, B., Shields, K.; Cycle Chemistry for Conventional Fossil Plants and Combined Cycle/HRSGs - PPChem 2004, 6(3).

² Hach Company ; Case History: Bristol-Myers Squibb/Hach Process Luminescence DO - S-P250, 07/2004.

³ Dooley, B., Shields, K.; Cycle Chemistry for Conventional Fossil Plants and Combined Cycle/HRSGs - PPChem 2004, 6(3).

⁴ Waltron LLC ; Dissolved Oxygen Analyzer: Aqualyzer® 9062 - 05/2009.

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