Sampling Considerations for Equilibrium Dissolved Oxygen Sensors

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Presented to
NUS 1996 International Chemistry On-line Process Instrumentation Seminar
Clearwater, Florida, November 20-22, 1996
Introduction
At standard temperature [25°C] and pressure [1 atmosphere], clean water in equilibrium with air contains 8.24 milligrams of oxygen per liter of water. This is called the air saturation value at 25°C and is usually reported as parts per million, ppm.

The control of corrosion in modern high pressure boilers commonly demands that the dissolved oxygen concentration in the water be less than 4 parts per billion, ppb, or 1/2000th of the air saturation value. The 8.24 micrograms of oxygen contained in one milliliter [ml] of air saturated water is enough to raise the dissolved oxygen concentration in 2000 ml of water by 4 ppb. Thus, if 2000ml of water containing 4 ppb dissolved oxygen were exposed to just one ml of air saturated water, the dissolved oxygen concentration in the 2000 ml would be doubled.

The concentration of oxygen in air is 20.9% by volume. The milligrams of oxygen per ml is calculated as follows:
From the ideal gas law, PV = nRT where P is pressure, V is volume, n is the number of moles [gram molecular weights], R is the gas constant and T is the absolute temperature, the volume of one mole of gas at atmospheric pressure and 25°C [298 K] is
\[ V = 1 \text{ mole} \times \left(0.08205 \text{ L-atm/mole K}\right) \times 298\text{K/1 atm} = 24.45 \text{ L} \]
The mg of oxygen per L is given by
\[ 1 \text{ L} \times \left[1 \text{ mole gas/24.45 L} \right] \times \left[0.209 \text{ mole O}_2/ \text{ mole gas} \right] \times \left[32,000 \text{ mg O}_2/ \text{ mole O}_2 \right] = 274 \text{ mg} \text{O}_2 \text{ per liter of air.} \]
This is about 33 times as concentrated as oxygen in air saturated water. The amount of oxygen in 1 ml of air is that which is required to double the concentration of [33 x 2000] 66,000 ml of water originally containing 4 ppb of dissolved oxygen.
Distinguishing between a leak and trapped air involves comparing results over time. With a [constant] leak, the relationship between flow rate and the error in reported dissolved oxygen should be constant. With trapped air, the contamination and the positive flow rate dependence should decrease with time. Often this effect is reported as a sensor with slow response at low ppb concentrations.

What’s really happening is the slow dissolution of trapped oxygen into the flowing sample. Once the trapped oxygen source is depleted, the sensor responds correctly.

**Conclusion**

Sampling systems for dissolved oxygen sensors should be devoid of leaks to the atmosphere, regions where air or stagnant water can communicate with the sample and downstream. Leaks and traps can be detected from the flow dependence and time-dependent flow dependence of the reported oxygen concentration. Each time a trap is exposed to air, such as during air calibration, the trapped oxygen source is reestablished and the “trap symptoms” described above reappear.

Leaks can be either “true leaks” — minute holes in the plumbing carrying the water usually observed at fittings — or diffusion of oxygen from the surrounding air through the walls of non-metal tubing. Non-metal tubing is not recommended but is frequently used because of its flexibility.

Any place where water fails to fill the plumbing or where the water flows down can become a dead spot and a source for oxygen contamination. An example of each is shown in Figure 1. Water flows up a sample line, over the oxygen-sensing portion of an equilibrium sensor, through the body of the sensor, out a side-arm outlet, down and then up a length of tubing leading to a funnel and, finally, over the top of the funnel. The funnel provides access to the water for the ampule of a wet chemical analysis of dissolved oxygen. The valve meters the sample flow and stops it for sensor calibration or servicing.

Two things are wrong with this picture. First, as shown in the cutaway, the side arm outlet from the equilibrium probe is situated only part way up a large internal cavity. The water fills to the level of the side arm but, at least initially, an air pocket significantly larger than the 1 milliliter discussed in the introduction exists in the upper portion of the cavity. While the air in this pocket must eventually dissolve into the water flowing through the sensor, until it does, it serves as a source for oxygen contamination that renders the results gathered by the wet chemical method unreliable. Consequently, independent measurement of dissolved oxygen in water flowing out of an equilibrium probe is not recommended.

The second error is allowing the water to the sampling funnel to flow down. Before flow starts, the tube will be filled with air. It is necessary to sweep the air from the tube before reliable results can be expected. Upflowing water will tend to lift air out above it. Downflowing water, however, can leave air bubbles trapped in the downflowing portion of the tubing. As long as the buoyant upward velocity of the bubbles exceeds the sample flow, the bubbles will remain in the downflowing portion of the tubing and will serve as a source of oxygen contamination until they are dissolved.

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Less obvious are the problems associated with the sampling system shown in Figure 2. Water normally flows through the equilibrium sensor and out its sidearm outlet as in Figure 1. When a wet chemical calibration check is to be performed, the valve in the sidearm outlet is closed, the valve below the funnel is opened diverting flow from the sensor to the funnel. The valve on the common line stops flow for calibration and service. Again, two problems present themselves.

When the flow to the sensor is stopped, the stagnant water in the sensor and the line to it will initially be at the sample dissolved oxygen concentration. However, unless the sensor has had water flowing through it long enough to dissolve the internal air pocket, oxygen from the pocket will immediately begin to diffuse into the water in the cavity and down the sample line. The question then will be whether this diffusion process is slow enough that the oxygen reaching the line flowing to the funnel will be negligible.

The other problem is a general one concerning allowing any stagnant water to communicate with the sample flow. In the normal operation, flow is to the sensor and goes past the piping to the funnel. The water in this stagnant leg is sealed from contamination by valve below the funnel. However, should this valve or any other fitting in this leg leak, oxygen can enter this stagnant leg and eventually reach the “T” below the sensor and begin contaminating the sample. This leak might be small enough to be negligible when its oxygen is continuously being diluted by the high flow recommended for the wet chemical analysis. However, a leak of similar magnitude might be large enough to contaminate the stagnant water and the water flowing to the sensor since this flow is usually much less than that recommended for the wet chemical method.

An arrangement eliminating sample communication with stagnant water is shown in Figure 3. Flow may be directed to either the sensor or the funnel and the 3-way valve isolates the sample flow from the stagnant water in both cases.

Two problems with the arrangement shown in Figure 3 remain. First, the sensor and the funnel cannot be supplied with sample simultaneously. It is desirable to be monitoring the dissolved oxygen concentration with the sensor exactly when the sample for the wet chemical analysis is gathered.

Simultaneous monitoring eliminates disagreements resulting from a fluctuating dissolved oxygen concentration. Simultaneous monitoring also allows a rapid return to the normal operation where the sensor only is monitoring without having to wait while air-contaminated water is purged from the line to the sample.

Second, dissolved oxygen sensors are normally calibrated in air. It is desirable to be able to expose the sensor to air without opening plumbing connections.

To achieve uncontaminated, simultaneous sampling and valve-controlled air calibration, the plumbing arrangement in Figure 4 is recommended.

Normal operation consists of allowing flow to be metered through the 3-way valve to the sensor. The stagnant water in the line to the funnel is protected from air contamination by a second shutoff metering valve.

The sensor is exposed to air by switching the 3-way valve to drain. If this valve is solenoid-actuated, air calibration can be executed automatically by activating a relay in a sufficiently sophisticated analyzer. Furthermore, initiation of the calibration can be based on a programmed time or by an event. Simultaneous flow to the funnel and to the sensor is controlled by the two metering valves.

Shown in Figure 5 is another arrangement that meets all of the requirements of uncontaminated simultaneous sampling and valve actuated calibration. The only drawback is that two connections into the main sample line flow are required.

**Consequences — Detection of Oxygen Contamination**

In spite of all the precautions described above, dead spaces can exist in complicated sampling arrangements and leaks can always occur. Their presence can be revealed by the response of the sensor.

The sensor’s dependence on sample flow rate is a key diagnostic. Equilibrium dissolved oxygen sensors are independent of flow rate. Within the sensor, oxygen is consumed at an electrode and its concentration determined from the direct current resulting from this process. The amount of oxygen consumed is balanced by oxygen produced electrochemically at a counter electrode. Net oxygen is consumed; there is no oxygen depletion in the sample; the sample just outside of the sensor need not be replenished so flow dependence is zero and oxygen may be measured in still water if desired, see Figure 6.

This is to be contrasted with oxygen sensors which consume oxygen electrochemically but which do not internally balance this consumption by a replenishing reaction. For these sensors, oxygen must continually diffuse from the sample, through a membrane, through some portion of an internal electrolyte solution to an electrode where it is consumed. Net oxygen is consumed from the sample. A concentration gradient develops from a point some distance from the sensor, through regions of diminishing dissolved oxygen concentration to the consuming electrode where the dissolved oxygen concentration is zero. The current from which the dissolved oxygen concentration is inferred depends on the diffusion path. If the flow rate past the sensor is diminished, replenishment of the consumed oxygen is lessened and the resulting drop in current is unrelated to the bulk dissolved oxygen concentration. Diffusion rate sensors demand a minimum flow rate below which the reported dissolved oxygen concentration will decrease with decreases in flow rate, see Figure 7.

How does all of this allow inferring the presence of a leak? From this discussion of how these sensors work, we see that a decrease in flow rate should result in either [1] no change in signal for an equilibrium sensor or [2] a decrease in signal for a diffusion rate sensor. If, however, a decrease in flow leads to an increase in signal, this is almost surely related to oxygen leaking into the sample. For a given leak rate, a decrease in flow would correspond to an increase in dissolved oxygen concentration because lowering the flow rate dilutes the leaking oxygen less.