# The truth about oxygen testing

**Oxygen measurement technology has advanced considerably in recent years as most manufacturers launch new optical sensors. As a result, a bewildering array is now available, so this article will seek to review the advantages and drawbacks of the most common oxygen sensors from a brewer's perspective.**

by ***Graham Meller***

Benefitting from over 40 years of experience in oxygen measurement for the brewing industry, staff at Hach Lange (working with the Orbisphere brand) are well placed to evaluate both amperometric and optical technologies. A number of critical issues will be addressed, including response time, long-term stability, and process condition effects as well as the benefits of the latest developments in the optical oxygen sensors.

## Background

The effect of oxygen on the different stages of beer production in addition to the importance of maintaining appropriate oxygen levels is well known. Once the fermentation step is complete, it is critical to avoid any further oxidation of the beer to maintain the taste and therefore the shelf life of the final product.

To prevent oxidation, the oxygen level must be maintained as low as possible. Careful beer handling in the brewery can result in packaged dissolved oxygen values of less than 100 ppb – at this level the shelf life will be greatly extended. To control the oxygen level accurately during beer processing, effective oxygen monitoring is required during the various movements from FV to package. Sources of air contamination and oxygen ingress include inadequately purged vessels, leaking pump glands or valves, and filter aid dosing pumps. By measuring throughout the process it is possible to identify the source of any oxygen contamination and act to minimise it.


*The Orbisphere M1100 optical oxygen sensor.*

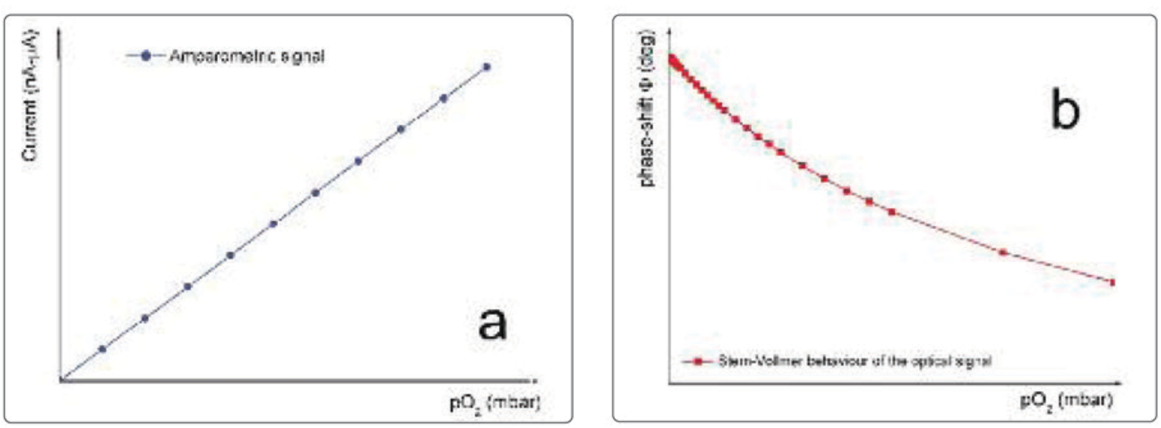
## Available methods to monitor oxygen

Until recently the vast majority of sensors used in the brewing industry were membrane covered amperometric sensors where oxygen diffuses through the membrane and the electrical current that is generated by the electrochemical reaction is in direct proportion to the partial pressure of the oxygen in the sample. The proportionality constant can be determined by a suitable calibration procedure using air as a source of known oxygen partial pressure.

More recently, optical oxygen sensors became available to the beverage industry. Optical sensing of oxygen is based on the measurement of the fluorescence of a dye/indicator illuminated with light; this dye fluorescence being quenched by the presence of oxygen (the more oxygen the faster the fluorescence disappears). Oxygen concentration can then be calculated by measuring the decay time of the fluorescence intensity. The higher the oxygen concentration, the shorter the decay time. By modulating the excitation, the decay time is transformed into a phase-shift of the modulated fluorescence signal, which is independent of fluorescent intensity and thus of potential aging. For both methods, Henry's law provides the link between partial pressure and dissolved concentration in the sample. Figure 1 shows the fundamental differences of the raw signal behaviour against the content of oxygen for both the amperometric and optical methods.

## Accuracy of the zero

As illustrated in Figure 1 the amperometric method can intrinsically provide a true physical zero (i.e. no oxygen means no signal). Whereas most amperometric systems show a drift of the zero and require a regular 'zero' calibration, Hach Lange's Orbisphere design is unique in guaranteeing a stable true zero over time. Laboratory and practical experience show that an accuracy as good as

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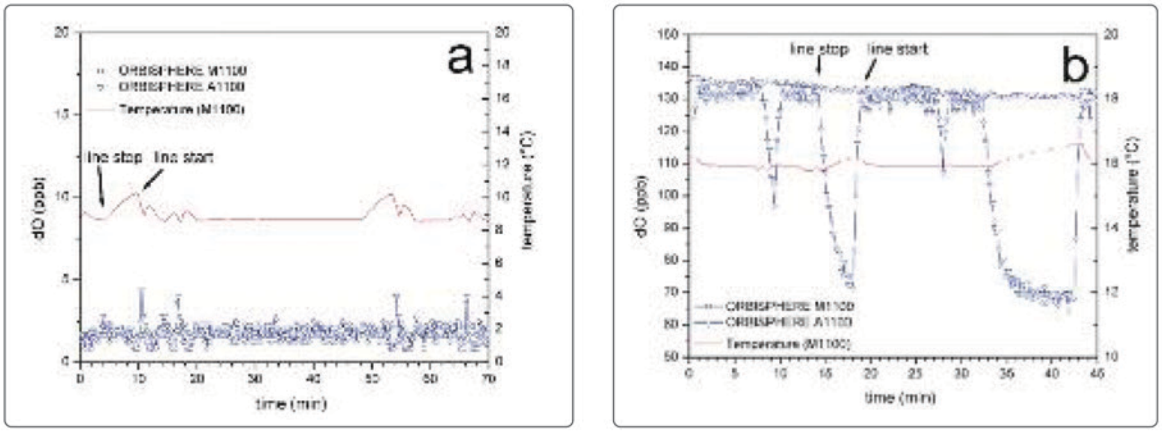



***Figure 2 shows the effects of lack of flow and pressure variations. In 2a, the spikes caused by the opening of a filling valve are observable, whereas 2b shows how the amperometric reading decreases over time in the absence of flow.***

±0.1 ppb can be obtained with these amperometric sensors. Conversely the parameter that varies the most with optical technology is the value in the absence of oxygen.

A zero calibration is generally performed by exposing the sensor to an oxygen free gas such as 99.999% nitrogen or 99.999% carbon dioxide. The accuracy of the zero is directly linked to the precision of the zero calibration which is influenced by: the quality of the calibration sample (± 0.4 ppb), the absence of leakage in the calibration set-up and the quality of the sensor signal. The accuracy that can be expected from this calibration is between ± 0.5 and 1 ppb. The stability of this technology over time will be discussed in a dedicated paragraph below.

### Calibration

Whereas the Orbisphere amperometric sensor only requires a simple one point calibration in air to determine the slope due to its 'true' zero, most amperometric sensors do require regular zero point and slope calibration. As previously mentioned, the parameter that varies the most with optical technology is the value in the absence of oxygen. Since the other parameters defining the phase-shift normally show negligible change over time, the key parameter to be adjusted is the zero. The calibration requires a specific set-up, a specific calibration sample and delivers an accuracy of between ± 0.5 and 1ppb. Together with the factory defined parameters describing the curve at high oxygen levels, the overall accuracy is in general around ± 1ppb or ± 2% of the measured value whichever the greater.

### Response time

The response time of an amperometric sensor is determined by the permeability of oxygen through the measurement membrane. For sensors used in beer processes, 90% of the sample change is typically detected in 30 to 60 seconds. Furthermore, sensors using a guard electrode that prevents the effect of the oxygen present in the sensor electrolyte show an improved response time (up to twice as fast) towards low oxygen values. A response time (t90) from air to zero of 10s has been reported for optical sensors in a recent paper[(1)]. This is only true in the gas phase where the N2 gas pushes the oxygen out of the luminescent spot (dye matrix); no response times have been published to date for dissolved oxygen measurement.

Measurement data published recently by the Weihenstephan Research Center for Brewing indicates a faster response to a change towards higher oxygen containing beer for the Orbisphere amperometric sensor (t90 = 45 s) than for another optical system that was used (t90 = 70s)[(2)].

### Effect of process conditions on the measurement

Amperometric technology consumes the oxygen that is measured and therefore requires a minimum flow to work accurately. This is not normally an issue in a beer process where the flow is sufficiently high. When the production line is stopped however, the absence of flow and hence oxygen consumption typically leads to low oxygen readings. Standard amperometric sensors are adapted for pressure conditions found in-line but changes in flow or pressure can cause the membrane to vibrate and generate noise in the measured signal. Pressure shocks caused by valves opening or closing can generate spikes on the oxygen signal whose duration strongly depends on the sensor design.

The effects of lack of flow, flow variation and sudden pressure changes are illustrated in Figure 2. On Figure 2a, the spikes caused by the opening of a filling valve are observable, whereas Figure 2b illustrates how the amperometric reading decreases over time in the absence of flow.

Although optical sensors do not intrinsically require any flow to measure accurately, a minimum flow is required to refresh the oxygen content in the spot and provide representative sample measurements. Static pressure and pressure changes have no effect on the measurement unlike amperometric sensors.

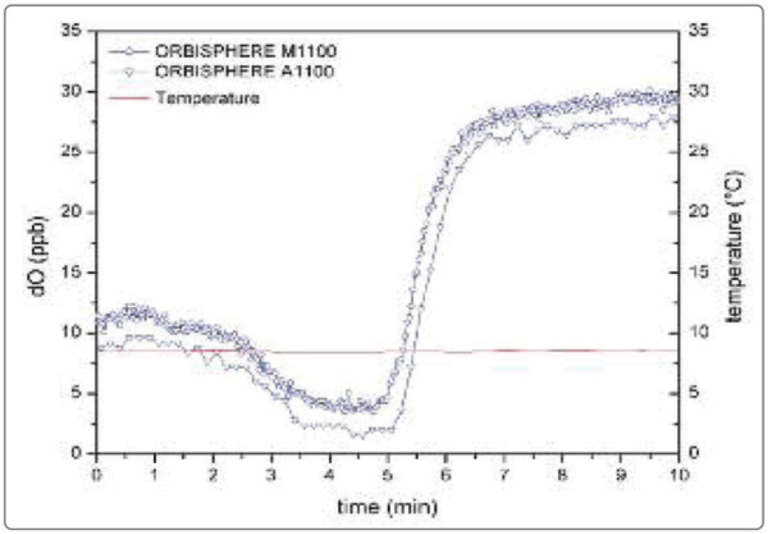
Figure 2a shows the absence of any pressure effect on the measurement as a valve is opened or the line stopped and Figure 2b the continuous accurate reading in the absence of flow. When amperometric sensors are exposed to high oxygen content and high temperature, such as during CIP, this can shorten maintenance intervals. However, such effects can be minimised by switching the sensor to stand-by position when the temperature is high.

Whilst optical sensors are also CIP compatible, exposure to high oxygen levels and high temperatures is the principal cause of drift which results in more frequent calibration. As for the amperometric sensor, an appropriate system configuration can protect the sensor by switching it off during high temperature conditions.

### Stability over time

All measurement devices drift with time and hence calibration is required at given intervals; the lower the drift the longer the interval between service and/or calibration. With the exception of the Orbisphere amperometric design that has no drift of the zero, all other amperometric sensors experience drift of both the zero point and of the slope – regular re-calibration is therefore a necessity. In beer applications, this re-calibration frequency is typically in the 1–3 months range for other amperometric sensors whereas the Orbisphere sensor only requires a calibration in air during the bi-annual maintenance due to its true zero with no drift.

Existing optical systems claim to require calibration once every two years[(1)]. The conditions to achieve this two year frequency are that the system runs for only 12 hours per day and is therefore switched off for the remainder of the time, and is configured to provide data points every 30 seconds. The




***Direct comparison of optical (M1100) and amperometric (A1100) sensors.***

reality, however, is for systems to be configured to operate continuously and provide data points every two seconds, this results in a calibration interval is of less than one month, because the drift is directly linked to the number of measurements performed.

## Maintenance requirements

Whereas the maintenance of the amperometric sensor has long had the reputation of being tedious, most modern sensors are fairly easy to clean and refurbish. The latest Orbisphere A1100 sensor is supplied with patented pre-mounted membrane kits that include pre-dosed electrolyte that reduces bi-annual maintenance to only 3 minutes. The maintenance of an amperometric sensor has to be performed at regular intervals because the sensor becomes dirty and the electrolyte is consumed. Optical sensors do not require such maintenance and the sensor head is normally cleaned during the CIP process. The only real maintenance is the replacement of the optical spot every 1–2 years depending on the process conditions.

## Latest developments

Hach Lange is committed to the provision of the most appropriate monitoring technology for all sectors. In the past, we have not offered our optical probes in the brewing industry even though we have experienced great success using optical technology in the Power and Wastewater sectors. However, the key goals are to provide long-term stability, a fast response time in liquids and a fast response to temperature changes – all of which are achieved by the recently launched Orbisphere M1100 optical dissolved oxygen sensor.

With the latest developments, Orbisphere can now offer an optical sensor with a calibration interval > 6 months when in continuous use and providing a data point every two seconds (without the need to switch off the instrument when no beer is flowing through the pipe).

In beer, the oxygen exchange between the sample and the luminescent spot as well as accurate temperature measurement are keys to provide a fast response time. We have proven that the latest optical sensor for beer has a response time equivalent to that of amperometric sensors in the beer process (see Figure 3). In addition, the oxygen levels measured correspond well to values from the amperometric sensor (within less than 3ppb).

In addition to the Orbisphere M1100 sensor stability during process changes, Figure 2 demonstrates the accuracy of the oxygen reading against the Orbisphere amperometric sensor. On a lager beer sample with an approximate content of 2ppb oxygen both sensors measure within 1ppb (Figure 2a). On beer/ syrup mix with an oxygen content of 135ppb both measure within 3ppb (Figure 2b). With such low deviations from the Orbisphere A1100 reference, the new Orbisphere M1100 offers the advantages of an optical sensor.

The M1100 offers high levels of precision and accuracy, allowing brewers to confidently maintain low oxygen levels, thereby controlling beer oxidation and improving flavour stability. Robust optical technology without membranes or electrolyte makes the M1100 Sensor highly resistant to rapid process and flow changes, reducing and simplifying maintenance. This adds up to increased production uptime and a lower total cost of ownership.

## Conclusions

Whereas the Orbisphere A1100 amperometric sensor gives the best detection limit (±0.1ppb) and the easiest calibration method (single point in air) and is an ideal solution for water applications requiring high accuracy, the new Orbisphere M1100 optical sensor is the best solution to fulfil brewers' needs offering a fast response time, reliability over time, and limited maintenance and calibration requirements, thus providing the most cost effective solution to accurately monitor oxygen in beer.

### References


1. Verkoelen F.; *Brewing and Beverage Industry International*, 2007, No1, 16.
2. Titze J., Walter H., Jacob F., Friess A., Parlar H.; *Brewing Science*, 2008, March/April, 66.