Oxygen Measurement Technologies in the Brewing Industry

As all major oxygen analyser suppliers have released an improved version of their existing products or launched a new product based on optical technology over the past 2 years, we thought it would be an appropriate time to review the existing technologies from a critical and objective viewpoint. Based on the oxygen measurement experience amassed by ORBISPHERE over 40 years in the brewing industry, and in both amperometric and optical technologies, we have evaluated the advantages and drawbacks of the most common oxygen sensors from the point of view of brewer's needs. Critical aspects such as response time, long-term stability, and process condition effects are discussed as well as the benefits of the latest development on the oxygen optical sensors.

Introduction

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 accurately control the oxygen level during the beer production process, accurate oxygen monitoring is required. A major source of air contamination in bright beer occurs when it is transferred between vessels. After every tank transfer, or operation such as filtration, the beer should be checked to ensure additional oxygen has not been absorbed. Other 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.

ORBISPHERE was the first, and for many years the only supplier, to offer inline ppb oxygen measurement. With brewing industry expertise in oxygen spanning almost 40 years using amperometric sensors and also 5 years of technical expertise using optical sensing methods, including 2 years commercial experience in critical applications in the power industry, ORBISPHERE has maintained its position as a leading innovator in the oxygen sector. Given the ongoing discussions over the most appropriate method to use, we wanted to critically review these two oxygen measurement methods in the beer process and discuss the advantages and drawbacks of each whilst presenting the latest improvements in optical measurement technologies.

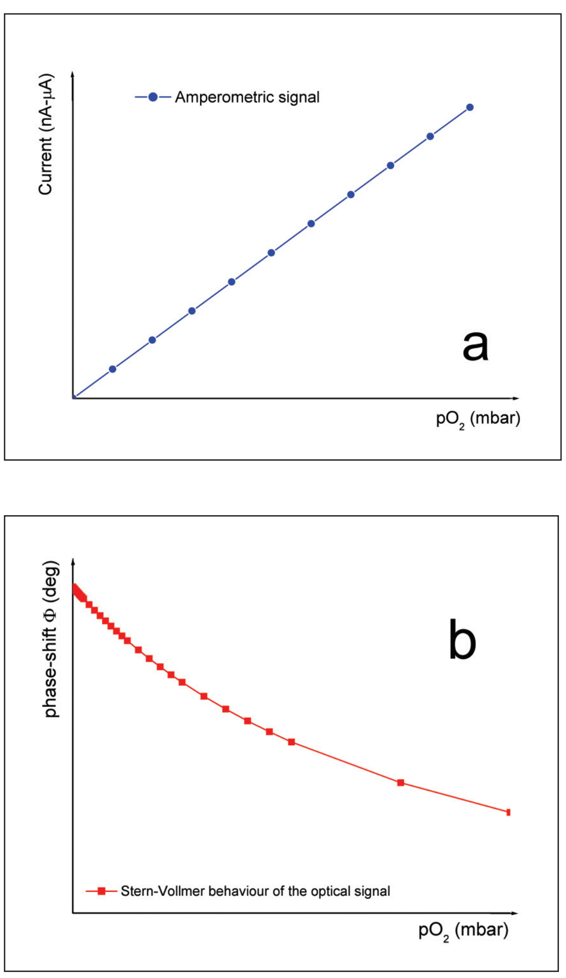


Figure 1. a) Linear current signal measured by an amperometric sensor as a function of oxygen partial pressure. b) Non-linear phase shift signal measured by an optical sensor as a function of oxygen partial pressure.

Available Methods to Monitor Oxygen

Until very recently the vast majority of sensors used in the brewing industry were membrane covered amperometric sensors. 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.

Two years ago, 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 con-centration 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, the proven ORBISPHERE unique design guarantees a stable true zero over time. Laboratory and practical experience show that an accuracy as good as ± 0.1 ppb can be obtained with an ORBISPHERE amperometric sensor.

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 like 99.999 % Nitrogen (N_2) or 99.999 % Carbon Dioxide (CO_2). 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. As described earlier the calibration requires a specific set-up, a specific calibration sample and delivers an accuracy of between ± 0.5 and 1 ppb. Together with the factory defined parameters describing the curve at high oxygen levels, the overall accuracy is in general around ± 1 ppb 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 s. 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 (t^{90}) from air to zero of 10 s has been reported for optical sensors. This is only true in the gas phase where the N_2 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 this year by the Weihenstephan Research Center for Brewing indicates a faster response to a change towards higher oxygen containing beer for the ORBISPHERE amperometric sensor (t^{90} = 45 s) than for the Haffmans optical system that was used (t^{90} = 70 s).

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 normally not 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 a 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 Cleaning In Place (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

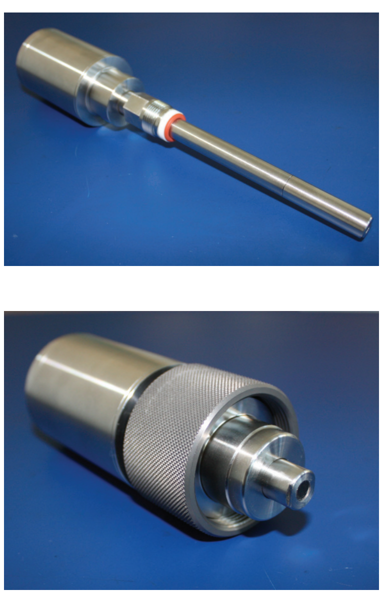
All measurement devices drift with time and hence calibration is required at given intervals; the lower the drift the longer the interval between service and/or calibration.

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 hence implied and required. 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 2 years: The conditions to achieve this 2 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 reality is that for systems configured to operate continuously and provide data points every 2 seconds, this results in a calibration interval is of less than 1 month, because the drift is directly linked to the number of measurements performed.

Maintenance Requirements



Picture 1. The new ORBISPHERE M1100 optical sensors in 28 mm and 12 mm versions

Whereas the maintenance of the amperometric sensor has long had the reputation of being tedious, all sensors today are fairly easy to clean and refurbish. The latest ORBISPHERE A1100 sensor is supplied with patented pre-mounted membrane kits that include pre-dosed elec-trolyte that reduces bi-annual maintenance to only 3 minutes. The main-tenance of an amperometric sensor has to be performed at regular intervals as the sensor gets dirty and the electrolyte 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 – Orbisphere M1100 Optical Oxygen Sensor

ORBISPHERE's customer commitment to offer the most performant solution in the brewing sector rather than launching a sensor not fit for its purpose has prevented us from releasing an optical sensor for the beer process, even though we have experienced great success using optical technology in the Power sector. Ensuring that we can provide at the same time long-term stability, a fast response time in liquids, and a fast response to temperature changes are key drivers and customer needs which can now finally be met with the ORBISPHERE M1100 (Picture 1).

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 2 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 ORBISPHERE's 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 3 ppb), unlike data obtained with the Haffmans optical system used by the Weihenstephan Center in their comparative tests where deviations of up to 30 ppb at 50 ppb have been reported, implying a 60 % deviation. 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 2 ppb oxygen both sensors measure within 1 ppb (Figure 2a). On beer/syrup mix with an oxygen content of 135 ppb both measure within 3 ppb (Figure 2b). With such low deviations from the ORBISPHERE A1100 reference, the new ORBISPHERE M1100 offers not only the advantages of an optical sensor but also the precision and confidence associated with ORBISPHERE.

Conclusion

The table below summarizes the key differences between the amperometric and the optical oxygen sensors discussed in this paper.

Whereas the ORBISPHERE A1100 ampero-metric sensor gives the best detection limit (± 0.1 ppb) 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 fulfill brewer's 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.

Characteristics	Typical amperometric sensors	ORBISPHERE A1100 amperometric sensor	Typical optical sensors	ORBISPHERE M1100 optical sensor
Calibration interval (Long-term stability assuming continuous use)	1-3 months	6 months	< 1 month	6 months
Response time in beer	60 s	30 s	30-60 s (depending on T changes)	< 30s
Accuracy of the zero (detection limit)	± 1 ppb	± 0.1 ppb	± 1 ppb	± 0.6 ppb
O_2 signal noise in a beer process (effect of conditions)	2-10 ppb	2-5 ppb	<2 ppb	1 ppb
Maintenance complexity	Medium	Low	Minimal	Minimal
Calibration method	2 points: zero + slope in air	Single point in air	Single point zero	Single point zero

Table 1. Summary of the main sensor characteristics discussed in this paper.

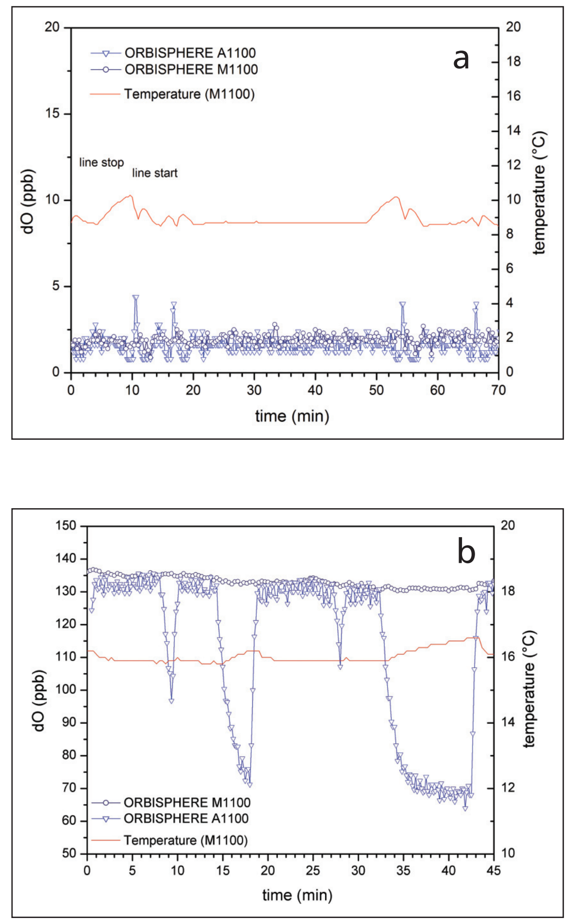


Figure 2. a) Oxygen measurement pre-filler on a Lager sample. b) Oxygen measurement pre-filler on beer/syrup mix.

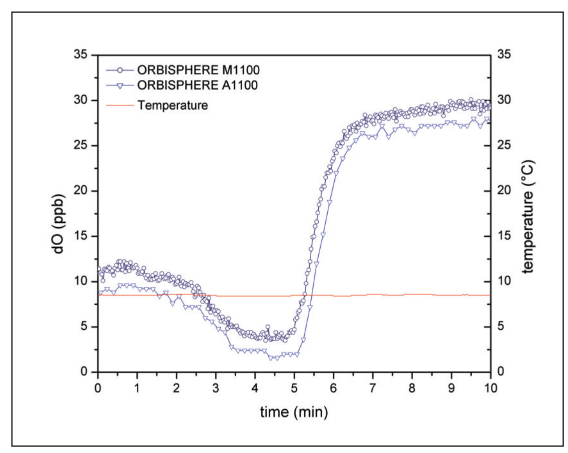


Figure 3. Typical response time in a beer line of the ORBISPHERE M1100 optical sensor as compared with an ORBISPHERE A1100 amperometric sensor. (sampling frequency of 2s for the optical sensor and 10 s for the amperometric sensor)

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