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THE TRUTH ABOUT OXYGEN MEASUREMENT TECHNOLOGIES

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ABSTRACT

As all major oxygen analyzer 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 appropriate to review 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

The effect of oxygen on the different stages of beer production in addition to the importance of maintaining appropriate oxygen levels has been reviewed in detail in other papers [1] [2]. 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 do this, accurate oxygen monitoring is required after every tank transfer, or operation such as filtration. By measuring throughout the process it is possible to identify the source of any oxygen contamination and act to minimize it.

ORBISPHERE was the first 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, ORBISPHERE has maintained its position as a leading innovator in the oxygen sector.

AVAILABLE METHODS TO MONITOR OXYGEN

Until very recently the vast majority of sensors used in the brewing industry were membrane covered amperometric sensors. Two years ago, optical oxygen sensors became available to the beverage industry.

For both methods, Henry's law provides the link between partial pressure and dissolved concentration in the sample.

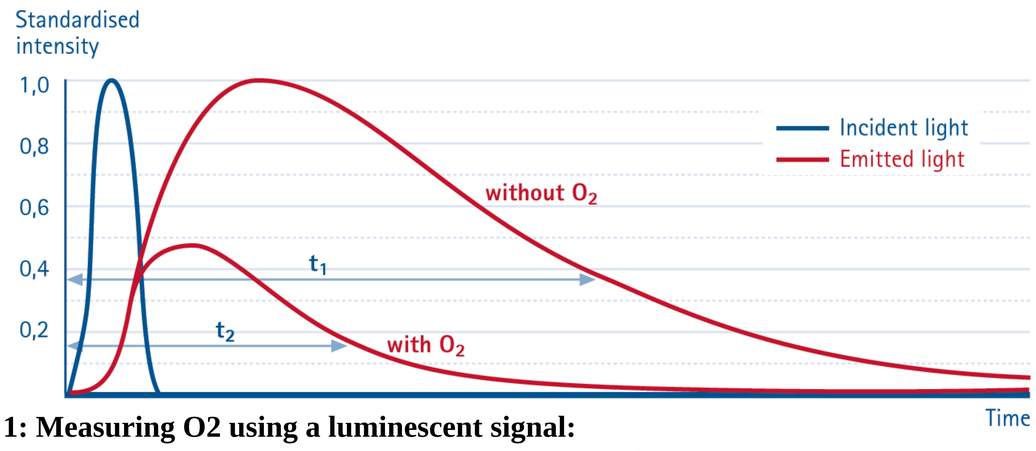
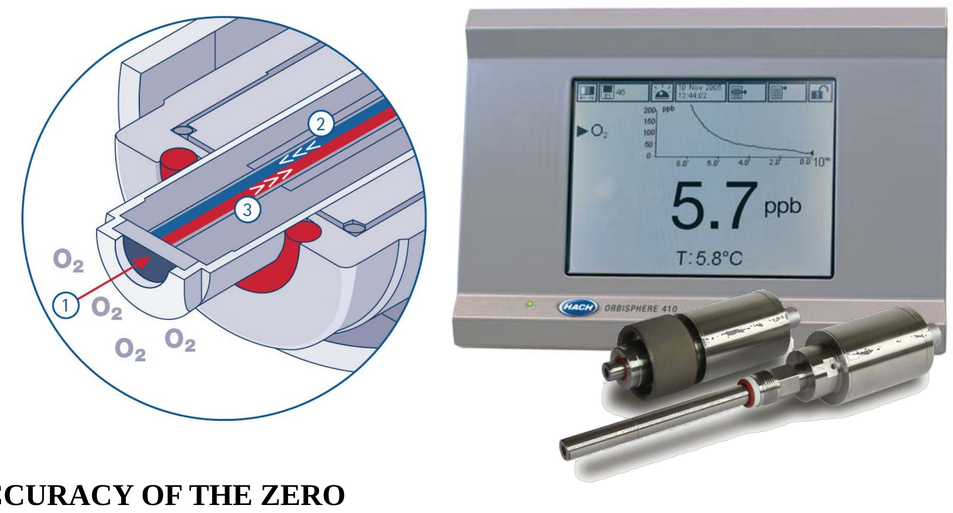


Fig. 1: Measuring O2 using a luminescent signal:
The more O2 the sample contains, the shorter the period of luminescence

Fig. 2: ORBISPHERE sensor schematic + ORBISPHERE M1100/410
Oxygen interacts with the active luminescent sensor to provide a signal:
1 Active luminescent spot; 2 Blue light (excitation); 3 Red light (detection)



ACCURACY OF THE ZERO

An 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 (N2) or 99.999% Carbon Dioxide (CO2). The accuracy that can be expected from this calibration is between ± 0.5 and 1 ppb.

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.

Existing optical systems claim to require calibration once every 2 years [3]: 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 and the number of CIP cycles completed.

EFFECT OF PROCESS CONDITIONS ON THE MEASUREMENT

Amperometric technology consumes the oxygen that is measured and therefore requires a minimum flow to work accurately. When the production line is stopped, the absence of flow and hence oxygen consumption typically leads to a low oxygen reading (see Figure 3). Pressure shocks caused by valves opening or closing can generate spikes on the oxygen signal whose duration strongly depends on the sensor design.

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.

When amperometric sensors are exposed to high oxygen content/high temp (during Cleaning In Place (CIP)), this can shorten maintenance intervals.

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. An appropriate system configuration as offered on all ORBISPHERE optical systems can protect the sensor by switching it off during high temperature conditions.

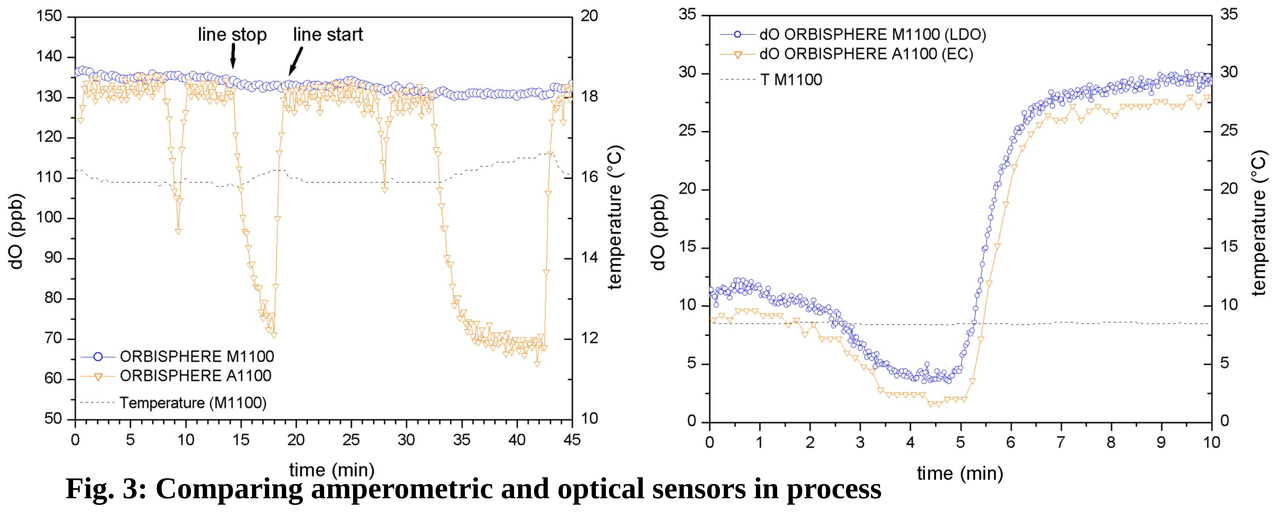


Fig. 3: Comparing amperometric and optical sensors in process

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.

The parameter that varies the most with optical technology is the value in the absence of oxygen. 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 ± 1ppb or ± 2% of the measured value whichever the greater.

MAINTENANCE REQUIREMENTS

Optical sensors do not require such maintenance; the sensor head is normally cleaned during the CIP process. The only real maintenance is the optical spot replacement every 1-2 years (frequency depending on process conditions).

ORBISPHERE M1100 OPTICAL OXYGEN SENSOR

With the latest developments, ORBISPHERE can now offer an optical sensor with a calibration interval > 6 months when in continuous use (data point every 2 seconds – no 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, oxygen levels measured correspond well to values from the amperometric sensor (within less than 3ppb), unlike data obtained with other optical systems used by the Weihenstephan Center in their comparative tests where deviations of up to 30 ppb at 50 ppb levels have been reported, implying a 60% deviation from the reference [4]. 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:

Characteristics	Typical amperometric sensors	ORBISPHERE A1100 amperometric sensor	Typical optical sensors	ORBISPHERE M1100 optical sensor
Calibration interval	1-3 months	6 months	< 1 month	6 months
Response time in beer	60 s	30 s	30-60 s (depends 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 beer process	2-10ppb	2-5 ppb	<2 ppb	< 1ppb
Maintenance complexity	Medium	Low	Minimal	Minimal
Calibration method	2 points: zero + slope in air	Single point in air	Single point zero	Single point zero

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 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.

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