

A New, Dissolved-Oxygen Analyzer for In-Line Analysis of Beer¹

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ABSTRACT

Experiments are described that prove the suitability of an Orbisphere membrane-enclosed dissolved-oxygen sensor for in-line use in a brewery. Also, a selection was made of the optimum membrane material and thickness for wort- and beer-monitoring tasks. Determinations are reported for four membranes of the usual parameters, such as the range of linear response to oxygen concentration, the sample flow requirement, and the speed of response to oxygen-concentration changes at various temperatures between 0 and 30°C. Resistance of the sensor to various physical and chemical conditions commonly encountered in a brewery was also investigated. The steady-state sensitivity of the sensor was unaffected by applied pressure in the range to 20 bars, and a simulated "hot-cleaning" operation at 90°C caused a temporary small increase of +3% in sensitivity which, after 2 hr, decayed to +1%. Extensive tests also showed that the specific sensitivity of the sensor towards oxygen was not influenced by the simultaneous presence of carbon dioxide, in both gaseous and beer samples. A preliminary report is given of 12 months of in-line experience with the sensor for oxygen monitoring at various points in a brewery.

Key words: Dissolved oxygen analysis, Feedback control of dissolved oxygen, Oxygen probe

It is becoming increasingly realized (1,3) that great attention should be paid to the control of dissolved-oxygen concentrations during the production and storage of beer. In the early stages of fermentation, high oxygen levels are essential because they promote vigorous growth of the yeast. Yet the boiling stage that precedes fermentation drives air out of the liquor. Therefore, it is desirable to accurately measure oxygen levels and to control the aeration of the wort by feedback to be certain that the desired high oxygen levels are attained before fermentation.

On the other hand, clarity, shelf life, flavor, and flavor stability of the finished beer are adversely affected by high levels of oxygen. Yet air pickup tends to occur during centrifugation, filtration, and storage of the beer. Many producers specify maximum dissolved-oxygen concentrations at the racking stage, and oxygen levels at this stage must be continuously monitored in order that these specifications are respected.

Oxygen sensors for in-line use in a brewery must satisfy several unique requirements. 1) They must not contaminate the beer, and at the same time their performance must not be affected by any of the ingredients of the beer. 2) They must tolerate the daily routine of the plant, including a hot-alkaline cleaning operation. 3) For wort monitoring, the measurement range of the sensor must extend upwards to at least 40 mg/kg to permit control of oxygenation as well as aeration. 4) For beer monitoring, the measurement range of the sensor must extend downwards to 2 µg/kg or so, which is typical of old finished beer. Also, the response time of the sensor must be reasonably short in spite of the low temperature in a cellar. 5) The sensors must function correctly under the physical conditions existing in the beer line. This implies that the flow rate of the beer must be sufficient for proper measurement, that turbulence in the fluid must not generate instability in the measurement, and that an overpressure should not affect the sensitivity of the sensor towards dissolved oxygen.

Details are given of a new sensor developed by Orbisphere Laboratories that has more than adequate sensitivity for the determination of typical oxygen levels in beer, that is unaffected by

continuous exposure to pressurized carbon dioxide, and that may be cleaned with hot detergent solutions of the type commonly used in breweries. Results obtained during in-line use of a dissolved-oxygen-monitoring system based on this sensor in a brewery environment are also given.

EXPERIMENTAL

All oxygen measurements were made with an Orbisphere model 2110 sensor contained in a model 2950 flow chamber and connected to a model 2606 instrument modified to enable display of sensor current at all temperatures.

The sensor (Fig. 1) is of the polarographic type; ie, it is an electrochemical cell containing an oxygen-detecting cathode of gold, a silver anode or reference electrode, and an alkaline potassium chloride electrolyte. The cell is enclosed and isolated from the beer by a fluorinated plastic membrane. A voltage is applied between the cathode and the anode by an external circuit that also measures the magnitude of the electric current flowing through the sensor.

The electric current is directly proportional to the dissolved-oxygen fugacity (partial pressure) in the beer, and is amplified and suitably scaled in the associated instrument to enable the display of oxygen concentration, or pressure, as desired.

Measurements were conducted at $25 \pm 0.1^\circ\text{C}$ in a water thermostat, unless otherwise noted. Recordings were made on a W+W model 1100 recorder.

Pure gases (Carba AG, Berne, Switzerland) were mixed with a Witt model KM60 2SE gas-mixing apparatus. This gas mixture was brought to experimental temperature before passing through the flow chamber by being led through a copper tube (1-m length, 6-mm o.d.) coiled and immersed in the thermostat bath.

Gas pressures were retained by a Nupro SS-6SG-MM needle valve placed after the flow chamber, and were measured by a Tescom H68A gauge. For response-time measurements, different gas mixtures were selected by means of a Whitey SS-43ZF2 five-way ball valve, or the pressure of a given gas mixture was changed suddenly.

Air-saturated water was generated by bubbling air through a glass frit into the thermostated water until the oxygen concentration in the water, as measured by an oxygen sensor, was constant. This water was circulated through the flow chamber with a Cole Parmer model K-7012-02 gear pump or a Sage Instruments model 351 syringe pump, passing first through the copper coil, as described above. Water flow rates were restricted with the Nupro

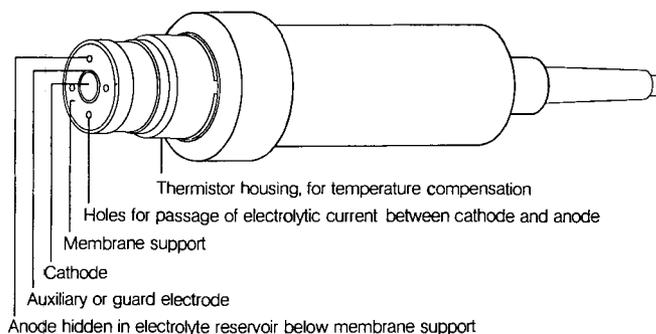


Fig. 1. Perspective view of oxygen sensor.

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needle valve and were measured manually by collection in a graduated cylinder. Measurements in beer were made with the aid of an Orbisphere Laboratories bottle-piercing unit, model 2997.

Known oxygen concentrations were dissolved in beer by first preoxidizing antioxidants in the beer by saturating for 24 hr with pure oxygen, then forcing CO₂-O₂ mixtures of known composition into the beer, under known pressure.

Studies were made with five different membranes mounted on the oxygen sensor, all of which were purchased from du Pont de Nemours & Company, Wilmington, DE. The membranes were of 0.1-mm thick polytetrafluoro ethylene (PTFE), 25.4- μ m thick polyfluoroalkoxy (PFA), 25.4- μ m thick ethylene-tetrafluoroethylene copolymer (ETFE), 12.5- μ m thick ETFE, and 12.5- μ m thick polyvinylfluoride.

RESULTS AND DISCUSSION

Range of Linear Response

The sensor generates a current linearly related to oxygen concentration in the current range from about 1 nA (10^{-9} A) to about 200 μ A (2×10^{-4} A). Corresponding limits of oxygen concentration measurable with the sensor appearing in Table I are obtained by dividing these current limits by the membrane permeabilities, quoted in amperes per unit concentration. These permeabilities are (at 25°C): 0.5 μ A/(mg/kg) for 1 mil ETFE and 4 mil PTFE; 2.5 μ A/(mg/kg) for 1 mil PFA; and 1 μ A/(mg/kg) for 1/2 mil ETFE. The linearity of the relationship between indicated and true oxygen concentrations is indicated for two membranes in Figs. 2 and 3.

At 25°C, the oxygen concentration in air-saturated water is around 8 mg/kg. Because this concentration is well below the

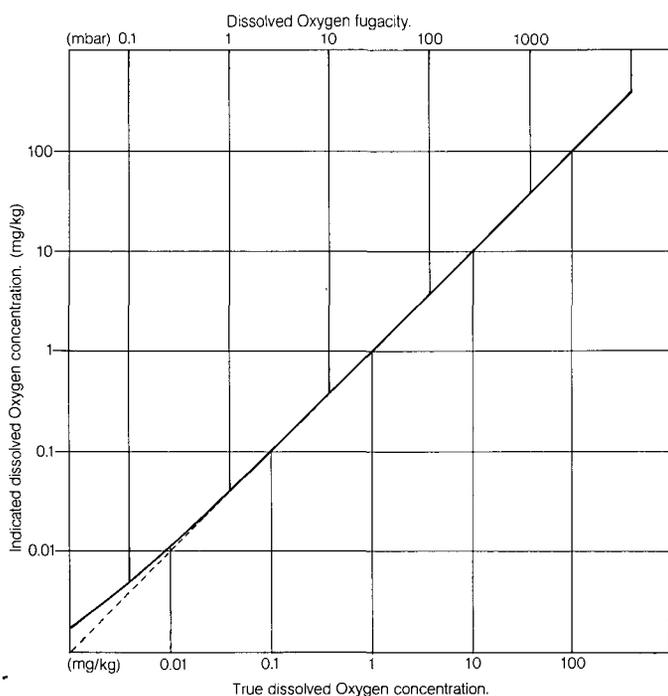


Fig. 2. Calibration line for sensor fitted with 1 mil ethylene-tetrafluoroethylene copolymer membrane.

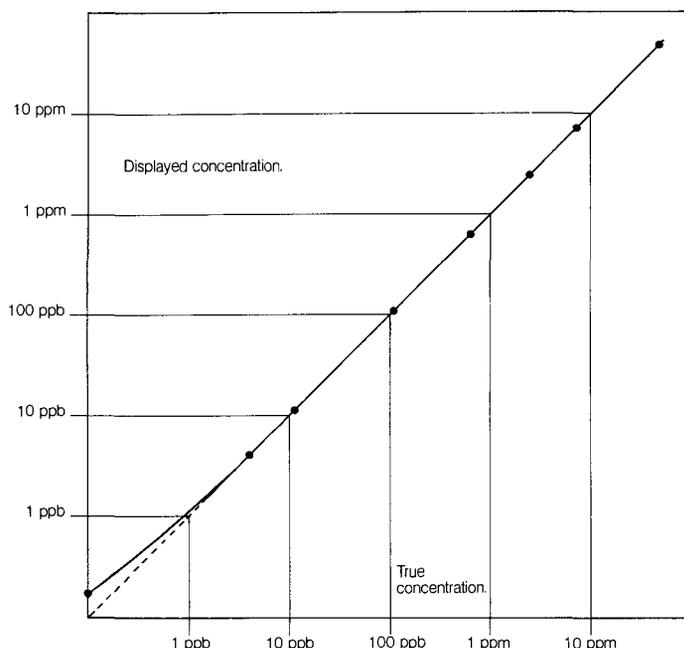


Fig. 3. Calibration line for sensor fitted with 1 mil polyfluoroalkoxy membrane.

TABLE I
Alternative Membranes, Their Properties, and Their Preferred Uses

Model No.	Membrane Material and Thickness	Concentration Limits ^a at 25°C		Flow Demand at 25°C		99% Response Time at 25°C	Application
		Lower (μ g/kg)	Higher (mg/kg)	Linear ^b (cm/sec)	Volume ^c (ml/min)		
2952	ETFE ^d 1 mil ^e	2	400	1 (30)	5 (25)	66 sec	General purpose
2955	PTFE ^f 4 mil	2	400	1 (30)	5 (25)	7 min	Wort monitoring
2956	PFA ^g 1 mil	0.4	80	80 (2,400)	40 (140)	12.5 sec	Beer monitoring in a bypass
2958	ETFE ^d 1/2 mil	1	200	3 (90)	10 (55)	16.5 sec	Beer monitoring

^aCorresponding limits of oxygen fugacity are obtained by multiplying by the factor 1 bar/40 (mg/kg).

^bMinimum linear velocity of beer past the sensor for a valid measurement. The first velocity produces a -5% error, and the second velocity (bracketed) produces a -1% error.

^cFlow-through model 2950 flow chamber. The first velocity produces -5% error, and the second velocity (bracketed) produces -1% error.

^dEthylene-tetrafluoroethylene copolymer.

^e1 mil = 1/1,000 in. = 25.4 μ m.

^fPolytetrafluoroethylene.

^gPolyfluoroalkoxy.

higher limit specified for all of the membranes listed in Table I, the air may be used as a reference source of oxygen for calibration purposes.

Flow Requirement

Figure 4 presents the dependence of sensor current due to oxygen reduction upon the rate of circulation of air-saturated water at 25°C through a special flow chamber enclosing the sensor (Orbisphere Laboratories, model 2950). The current tended to an asymptote at a high flow rate, and currents at lower flow rates were normalized with respect to this limit. Also, this limit was identical to the current measured in water-saturated air at the same temperature, a fact that may be exploited for calibration purposes, provided that sample circulation rates are required to exceed the

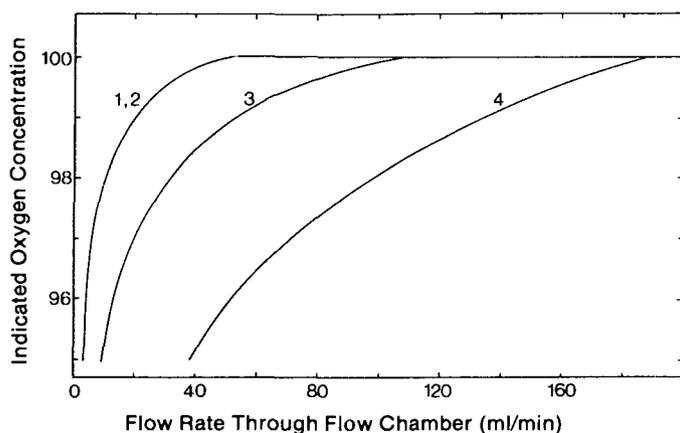


Fig. 4. Variation of indicated oxygen concentration with flow rate of sample for various membranes. Concentration presented as percentage of indication at infinite flow rate. Flow rates through special flow chamber in milliliters per minute. 1, 4 mil polytetrafluoroethylene; 2, 1 mil ethylene-tetrafluoroethylene; 3, ½ mil ethylene-tetrafluoroethylene; 4, 1 mil polyfluoroalkoxy.

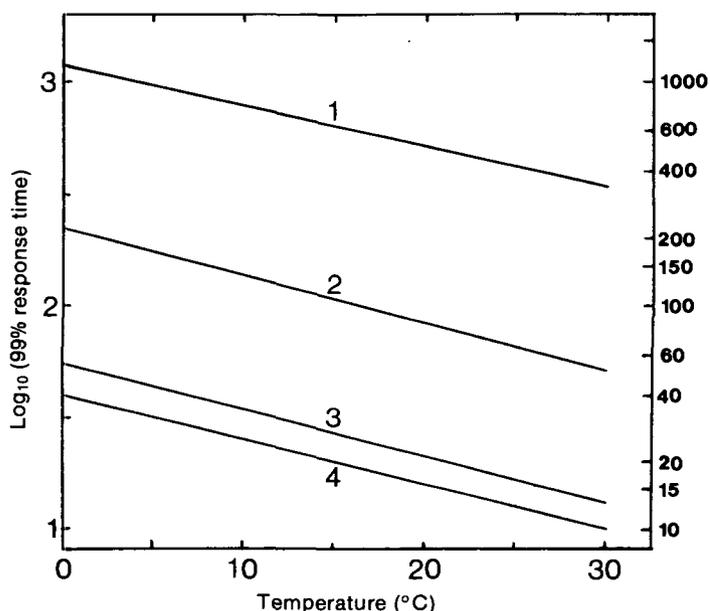


Fig. 5. Variation of 99% response time with temperature for various membranes. 1, 4 mil polytetrafluoroethylene; 2, 1 mil ethylene-tetrafluoroethylene; 3, ½ mil ethylene-tetrafluoroethylene; 4, 1 mil polyfluoroalkoxy.

threshold at which the current limit is attained.

Figure 4 shows that this threshold depends upon the thickness and nature of the membrane material, and Table I lists the flow demands for various membranes available with the sensor. The thresholds are quoted at which the current approaches within 5% and within 1% of the current limit.

In a similar fashion, the sensor current depends upon the linear flow velocity of a stream flowing parallel to the sensing face. Table I also lists the threshold velocities for this configuration.

Response Time Measurements at Various Temperatures

The response of the sensor was measured upon suddenly changing the oxygen partial pressure in a gas mixture flowing past the sensor. Provided the ratio r of the initial to the final pressures fell in the approximate range $0 < r < 2$, the transient current could be described by the equation (2):

$$\frac{i - i_0}{i_\infty - i_0} = 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp[-n^2 \pi^2 \tau]$$

where $\tau = D_m t / X_m^2$ is a dimensionless time parameter. In this equation, i = instantaneous detector current during the transient, i_0 = initial current, i_∞ = final current, D_m = diffusion coefficient of oxygen in the membrane, X_m = thickness of membrane, and t = time.

The quantity $\theta = X_m^2 / D_m$ is a characteristic time for diffusion across the membrane. Ninety-nine percent of signal change occurs in the time 0.53θ 95% in 0.37θ and 90% in 0.305θ . θ was determined for four membrane materials at a variety of temperatures in the range 0–30°C, by analysis of the signal transients with the foregoing equation. Figure 5 shows the variation of 99% response time with the temperature for each of the membranes.

When the ratio of initial to final oxygen partial pressure was large, the response of the sensor was slower than would be predicted from the foregoing equation. A small (~5%) contribution to the total current arises from sources inside the sensor relatively distant from the cathode, which equilibrate with the sample through the membrane. Hence, the total current is proportional to the pressure of oxygen in the sample, but this small

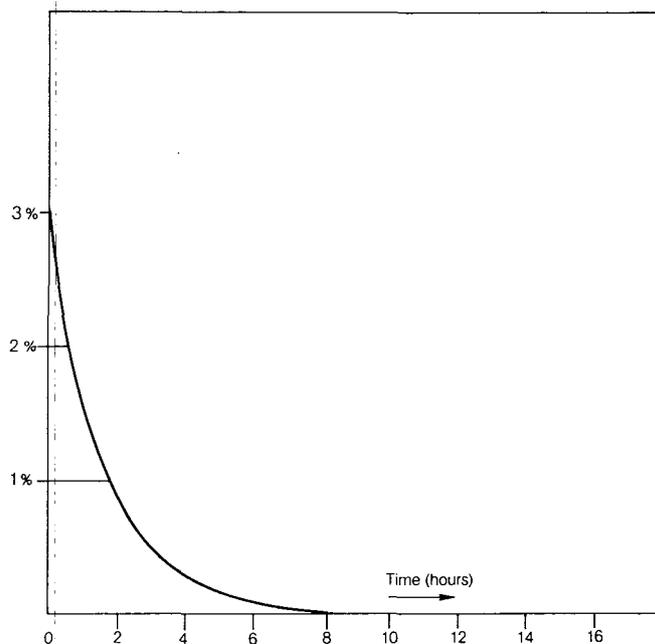


Fig. 6. Increase in sensitivity of sensor caused by hot cleaning at 90°C.

contribution is slower to respond to changes in sample oxygen pressure than is the principal membrane-controlled contribution. A period of up to 2 hr can be required for final stabilization of a sensor transferred to a sample having 5 $\mu\text{g}/\text{kg}$ dissolved oxygen after long exposure to the air.

Effect of Hot Cleaning

Figure 6 shows the effect of a simulated hot-cleaning operation. The sensor was first stabilized in air-saturated water at 25°C to determine its precise sensitivity towards dissolved oxygen, then warmed to 90°C in hot water and held at this temperature for 30 min, and finally returned to the 25°C air-saturated water to redetermine its sensitivity. The recording of the sensor output in the ensuing 10 hr (Fig. 6) shows a temporary small increase (about 3%) in the sensitivity towards oxygen immediately after the heat treatment, decaying quickly to about +1% after 2 hr, and tending asymptotically to the original sensitivity. No cumulative drift of sensitivity was noticeable after 10 repetitions of this treatment.

There was a risk that the membrane would inflate and require replacement if the sensor was too rapidly heated. The temperature rise should not exceed about 3°C/min, so that the electrolyte and all solid parts of the sensor remain at about the same temperature. In practice, the actual rate of temperature rise in a typical brewery is usually compatible with this requirement because of the large heat capacity of the plant.

Pressure Independence of Detector Sensitivity

Oxygen measurements in beer are almost invariably made at an overpressure in the range of 0–4 bars, yet calibration of sensors is normally effected at atmospheric pressure. It must be shown, therefore, that the current generated by the sensor per unit oxygen concentration is invariant in the specified pressure range.

A direct experimental test of this effect was made by measuring the sensor current at elevated pressures of pure oxygen. The sensor was enclosed by the polyvinylfluoride membrane and held at $25 \pm 0.1^\circ\text{C}$. It was first calibrated in oxygen at 1 bar, the sensor current being about 1 μA . Elevated pressures were measured directly at the oxygen cylinder. Figure 7 shows the result as a plot of oxygen pressure, as measured by the sensor, against oxygen pressure as measured by the pressure gauge. Linearity was good in the pressure range to 21 bars absolute pressure.

Effects of Carbon Dioxide

Fluorinated membranes such as those used on the Orbisphere oxygen sensor are highly permeable to carbon dioxide. Consequently, the electrolyte of the sensor is quickly saturated with the pressurized gas after exposure of beer with consequent formation of carbonates and a shift of pH. Experiments were therefore performed to compare the sensitivity of the sensor towards oxygen, in the presence of carbon dioxide, with that in the absence of carbon dioxide.

The sensor, fitted with a 12.5 μm ETFE membrane, was exposed to dry air at 25°C, and the oxygen reduction current was measured to be 7.20 μA . The sensitivity in the absence of carbon dioxide was therefore

$$\frac{7.20}{21} = 0.343 \mu\text{A}/1\% \text{O}_2,$$

corresponding to about 0.9 $\mu\text{A}/(\text{mg}/\text{kg})$ dissolved oxygen.

Next, the sensor was exposed to pure carbon dioxide gas at 1 bar pressure for some time, after which the "residual" current had decayed to 0.64 nA. The entry port of the sensor was then switched to the output from a gas-mixing apparatus, supplied with a carrier gas of carbon dioxide, and a bleed from a cylinder containing 0.1% $\text{O}_2/99.9\% \text{N}_2$. By this means, the oxygen content of the gas routed to the sensor at 1 bar absolute pressure was adjusted to various levels in the range to 0.05% O_2 . At 0.01% O_2 , for example, the composition of the gas mixture was: 0.01% O_2 , 9.99% N_2 , 90% CO_2 .

Figure 8 shows the dependence of the steady state current from

the oxygen sensor, corrected for the residual of 0.64 nA, upon the percentage of oxygen in the gas mixture. The slope of the straight line is 0.356 $\mu\text{A}/1\% \text{O}_2$, in good agreement with the sensitivity determined in dry air; hence, the simultaneous presence of carbon dioxide does not interfere with the detection of oxygen by the sensor. A gas containing 0.01% O_2 generates the same current from the sensor as an aqueous sample containing about 4 $\mu\text{g} \text{O}_2/\text{kg} \text{H}_2\text{O}$.

In a second experiment, beer that had been preoxidized by having pure oxygen bubbled through it for 24 hr was saturated at a room temperature of $18 \pm 1^\circ\text{C}$ and at 2 bars absolute pressure with gas from a cylinder containing 0.1% O_2 –99.9% CO_2 . This generated

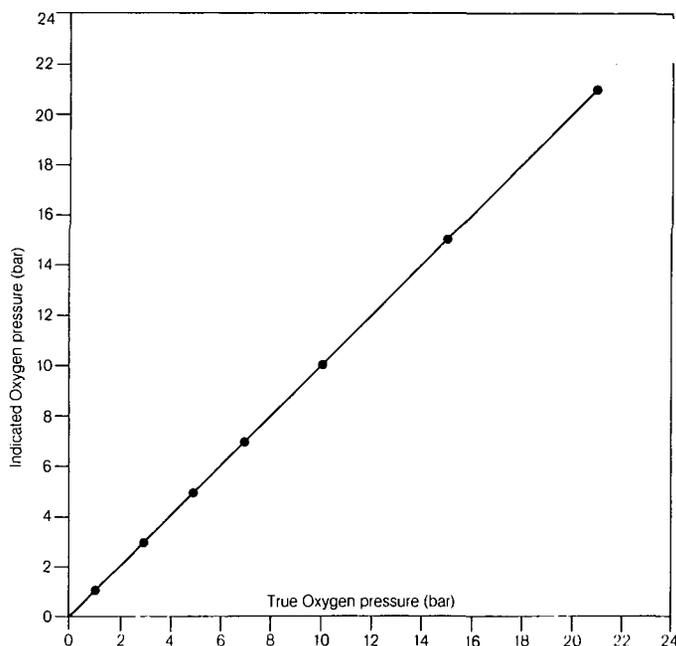


Fig. 7. Linearity of oxygen measurement at elevated pressures showing pressure insensitivity of sensor.

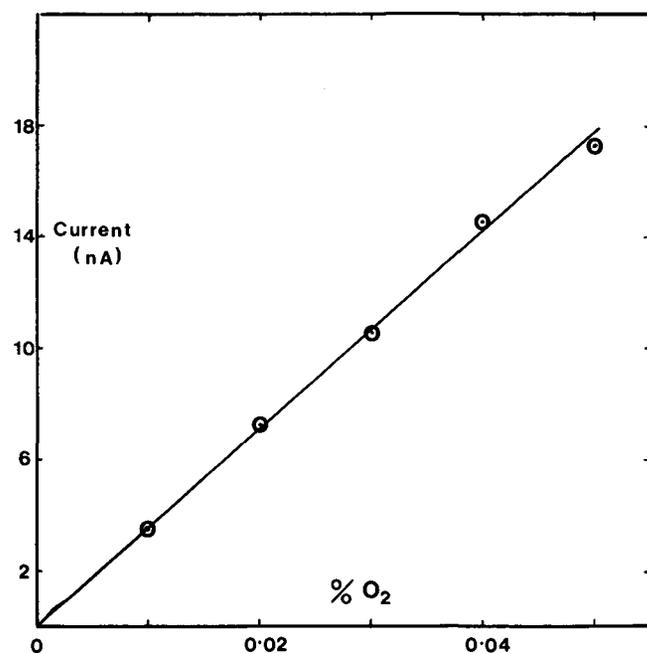


Fig. 8. Low-level response of oxygen sensor in the presence of carbon dioxide.

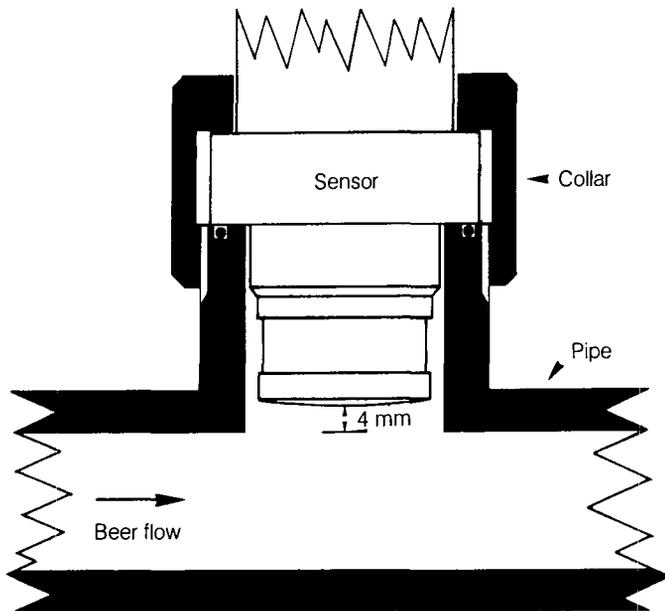


Fig. 9. Preferred method of mounting sensor in-line.

a dissolved-oxygen concentration in the beer of about $94 \mu\text{g}/\text{kg}$. When the beer-saturated gas was routed to the sensor, a steady current of 85.7 nA was measured. When the pressurized beer was forced through the flow chamber, a similar current magnitude of $85 \pm 5 \text{ nA}$ was measured; the current range was caused by flow-rate variations. Finally, when the beer was allowed to depressurize and therefore to "degas" immediately before encountering the sensor, a reading of 40 nA was obtained.

The agreement between the currents measured in the pressurized gas and beer is to be expected, in view of the fact that the response of the sensor is proportional to oxygen partial pressure, because at equilibrium the oxygen partial pressures in the gas and liquid phases is equalized. Furthermore, the sensor response corresponds to a specific sensitivity towards oxygen of

$$85 \text{ nA}/94 (\mu\text{g}/\text{kg}) = 0.904 \mu\text{A}/(\text{mg}/\text{kg}),$$

which is in good agreement with the sensitivity as determined by exposure to carbon dioxide-free media such as air-saturated water. Once again, therefore, the presence of carbon dioxide in addition to oxygen was shown not to influence the steady state performance of the sensor.

Finally, the measurement in depressurized beer corresponds to the response that would be expected either in a gas containing $0.01\% \text{ O}_2$ at 1 bar absolute pressure, or in beer equilibrated with such a gas. This result demonstrates that oxygen is very rapidly partitioned between the gas and liquid phases formed as a result of decompression, and is a warning that a valid measurement of dissolved oxygen in beer can only be made under pressurized conditions when gas-bubble formation is prevented.

A purely mechanical problem arises, because carbon dioxide enters the sensor. Carbon dioxide barely affects in-line use of sensors but is of importance in off-line use. The fragile membrane can support pressure differences up to 20 bars (or optionally to 100 bars), provided the exterior pressure is greater than the interior one, but is very weak when subjected to pressure differences where the interior is greater than the exterior. After the sensor has been equilibrated with an overpressure of carbon dioxide, therefore, it should not be suddenly depressurized. Depressurization rates up to 10 bars per minute are tolerated.

In-Line Oxygen Analysis in a Brewery Environment

The sensor was tested at several different in-line locations in Samuel Websters' Brewery, Halifax, England, for periods up to 12

months. Positioning of the sensing membrane in the beer stream inside a pipe is critical. If the sensor projects too far into the flow, it produces a noisy recording of oxygen concentrations, presumably because of the effects of pressure and turbulence on the membrane. Satisfactory results were obtained by withdrawing the probe into a side arm, so that the membrane surface was parallel to the flow lines but about 4 mm further from the axis than the inner radius of the pipe (Fig. 9).

The sensor was successfully tested when mounted in-line on the racking plant, monitoring low levels of dissolved oxygen. It was subjected, together with the pipework and the remainder of the plant, to the daily cleaning and sterilizing routine, which included a hot detergent wash at temperatures that reached 90°C .

Continued proper functioning of the sensor during the whole period was verified in two ways. First, the accuracy and reproducibility of the measurement by the system of the oxygen level in cold aerated water, used to wash the detergent out of the plant, was checked each day. Second, periodic checks of dissolved oxygen concentrations in the beer by off-line equipment were compared with the indications derived from the in-line sensor. Results were in excellent agreement at all times. Throughout the periods, ales and lagers were processed through the plant, and concentrations of dissolved oxygen were continuously monitored.

Similar successful tests were made with sensors located after the filter. Again, off-line checks of oxygen levels agreed with indications by the in-line analyzer.

An average service frequency (anode and cathode cleaning, and electrolyte and membrane replacement) of about once per month was adequate.

Membrane Selection

The sensor is available with a selection of four alternative membranes: one most suited to wort monitoring, two for beer monitoring, and one for both uses. The suitability of the sensor for one application or the other is determined by its sensitivity towards dissolved oxygen, its rate of response to an oxygen-concentration change, and the minimum flow rate of the sample fluid required by the sensor for a valid measurement. These properties, in turn, are determined by the thickness and the oxygen permeabilities of the membrane materials. Table I lists the alternative membranes, their properties, and their preferred uses.

For wort monitoring, 0.1 mm -thick PTFE is preferred because its greater thickness and low permeability enable maximization of service life. Entrained particles in the wort tend to erode or accumulate on the sensor membrane, and thicker and less permeable membranes are less affected by this phenomenon. The response time might be excessively long, however, in which case $25\text{-}\mu\text{m}$ ETFE is the best alternative.

For beer monitoring, $25 \mu\text{m}$ PFA would be ideal because of its measurement accuracy, but its flow demand is far too high to permit its use in-line. When it is used, the sensor must be put in a bypass.

For in-line use, therefore, $12.5\text{-}\mu\text{m}$ ETFE is the best choice for beer monitoring. The accuracy of $\pm 1 \mu\text{g}/\text{kg}$ is adequate, the flow requirement is compatible with the usual flow velocities found in a brewery, and the response time is excellent even at a low temperature. Although a little less accurate and slower to respond than the thinner, $12.5\text{-}\mu\text{m}$ membrane in the same material, $25\text{-}\mu\text{m}$ ETFE demands a lower flow rate and requires less frequent maintenance. It is, therefore, a good alternative choice for beer monitoring and can be recommended as a general-purpose membrane for all monitoring tasks in a brewery.

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