

Chapter I.2 Calibration and Accuracy of Polarographic Oxygen Sensors

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1 Introduction

A membrane-covered polarographic oxygen detector, or polarographic oxygen sensor (POS) as it is called here, is an electrochemical device in which the steady-state current at the working electrode (the cathode) is, in the ideal case, linearly proportional to the concentration, or more strictly the activity, of oxygen in contact with the external surface of the membrane. This proportionality is most simply expressed by the equation originally derived by Mancy et al. [15]:

$$I_1 = \frac{nFAP_m c_s}{z_m}, \quad (1)$$

where the symbols are defined in the discussion below. According to this equation, a plot of detector current, I_1 , against oxygen concentration, c_s , will be linear with a slope of $nFAP_m/z_m$. This slope can be regarded as the calibration factor for the sensor.

However, of the terms in this factor only F , the Faraday, is truly constant. All the other terms can be variable. Clearly, A , the cathode area, can be different for different sensors, but even for a given sensor it can change during use. For example, in a polluted environment there may be partial poisoning of the cathode, leading to a reduction in the active area, while in a dirty environment fouling of the membrane could occur, causing a reduction in the effective area through which the oxygen flux can reach the cathode by diffusion normal to the electrode surface. The membrane thickness, z_m , may vary for membrane samples of the same nominal thickness, while P_m , the permeability coefficient (Chap. I.3), can be very different for membranes of the same plastic but from different sources; different techniques of film preparation can give rise to different degrees of crystallinity and hence membrane permeability [10]. Once a given membrane is mounted on the sensor there is still no guarantee that z_m and P_m will not vary with time. Plastic films used for POS membranes are elastic to some extent and so can be readily stretched when they are mounted on the sensor. Gradual relief of the applied stresses will cause z_m to change slowly, and may also be accompanied by internal restructuring, giving crystallinity changes and concomitant permeabil-

ity changes. Finally, n , the number of electrons associated with the oxygen reduction, need not be equal to the maximum value of 4. Competing electrode processes and the nature of the electrolyte can cause the value of n to be less than 4 and to be time-dependent [10].

In view of the uncertainties associated with the values of the terms in the calibration factor it is apparent that one cannot calculate with any degree of confidence the value of this factor. Therefore one has to rely upon a calibration procedure based on standard oxygen-containing test samples. Furthermore, since there may also be changes with time of the calibration factor any such procedure should be straightforward and easy to carry out. Some methods that are commonly used are described later, but first we consider calibration standards that can be used in these methods.

2 Calibration Standards

The basic requirement of a calibration standard is that it should have a known oxygen activity. This is because the current of the sensor is dependent on the oxygen flux through the membrane, and this flux is, in turn, determined by the difference in activity or chemical potential of oxygen across the membrane [10]. A practical measure of activity is the partial pressure, p_{O_2} – more strictly the fugacity, f_{O_2} , should be used (Chap. I.1) – and Eq. (1) in terms of p_{O_2} is

$$I_1 = \frac{nFAS_m D_m p_{O_2}}{z_m}, \quad (2)$$

where S_m and D_m are the solubility coefficient and diffusion coefficient, respectively, of oxygen in the membrane. Thus the simplest calibration standard is a gas mixture of known oxygen partial pressure, and the most readily available such mixture is air. Dry air contains 20.95% of oxygen [9] and the oxygen partial pressure in this case will clearly be 20.95% of the total air pressure. Air is, however, very rarely completely dry but has a relative humidity associated with it. This humidity will contribute toward the total pressure, and unless the partial pressure arising from the water vapor is subtracted before the oxygen partial pressure is calculated an erroneous calibration will be made. Unfortunately, the determination of relative humidity is difficult to do with any accuracy, and so in order to use air as a calibration standard it should either be dried before use or brought to 100% relative humidity.

If a calibration check at other partial pressures is required, then this can be done with suitable gas mixtures of known oxygen partial pressure (App. B). In practice linearity is found (Fig. 1), as would be expected from Eq. (2). For gas phase calibration at zero oxygen level the detector can be simply placed in an inert gas; e.g., N_2 , Ar, He, etc.

Gaseous calibration standards are the obvious choice if subsequent measurements are to be in the gas phase. For measurements of dissolved oxygen, whether in aqueous or nonaqueous solvents, the gaseous standards discussed above can also be used. Since, as has been mentioned, a POS responds to activity or partial pressure, then such a calibration will allow the direct measurement of dissolved oxygen in terms of oxygen

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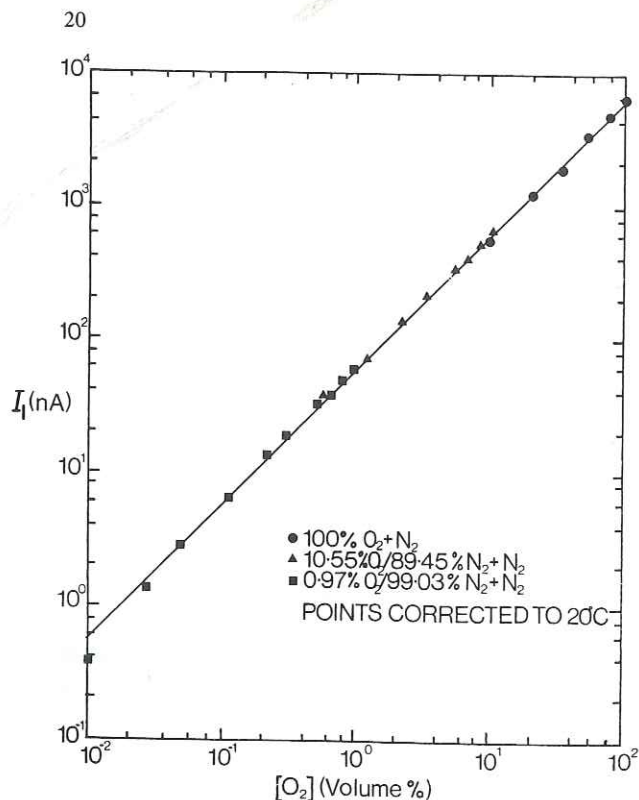


Fig. 1. Calibration curve for a POS. The different oxygen concentrations were obtained with the gas mixtures shown [10]. (Reproduced by permission of John Wiley and Sons, Inc.)

activity. However, if it is necessary to have a measure of dissolved oxygen in terms of concentration, then the calibration is somewhat more complicated since the Henry's law proportionality constant relating activity and concentration at the given temperature and liquid composition must be known (Chap. I.3). The value of this proportionality constant cannot, in general, be predicted, and so one has to rely upon the empirical determinations of solubilities in order to obtain it. For pure, nonaqueous liquids the solubility of oxygen is given in a number of compilations (e.g., [12]), but the data are often only at one temperature and it is difficult to evaluate the accuracy of the data. Hopefully the volume for oxygen in the new Solubility Data Series [1] will remedy this. For water, on the other hand, extensive investigations have been made of the solubility of dissolved oxygen as a function of temperature and pressure (App. A). Using the appropriate equations allows a direct correlation between a calibration made, in terms of partial pressure, with a gaseous standard and the dissolved oxygen concentration at a given temperature. Some caution is needed, however, with subsequent measurements, since the POS will always be measuring oxygen activity and not concentration and the relationship between these two may change; for example, when salting-out occurs (App. A).

For dissolved oxygen measurements it is sometimes more convenient to make the calibration with a dissolved oxygen standard. The standards to be used would then be samples of the pure liquid saturated with oxygen at a known partial pressure. The most common sample of this kind is air-saturated water. Calibration in terms of partial pressure is straightforward, once allowance is made for the vapor pressure of the water

(App. A) at the calibration temperature, while calibration in terms of oxygen concentration has again to rely on solubility tables. The zero oxygen level for liquid phase calibration can be checked either with a deaerated sample of the liquid or with a sodium sulfite solution.

3 Methods of Calibration

3.1 Preparation of Calibration Standards

If air is to be used as a calibration standard it should, as we have pointed out, be either completely dry or brought to 100% relative humidity. Drying of air can be done by several methods [5]. One technique is to pass the moist air along a tortuous path through a column containing a solid drying agent; e.g., silica gel or calcium chloride. Another method is to bubble the air slowly through a hygroscopic liquid; e.g., concentrated sulfuric acid or concentrated phosphoric acid. A third method of drying is to freeze out the water by passing the air through a tubular metal coil immersed in a cold bath. The most convenient freezing agent is dry ice (-56.6°C) which will give air with a partial pressure of water vapor of < 0.004 kPa and will not freeze out any other common constituent of air. After freezing out the water the dry air should be brought back to ambient temperature by passing it through a second coil in the ambient.

Saturating the air with water vapor is not quite as straightforward as might be imagined if one wishes to humidify a given volume of gas, since it involves not only the mass transfer of water from the liquid to the gaseous phase but also heat transfer, arising from the vaporization of the water, and its interaction with the mass transfer. One should use a device such as an adiabatic saturator [16], where gas passing through an adiabatic spray chamber is cooled and humidified. The exiting gas is, however, only fully saturated at a temperature equal to or less than the water temperature in the saturator, and so must not be allowed to warm up. A far simpler method of obtaining an air calibration standard with 100% relative humidity is to use the air a short distance (a few mm) above the surface of a clean sample of water; this is, in fact, the most commonly used gaseous calibration standard for POS. It is, of course, always necessary to know the temperature of the water used for saturation in order to obtain the appropriate water vapor pressure to subtract from the total air pressure.

For checking of the zero oxygen level of a POS with a gas it is merely necessary to flush out a closed volume with an inert gas (e.g., N_2 , Ar, He). Since one is supposed to be measuring zero oxygen partial pressure it is not essential that the inert gas be either at a known total pressure or have a known water vapor content. Gas mixtures with intermediate oxygen partial pressures are available commercially or are readily made up with a high degree of accuracy from pure oxygen and an inert gas using calibrated flow meters or mass flow controllers.

Liquid phase calibration standards are prepared by saturating a sample of pure liquid with oxygen at a known partial pressure. For air-saturated water, a short period (some minutes) of bubbling air through a gas tube dipping into a volume (typically several hundred cm^3) of clean water is often considered to be adequate. Since the water may very well be close to being saturated with air beforehand this preparation

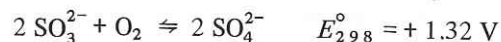
is probably enough for the air standard, but with other oxygen partial pressures considerably greater care is needed. This is largely because of the very limited contact between gas and liquid that a simple bubbler produces. In general the total mass transfer to and from a bubble takes place at a rate governed by the difference in partial pressure of the gas in the bubble and the liquid, the interfacial area for transfer, and the mass transfer coefficient in the liquid phase. For a given gas/liquid system it can be shown [16] that this transfer rate (J_o) is fairly well represented by

$$J_o = Ak_1 P^{0.4} (V_g/u_b)^{1/2}, \quad (3)$$

where A is a constant for the system, k_1 is the mass transfer coefficient in the liquid, P is the power input/unit volume to an agitator or stirrer, V_g is the volumetric gas feed rate/cross-sectional area of the containing vessel, and u_b is the bubble rise velocity. It is found that k_1 is approximately independent of the power input and impeller characteristics and so, for a given system, can be taken as a constant. Thus for efficient mass transfer to and from the gas bubbles it is necessary to fulfil three requirements. First, to have a large power input to the stirrer to give a high agitation rate and ensure a thorough dispersion of the bubbles throughout the liquid. Second, to have a large volumetric feed of the gas into the liquid to give a high volume fraction of bubbles in the system and so promote a large interfacial area across which mass transfer can occur. Third, to have a slow rise rate for the bubbles in order to provide adequate opportunity for mass transfer to take place during the passage of the bubbles through the liquid.

Apart from bubbling, other means of gas exchange [2] can also be employed to prepare calibration samples with various oxygen concentrations. Electrolytic generation of oxygen [14] and the catalase catalyzed decomposition of hydrogen peroxide [17] have been suggested for the preparation of dissolved oxygen calibration standards, but these techniques would seem to have no real advantages over the more straightforward gas-bubbling method. Indeed, with both electrolytic oxygen generation and hydrogen peroxide decomposition there is the danger of a wrong calibration due to less than 100% efficiency in oxygen production.

Water samples for zero point calibration can be produced by de-aerating with an inert gas. However, because the purging is essentially a first-order rate process the rate of de-aeration will fall off with time as the oxygen partial pressure gradient between the liquid and the bubbles decreases. Therefore it is especially important here to make the rate constant for the process as large as possible by ensuring efficient mass transfer between the two phases. This is particularly necessary if measurements are to be made at the ppb level. An alternative method of producing de-aerated water is simply to boil off the dissolved oxygen and let the water cool down under an inert atmosphere. Or one can take advantage of the thermodynamically, strongly downhill reaction



and use a 2%–5% solution of Na_2SO_3 which, as a simple calculation shows, should, and in practice is found to, contain infinitesimally small amounts of dissolved oxygen.

The above discussion of the preparation of liquid phase calibration standards has been in terms of aqueous standards, which are the most common form. For dissolved oxygen analysis in nonaqueous solutions then, provided that measurements are to be

made in terms of oxygen partial pressure, there is no fundamental reason why aqueous calibration standards should not be used since the oxygen activity in an aqueous and nonaqueous environment will be the same for a given oxygen partial pressure in the gas phase above the liquids. Even for analysis in nonaqueous solutions in terms of oxygen concentration, aqueous calibration standards can still be used if a partial pressure calibration is made since one can then convert the pressure to a concentration knowing the Henry's Law constant for the pure, nonaqueous liquid at the calibration temperature. This constant will not, however, be the same as that for water, and so a calibration with aqueous standards for dissolved oxygen concentration cannot be used for nonaqueous samples. If a direct calibration of oxygen concentration in a nonaqueous standard is required then, provided that the Henry's Law constant is known, such a standard can be prepared using the gas exchange methods described earlier; direct nonaqueous calibration may be demanded by the need, for example, to avoid contamination of the nonaqueous medium with traces of moisture that could be left on the surfaces of the POS from an aqueous calibration.

3.2 Use of Calibration Standards

Whichever form of standard is used, it is obvious that adequate precautions must be taken to prevent contamination of the standard sample by extraneous gases. In the case where air is the basis of the standard this should not present any real problem, but where the standard has an oxygen content different to that of air, particularly when a zero point calibration is being made, then leakage of air has to be avoided and a suitable calibration chamber must be used. For both gaseous and liquid calibrations continuous flushing with gas is recommended and the outlet from the chamber should be designed so that back-diffusion of air against the gas flow is negligible. Some idea of the conditions needed to fulfil this can be obtained by using the equation [3].

$$\frac{c}{c_\infty} = \exp(-\langle v \rangle l / D_a), \quad (4)$$

where c_∞ is the gas concentration in the atmosphere at the exit of a flushing tube, c is the concentration at a distance l from the exit inside the tube, D_a is the diffusion coefficient of the gas, and $\langle v \rangle$ is the mean velocity of the flushing gas. The dimensionless term $\langle v \rangle l / D_a$ is known as the Peclet number, Pe , and it is a measure of the relative importance of forced convection and diffusion for the transport of matter. When $Pe \gg 1$ the flow is predominantly convective, whereas when $Pe \ll 1$ it is mainly diffusive. Therefore in order that back diffusion of air against the gas stream can be neglected we can say that it is necessary for

$$D_a \langle v \rangle l / 7, \quad (5)$$

if we take $c \approx 0.001 c_\infty$ as being negligible. At atmospheric pressure and normal operating temperatures ($\approx 20^\circ\text{C}$) for air $D_a \approx 0.3 \text{ cm}^2 \text{ s}^{-1}$ and so values of $\langle v \rangle$ and l required to fulfil the criterion can be calculated. For example, with a gas flow $1 \text{ cm}^3 \text{ s}^{-1}$ and an exit tube cross-sectional area of 1 cm^2 the tube length required is $\approx 2 \text{ cm}$. A flow of $1 \text{ cm}^3 \text{ s}^{-1}$ is not unreasonable for flushing a liquid or a gas chamber, but if for a liquid calibration standard a lower rate of flushing is desired then a rather longer

and/or narrower exit tube should be used, or gas should be simultaneously flushed over the surface of the liquid but at a higher rate than the flushing through the liquid.

In addition to ensuring that the calibration standard has the oxygen partial pressure expected it is also essential to make sure that this partial pressure prevails right up to the outer surface of the membrane of the POS. In other words, that there is no depletion of the oxygen close to the membrane due to mass transfer limitations. A very simple criterion for this is that the rate of mass transfer through the membrane must be much slower than the transfer through the diffusion layer at the outer face of the membrane in the calibration medium. This criterion for diffusion in the membrane to be rate-determining can be expressed by

$$\frac{\delta_s}{D_s} \ll \frac{z_m}{P_m}, \quad (6)$$

where δ_s is thickness of the diffusion layer in the test environment, D_s is the diffusion coefficient for O_2 in this environment, and z_m and P_m have the same meaning as in Eq. (1) (cf. Chap. I.4). Considering first the case of gaseous calibration then, assuming that the gas flows tangentially past the membrane, it can be shown [11] that

$$\delta_s \sim \left(\frac{l D_s}{\langle v \rangle} \right)^{1/2}, \quad (7)$$

where l is a length along the membrane surface and $\langle v \rangle$ is the mean gas velocity. Condition (6) then becomes

$$\langle v \rangle \gg \frac{l}{D_s} \left(\frac{P_m}{z_m} \right)^2. \quad (8)$$

Taking typical values of $l \approx 1$ cm, $D_s \approx 0.2$ cm² s⁻¹, $P_m \approx 10^6$ cm² s⁻¹ and $z_m \approx 25$ μm, then it is only necessary for $\langle v \rangle$ to be much greater than $\approx 10^6$ cm s⁻¹, and this will always be true since even natural convection will provide a flow greater than this. With very thin and highly permeable membranes it is still unlikely that the criterion will not be valid. So with gaseous calibration there is no need to be concerned about oxygen depletion near the outer surface of the membrane.

With liquid calibration there is more of a problem. The diffusion layer thickness is now given by ([10]; cf. Chap. I.1)

$$\delta_s \sim D_s^{1/3} \nu_s^{1/6} \left(\frac{l}{\langle v \rangle} \right)^{1/2}. \quad (9)$$

where ν_s is the kinematic viscosity of the liquid. Condition (6) now becomes

$$\langle v \rangle \gg \frac{l}{D_s} \left(\frac{P_m}{z_m} \right)^2 \left(\frac{\nu_s}{D_s} \right)^{1/3}. \quad (10)$$

Taking values of l , P_m and z_m as before, and with typical values of ν_s and D_s of 10^{-2} cm² s⁻¹ and 10^{-5} cm² s⁻¹ respectively, the right hand side of the inequality is ≈ 0.2 cm s⁻¹, which is a much more demanding criterion. For example, if we take the inequality as being valid only at the 1% level then a liquid flow rate of 20 cm s⁻¹ is required. In practice it is found that the sensitivity of a POS is indeed independent of test solution

flow rates only at higher levels than this [10, 15]. Thus the great care in having adequate agitation when making calibration with liquids is emphasized. Also highlighted is a problem often encountered when calibrating in a gaseous environment for measurements eventually to be made in a liquid. Because of the difficulty of providing sufficient agitation to eliminate the effects of the diffusion layer in a liquid, a gas phase calibration (e.g., with air a short distance above an air-saturated water) can give a higher reading than a liquid phase calibration (e.g., with the water). If there is any possibility of the liquid flow rate being inadequate then it is probably better to calibrate in the liquid with the same stirring as will be used for the measurement. In this way calibration and measurement will at least be done under equivalent conditions.

We have already pointed out in the previous section the need for temperature control when using for calibration a gas sample with 100% relative humidity in order that the appropriate water vapor correction can be made. In fact, some form of temperature control is necessary with any form of calibration standard because of the large temperature coefficient of the current of a POS [10]. Automatic compensation can help to alleviate this problem. Typical errors quoted for automatic correction of commercial system are $\pm 1\%$ for temperatures within $\pm 5^\circ\text{C}$ of the calibration temperature and $\pm 5\%$ over the complete temperature range of $0^\circ\text{--}50^\circ\text{C}$ usually encountered (cf. Chaps. I.10, III.1). However, membrane characteristics often show a strong hysteresis when subject to large temperature changes and so some caution is necessary in using compensating circuits. For the most accurate work automatic compensation should not be relied upon and a calibration should always be made either at the same temperature at which the measurement is to be made, or as close as possible in order to allow a correction [10] to be made with confidence.

The calibration of a POS can change with time as a result of variations in the terms of the calibration factor. There may also be in addition external factors causing instabilities or changes in the sensor current (Chaps. I.1, I.6). Because of the very nature of many of these influences it is not possible to give a frequency for calibration checks categorically. All that can be said is that certainly a check should be made whenever the membrane is changed and when the sensor has not been used or checked for some time. For the rest one must rely upon both scientific and basic common sense.

As far as the number of calibration points is concerned, according to Eq. (2) only a single point is needed. In practice, because of residual currents an additional zero check has generally to be made in order to back-off any such residuals. It is probably also worthwhile to check the linearity of response from time to time with intermediate calibration standards. This is especially so at low oxygen partial pressures where deviations are most likely to occur as a result of the residuals.

3.3 Minimizing Residual Currents

Because residual currents are rarely constant in time frequent zero checks and/or calibration at low levels must be made, and so a better solution would be to attempt to eliminate the residuals altogether. But any attempt at eliminating residuals presupposes that the cause of such currents is known. Therein lies a problem, in that there is very often more than one cause and it is not always obvious which one is predominant.

Two sources that can give rise to varying current residuals are the reduction of surface oxides on the cathode [10] and the charging of a pseudocapacitance arising from the formation of adsorbed intermediates at the electrode surface. Both these phenomena are, however, only likely to contribute significantly to the residual current during the settling down of the detector when it is switched on, and once a true steady-state situation has been reached they will probably only make a small contribution to the overall residual.

Residual currents can also arise from reduction of species other than dissolved oxygen in solution. For example, if the electrolyte is not completely stable to oxidation then reduction of the oxidation products can occur at the cathode (Chap. I.5). Some detectors use an iodide electrolyte and the I^- anion, as is well known, is readily oxidized to I_2 in the presence of light. The I_2/I^- couple has a high, positive standard potential ($E_{298}^{\circ} = 0.535$ V) and so I_2 is easily reduced at the cathode. Electrolytes not resistant to oxidation, or indeed showing any form of instability, are to be avoided.

Other reducible species that can appear in the detector electrolyte are heavy metal ions. A POS that has been running for some time will have an electrolyte containing such ions as a result of the anodic dissolution of the auxiliary/reference electrode. The concentration of these cations and the resulting residual current from their reduction will depend very markedly on the anode couple used. For a POS with a Ag/AgCl anode in an electrolyte of 2 mol dm^{-3} KCl the Ag^+ concentration will be $\approx 10^{-10} \text{ mol dm}^{-3}$ and this concentration could be expected to produce a maximum current density $\approx 1\%$ of that generated by 1 ppb of dissolved oxygen. On the other hand for a Ag/Ag₂O anode with an electrolyte of 2 mol dm^{-3} KOH the Ag^+ concentration will be $\approx 10^{-8} \text{ mol dm}^{-3}$ (the solubility product of Ag₂O being about 100 times greater than that of AgCl) and the maximum current from the reduction of this concentration will be comparable to that from 1 ppb of dissolved oxygen. Therefore some care is needed in the choice of anode couple if low level oxygen calibrations are to be made. Here it is worth noting that any electrolyte which does not initially have a low pH or which is not strongly buffered will ultimately become alkaline anyway [8]. This change of pH will, of course, take some time to establish and during this period one may expect to observe a drift in the detector sensitivity. It is therefore better to start off with a high pH electrolyte, but at the same time to have a high concentration of an anion which has a low solubility product for the cations formed by the anodic dissolution of the anode.

Another reason for using a high pH electrolyte is to discourage, right from the moment of switching on the detector, the formation of hydrogen peroxide at the cathode. This is produced by incomplete reduction of oxygen at low pH values and it can build up to a steady concentration in the bulk of the electrolyte [6]. Calibrations made at low oxygen levels with a detector which initially had a low pH electrolyte and which has previously been used at high oxygen partial pressures can show residual currents arising from either the direct reduction of the H_2O_2 or from reduction of oxygen produced by the catalytic decomposition of the H_2O_2 on the cathode. Hydrogen peroxide formation is also minimized by using a high reduction potential [6], but too negative a potential can lead to a current residual from another source – the reduction of the solvent. Thus a compromise must be achieved. In this context it should be

noted that Pt is a significantly better catalyst for hydrogen evolution than Au [4], so that Au is to be preferred to Pt from this point of view.

All that we have said so far has concerned residual currents arising from processes other than the reduction of oxygen. In order to minimize these residuals it can be seen that one must simultaneously satisfy a number of requirements: anode couple producing low concentration of soluble cations; stable electrolyte of high pH and with anions to precipitate cations from the anode dissolution; cathode with high overpotential for water reduction; high applied potential. These conditions are probably most satisfactorily fulfilled with a POS having an Au cathode, a concentrated KCl electrolyte with a pH ≈ 13 , an Ag/AgCl anode, and an applied potential of -0.8 V.

In addition, however, to residuals from these various sources there is also the possibility of residual currents from oxygen reduction itself. This oxygen is in excess to that in the test or calibration environment and is, in fact, residual oxygen left behind in the detector from a time when the sensor was in an oxygen-rich environment. It can accumulate in various places, such as in the electrolyte reservoir, in electrolyte in microcracks in between the cathode and the insulating region surrounding it, and even in the body of the sensor itself. But whatever the final source, it is clear that this oxygen reaches the cathode by radial diffusion in contrast to the diffusion normal to the cathode of the oxygen from outside the membrane of the POS. The problem of the contribution to the current of a POS from oxygen diffusing to the cathode radially from the electrolyte reservoir has been examined in some detail [13]. This solution is complex, involving modified Bessel functions, but a simpler, approximate solution can be obtained which allows one to obtain a good estimate of the current from radial diffusion of oxygen [7]. We consider the differential equation for radial diffusion:

$$\frac{\partial}{\partial r} \left(r \frac{\partial c}{\partial r} \right) = 0 \quad (11)$$

with the boundary conditions

$$r = r_o \quad c = 0 \quad (12)$$

$$r \geq r_E \quad c = c_e \quad (13)$$

The boundary conditions apply to a detector design with a central disk cathode of radius r_o . The distance from the center of the electrode to the edge of the insulating land between the cathode and the electrolyte reservoir is r_E , and in the reservoir it is assumed there is a constant oxygen concentration, c_e ; since this will, in practice, clearly not be the case, because of loss of oxygen through the membrane and also removal by the radial diffusion process, any contribution to the current from radial diffusion will be less than what we shall estimate here. It is also assumed that the cathode is a cylinder with a radius equal to that of the actual disk cathode; this is a good approximation since the thickness of the electrolyte layer is, in general, much less than r_E . Solving Eq. (11) subject to Eqs. (12) and (13) gives

$$c = c_e \frac{\ln r/r_o}{\ln r_E/r_o} \quad (14)$$

and so the radial diffusion current I_r is

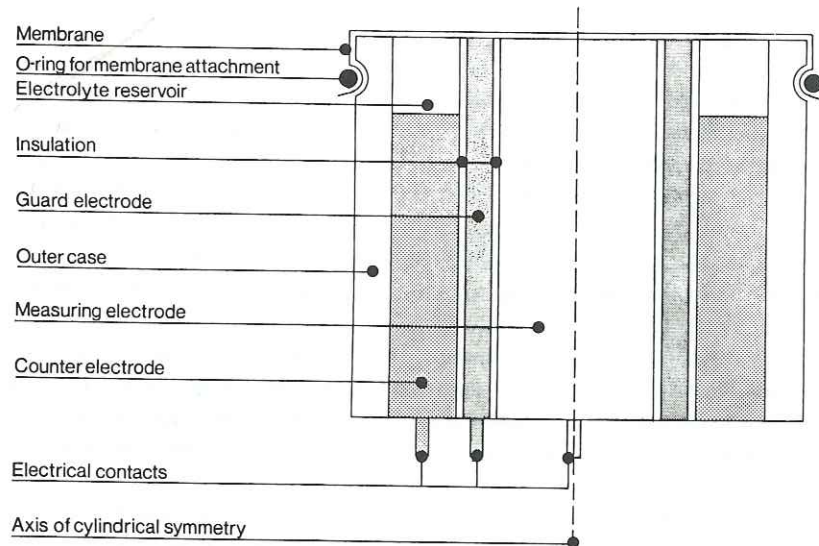


Fig. 2. A POS with a guard ring. (Reproduced by permission of Orbisphere Corporation)

$$I_r = nFAD_e \left(\frac{\partial c}{\partial r} \right)_{r=r_0} = \frac{8\pi z_e F D_e c_e}{\ln r_E/r_0}, \quad (15)$$

where z_e is the thickness of the electrolyte film over the cathode and D_e is the diffusion coefficient for oxygen in the electrolyte solution. The concentration of oxygen in the electrolyte reservoir will be less than that in air-saturated water because of the salting-out effect, and might typically be $125 \mu\text{mol dm}^{-3}$ at 25°C [10]. Then with $z_e \approx 5 \mu\text{m}$ and with $r_E/r_0 \approx 1.2$, which is typical for many POS, the value of $I_r \approx 9 \text{ nA}$. With a POS having a cathode area $\approx 0.3 \text{ cm}^2$ the corresponding current density is $\approx 30 \text{ nAcm}^{-2}$ and current residuals are often at this level; i.e., equivalent to $\approx 2 \text{ ppb}$ of dissolved oxygen. As we have pointed out, the value of I_r we have calculated will be greater than any actual value, but clearly radial diffusion of oxygen dissolved in the electrolyte reservoir could be a cause of the residual currents commonly found. Equation (15) shows that to reduce the current from radial oxygen diffusion one requires a thin electrolyte layer and as long a length as possible of this layer between the edge of the cathode and the electrolyte reservoir. In practice, one is limited by the requirement that the ohmic drop between cathode and anode should not be too high, and additional precautions may need to be taken. For example, by designing the sensor so that there is only a small area of the electrolyte reservoir exposed to the ambient atmosphere, or by incorporating a second cathode into the sensor which guards the current measuring cathode from oxygen diffusing radially from the reservoir. Figure 2 shows schematically the design of a three-electrode sensor. The guard electrode and measuring electrode both function as cathodes and reduce oxygen, but only the current from the central electrode is used as a measure of the oxygen in the test or calibration environment. Calculations show that the guard electrode will remove all but 0.001% of the oxygen diffusing radially from the reservoir.

One final point about residual currents should be made. The term polarographic oxygen sensor is taken to include both amperometric and galvanometric POS. The residual currents in all cases arise from processes occurring at the cathode and there is no fundamental electrochemical difference between these processes in the two types of cell. The interfacial potential at the cathode/electrolyte interface, which is the potential difference that governs any current, is the same whether the cell potential is being applied from an external source (amperometric POS) or arises from the intrinsic relative potential difference between cathode and anode (galvanometric POS). The methods suggested for minimizing residual currents therefore apply to both types of sensor.

In conclusion, we can say that while it may be a relatively easy matter to produce a calibration standard of zero or low oxygen content using such a standard to give an accurate calibration is by no means trivial. Indeed, if one wants to do more than just make an electrical adjustment to back-off any residual current considerable problems can arise.

4 Accuracy of Calibration

Having decided on the calibration standards to be used, and having taken all the necessary precautions to make sure that they have been used correctly, the final question to be discussed is the following: How accurate (i.e., how close to the true value) will a measurement with a POS be? Before we can answer this question it is necessary to ask some further questions in order to define the boundary conditions within which we are going to operate. So, for example, are we going to assume that the sensor is stable and that there is no long-term drift (Chap. I.1)? Is there going to be no poisoning of the detector by gaseous pollutants (Chap. I.6)? Is the measurement going to be made in an identical environment to that in which the calibration was made (Chaps. II.10, III.1)? As indicated, the problems of signal instability and electrode poisoning are dealt with in other sections, and here we just briefly consider the question concerning "identical environment". By this term we mean not only the same form of environment, but also all the same conditions except, of course, for the oxygen partial pressure. Thus, as we mentioned earlier, gaseous calibration standards are the logical choice for gaseous measurements, but, as we have also discussed, the temperature of the measurement and the calibration should ideally be the same because of the large temperature coefficient of the sensor current. If the read-out is to be in terms of volume percent rather than oxygen partial pressure, then there is the further constraint that there must be the same conditions of total pressure and relative humidity for both measurement and calibration.

For measurements in solution, gaseous calibration standards can be used, but there is then the problem of providing adequate agitation of the test solution to allow the calibration to be valid. For this reason it is probably better to calibrate with dissolved oxygen standards for dissolved oxygen measurements. As with gaseous phase measurements, calibration and measurement should preferably be done at the same temperature, and even with automatic compensation the difference in temperature should be

$\pm 5^{\circ}\text{C}$ at the most if an accuracy of $\pm 1\%$ or better is required. Read-out of dissolved oxygen can be as partial oxygen pressure or oxygen tension, p_{O_2} [kPa], as concentration [mmol dm^{-3}], or percent saturation. With partial pressure no particular problems arise, but with concentration and percent saturation a number of factors can lead to errors. As has been emphasized several times, a POS measures oxygen activity rather than concentration (Chap. I.3), and so any deviation from the expected relationship between the two – when, for example, measurements are made in saline solution or at great depths – will give a wrong concentration reading.

So in answer to our original question “How accurate will a measurement with a POS be?” we can say that if the answer to each of the supplementary questions is “yes”, then there is no reason why a measurement should not be made with an extremely high degree of accuracy. If the answer, on the other hand, to any of the supplementary questions is “no”, then the measurement will be inaccurate to a greater or lesser extent. But to put a general figure to the level of inaccuracy is not possible – in spite of what many manufacturers of POS would like us to believe.

References

1. Battino R (1979) Solubility data series, vol V. Oxygen and ozone – gas solubilities. Pergamon Press, Oxford
2. Battino R, Clever HL (1966) The solubility of gases in liquids. *Chem Rev* 66:395–463
3. Beek WJ, Muttzall KMK (1975) Transport phenomena, ch 1. John Wiley and Sons, New York, x + 298 pp
4. Bockris JO'M, Reddy AKN (1970) Modern electrochemistry, vol II, ch 10. Plenum Press, New York, lvi + 709 pp
5. Coulson JM, Richardson JF (1968) Chemical engineering, vol II, ch 15. Pergamon Press, Oxford, xvii + 790 pp
6. Hahn CEW, Davis AH, Albery WJ (1975) Electrochemical improvement of the performance of $p\text{O}_2$ electrodes. *Respir Physiol* 25:109–133
7. Hale JM, Hitchman ML (1979) Some considerations of the steady-state and transient behaviour of membrane covered dissolved oxygen detectors. RCA Tech Rep ZRRL-79-TR-002, 52 pp
8. Hale JM, Hitchman ML (1980) Some considerations of the steady-state and transient behavior of membrane covered dissolved oxygen detectors. *J Electroanal Chem* 107:281–294
9. Handbook of chemistry and physics (1969), 50th ed. Weast RC (ed) Chemical Rubber Co, Cleveland, p 151
10. Hitchman ML (1978) Measurement of dissolved oxygen. John Wiley and Sons, New York, xvi + 255 pp
11. Hitchman ML (1980) A consideration of the effect of the thermal boundary layer on CVD growth rates. *J Cryst Growth* 48:394–402
12. Washburn EW (ed) (1928) International critical tables, vol III. McGraw Hill, New York, xiv + 444 pp
13. Jenson OJ, Jacobsen T, Thomsen K (1978) Membrane covered oxygen electrodes. I Electrode dimensions and electrode sensitivity. *J Electroanal Chem* 87:203–211
14. Keidel FA (1960) Coulometric analyser for trace quantities of oxygen. *Ind Eng Chem* 52:490–493
15. Mancy KH, Okun DA, Reilley CN (1962) A galvanic cell oxygen analyser. *J Electroanal Chem* 4:65–92
16. McCabe WL, Smith JC (1976) Unit operations of chemical engineering, 3rd edn, ch 22, 24. McGraw-Hill, New York, ix + 1028 pp
17. Wingo WJ, Emerson GM (1975) Calibration of oxygen polarographs by catalase catalysed decomposition of hydrogen peroxide. *Anal Chem* 47:351–352