Measurement of Oxygen Diffusion Rates with the Platinum Microelectrode

I. Theory and Equipment
   J. Letey and L. H. Stolzy

II. Factors Influencing the Measurement
   D. E. Birkle, J. Letey, L. H. Stolzy, and T. E. Szuszkiewicz

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   L. H. Stolzy and J. Letey
In 1952, E. R. Lemon and A. E. Erickson introduced a method for measuring the rate of oxygen diffusion to a small platinum wire electrode inserted into the soil. This was considered analogous to measuring the oxygen movement to a plant root that would be in the same position as the wire electrode.

In spite of certain limitations, the platinum microelectrode technique appears still to be the best method available at present for providing a measurement of oxygen conditions in soil which can be interpreted with respect to biological behavior.

The first two papers of this series discuss theory, equipment, and the factors that can influence measurements. The third paper reviews the literature reporting research on correlation of oxygen diffusion rates to biological response.

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I. Theory and Equipment

INTRODUCTION

Early methods of measuring and characterizing soil aeration conditions consisted of extracting gas samples from soil pores and analyzing the samples for oxygen and carbon dioxide concentration. Later, diffusion rates of oxygen through the gas phase were measured. In general, the results of these measurements could not be correlated with biological response in the soil. The diffusion coefficient of oxygen is approximately 10,000 times lower in water than in air, and soil oxygen must usually pass through a liquid film before arriving at a respiration site. Therefore, the limiting factor in oxygen supply is very likely the rate of movement through the liquid (rather than the gas) phase, and it is that movement which should be measured.

DIFFUSION THEORY

When a certain electrical potential is applied between a platinum electrode inserted in the soil and a reference electrode, oxygen is reduced at the platinum surface. The electric current flowing between the two electrodes is proportional to the rate of oxygen reduction. This, in turn, is related to the rate of oxygen diffusion to the electrode. The oxygen diffusion rate (O.D.R.) can therefore be calculated from the measured electric current.

Kolthoff and Lingane (1952) related the oxygen flux at the electrode surface to

\[ f_z = a, \ t = D \left( \frac{\partial c}{\partial z} \right)_{z=0} = a, \ t \]  

where \( D \) is the oxygen diffusion coefficient in solution and \( c \) is the oxygen concentration in solution. This equation was stated by Lemon and Erickson (1952) and by Poel (1960), in connection with making measurements in soil (the O.D.R. is identical with the flux). The O.D.R., therefore, is related to the diffusion coefficient and to the concentration gradient at the electrode surface at steady state.

Equation (1) is valid for linear diffusion; but in the use of the platinum microelectrode, a cylindrical coordinate system is more appropriate than a rectangular coordinate system. The general steady-state diffusion equation in cylindrical coordinates is

\[ \frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} = 0 \]  

Assuming the boundary conditions

\[ c = c_1 \text{ when } r = a \text{ (electrode radius)} \]
\[ c = c_2 \text{ when } r = r_1 \]

integration of (2) leads to

\[ \frac{\partial c}{\partial r} = \frac{c_2 - c_1}{a(\ln r - \ln a)} \]  

1 Submitted for publication October 2, 1963.
2 The research reported in all three papers was supported in part by Atomic Energy Commission Contract AT11-1-34 P92 and by National Science Foundation Grant GB-84.
3 See "Literature Cited" for citations referred to in the text by author and date.
The flux is equal to the diffusion coefficient times the concentration gradient.

\[ f_{\text{r=a}} = \frac{D_e(c_2 - c_1)}{a(\ln r_1 - \ln a)} \]  

(4)

The value \( r_1 \) is the distance from the electrode center to the point at which the concentration changes very slowly from \( c_2 \) (the initial uniform concentration), so that an apparent steady-state condition has been achieved. In some cases, with unsaturated soil, this value may correspond to the distance to the edge of the water film surrounding the electrode. \( D_e \) is the effective diffusion coefficient, and is related to the diffusion coefficient in pure water \( (D_0) \) by

\[ D_e = D_0 \tau \gamma S \]  

(5)

where \( S \) is the fraction of the area not occupied by soil particles and therefore available for diffusion, \( \tau \) is the tortuosity factor in the diffusion path length, and \( \gamma \) is the interaction between oxygen and soil. The value of \( \gamma \) is probably near 1.

Equations (4) and (5) show that an O.D.R. value includes the effect of the diffusion coefficient of oxygen in water, the oxygen concentration in solution, the thickness of the water film around the electrode, the porosity of the soil around the electrode, and the tortuous path encountered by the oxygen molecule as it diffuses to the electrode. These factors would also influence the rate of oxygen movement to a root. Unfortunately the electrode radius is also included in the results in such a way that it cannot be readily factored out without a knowledge of the value of \( r_1 \). Therefore, under identical conditions, a different O.D.R. would be expected with electrodes of differing radii.

The relative effect of electrode radii on the O.D.R. was determined by calculations on a model system. In making the calculations, a mass of water in cylindrical forms of varying radii was assumed. The resulting changes in radius as the various electrodes were inserted into the water were calculated. Assuming that the outer cylindrical edge always had an oxygen concentration in equilibrium with air \( (8.38 \times 10^{-6} \text{ gm cm}^{-3}) \) and that the oxygen concentration at the electrode surface was zero, the steady-state O.D.R. was calculated, using the diffusion coefficient of \( 2.4 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1} \) and the various electrode radii, and distance to cylindrical edge, \( r_1 \). Results of these calculations are shown in figures 1 and 2.

At a high radius, which corresponds to a very wet soil, the measured O.D.R. would be highest for a 25-gauge (.023 cm radius) electrode and would decrease as the electrode size increases. At low values for \( r_1 \) the trend is reversed. It should be remembered that the method of calculation was to assume a...
The factors 60 and $32 \times 10^8$ are included in equation (7) in order to express results in minutes and micrograms.

$$O.D.R. = i \times 10^{-6} \times 60 \times 32 \times 10^8$$

where $i$ is the electric current in microamperes, $n$ is the number of electrons required for the reduction of one molecule of oxygen, and is $4$, $F$ is the Faraday constant, $A$ is the surface area of the platinum electrode (in cm$^2$) and $f$ is the flux or oxygen diffusion rate to the electrode surface in number of moles of oxygen per second per cm$^2$.

The O.D.R. generally reported is identical with flux ($f$) in equation (6). The O.D.R. is calculated by

$$O.D.R. = \frac{i \times 10^{-6} \times 60 \times 32 \times 10^8}{4 \times 96,500 \times A}$$

The factors 60 and $32 \times 10^8$ are included in equation (7) in order to express results in minutes and micrograms.

Fig. 2. Theoretical O.D.R. values resulting from inserting electrodes of various sizes into a cylindrical volume of solution of varying radii. For a given radius on the abscissa, the water film around the larger electrode is thinner than around the smaller electrode.
rather than moles and seconds. Therefore, the O.D.R. is calculated by dividing the current by the electrode area and multiplying by a constant.

Variability of Results

Results with the platinum microelectrode technique vary widely. Macroscopically the soil appears to be homogeneous, but microscopically it is heterogeneous. If the electrode is inserted into an aggregate of relatively large pore sizes (5-mm diameter) that is completely saturated with water, a low reading will result. Slight movement of the electrode could place it in an environment with only a thin water film, and result in a high reading. Obviously, the average of several measurements must be taken to insure proper assessment of the soil oxygen status.

Figures 1 and 2 illustrate a large difference in O.D.R. with a small change in liquid film size when the moisture content is low. On the other hand, O.D.R. would be expected to be more nearly uniform in a very wet soil. Indeed, in a bentonite suspension, accuracy of results is limited only by the precision of the ammeter and the exactness with which electrode size can be measured.

EQUIPMENT

The simplest apparatus would consist of a battery, variable resistor, voltmeter, ammeter, reference electrode, and platinum electrode. Since about four minutes are required after the application of potential for a constant current to develop, and since several measurements are necessary, a more complex apparatus that will allow 10 measurements to be made in essentially the same time is desirable. While an assembled apparatus is commercially available, the parts and assembly of the portable unit described here have some desirable features that differ from those of the commercial equipment.

The apparatus shown in figure 3 has three functions: (1) to provide an external electric potential; (2) to measure the current in the external circuit connecting the two electrodes; and (3) to apply a holding voltage to the other nine electrodes.

The instrument circuit (fig. 4) is in three main parts: (1) applied potential and measuring section; (2) electrode selector; and (3) battery charger.

The saturated calomel and the saturated silver-silver chloride electrode are commonly used with the plantinum microelectrode. Their standard oxidation potentials are -0.246 and -0.222, respectively. The silver-silver chloride cell (fig. 5) was used with our equipment.

Platinum Microelectrode

The choice of platinum wire for the electrode involves a compromise between wire of large diameter, for durability, and that of small diameter, for better simulation of the plant root and its environment. One of the main advantages in using platinum microelectrodes for characterizing soil oxygen status is that the effect of water surrounding a root or organism is included in the measurement. When large-diameter wire is used or is incorporated as part of a rugged tip such as that used by Wiersum (1960), the existing solid-liquid-gas geometry is greatly altered so that the measurement does not properly characterize the oxygen diffusion to a root growing in that environment. This problem is less serious under high moisture conditions, but becomes more critical as the moisture decreases. Fail-

Fig. 3. Equipment used in making oxygen-diffusion measurements: meter, silver-silver chloride cell, platinum microelectrodes. Meter has sloping panel containing voltmeter (left) and microammeter (right). At left is a double-pole double-throw switch. At "off" position, circuits in voltmeter and microammeter are shorted to prevent excessive swing of meter needle. At "on" position, potential is applied. It can be adjusted by middle knob, and is read on voltmeter. Right-hand knob is selector switch used to connect microammeter in series with individual platinum electrodes. Quick-coupling, lock-type amphenol plug and socket connecting electrodes to meter circuit are on side of meter. The silver-silver chloride electrode is connected to meter by means of a bannan jack.

ure to wet the large electrodes completely as the moisture content of the soil decreases could also influence the accuracy of measurements.

Although some breakage occurs, the 25-gauge (.023-cm radius) wire electrode has been successfully used in making measurements in greenhouse experiments. Wire of this size is too fragile, however, for field experiments. Electrodes constructed of 22-gauge wire (.032-cm radius) have been successfully used in the field. Some researchers have used 18-gauge (.051-cm radius) platinum wire electrodes. Considerable difficulty will be encountered with all sizes if gravel or stones are present in the soil to be sampled.

All 25-gauge electrodes and some 22-gauge ones used in these studies were constructed by the authors. Some 22-gauge electrodes were also purchased from a commercial supplier. To make 25-gauge electrodes, platinum wire was fused to 20-gauge copper wire. The length of the copper wire was determined by the over-all length desirable for the completed electrode. The end of the copper wire was heated in a gas flame until it became soft; it was then brought into contact with the end of the platinum wire, with the point of the flame kept on the copper. After fusion, the platinum wire was cut so that 4 cm remained attached to the copper. A piece of 4-mm (O.D.) Pyrex glass tub-

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Fig. 4. Circuit diagram of oxygen-diffusion meter, electrode selector, and battery charger. Nickel-cadmium battery (B-1) is source of potential. When switch (S-1) is on, voltage is applied through voltmeter (M-2). Potential is changed by voltage-adjust knob connected to potentiometer (R-1). Adjustable post of potentiometer goes to electrode selector's common source (A). The resistor (R-2) is in circuit to compensate for resistance of microammeter. Applied potential has two pathways: either through R-2 to A, and thus to 9 or 10 platinum electrodes, or through the microammeter (M-1) to B and one platinum electrode, depending on electrode selector.

Electrode selector (S-2) is connected to main circuit at points A and B. Connection A is a ring connecting 10 electrodes to a common source. When right-hand knob (fig. 3) is at "on" position with potential applied, the 10 electrodes are connected through contact A. As selector rotates to position 1 (figs. 3 and 4), ring (contact A) is disconnected from number 1 electrode and reconnected through microammeter (M-1) to contact B. In this way the potential can be continuously applied to all electrodes, and the current through each can be measured successively.

There is, however, a voltage drop across the microammeter. In order to maintain a constant potential on all electrodes during measurement of an individual electrode, a 4700 resistor (R-2) was placed in series with contact A. Value of resistor (R-2) was determined experimentally so that the applied potentials at A and B were nearly equal.

Battery charger consists of transformer that will plug into any 115-v AC current and reduce voltage to 1.5. Arrangement of diodes (D-1, D-4) rectifies AC to DC voltage. Capacitor (C-1) smooths out pulsating current before it reaches battery (B-1). Charger is designed to prevent battery damage by an overcharge.

ing was used to give the electrode rigidity. The end of the glass tube to be fused with the platinum was heated until the end was drawn to a diameter slightly larger than the platinum wire. The wire was then passed through the glass tubing until approximately 5 mm of platinum protruded from the end. The glass was heated until it was fused to the platinum wire. When necessary, the platinum wire was cut so that approximately 4 mm of wire were exposed. Some of the common problems encountered in the construction of these elec-
Fig. 5. Silver-silver chloride reference cell. Electrode is connected to soil through saturated KCl salt bridge. Lucite container for electrode and salt solution has outer diameter of 8.3 cm and is 18 cm long. Silver foil (.0127 cm thick) with a total surface area of 2000 cm² (both sides) was rolled to fit inside container. Nylon tubes separate the silver foil. Tongue of foil was passed through slit in container wall for connection to anode plug. Slit in container was made with hot spatula; resealed with epoxy adhesive. Tygon tubing and a porous ceramic cup complete the salt bridge. Ceramic cup was filled with KCl-saturated agar to reduce flow of salt solution into soil. Silver chloride deposit was formed on silver by inserting platinum electrodes and salt bridge into soil and applying potential for one hour.

Fig. 6. Various results in construction of platinum electrodes. Electrode A is poorly constructed; note concavity at junction of glass and platinum that prevents measurement of area of electrode. Electrode B was overheated, and glass flowed down one side. Strain such as that encountered on inserting electrode into soil will crack glass shoulder, thus modifying electrode dimensions and possibly causing a leak along platinum wire. Electrode C shows poor sealing between glass and platinum as indicated by ink drawn into glass tube. Such electrodes give erratic and erroneous results. Electrode D is well constructed.
trodes are illustrated in figure 6. If the platinum wire broke after use, the glass was broken away and the wire sealed in a new tube. This procedure was continued until the entire 4 cm of platinum were used.

The 25-gauge electrode is too fragile for use in field measurements or in any situation in which the electrode must be pushed to a depth of more than 10 to 15 cm into the soil. In place of glass tubing, 12-gauge, plastic-insulated copper wire (U. S. wire 12, solid TW, 600v) may be used to make 22-gauge electrodes as follows: (1) cut the copper wire to desired length; (2) slip insulation off the copper; (3) fuse the platinum to the copper; (4) cut the platinum wire to leave 8 mm; (5) after fusing, file the copper wire to its original character if necessary; (6) slip insulation back onto the copper wire down to the copper-platinum union; (7) apply epoxy adhesive to the edge of the insulation and taper it to a point half way down the platinum wire; (8) cut the insulation at the other end of the wire, leaving 2 to 3 cm of copper wire exposed for contact with the

Fig. 7. Construction problems with 22-gauge electrodes. Electrode A has copper exposed and part of platinum filed. Electrode B has adhesive smeared down side. Electrode C is well made.
**MATERIALS REQUIRED FOR OXYGEN DIFFUSION METER**

<table>
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<tr>
<th>DESCRIPTION</th>
<th>MODEL No.</th>
<th>MANUFACTURER</th>
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<tr>
<td>Box chassis</td>
<td>HC-253</td>
<td>California Chassis</td>
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<td>Power and meter shorting switch—OPDT (S-1)*</td>
<td>.8363-K7</td>
<td>Cutler-Hammer</td>
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<tr>
<td>Nickel-cadmium battery—1.25 v (B-1)</td>
<td>N-83</td>
<td>Eveready</td>
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<td>Microammeter—0-30 μA (M-1)</td>
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<td>Triplett</td>
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<tr>
<td>Voltmeter—0-0.8 VDC (M-2)</td>
<td>420</td>
<td>Triplett</td>
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<tr>
<td>Potentiometer—100-2W (R-1)</td>
<td>Cu-10001 Ohmite</td>
<td></td>
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<tr>
<td>470Ω ± 1 per cent carbon resistor—½ W (R-2)</td>
<td>MDC</td>
<td>IRC</td>
</tr>
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<td>Electrode selector (S-2)</td>
<td>Pa-300</td>
<td>Centralab and PA-11</td>
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<tr>
<td>Electrode socket (J-1)</td>
<td>165-12</td>
<td>Amphenol</td>
</tr>
<tr>
<td>Plug</td>
<td>165-9</td>
<td>Amphenol</td>
</tr>
<tr>
<td>Diodes (D1–D4)</td>
<td>IN 3208</td>
<td>Motorola</td>
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<tr>
<td>Capacitor—1000 MFD, 15 v, DC (C-1)</td>
<td>TVA-1163</td>
<td>Sprague</td>
</tr>
<tr>
<td>Transformer—1.5 v, 3 amps (T-1)</td>
<td>FT-1</td>
<td>UTC</td>
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<tr>
<td>Fuse—½₁₆ amp., 115 v (F-1)</td>
<td>3AG</td>
<td>Littlefuse</td>
</tr>
</tbody>
</table>

*Letters in parentheses refer to figure 4. Total cost of materials is approximately $150.

Alligator clips. These electrodes are illustrated in figure 7. Examine the electrodes periodically to make sure that copper does not become exposed.

**Calibration of electrodes.** The area of the electrode must be known in order to calculate oxygen diffusion rates by equation (7). That area may be determined (1) by use of a traveling microscope to measure the length of the exposed platinum; or (2) by standardizing to an electrode carefully constructed and measured. In the first method, the platinum wire was first squared on the end; length was then measured on at least three different sides of the wire, and measurements were averaged. The diameter was measured with a micrometer. The area was calculated from the combined information. In the second method, the standard electrode was inserted with nine other electrodes, into a 3 per cent bentonite suspension that had previously been mixed for a few minutes in a milk-shake mixer to bring the solution into equilibrium with atmospheric oxygen. The suspension was allowed to stand for 5 minutes after stirring, before the potential was applied, and another 10 minutes before the readings were made. The unknown length \((X)\) was calculated by the equivalent ratios

\[
\text{unknown lgth. (X)} = \frac{\text{eur. of unknown}}{\text{eur. of standard}} \times \text{standard length}
\]

A comparison of measured electrode lengths with a calculated length based on a standard electrode is made in figure 8. Statistical analysis of the data for the 20 good electrodes in figure 8 shows a coefficient of variation for the measured electrode values to be 4 per cent while the calculated values had a coefficient of variation of 0.2 per cent. A “t” test by methods of paired observations (Li, 1957) shows

\[
t = \frac{2.0 - 0}{0.1041} = 19.2
\]
The difference between the means is highly significant at the 0.1 per cent level. These data clearly show that more reproducible results would be obtained from electrode lengths calculated in a standard medium than from measured values.

When new electrodes are first inserted into the soil, readings may be higher for a period and then drop. This was noted for all electrodes and may possibly be the result of preoxidizing treatments. When new electrodes are made, they are subjected to an open flame, and their surface becomes oxidized. An oxidized platinum surface has been shown to give different readings from those obtained with a nonoxidized or pre-reduced surface (Sawyer and Interrante, 1961). To obtain less variable readings, the oxidized surface film should be scratched off by rubbing lightly with steel wool before calibration in the bentonite suspension.

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**LITERATURE CITED**

KOLTHOFF, I. M., and JAMES J. LINGANE

LEMON, E. R., and A. E. ERICKSON

LI, JEROME, C. R.

POEL, L. W.

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