THE DETERMINATION OF OXYGEN CONCENTRATION IN SOIL WITH COLLODION COATED SILVER WIRE ELECTRODES

Thesis for the Degree of Ph. D.
MICHIGAN STATE UNIVERSITY
TSE CHUN YANG
1970

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ABSTRACT

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An instrument was designed to measure oxygen concentration in soil. It is an amperometric measurement which uses a silver microelectrode coated with collodion as cathode and a silver-silver chloride anode. An integrated current of short duration is measured shortly after closing the circuit. The current is shown theoretically and experimentally to be related with oxygen concentration of the medium. Oxygen concentration is expressed in terms of oxygen saturation thus eliminating temperature correction. Consistent readings were obtained when measurements were taken from a silt sample in 0.02 N KCl at 70 cm tension. The meter is shown to be useful to measure oxygen concentration in soil at or near saturation.

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By

Tse Chun Yang

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
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DOCTOR OF PHILOSOPHY

Department of Crop and Soil Sciences

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To

My Parents and Wife

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I. INTRODUCTION

It is well-known that an oxygen deficient soil suppresses the growth of most plants and their associated soil microorganisms. Monitoring soil oxygen status in the rhizosphere of poorly aerated soil is an important soil measurement for studying crop production.

Two parameters are needed for the complete expression of the soil oxygen status: oxygen concentration and oxygen flux. The oxygen status of a soil, due to the microheterogeniety of the soil, is not uniform. In a location it may differ greatly between two peds from that within the peds. Therefore, soil oxygen status described in micro-terms would be more meaningful than in macro-terms. Soil oxygen flux has been successfully measured,[1] since Lemon and Erickson (1952) introduced the oxygen diffusion meter. The use of platinum microelectrode provided good spatial resolution of oxygen flux. The oxygen flux as seen by a fine root is closely simulated by a thin wire electrode. However, an apparatus for determining dissolved soil oxygen concentration of comparable resolution has not yet been realized. The purpose of this study is to investigate the possibility of constructing such an instrument.

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[1] Under favorable conditions described on page 3.

II. REVIEW OF LITERATURE

Numerous writers have discussed the importance of soil oxygen to plant growth and to soil chemical reactions. Some reviews of the literature are Bergman (1959), Black (1968), Brandt (1963), Grable (1966), and Russell (1952). In this study, therefore, the focus is on the development of instruments for measuring oxygen concentration and factors affecting such measurements. Some of the instruments are not for soil use, but they certainly play a role in the sequence of development. The principle and design of these instruments may enlighten ideas for further improvement.

INSTRUMENTS FOR OXYGEN MEASUREMENT

In 1897, Danneel (11) found that current passing through two platinum electrodes in aqueous solution depends on oxygen concentration. Precise measurement of dissolved oxygen was later achieved by using a dropping mercury electrode or a rotating electrode (Kolthoff and Lingane, 1952). The applicability of stationary electrodes to *in situ* and *in vivo* measurement received, naturally, more attention from biologists and related scientists.

Blinks and Skow (1938) used a stationary platinum electrode to measure oxygen concentration change at the surface of green leaves in solution. Lemon and Erickson (1952) introduced the platinum microelectrode method to measure soil oxygen diffusion rates and this method has been widely adopted. Satisfactory results can be obtained when a clean electrode is completely covered with soil solution and the cell resistance is within a favorable range which is in the range of soil oxygen deficiency to plants (Van Doren and Erickson, 1966).

Davies and Brink (1942) constructed a recessed microelectrode for measuring oxygen concentrations in the cat brain. The platinum wire was sealed 1 mm inside the opening of a glass tube. This construction for oxygen concentration measurement was supported by a sound diffusion theory treatment. In blood oxygen measurements, the undesirable effect of blood cells was minimized by coating a platinum electrode with collodion (Drenckhahn, 1951) or cellophane (Clark, Wolf, Granger, and Taylor, 1953).

Clark (1956) enclosed a platinum cathode and a silver anode together behind a polyethylene membrane for blood oxygen determination. Material such as teflon (Sawyer, George, and Rhodes, 1959; Krog and Johansen, 1959) and silicon rubber (Flynn, Kilburn, Lilly, and Webb, 1967) are also used as membranes. These membranes are permeable to oxygen but restrict other substances from diffusing through them. Poisoning can thus be minimized and electrode stability greatly improved.

Another outstanding feature of the membrane covered electrode is that regardless of whether measurements are made in gas or in liquid phase the readings are almost the same, provided both are at the same oxygen tension (Reeves, Rennie, and Pappenheimer, 1957; Krog and Johansen, 1959).

Carritt and Kanwisher (1959) incorporated a thermister in the electrode system to compensate for the high temperature dependence of the diffusion rate (8.5% per degree at $25^{\circ}C$ for polyethylene) in the cell. McIntyre and Philip (1964) used this electrode system in their apparatus to study gas diffusion into soil. Mancy, Okun and Reilley (1962) felt that a single fixed thermister *per se* cannot offer adequate temperature compensation because the permeability coefficient of plastic sheets vary from one batch to another (membrane requires frequent replacement) and because of variable distortion applied to the membrane on mounting. They provided nomograph charts for temperature correction with their oxygen analyzer which has a silver cathode and a lead anode in 1 M KOH. The spontaneous cell reaction eliminates the requirement of an external current source. Current from a membrane-covered electrode is independent of the variation in oxygen solubility due to types and concentration of salt in the medium measured.

All the membrane covered cells require a minimum amount of stirring while taking measurements, except in the case of gases which mix readily. Insufficient stirring gives readings dependent on the diffusion impedence of the medium measured. Enoch and Falkenflug (1968) suggested to use an additional sheet of membrane to enclose a thin gaseous volume on the end of a Beckman oxygen sensor (no. 39065). This volume which is in equilibrium with the soil environment through a greater surface than with the original effective surface of the electrode, in effect reduces the diffusion impedence effect of the environment. The time required to reach a steady current reading increases with the spacing between the two membranes. Some stirring was still applied by bubbling the solution with gas in their experiment. A good membrane-covered sensor to be used in soils should, at least, give consistent readings when it is placed in gas and in unstirred aqueous solution of the same oxygen tension.

Willey and Tanner (1963) designed a rugged membrane-covered electrode with temperature compensation for measuring oxygen concentration in soil. Steady readings can be attained 2 1/2 minutes after the circuit is closed. The electrode, when placed in an access tube, has a diameter of about one inch. Because of its large size it may be difficult to use in the field to measure the microenvironment of roots. However, it still seems to be the best and most compact tool available for soil oxygen concentration investigations.

Brandt (1953) attempted to use a bare platinum wire electrode to estimate oxygen concentration in bentonite suspensions and in soil. Oxygen concentration was calculated from the transient currents, recorded photographically from an oscillograph trace, after a few tenths of a second of circuit closure. Using the diffusion current after a short duration of circuit closure virtually limits the diffusion path. Only the diffusion character in the immediate vicinity of the electrode surface is important. Good agreement was attained between the measured and actual oxygen concentration of a bentonite suspension; but the results were erratic when soil oxygen concentration was measured. The variability due to the platinum electrode itself, as pointed out by Brandt, was later successfully overcome by using silver electrodes (Erickson, Fulton and Brandt, 1964; Wu, 1967). Wu (1967) used a set of timers and an integrator to substitute for the time-consuming oscilloscope photography for reading transient current. Reasonably consistent readings were obtained from saturated sands and sandy loams of the same oxygen concentration. But variations were found at higher moisture tensions, around 10 cm for sands and 50 cm for sandy loams, and high electrical resistances, approximately 50 kilo-ohms between the Ag and Ag-AgCl. Both Brandt and Wu assumed that the diffusion coefficient of oxygen in soil in the immediate vicinity of the electrode is constant. The validity of this assumption was not explained.

Non-polarographic methods for determining oxygen concentration in unsaturated soil are also available. Hutchins (1921) determined oxygen supplying power by burying a porcelain cup in soil and flushing it with nitrogen gas. Oxygen in the outflowing gas was absorbed by a solution of pyrogallol and potassium hydroxide, and determined colorimetrically. The apparatus is too clumsy for field use. A relatively compact diffusion tube was designed by Raney (1950). It has a lateral port and a valve at the lower end. After 10 minutes of diffusion the gas in the chamber was analyzed by a Beckman model D oxygen analyzer. Similar kinds of apparatus were also described by Taylor and Abraham (1953) and van Bavel (1954). This could be used for oxygen concentration determination if the time of diffusion was long enough to allow equilibrium to be established.

Hack (1956) was able to take a small soil air sample, as little as 0.01 cc, by inserting a microsyringe with a lateral port into the soil. Small samples and large samples were compared. Results showed that small samples are more sensitive to oxygen concentration changes in soil than are large samples. Yamaguchi, Howard, Hughes, and Flocker (1962) used a syringe to take air samples from a diffusion chamber so that sampling depth is not limited by the length of the needle.

No apparatus is available to successfully detect oxygen concentrations in saturated and unsaturated soils with a micro-spatial resolution similar to the plant root environment.

OXYGEN REDUCTION AT A METAL CATHODE AND FACTORS AFFECTING IT

Laitinen and Kolthoff (1941) showed the presence of H_2O_2 as a product of electrolysis of oxygen at a platinum electrode in KNO_3 solution. Lingane (1961) reported that direct reduction of oxygen at a platinum cathode is diffusion controlled in the presence of a small amount of platinum oxide (about one-tenth the amount on a fully oxidized electrode is sufficient), but kinetically controlled if the oxide is not sufficient. He also concluded, by using an anodized platinum electrode in 1 M H_2SO_4 and 1 M NaOH, that in both acid and basic aqueous media, oxygen was reduced all the way to water rather than to H_2O_2. At the same time, Sawyer and Interrante (1961), working on both oxidized and reduced electrodes of various metals including Pt, Pd, Ni, Ag, Au, Ta, W, Cu, and Pb, pointed out that the reduction does not involve H_2O_2 at the oxidized electrodes but does produce H_2O_2 at the reduced platinum electrode. Reaction mechanisms were also proposed, i.e., at an oxidized electrode,

$$Pt(OH)_2 + 2e^- \rightarrow Pt + 2OH^-$$
$$2Pt + O_2 + 2H_2O \rightarrow 2Pt(OH)_2,$$

and at a reduced electrode,

$$Pt(OH_2)_n + O_2 + e^- \rightarrow Pt(OH_2)_{n-1}(OH)^- + HO_2 \quad \text{slow}$$
$$Pt(OH_2)_{n-1}(OH)^- + H_2O \rightarrow Pt(OH_2)_n + OH^- \quad \text{fast}$$
$$2HO_2 \rightleftharpoons H_2O_2 + O_2 \quad \text{fast.}$$

Later Sawyer and Day (1963) concluded that the mechanism at the oxidized electrode is dependent upon the electrode material, whereas the mechanism at the reduced electrode is largely independent of electrode material. The cyclic reactions of platinum hydroxides coincides with Lingane's conclusion, i.e., if the platinum electrode does not have enough oxide, the reaction becomes rate limiting rather than diffusion controlled. The presence of platinum oxides was confirmed earlier by Anson and Lingane (1957). The PtO and PtO_2 are in 6 to 1 molar ratio regardless of degree of oxidation. Feldberg, Enke and Bricker (1963) defined three surface states of platinum electrode: reduced or "clean" state (Pt), the oxidized state ($Pt(O)_x$) and the half-reduced state ($Pt(OH)_x$). The $Pt(OH)_x$ film enhances electron transfer in the oxidation-reduction reaction. A platinum electrode can be activated by strong oxidation and subsequent reduction producing the half-reduced oxide.

Sawyer and Interrante found that reduction of oxygen at all preoxidized metal electrodes, except Ag and Au of all the various metals tested, appears to occur by the same mechanism. For the Ag and Au electrode, the oxide is reduced prior to the oxygen wave, and thus these electrodes act as reduced electrodes for oxygen wave. Mancy et al. (1962) indicated that better performance stability was achieved by using silver than using platinum. Wu (1967) showed silver produces lower residual current than platinum in oxygen concentration measurement.

The pH dependence of oxygen reduction at a platinum cathode was first shown by Laitinen and Kolthoff (1941). Their current-voltage curves indicate the reaction rate is quite independent of pH (within the tested range of 3 to 12) as long as the potential (vs. AgCl) is above -0.5 v, but varies greatly with pH as voltage becomes more negative. Unfortunately, they did not state the oxidation condition of the platinum electrode. It was made clearer by Sawyer and Day (1963) that oxygen reduction at oxidized electrodes occurs by a pH-dependent mechanism, whereas at reduced electrodes in acidic solutions oxygen is reduced by a pH-independent mechanism.

Since platinum electrodes with different oxidized conditions may perform differently in the soil oxygen diffusion rate (O.D.R.) measurement, Black and Buchanan (1966) determined the current-voltage (i-v) curve at pH 3.6 and 6.2. They found the i-v curves to vary with pH using oxidized electrodes but not with reduced and aged-oxidized electrodes. However, Black and West (1969) demonstrated the pH dependence of i-v curves in acidic soil, and attributed it to the reduction of the carboxylic acid group of humic acid to the hydroxyl group at its solid state. The proposal is based on the fact that the i-v curve differs when the electrode is in a humic acid-water slurry from what it is in the supernatant liquid from the slurry. A similar curve was obtained when the electrode was in the supernatant liquid from a carboxylic cation resin. The current was independent of pH at an applied voltage of -0.4 v (vs. S.C.E.). It is hard to evaluate their work because of their failure to mention the electrode conditions.

III. THEORETICAL ANALYSIS

In a polarographic determination of oxygen, the diffusion of oxygen to a metal wire anode follows Fick's second law in cylindrical coordinates. In an isotropical medium the law states

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial r^2} + \frac{1}{r}\frac{\partial C}{\partial r} + \frac{1}{r^2}\frac{\partial^2 C}{\partial \theta^2} + \frac{\partial^2 C}{\partial Z^2}\right), \tag{1}$$

where C is the concentration of oxygen at the point $p(r,\theta,z)$ and time t, and D is the diffusion coefficient of oxygen in the medium surrounding the electrode. By assuming azimuthal symmetry of the concentration and if the exposed part of the wire is long, equation (1) reduces to

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial r^2} + \frac{1}{r}\frac{\partial C}{\partial r}\right). \tag{2}$$

At steady state it becomes

$$\frac{d^2 C}{dr^2} + \frac{1}{r}\frac{dC}{dr} = 0. \tag{3}$$

The general solution of (3) is

$$C = A + B \ln r,$$

where A and B are constants. Assigning the boundary conditions

$$C = C_1 \quad \text{at} \quad r = a \text{ (radius of metal wire)}$$

$$C = C_2 \quad \text{at} \quad r = b,\ a \leq r \leq b,$$

the specific solution becomes

$$C = C_1 - \frac{(C_1 - C_2) \ln ar}{\ln(a/b)} \quad .$$

Differentiating with respect to r gives

$$\frac{dC}{dr} = \frac{C_2 - C_1}{r \ln(b/a)} \ . \tag{4}$$

At time $t > 0$, C_1, the concentration at the electrode surface, is much smaller than C_2, the oxygen concentration at $(b - a)$ from the electrode surface. The flux written as $f = D\ dC/dr$ at the electrode surface is then

$$f_{r = a} = \frac{D\ C_2}{a \ln(b/a)}, \ t > 0 \ . \tag{5}$$

The flux is also related to the measured current by

$$I = n\ F\ A\ f, \tag{6}$$

where I is the current in amperes, n is the number of electrons used for reducing one molecule of oxygen, F is the Faraday constant, A is the area of electrode in cm^2 and the flux is in number of moles of oxygen transferred per second per cm^2. Substituting (5) into (6) gives

$$I = \frac{n\ F\ A\ D\ C_2}{a \ln(b/a)} \ . \tag{7}$$

If the diffusion coefficients of a set of media are all the same, and b is adequately chosen such that when an apparent steady-state[2] is reached before reading the current, then the current passing through an electrode of fixed size is a function of oxygen concentration C_2 only. Now let

$$C_0 = C_2 + \epsilon$$

where C_0 is the initial uniform concentration and ϵ is any positive value. The value of ϵ can be made as small as we want if we choose b sufficiently large. A precise treatment can be shown by relating it with equation (11). If b is adequately chosen so that ϵ is negligible, then equation (7) becomes

$$I = \frac{n\ F\ A\ D\ C_0}{a\ \ln(b/a)} \tag{8}$$

or

$$I = k\ C_0\ , \tag{8a}$$

where k is a constant and equivalent to the right-hand side of equation (8) except C_0. Equation (8a) allows us to measure the oxygen concentration of a set of samples of identical diffusion coefficients provided one of the sample's oxygen concentrations is known.

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[2] At $t = \infty$, the solution of equation (2), $C = C_2 \int_0^z y^{-1} e^{-y^2} dy$ where $z = \frac{r}{2\sqrt{D\ t}}$, goes to zero. This implies a real steady-state can never be reached. An apparent steady-state can, however, be arbitrarily chosen from the current-time curve where the slope is small without essentially losing validity of the steady-state assumption.

The accuracy of the measurement of oxygen concentration using a metal wire electrode depends on how close these assumptions are followed. Difficulties may be encountered when the foregoing theory is applied to measure soil oxygen concentration. For convenience the assumptions of equation (8) are iterated:

(i) The diffusion coefficient is the same everywhere in the vicinity of the electrode.

(ii) The diffusion is with azimuthal symmetry.

(iii) The exposed part of the electrode is long.

(iv) An apparent steady state must be reached before recording the current.

(v) The value of b is chosen sufficiently large so that the difference between C_0 and C_2 is negligible.

(vi) The diffusion coefficient of all media of interest must be identical. This includes samples of known oxygen concentrations. For easy preparation of the latter, an aqueous salt solution is preferable.

Assumption (i) can be satisfied if the medium of interest is isotropical, e.g., a liquid or a suspension. Soil is hardly isotropical and particularly not as is seen by a thin wire electrode. When (i) is satisfied, (ii) will be satisfied automatically for a wire electrode. Assumption (iii) requires a relatively long wire with respect to its radius. For the assumptions (iv) and (v), the value of b depends on the time chosen to reach a steady-state. A longer time gives a better approach to a steady-state, but requires a larger b. A detailed account on these two parameters will be discussed in the next section. Assumption (vi) is as difficult to fulfill as (i) in the case of soil.

It is obvious now that the difficulty in determining soil oxygen concentration with a metal wire electrode arises primarily from the heterogeneity of soil to satisfy assumption (i) and (vi). A promising solution to the problem is to coat the electrode with a layer of porous material. If the thickness of the coating can be made equal to the parameter b required to satisfy equation (8) and if the coatings can be made so reproducibly porous that their diffusion coefficients are identical, then assumptions (i) and (vi) are satisfied. A minor deviation to satisfy assumptions (i) through (iv) may cause equation (8a) to be non-linear and to not intercept the origin in a current-concentration plot. The resulting errors in estimating the oxygen concentration may be corrected empirically. A common way to do this is to make a standard current-oxygen concentration curve and determine the oxygen concentration by interpolation.

The following procedure could be used in the measurement of oxygen concentration. Let the coated electrode first equilibrate in the sample, which may either be an aqueous solution or a soil, then apply a negative current to the electrode of such a duration that the concentration gradient that is built up is essentially only within the coating.

At the end of this time a current reading is taken. A set of solutions of known oxygen concentrations may be used to plot the current-concentration relation. Oxygen concentrations of the unknowns can be found from the plotted curve of standard solutions.

IV. THE POROUS COATING

From the theoretical consideration, the porous coating on a thin wire electrode is expected to satisfy the following requirements:

(1) The coating must be lyophilic and of adequate porosity.

(2) It must be sufficiently thick.

(3) It must be reasonably strong and rigid.

The porosity of the coating should be such that the oxygen molecules as well as water and the principle charge-carrying ions can move freely through and within the coating. This can be determined experimentally by (i) the time required to establish oxygen concentration equilibrium between the coating and the outside medium, and (ii) the electrical conductance of the coating in a salt solution. The coating thickness must be greater than (b - a) so that the requirement set by equation (8) is satisfied. Details will follow. The coating must also be able to maintain its rigidity. No significant deformation should occur when the electrode is inserted into a soil. Durability is also required for repeated usage of an electrode.

DETERMINATION OF THE THICKNESS OF COATING

For simplicity, adequate thickness can be estimated by use of the linear diffusion law given by Ficks. In essence, any thickness greater than the required value of (b - a) is satisfactory. For a thin coating, the linear diffusion law approximates well and will give a slightly greater value than is actually needed. Within a uniformly porous coating, the diffusion coefficient of oxygen may be considered constant, then it follows

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad ,$$

where C is the oxygen concentration at a distance x from the electrode surface at time t, D is the diffusion coefficient. A solution of the equation is

$$C = a \int e^{-z^2} dz, \tag{9}$$

where

$$z = \frac{x}{2\sqrt{D\ t}} \quad , \tag{10}$$

and a is a constant determined by boundary conditions. At the initial and boundary conditions,

$$C = C_o \text{ (initial concentration) when } t = 0$$

$$C = 0 \quad \text{at} \quad x = 0 \qquad \text{when } t > 0 \ ,$$

equation (9) becomes

$$\frac{C}{C_o} = \frac{2}{\sqrt{\pi}} \int_o^z e^{-y^2} dy \ . \tag{11}$$

The right-hand side is called the error function and its values are tabulated versus z in many books, e.g., Kolthoff and Lingane (1952, page 23).

If x is taken as the thickness of the coating, then C is the concentration at the outer boundary of the coating. It is desirable to have C as close to C_0 as possible so the oxygen gradient is built up essentially only within the coating at time t during which the current is recorded. Under this condition, the diffusion coefficient D in equation (10) is determined by the coating only. This satisfies the requirement of constant D for equation (8).

From the assigned value of C/C_0, a corresponding value of z can be found. If the diffusion coefficient in the coating is known and t is adequately chosen, then x, the thickness of the coating, can be calculated from equation (10). Here t is the time required to approach a steady-state. A longer time gives a better approach but requires a thicker coating. Therefore t is chosen at a value at which the thickness of the coating reaches its upper optimum limit. On the other hand, a thin coating is preferred, because a thick coating requires a longer time, prior to $t = 0$, to equilibrate the oxygen concentration inside and outside the coating and at the same time allow the surrounding medium to recover to its original oxygen concentration. In addition, a thick electrode, in which the oxygen concentration is to be measured, tends to disturb more of the soil than a thin electrode and is not desirable.

ESTIMATION OF THE DIFFUSION COEFFICIENT IN THE COATING

In order to find z by equation (10), D must be known. Estimation of D in the coating is possible by applying equation (8). Let I_1 and I_2 denote the currents measured by using coated and uncoated electrodes, respectively. If the measurements are made in one solution and the electrodes have the same exposed areas, then by equation (8) we have

$$I_1 = \frac{n\ F\ A\ D_1\ C_0}{a\ \ln(b_1/a)} \quad \text{coated}$$

$$I_2 = \frac{n\ F\ A\ D_2\ C_0}{a\ \ln(b_2/a)} \quad \text{uncoated,}$$

where D_1 is the diffusion coefficient in the coating and D_2 is the diffusion coefficient in the solution. Usually D_1 is smaller than D_2 due to the torturosity of the diffusion path in the coating material. Hence b_2 is usually greater than b_1, when both satisfy equation (8) to the same extent or produce the same value of ϵ, as can be seen from equation (10). In fact any increase in the thickness of the coating beyond b_1 gives a deviation of the estimated concentration insignificantly small and within tolerance of the instrument. The value of b_1, therefore, need not be as large as b_2. Let us simply imagine the outer solution to be an additional coat and make the thickness of the entire coating equal $(b_2 - a)$. Dividing I_1 by I_2 gives

$$\frac{I_1}{I_2} = \frac{D_1}{D_2}\ , \text{ or } \quad D_2 = \frac{D_1 I_2}{I_1}\ . \tag{12}$$

Let D_1 be the diffusion coefficient of oxygen in water which is known, then D_2 can be calculated from the two current readings.

A STANDARDIZATION PROCESS

It is difficult to make the collodion coatings reproducibly porous so that the diffusion coefficients of oxygen in the coatings are all identical. In addition, the porosity of a coating may change with time, and so does the "reactive" surface area of the electrode. If these changes occur the current measured will be influenced according to equation (8).

A simple but effective way to minimize these variations is to use the same electrode and take a current reading from a solution of known oxygen concentration (air saturated KCl solution is most convenient) after the measurement of an unknown.

For the convenience of discussion, we define: (1) standardized current as the ratio of the current reading of the unknown sample to that of air saturated 0.02 N KCl (the two measurements should be made consecutively at the same temperature and atmospheric pressure using a single electrode); (2) oxygen saturation as the ratio of quantity of oxygen present in a solution to the greatest amount possible at the same temperature and pressure. Complete saturation of the solution is designated by 100% oxygen saturation and that equilibrated with air as 20 (air has 20% oxygen by volume).

Denoting I_x and C_x the current and concentration, respectively, of the unknown, and I_{air} and C_{air} that of the air-saturated solution and substituting these values into equation (8a) yields

$$\frac{I_x}{I_{air}} = \frac{C_x}{C_{air}} \qquad (13)$$

The left-hand side of (13) is the standardized current of the unknown. Since C_{air} is a constant at a specific temperature and pressure, standardized current is, therefore, a function of the concentration of the unknown only. The dependence of the current on the surface area of the electrode and diffusion coefficient of oxygen in the coating is eliminated.

It might be better to express oxygen concentration in a soil in terms of oxygen saturation. This expression describes both the oxygen concentration in soil air and soil solution at electrode surface provided they are in equilibrium.

The standardized current and the oxygen saturation are independent of temperature and atmospheric pressure at which measurements are made; hence, a current vs. concentration curve expressed in terms of these two parameters can be used as a standard at all temperatures and pressures.

V. THE OXYGEN CONCENTRATION METER

Applying the foregoing principles, an instrument was constructed for measuring soil oxygen concentration. A silver wire is used as the cathode and silver-silver chloride in saturated KCl solution as the anode. After a short duration of circuit closure, a portion of transient current is integrated and amplified. The output signal of the integrated current is read as voltage which relates directly with oxygen concentration. Ten electrodes can be used at a time. Block and wiring diagrams are shown in Figure 1, and the wiring diagram and description of the panel are in Appendix A.

The main parts of the system are discussed separately. For added convenience, the meter is also wired for taking oxygen diffusion rate measurements.

THE ELECTRODE SYSTEM

Although platinum has been commonly used as the cathode in polarographic measurement of dissolved oxygen, the requirement of platinum oxide at electrode surface complicates the oxygen reduction mechanism (Lingane, 1961). On the other hand, the oxygen reduction mechanism is independent of the

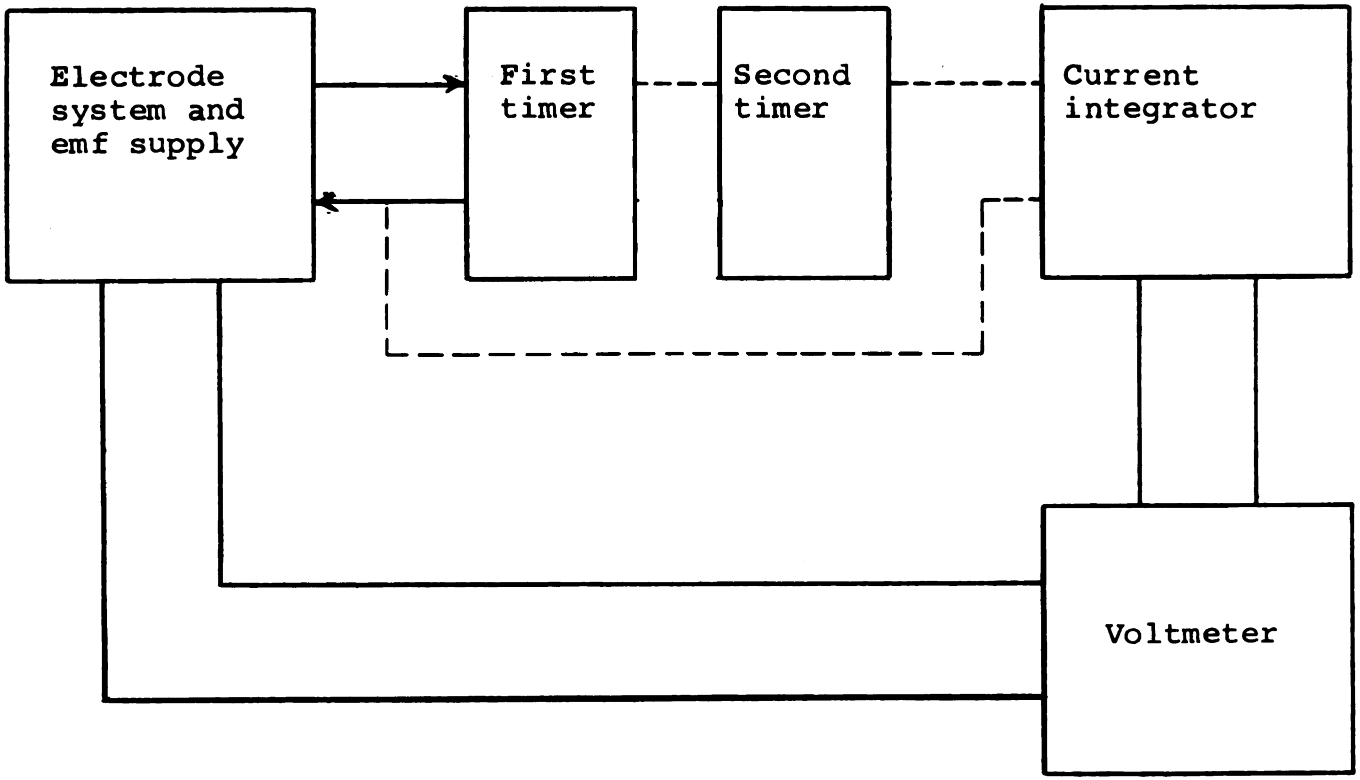

Figure 1. Block diagram of the oxygen concentration meter. Current first passes through the solid arrowed line to establish an apparent steady-state and then through the second timer to the integrator for recording.

previous history of oxidation at silver and gold surfaces (Sawyer and Interrante, 1961). By using a silver instead of platinum electrode in oxygen concentration measurement, better stability (Mancy et al., 1961) and lower residual current (Wu, 1967) were achieved. For these reasons, silver is chosen as the cathode material.

The cell consists of a rectangular plastic box containing a loosely folded silver foil[3] in a saturated KCl solution with KCl crystals. The silver sheet is plated with AgCl. The box connects to a fritted filter candle through tygon tubing. The fritted section has a length of 2 cm and a diameter of 1.2 cm. To assure good electrical continuity with the soil sample, the bottom of the candle must also be porous. The fritted part is impregnated with 1.5% agar in saturated KCl. This slows down the mass flow rate of the saturated KCl solution into the sample without appreciable impairment to the conductance of the system.

A 6 cm long 22 gauge silver wire is used to construct the electrode. The wire tip is first heated until one end is just rounded without protrusion in diameter. This can be accomplished by heating the wire near the bottom of a small gas flame. The tip is further heated so that the 1 cm end section becomes dull. This provides a better grip of the coatings to the electrode. The rounded tip is then coated

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[3] It is the same one used in the commercial oxygen diffusion maters made in Dicks Machine Shop, Lansing, Mich.

with tygon paint (black, TP-21, U. S. Stoneware, Akron, Ohio 44309) to a length of 1 to 2 mm by withdrawing the wire slowly from the paint so that the coating is thin and uniform. It was repeated twice; allowing for drying between coats. The other end of the wire is soldered to a plastic covered 22 gauge stranded copper wire. If the sites to be measured are more than 5 cm deep, the wire is first soldered to a plastic covered jumper wire then to a stranded wire. The exposed portion of the wire including the soldered connection is painted with tygon but a 4 ± 0.5 mm exposure is left at the end. The soldered part is wrapped with electric tape and two additional coatings of paint are applied. If the electrodes are not to be used fairly soon, it is suggested the electrodes be stored at this stage rather than a later stage.

The collodion solution is prepared by mixing 10 parts of collodion (Mallinckrodt, U.S.P.) with 1 part (by weight) of glycerol. Since the collodion solution is extremely volatile, the following provides a quick way of preparation of the mixture without excessive evaporation. 15 ± 5 g of collodion is poured into a tared narrow-necked 50 ml bottle, stoppered and weighed on a single-pan balance. While keeping the bottle on the balance, the required amount of glycerol is added with a medicine dropper. The contents in the bottle are mixed well in a reciprocating shaker. To achieve a better reproducibility of coating thickness and porosity, the mixture is preferably prepared just prior to the application of the coating.

Before applying collodion coating, the tygon-coated wire is washed by rubbing it between gloved fingers with floride-free toothpaste. Cleaning was stopped before the silver surface becomes shiny again. The wire is rinsed thoroughly in tap water and then placed in distilled water. After all electrodes are cleaned, they are dried with tissue paper and air dried for a few minutes. To coat the electrodes, they are dipped directly into the bottle of collodion mixture, then air dried for 5 seconds. While drying the electrodes are held horizontally and kept turning. They are held only by the plastic covered copper wire, not the silver part (which is an excellent heat conductor) to avoid evaporation of the solvent from inside the coating. Electrodes with visible bubbles within the coating should be discarded. The coating process is repeated 8 times, then the electrodes are air dried for 60 min. The electrodes are stored in a 250 ml flask half-filled with 0.02 N KCl. It is important that the coated electrode not be taken out of the KCl solution and exposed to air for more than a few seconds. Longer exposure may cause sufficient drying to ruin the coating. If longer exposure is desired, such as in the case of checking the thickness of the coating, the electrode should be dipped in 1:1 glycerol-water solution before exposure. The collodion mixture must be kept stoppered to avoid evaporation and should be swirled well, which produces less foam than shaking, before coating each electrode. A new electrode usually has a high resistance which can be lowered by passing a current at -1.2 v (vs. AgCl) for 15 minutes. A good electrode should give a resistance of less than 4 kilo-ohms between the AgCl and the electrode, while in 0.02 N KCl.

THE TIMING RELAYS

Two identical time-delay relays[4] are used in series. The activation of the first relay is simultaneously accompanied by a closing of the circuit of the electrode system. At the end of 0.4 second, the first relay activates the second relay which sends the current to the integrator for 0.1 second.

THE INTEGRATOR

The transient current flowing through the electrode is registered by the Keithley[5] model 301 solid state electrometer operational amplifier. The amplifier integrates the input current I and yields an output voltage V as given by

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[4] Intermatic model SS10223B-1, International Register Company, 4728 W. Montrose Ave., Chicago, Ill. 60641. The model is a surface mount type and has an operating range of 0.05 to 0.5 second.

[5] Keithley Instruments, Inc., 28775 Aurora Road, Cleveland, Ohio 44139.

$$V = -\frac{1}{C_f} \int I \, dt \; . \qquad (14)$$

The degree of amplification is determined by the feedback capacitor C_f.

At steady state,[6] I is independent of t, then

$$V = -\frac{I}{C_f} \Delta t \; . \qquad (15)$$

If Δt, the duration of time in which the current is integrated, is invariant, and the same feedback capacitor is used in all measurements, then the measured voltage V is directly proportional to the input current I. Applying equation (15) to (13) yields

$$\frac{V_x}{V_{air}} = \frac{C_x}{C_{air}} = \left(\frac{I_x}{I_{air}}\right) , \qquad (16)$$

where V_x is the voltage measured from the unknown and V_{air} is the voltage measured from the air saturated solution. The voltage ratio is, therefore, the standardized current.

THE VOLTMETER

A 20 milliampere ammeter is used to construct the voltmeter. It gives a full-scale reading of 1.0 v, 0.5 v and

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[6] If the steady-state is not obtained but Δt is small, the current-time curve within Δt can be approximated by a straight line. The average I within Δt is then simply the current at $t + \frac{\Delta t}{2}$. We can substitute this average I for I in equation (14) and also obtain equation (15).

0.25 v for measuring the output voltage from the integrator. The meter serves also as the indicator of the O.D.R. current, the emf of the electrode system, and for checking the voltages of the batteries which power the integrator and timers.

VI. RESULTS AND DISCUSSION

Bare electrodes were used in the early stage of this study to measure oxygen concentrations in bentonite suspensions and dilute potassium chloride solutions. Highly reproducible current readings were achieved under carefully controlled surface area and surface conditions of the electrodes. It was found effective to rub electrodes with toothpaste in providing uniform surface conditions among electrodes. Measured current-oxygen concentration relationship agreed well with that given by Brandt (1963) and Wu (1967). However, when measurements were made in sand and silt, readings became erratic and were usually lower than that measured in pure solution of the same oxygen concentration. Theoretical analysis of the problem, as discussed in section III, pointed out that oxygen concentration is proportional to current only when the diffusion coefficients of oxygen in the sample media are constant. This constancy may not be obtained in soil due to its diverse combination of solid, liquid and gaseous phases. Coating the electrode with a porous medium was then proposed and a search for such porous medium was conducted. It was found that electrode coated with 10:1 collodion-glycerol mixture provided a good porous coating. The coating is easy to prepare and adheres to the electrode very well and has sufficient strength and rigidity. Experiments were then conducted to test the adequacy of the coating thickness as well as the factors that may affect the oxygen concentration measurement.

In measuring oxygen concentrations, the electrodes and the salt bridge were inserted into the sample 1 cm above the site to be measured; while in aqueous solution, the electrodes were inserted directly into the final positions. An emf of -0.65 v was applied to the electrodes for five minutes. The electrodes were then inserted 1 cm deeper and after a 5 minute wait, to let the oxygen concentration in the sample equilibrate with that in the coatings, the circuit was closed and current readings were taken. A detailed procedure is shown in Appendix B.

THE COLLODION COATING

Calculation of coating thickness, by using equation (11), requires the knowledge of (i) the concentration ratio C/C_0, where C is the oxygen concentration at the outer boundary of the coating and C_0 is the initial oxygen concentration, (ii) the diffusion coefficient of oxygen in the coating, and (iii) the time required to reach an apparent steady-state. The choice of the C/C_0 in (i) determines the accuracy of the instrument. For the second parameter, a value close to the upper limit will minimize the possibility of underestimating the coating thickness. The third has little effect on the accuracy of the measurement because by using standardized current the errors will cancel out. However, it is related to the sensitivity of the measurement as will be seen later.

The concentration ratio

The best choice of the concentration ratio should give a deviation similar to the component of the instrument that gives the poorest reproducibility. The timers which have a reproducibility in the order of 1% most likely have the poorest reproducibility of all the components. The C/C_0 is, therefore, set at 0.995. This restricts a concentration drop of only 0.5% at the boundary provided the diffusion coefficients of oxygen in the soil and in the collodion are the same. Any moderate departure of the two diffusion coefficients may not change the concentration at the boundary very much and the ratio C/C_0 could be considered as unaltered. This ratio gives a z value of 2.0 by equation (11).

The diffusion coefficient in the coating

The oxygen diffusion coefficient in the collodion coating depends greatly on the porosity and age of the coating. The porosity can be controlled somewhat by the ratio of glycerine to collodion. More glycerine gives a higher porosity. By applying equation (12), the estimated diffusion coefficient ranged from 1/2 to 2/3 that of water. In water D has a value of 2.38×10^{-5} cm^2 sec^{-1} at 25°C (Millington, 1955), and 2/3 of it yields a D value of 1.6×10^{-5} cm^2 sec^{-1}.

The choice of the steady-state time

Since there is no real steady-state in the oxygen diffusion current the choice of steady-state is rather subjective. However, the current-time relationship, as revealed by the oscilloscope photo (Figure 2), indicated that the background current (the N_2 curve) decreases, relative to that of air saturated solution, with time. This means the sensitivity of the instrument can be improved by increasing the time. The improvement is greatest before 0.3 second and relatively slow thereafter. In order to have a useable sensitivity and have a thin coating the t in equation (10) was chosen as 0.45 second and the current was integrated between 0.4 and 0.5 second.

These values substituted into equation (10) yield a coating thickness of 0.107 mm, which is about 1/3 the radius of the silver wire. A test was made to show whether the calculated thickness is appropriate.

Testing the thickness of coating

A preliminary examination was made to compare the variability of measured oxygen concentration of a several

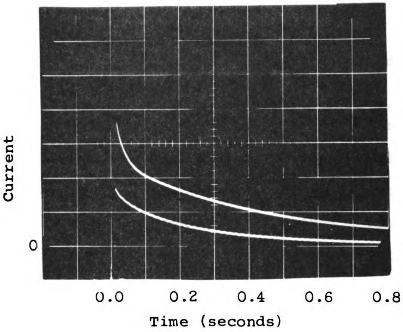

Figure 2. Oscilloscope photo showing current-time relationships after a -0.65 v emf was applied to a collodion coated silver electrode.

The upper curve was obtained from air-saturated 0.02 N KCl solution and the lower curve from N_2 saturated. The base line for both curves is the horizontal line just below the lower curve.

thicknesses of coating at different conditions. Current readings were taken in medium sand and silt samples in 0.02 N KCl at various moisture tensions. It seems evident, as shown by Table 1, that readings from thin coatings were affected more by the blocking effect of solid particles, moisture tension and consequently the presence of air than the thicker coatings, whereas the bare electrodes showed the highest variation.

The same electrodes were then tested by the variances (Table 2) at the most discriminating conditions, i.e., using the silt sample at 70 cm tension. In each of the five coating thickness readings were obtained from 2 electrodes of similar thickness with 11 repetitions. The estimate of the component of variance due to measurements is over 15 times as large as the component due to electrodes. This means that the variance of a single observation on an arbitrary electrode

$$\begin{aligned} s^2 &= s_M^2 + s_E^2 = 0.00147 + 0.0000881 \\ &= 0.00156 \end{aligned}$$

has much smaller error due to electrode construction than due to the error of measurement. This single observation gives a standard error ± 4% of the standardized current, or less than ± 1.5% of the oxygen saturation. The latter may drop to ± 0.3% when single measurements are made using 10 electrodes to determine the oxygen concentration in a soil.

Table 1. Comparison of the standardized currents from air saturated media as measured by electrodes of various coating thicknesses.

Electrode number	Coating thickness mm	Standardized current					0.02 N KCl only
		Medium sand in 0.02 N KCl			Silt in 0.02 N KCl		
		Saturation	40 cm tension	60 cm tension	Saturation	70 cm tension	
6-1	0	0.81	0.85	0.91	0.64	0.54	1.00
6-2	0	0.80	0.85	0.89	0.60	0.54	1.00
20-127	0.036	1.12	1.23	0.99	1.00	0.97	1.00
20-128	0.036	1.13	1.24	0.99	1.04	1.01	1.00
20-141	0.051	1.01	0.90	0.97	1.03	0.74	1.00
20-142	0.051	1.01	0.93	0.97	1.04	0.78	1.00
20-143	0.079	0.98	1.05	0.99	1.04	0.96	1.00
20-144	0.079	1.00	1.04	0.93	1.01	0.93	1.00
20-145	0.111	0.99	1.06	1.02	1.00	1.03	1.00
20-146	0.111	0.99	1.05	1.07	1.01	0.95	1.00

The medium sand contains 70% medium sand and 30% fine sand.
The silt contains 39% very fine sand and 61% silt.

Table 2. Analysis of variance for the standardized currents measured in a silt sample leached with air saturated 0.02 N KCl and equilibrated at 70 cm tension using electrodes of various coating thicknesses.

Source of variation	d.f.	M S	Expected Mean Square
Thickness	4	1.042	$\sigma_M^2 + 11\sigma_E^2 + 22K_T^2$
Electrode	5	0.00244	$\sigma_M^2 + 11\sigma_E^2$
Measurement	100	0.00147	σ_M^2

With m measurements per electrode and e electrodes the variance of the mean of any thickness is

$$s_{\bar{x}}^2 = \frac{s^2_M}{me} + \frac{s^2_E}{e}$$

and when m = 11 and e = 2

$$s_{\bar{x}}^2 = 0.000101.$$

Thus Tukey's critical value is

$$\text{HSD}_{0.05} = Q_{0.05}s_{\bar{x}} = (5.67)(0.0100)$$
$$= 0.0567$$

As shown by Table 3 the differences between the coated and the uncoated electrodes were significant at 5% level, but the differences between the coated electrodes were nonsignificant. In other words, coating thickness as thin as

Table 3. Differences of the standardized currents from electrodes of various coating thicknesses as measured in a silt sample leached with air-saturated 0.02 N KCl and equilibrated at 70 cm tension.

	Coating thickness	$\bar{x}_i$	$\bar{x}_i - \bar{x}_0$	$\bar{x}_i - \bar{x}_1$	$\bar{x}_i - \bar{x}_3$	$\bar{x}_i - \bar{x}_4$
x_2	0.051	1.0086	0.4937	0.0243	0.0055	0.0005
x_4	0.111	1.0081	0.4932	0.0238	0.0050	
x_3	0.079	1.0031	0.4882	0.0188		
x_1	0.036	0.9483	0.4694			
x_0	0	0.5149				

The differences above the dotted line exceed the critical value 0.0567 at 5% level for Tukey's test.

0.036 mm, which is only 1/3 that of calculated thickness, seemed satisfactory and an increase in the thickness gave little improvement in the consistency of the standardized currents. It should be noted, however, that the adequacy of the coating thickness depends on the diffusion coefficient in the testing sample. Media denser than this silt (which is quite dense) could increase the current differences between 0.036 mm and the thicker coatings. Therefore, the calculated thickness which provides a safety factor of over 3 with respect to the tested condition, may be reasonable. The adequacy of the coating thickness may also be revealed by the standard curves of various coating thicknesses.

The coating thickness and sensitivity

A standard current-oxygen concentration curve is required to convert standardized current into oxygen saturation. Figure 3 shows the curves made by using electrodes of various coating thicknesses. The curves indicate that oxygen concentration resolution decreased with increasing coating thickness but approach a limit at a thickness somewhere between 0.111 and 0.079 mm. This reveals that the standard curve is dependent on the coating thickness when it is insufficient; and it is independent of coating thickness when it is near the calculated thickness, i.e., 0.107 mm. This supports the calculated thickness as a good approximation.

The top curve in Figure 3 may be used as the standard curve for converting standardized current into oxygen saturation.

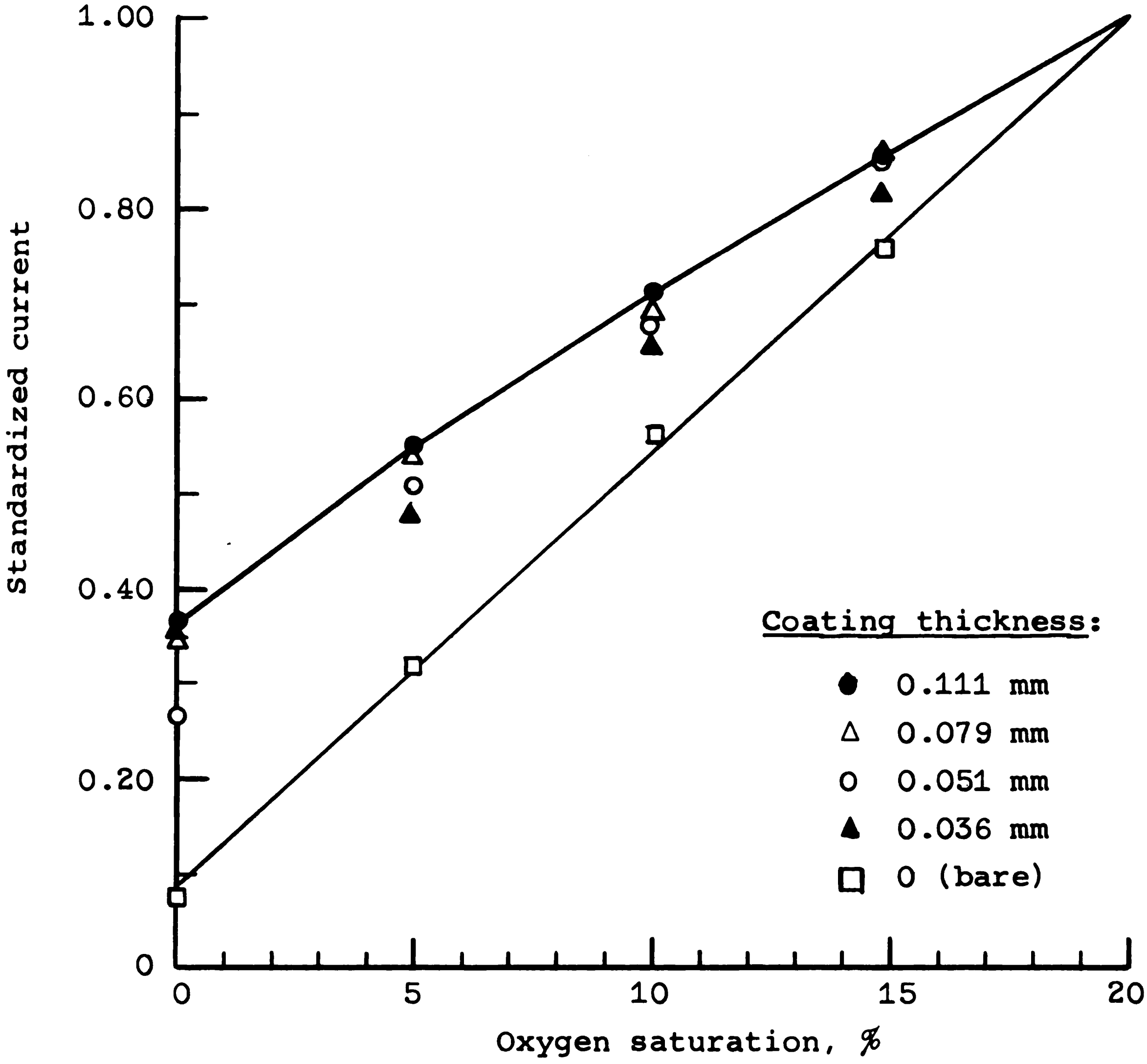

Figure 3. Standard curves obtained from electrodes of various coating thicknesses.

THE EFFECT OF APPLIED E.M.F.

A flat plateau in an ideal polarographic curve would indicate that the current is independent of the applied voltage in the vicinity of the chosen emf for measurement. Figure 4 shows the emf and current relationship of a collodion-coated electrode. The gentle slope between -0.6 and -0.8 volt indicated that the current depended only slightly on emf. An emf of -0.65 volt was chosen for oxygen concentration measurements.

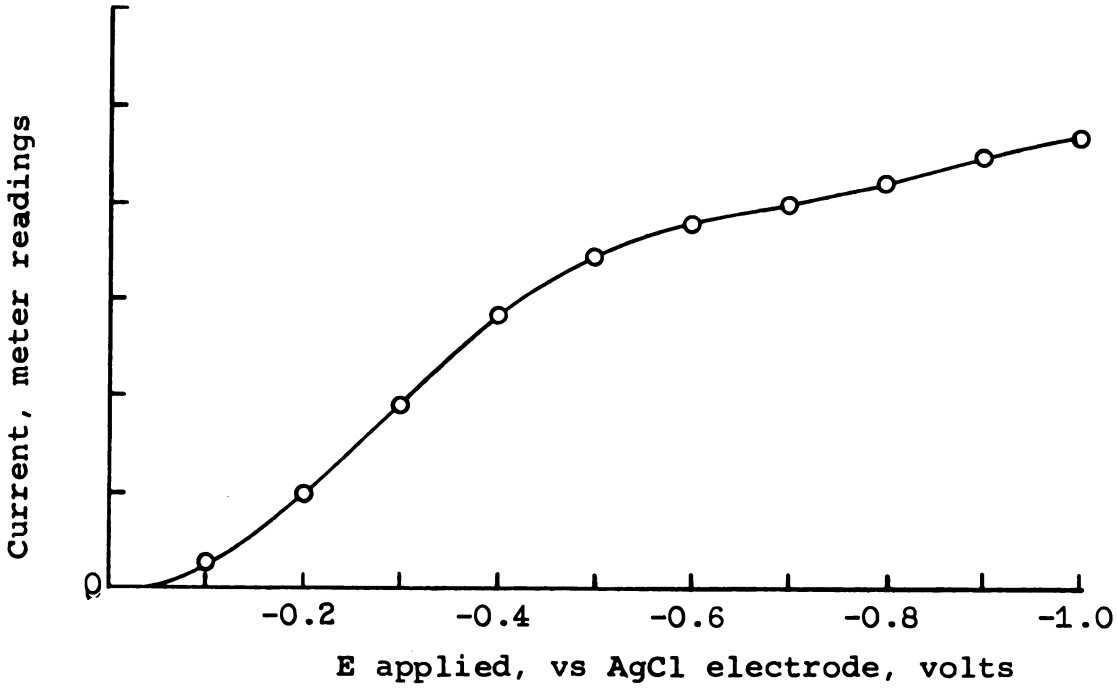

Figure 4. Oxygen diffusion current at various applied emf.

THE EFFECT OF SALT CONCENTRATION

The oxygen reduction current is conducted by ions in the solution of the sample. In soil, most of these ions are in the form of dissociated salt. The overall concentration of these ions should always be sufficient so that the current is limited by oxygen concentration only. It is necessary to find the lower limit of salt concentration at which the measured oxygen concentration is within acceptable precision. To specify this limit, currents were determined in air saturated solutions of various KCl concentrations.

Within a wide concentration range of 0.0015 to 0.05 N KCl, a ± 4% variation of standardized current was obtained (Figure 5). This corresponds to ± 1.5% of oxygen saturation. The current increased slowly with decreased salt concentration and reached a maximum at about 0.005 N KCl, then fell down slowly. An interesting phenomenon was that the maximum coincided with the current-resistance curve (Figure 6) where the resistance was controlled by an added variable resistor in series with the cell system. Both maxima had a total cell resistance of about 5 kilo-ohms. It was concluded then that the change of the standardized current with salt concentration accounted mainly for the resulting resistance effect. A possible explanation of the increased current with resistance is that the increased resistance may restrict, as expected by Ohm's law, the current flow in the

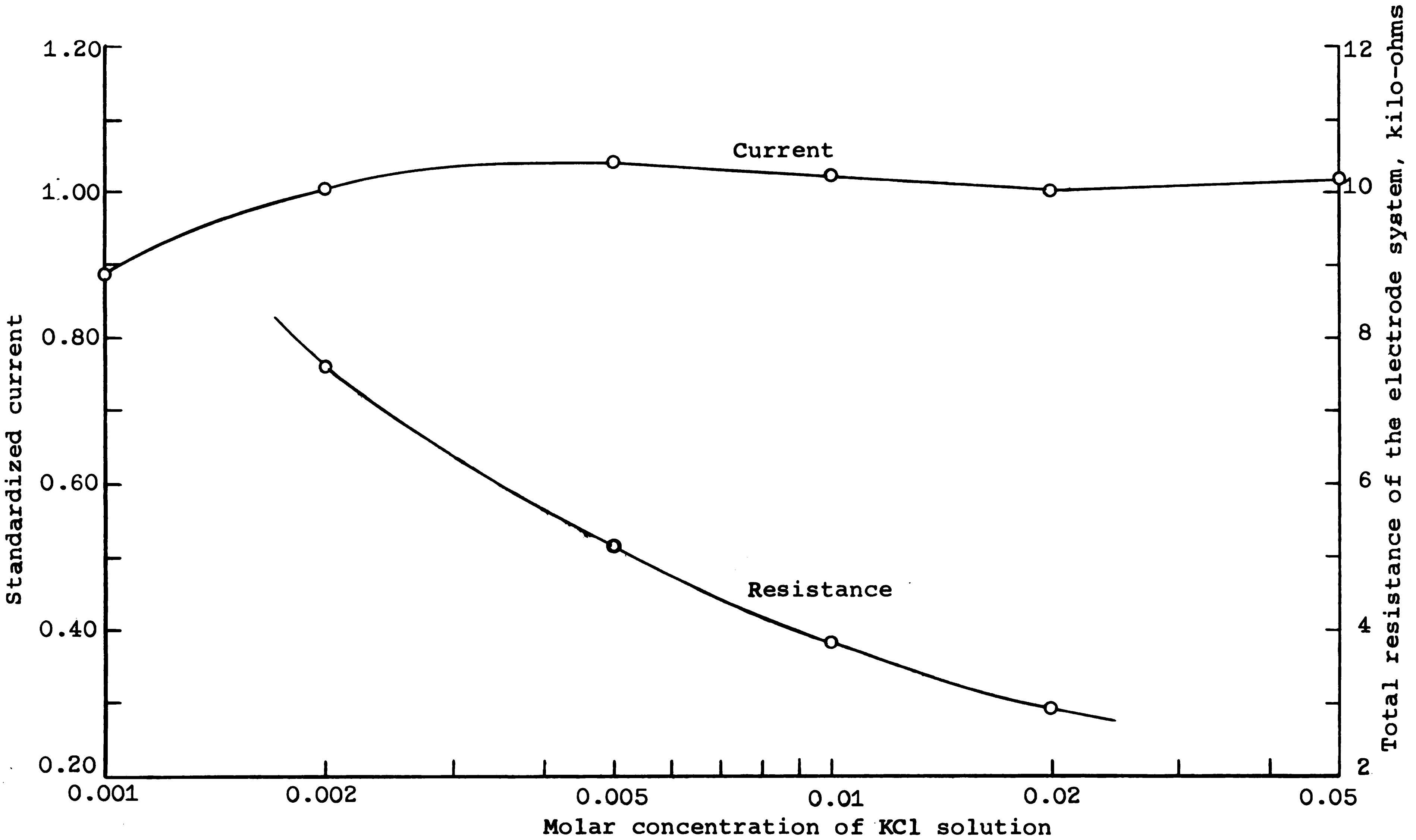

Figure 5. Oxygen diffusion currents measured in KCl solutions at air saturation.

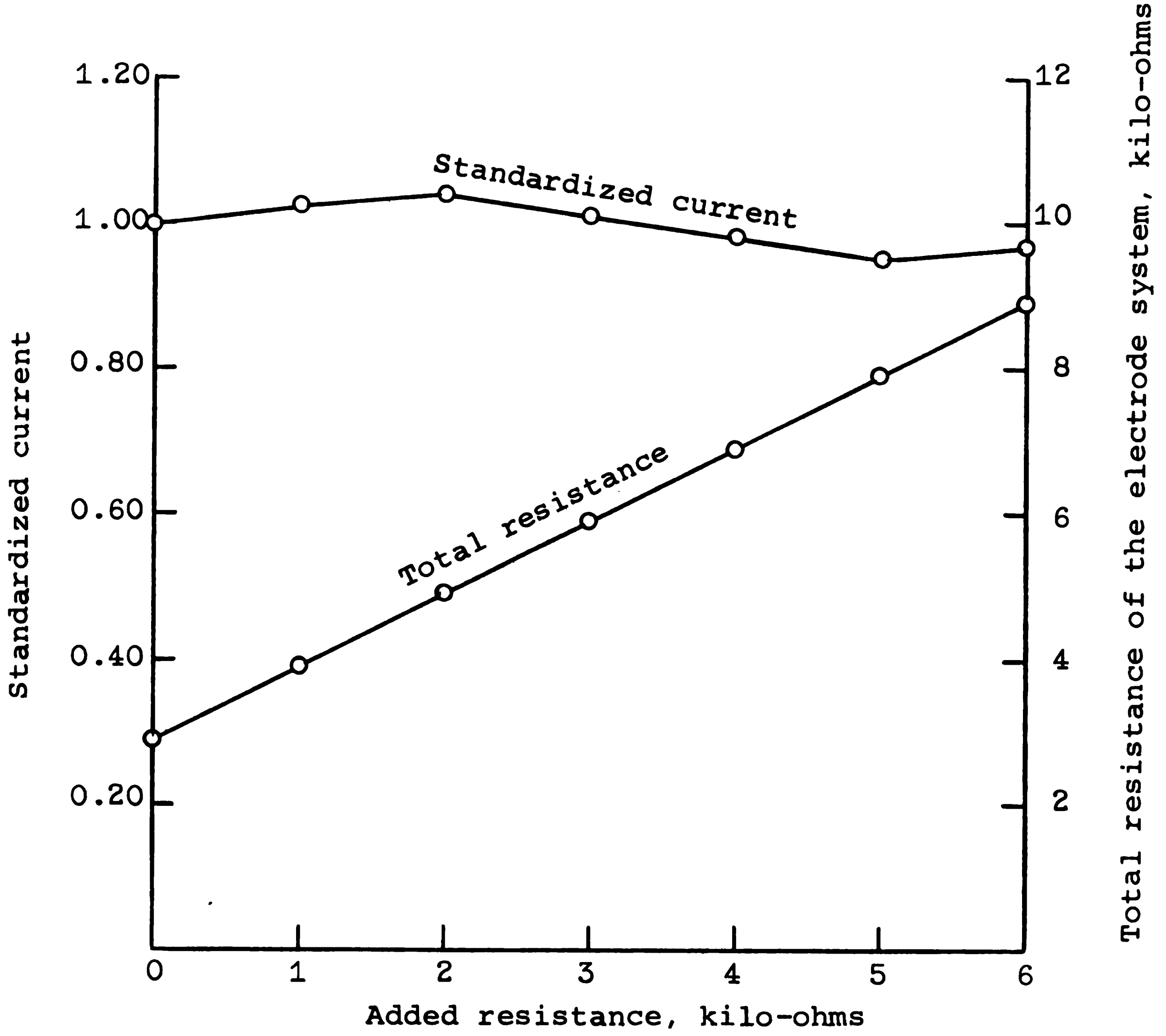

Figure 6. Oxygen diffusion currents measured at various added resistances.

very early stage of current flow where much higher current drain is required (see Figure 2). The formation of a concentration gradient may thus be slightly retarded even at later stages when the current is not limited by salt concentration. The gross oxygen concentration is, therefore, slightly higher than would be expected, and results in a corresponding higher current reading.

The coincidence of the two curves of Figure 5 and 6 suggests such deviation can be corrected, at least to some extent, by the following method. The system resistance of the unknown is measured following the current measurement. The resistance of the air saturated 0.02 N KCl system is then adjusted to the resistance of the preceding sample with a variable resistor in series before the reference current reading is taken. The ratio of the two readings gives a resistance-corrected standardized current. Since the standardized current dropped rapidly beyond 8 kilo-ohms in Figure 5 but did not show so in Figure 6, oxygen concentation measurement will thus be inaccurate in media with resistances higher than 8 kilo-ohms. The resistance can be conveniently measured by the Bouyoucos moisture meter.[7] Since error due to salt concentration accounts for less than 2% of oxygen saturation, the correction for resistance might not be necessary when

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[7] Model BN-2A, Industrial Instrument Inc. The portable unit produces an alternating current for resistance measurement and has a full-scale resistance of 10 kilo-ohms.

that error is acceptable; but such a resistance measurement is still strongly suggested especially when the sample's resistance is low.[8]

OXYGEN CONCENTRATION MEASUREMENTS IN FLOODED AND WET SOILS

The instrument should be useful in monitoring the oxygen concentrations in paddy soils or wet soils. In such situations oxygen depletion is likely to occur. To test the instrument, a number of flooded conditions were simulated in the laboratory and greenhouse in which oxygen concentrations were measured. Measurements were also made in the field when the soil was wet. The results are discussed as follows.

Two experiments were made in flooded soils. In the first experiment two pots were filled with air dried loam soil. One pot was watered with aerated tap water and the other was watered with non-aerated tap water. Oxygen concentrations were measured right after the watering. Six to 10 readings were taken from each pot. The average oxygen saturation of the soil irrigated with aerated tap water was 11.1 ± 1.3%[9] and that of the soil irrigated with non-aerated

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[8] For instance, the electrode itself may change its conductance due to excessive exposure to air.

[9] Standard error for the average value.

tap water was 2.2 ± 0.4%. Measurements were repeated two days later, after watering, and the average oxygen saturations of the soil irrigated with aerated and non-aerated tap water were 8.9 ± 1.5% and 2.0 ± 0.7%, respectively. The results indicated that non-aerated tap water has a very low oxygen concentration and irrigation with such water could be detected with the instrument.

In the other experiment, two soil samples of Sims sandy loam were taken from a rotation experiment at the Ferden Farm, near Chesaning, Michigan. Rotation 6 consisted of corn-sugar beet-barley-bean-wheat, whereas rotation 1 consisted of corn-sugar beet-barley-2 years of alfalfa brome. Rotation 1 showed a better long-term average physical condition than rotation 6. To assure soil homogeneity, so that consecutive concentrations could be comparable, soil was first air dried and passed through a 2 mm sieve. A plastic tray (27 cm x 19 cm x 6 cm deep) was half filled with air saturated 0.02 N KCl. Soil was poured slowly into the tray until the soil was 4.5 cm thick, but with the KCl solution constantly covering it. More KCl solution was added until it was 0.5 to 1 cm above the soil surface. The tray was covered with another tray but with a small gap for air exchange without excessive evaporation. The temperature was maintained at 25 ± 1°C. Aerated distilled water was added following measurement to replenish evaporation loss. The results are shown in Figure 7 where each point was the

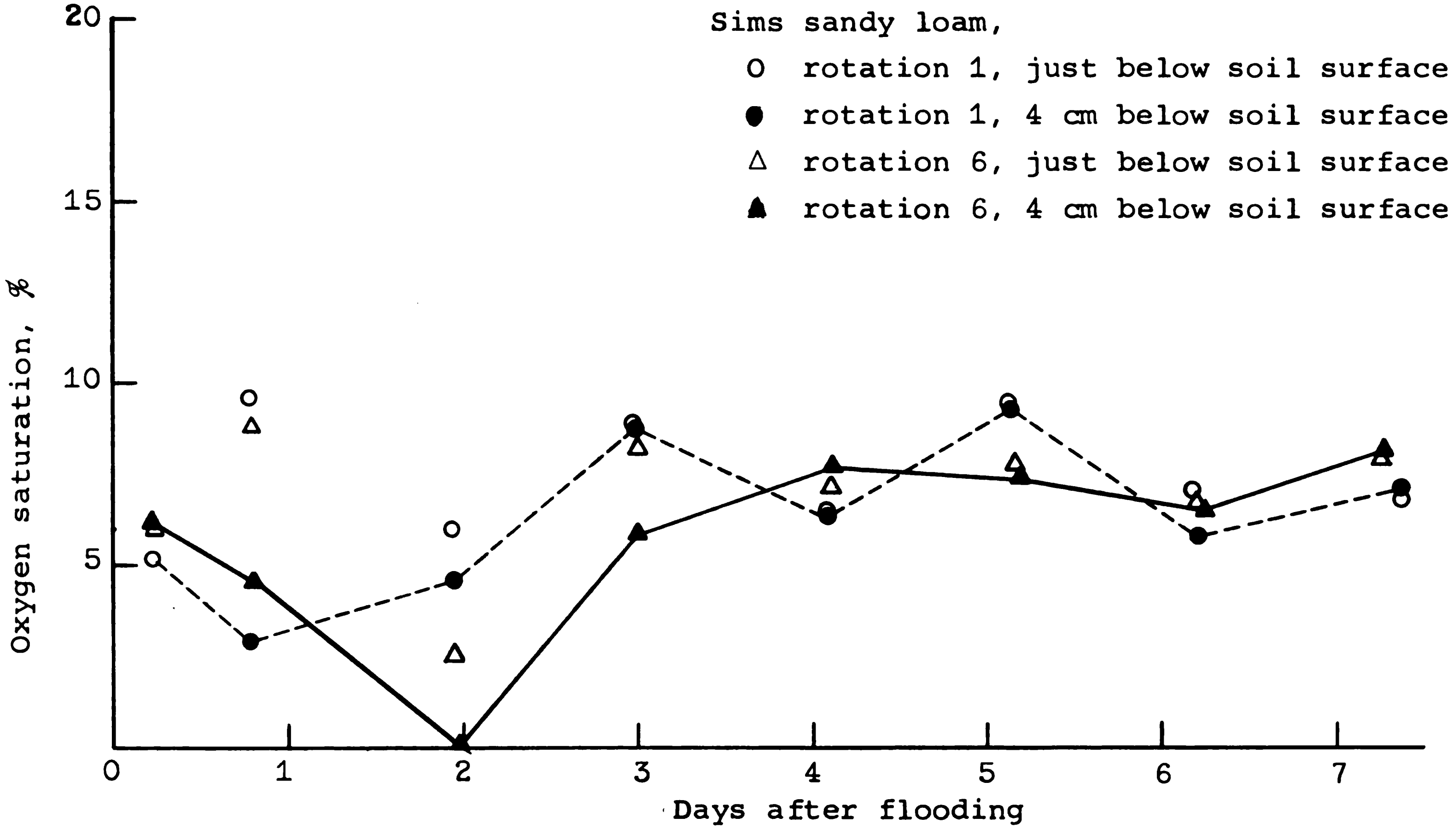

Figure 7. Oxygen concentration in sieved soils after being submerged under air-saturated 0.02 N KCl.

average of 8 electrode readings. It was interesting to note that oxygen concentration dropped to a minimum (0 to 3% oxygen saturation) after 1 to 2 days of flooding and then increased and remained quite constant (6 to 9%) after the third day. If the field response is similar, plants would most likely suffer from oxygen depletion between the first and second days after irrigation (or heavy rain) in poorly-drained soil.

Oxygen concentration measurements were also made in the University's Soils Farm. The soil is a Hillsdale sandy loam. The results are shown in Table 4. The data in columns 1 to 4 indicates that the oxygen concentrations in the bare soil were a little higher than that in the turf grass covered soil. Both soils showed very low oxygen concentrations. This was partly due to the low conductivity of the soil. The resistances between the Ag electrode and the reference cell were over 10 kilo-ohms. Such higher resistances were not correctable by the resistance compensation device of the meter. The measured oxygen concentrations were thus considerably lower than the actual oxygen concentrations. However, they do show the relative effect and the influence of the root respiration of the turf. To correct the high resistance of the soil, the same plots were later fertilized with ammonium nitrate prior to take measurements. The results are shown in columns 5 and 6. This time the turf-covered showed higher oxygen concentrations than the bare.

Table 4. Oxygen concentrations and Oxygen diffusion rates in the top soil (2-4 cm) at the University's Soils Farm.

	1	2	3	4	5	6	7		8	
Date	May 21		May 22		June 3, 1970					
Soil Temp.	26^{o}C		25^{o}C		19.5^{o}C					
Weather condition	Sunny on the day and the previous days				Sunny and cool on the day but rainy on the preceding days					
Crop cover	Bare	Turf	Bare	Turf	Bare	Turf	Bare		Turf	
Measurement	Oxygen saturation, %						O.D.R.			
	5.7	0	3.8	0	8.2	18.6	3.0	1.3	10.6	1.3
	3.1	0	4.3	0	5.6	14.9	0.6	2.4	5.6	1.7
	1.3	0	7.0	0	9.2	14.9	6.7	1.6	1.8	2.8
	5.3	0	6.9	0	9.0	14.6	3.3	0.5	6.8	1.9
	1.1	0	6.2	0	10.3	12.1	5.1	2.5	6.8	3.4
	1.2	0	6.8	0	5.9	15.9	0.4	5.4	1.5	0.9
	2.8	0	5.9	0	9.1	12.8	0.4	1.2	3.8	3.9
	4.2	0	3.1	0	13.1	17.2	1.8	0.9	1.6	8.8
	1.0	0	2.2	0	7.4	13.5	0.4	1.3	0.8	0.9
	---	---	5.0	0	12.8	13.6	2.1	4.4	0.9	---
Average	2.73	0	5.12	0	9.06	14.81	2.38	2.15	4.02	2.56
Standard deviation, s	1.86		1.71		2.52	2.00	2.18	1.59	3.31	2.48
Standard error, $s/\sqrt{n}$	0.62		0.54		0.80	0.63	0.69	0.50	1.05	0.83
Remark	Sprinkler irrigation				Same as (7)	Same as (8)	Heavy rain in the previous day and fertilized. Water standing at surface.		Heavy rain in the previous day, and fertilized and hose irrigated before measurement.	

The same trend was found for O.D.R's. The high oxygen concentration in the turf-covered soil may be due to the cool rainy weather in the preceding days, and the loose matrix at the soil surface and the incomplete watering prior to take measurements. The fallowed plot had water standing while the turf did not. The thin wire electrodes had no difficulty to be inserted into the saturated bare soil but did find difficulty at times (about 2 out of 10 electrodes) when inserting them into the densely rooted turf-covered soil. In the latter case, about 50% of the electrodes were with broken coatings after couple times of service but none in the former case. Readings from broken electrodes were excluded from Table 4.

VIII. SUMMARY AND CONCLUSIONS

An instrument that is capable of measuring oxygen concentration in soil at or near saturation has been designed, constructed and tested. It uses a collodion-coated, silver electrode less than 1 mm in diameter. With an electrode of this size good spatial resolution can be achieved without seriously disturbing the soil structure. The instrument measures an integrated current 0.4 second after closing the circuit. The reading is independent of oxygen diffusion coefficient of the soil. Drift due to change of surface character of electrode is minimized by taking a reading in air saturated 0.02 N KCl immediately following the unknown, both are at the same temperature. The ratio between the two currents, called standardized current, is a measure of the oxygen concentration of the soil. Oxygen concentration expressed in terms of oxygen saturation eliminates the requirement for temperature correction. The resistance of the cell system and soil influences the standardized current. The effect of resistance is corrected by putting a variable resistor in the system so the current reading in air saturated KCl solution can be measured at the same resistance as that of the preceding unknown. Oxygen concentration measurement in media with resistances between the Ag electrode and the reference cell higher than 8 kilo-ohms are not suggested because such high resistances are not correctable.

The instrument has been tested in saturated soils in the laboratory, greenhouse and field. It should be useful in measuring oxygen concentration in paddy soils and in other soils following irrigation or a heavy rainfall when oxygen depletion is likely to occur.

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APPENDICES

APPENDIX A

DESCRIPTION OF THE OPERATING CONTROLS AND TERMINALS OF THE OXYGEN CONCENTRATION METER

This appendix gives a brief description of all the panel controls on the oxygen concentration meter. The controls are listed by their reference numbers as it appears in both Figures 8 and 9.

1. Positive emf supply.
2. Negative emf supply.
3. Positive emf output to reference cell.
4. External power post for integrator, + 28.5 v.
5. External power post for integrator, common.
6. External power post for integrator, - 28.5 v.
7. External power post for timers, + 25.5 v.
8. External power post for timers, - 25.5 v.
9. Power switch for emf supply.
10. Power switch for the timers. "ON" uses internal batteries, "OFF" connects to external batteries.
11. Power switch for integrator. "ON" uses internal batteries, "OFF" connects to external batteries.
12. Timer, set at 0.4 second.
13. Timer, set at 0.1 second.

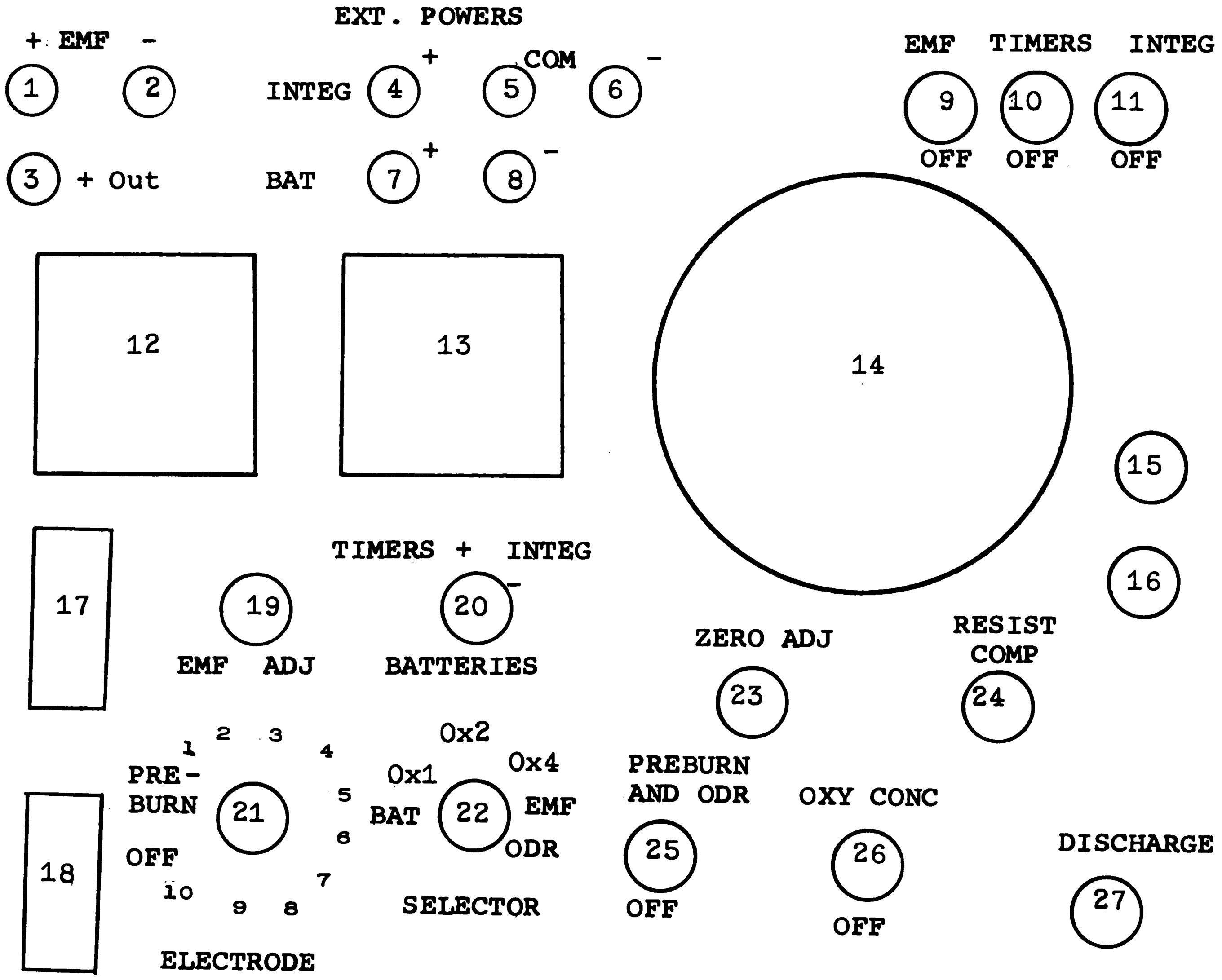

Figure 8. Pictorial diagram of the oxygen concentration meter.

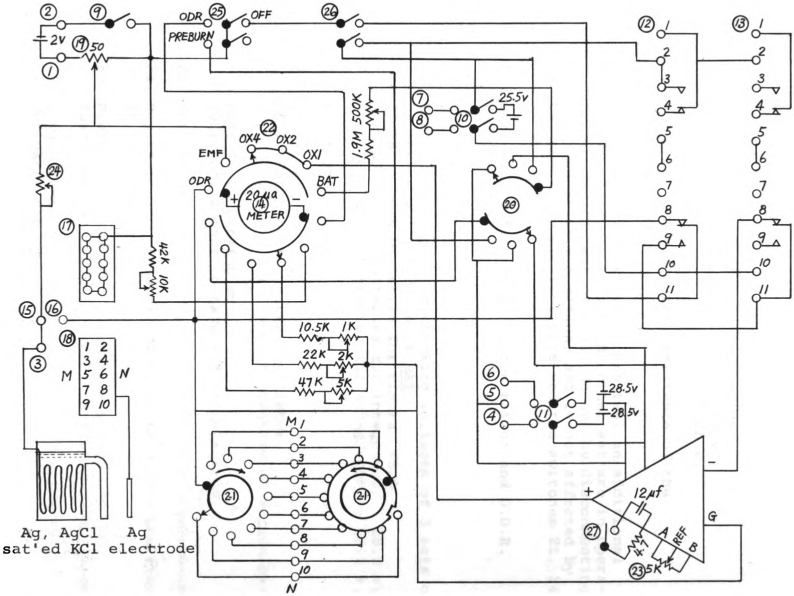

Figure 9. Wiring diagram of the oxygen concentration meter.

14. Meter provides following full-scale readings.

    emf: 1.0 v
    Batteries: 40 v
    ODR: 20 μA
    Oxygen concentration, Ox1 : 1 v
    Ox2 : 0.5 v
    Ox4 : 0.25 v.

15,16. Posts for measuring the resistance of the electrode systems.

17. -emf output to preburn (5 minutes) an additional set of electrodes while the other set are in operation. The current can only be cut by disconnecting the plug at this position, and is not affected by the operation of the timers and the switches 21, 24, 25 and 26.

18. -emf output for oxygen concentration and O.D.R. measurements.

19. emf adjustment.

20. Battery selector--for checking voltages of 3 sets of batteries while (22) is at BAT.
    TIMER: check batteries for timers, 25.5 v.
    + INTEG: check batteries for integrator, + 28.5 v.
    - INTEG: check batteries for integrator, - 28.5 v.

21. Electrode selector.

22. Selector--
    BAT: For checking battery voltages
    Ox1, Ox2, Ox4: For oxygen concentration determination.
    EMF: For checking emf.
    ODR: For measuring oxygen diffusion rate.

23. Zero adjustment for oxygen concentration measurement.

24. Resistance compensator--This switch adds a resistance in the cell system.

25. Preburn and ODR--For 5 minutes preburn and ODR measurements. Keep at "OFF" in all the other cases.

26. Oxygen concentration--Switch in "ON" position it activates the timers.

27. Discharge button--to discharge the feedback capacitor in the integrator and thus zeroes the meter.

APPENDIX B

OPERATING INSTRUCTIONS OF THE OXYGEN CONCENTRATION METER

The meter is designed for both oxygen concentration measurements and oxygen diffusion rate (O.D.R.) measurements. Collodion coated silver electrodes are used for the former and bare platinum electrodes are the latter.

Front panel operation controls are shown in Figure 8, and the corresponding components are shown in Figure 9.

IMPORTANT: To save batteries, switches 9, 10, and 11 must be kept at "OFF" when the meter is not in use.

I. The Measurement of Oxygen Concentration

Check batteries

1. Turn 10 and 11 "ON".
2. Turn 22 to BAT. The full-scale reading is 40 v.
3. Turn 20 to "TIMERS". The reading will be 25.5.v.

   Turn 26 on. Two clicks will be heard from the timers, and the voltage drop should be less than 3 v.
4. Turn 20 to "+ INTEG". The reading should be no less than 26 v. The same should be satisfied when 20 is turned to "- INTEG".
5. Check the position of the balls of the wet cell.

Operation

1. Turn 9 and 10 "ON", keep 11 at "OFF".
2. Set 12 at 0.4 second and 13 at 0.1 second.
3. Set 24 at counter-clockwise limit.
4. Set both 25 and 26 at "OFF".
5. Connecting electrodes to 18. Insert electrodes to the sample (1 cm above the place to be measured). Turn 21 to "PREBURN".
6. Adjust emf to 0.65 v by turning 22 to emf and adjust 19. The full-scale reading is 1v. Turn 22 to "Ox2" (or "Ox1").
7. Turn 25 to "PREBURN", keep the preburn on for 5 minutes, then turn it "OFF".
8. Insert electrodes 1 cm deeper, wait another 5 minutes to insure diffusive equilibrium. Repeat 6 while waiting.
9. Turn 11 "ON", zero the meter by adjusting 23 while pushing 27.
10. Turn 21 to "1".
11. Turn 26 "ON". After hearing two clocks from the timers, turn 26 "OFF".
12. Record the meter reading. The reading can be doubled or halved by turn 22 to "Ox4" or "Ox1", respectively.
13. Turn 21 to the next electrode. Repeat 11 through 13 until all the electrodes are measured.
14. While electrodes are still in the sample, measure the resistances of the electrode system through pole 15 and 16 with the Bouyoucos moisture meter.
15. Place the same electrodes in air saturated 0.02 N KCl. Force bubble the KCl solution well to insure air saturation.
16. Repeat steps 6 and 7. Wait another 5 minutes.

17. Turn <u>21</u> to "1".

18. Turn 17 to match the resistance in KCl solution to that in sample.

19. Repeat steps 11 and 12.

20. Turn <u>21</u> to the next electrode and repeat 18 through 20 until all electrodes are measured.

21. Return <u>24</u> to counter clockwise limit.

22. Divide the reading from 17 by the reading from 20 to calculate the standardized current.

23. Oxygen concentration (in terms of oxygen saturation) can be obtained from the top curve in Figure 3 by interpolation.

II. <u>The Measurement of Oxygen Diffusion Rate</u>

1. Turn <u>9</u>, <u>10</u>, <u>11</u>, <u>25</u> and <u>26</u> to <u>OFF</u>.

2. Turn <u>21</u> to <u>PREBURN</u> and <u>24</u> to counter-clockwise limit.

3. Insert the bare platinum microelectrodes into the soil and connect them to <u>18</u>.

4. Turn on <u>9</u>.

5. Turn <u>22</u> to <u>EMF</u> and adjust the emf to 0.65 v (1 v full scale) with knob <u>19</u>.

6. Turn <u>22</u> to <u>ODR</u>.

7. Turn <u>25</u> to <u>ODR</u> and wait 5 minutes.

8. Take ODR readings of individual electrodes by turning <u>21</u>.