DETERMINATION OF DISSOLVED OXYGEN CONCENTRATION IN SOIL WITH BARE SILVER WIRE ELECTRODES

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THESIS





ABSTRACT

DETERMINATION OF DISSOLVED OXYGEN CONCENTRATION IN SOIL WITH BARE SILVER WIRE ELECTRODES

by Tung-kai Wu

A modified microelectrode technique was developed to measure oxygen concentration in the soil solution within the root environment. The oxygen diffusion currents at a relatively short time (0.1 to 0.3 second) are measured by an electrometer operational amplifier. The apparatus reading can be converted to the oxygen concentration in the medium by applying linear diffusion theory.

Electrical resistance between the silver and reference electrodes up to 5 kiloohms has no effect on the concentration measurement using an applied voltage of -0.65 volt. When a high resistance was present in the soil, a standard curve was successfully used to calibrate the oxygen concentration.

The coefficient of variability of the ten electrode measurements in soil is about 13%, this is quite satisfactory for the determination of oxygen concentration in the heterogeneous soil system. Nevertheless, it is necessary always to standardize the electrodes before in situ measurements. The silver microelectrode method of measuring soil oxygen concentration has several advantages over other methods. It is portable, inexpensive, has a rapid response, and it can measure oxygen in an environment where this has heretofore not been possible. This makes it a valuable tool for field studies.

DETERMINATION OF DISSOLVED OXYGEN CONCENTRATION

IN SOIL WITH BARE SILVER WIRE ELECTRODES

By

Tung-kai Wu

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I. INTRODUCTION

In 1952, E. R. Lemon and A. E. Erickson introduced a method for measuring oxygen diffusion rate of soils with bare platinum wire electrode(13). This microelectrode technique appears 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.

According to Fick's second law, oxygen diffusion rate is a function of the concentration of dissolved oxygen (9). In soils, the latter is related to the rate of oxygen consumption by plant roots and microorganism in the soil mass which has been referred to as the "activity" of the soil (18). If a method could be used to measure the dissolved oxygen concentration associated with each diffusion measurement, it would be possible to calculate a purely physical aeration parameter for a given soil matrix by combining with appropriate diffusion theory. This parameter would be unaffected by biological activities of the soil and only governed by other physical factors such as structure and moisture of the soil.

Generally, in all living cells, increasing metabolic uptake of oxygen is a hyperbolic function of increasing oxygen in the immediate environment (12). Therefore it is important to determine the critical oxygen concentration at the root surface to insure an adequate supply throughout the tissue. The microelectrode technique which is considered to measure the oxygen conditions analogous to those plant roots could be used in these studies.

The rate of oxygen consumption by the active microbiological processes in the soil may depend upon the existing oxygen concentration. Since oxygen diffuses 10,000 times faster through air than through water, there are always large variations in the oxygen concentration in the soil water and only small variations in oxygen partial pressures in the soil atmosphere. It is the oxygen concentration in soil water on the surfaces of the respiring bodies that is correlated with their activities. In addition, respiration tends to take place within the crumbs rather than between them (4). Therefore, it is the oxygen concentration in soil water on the surfaces of the respirating microbes within the crumbs which should be measured and only the microelectrode technique could be used in these kinds of studies.

According to the brief discussion above, measurements of oxygen concentration with microelectrodes should be very useful for studying the biologic demand for oxygen throughout the soil fabric and for correcting the oxygen diffusion rates for those differences in oxygen concentration. The diffusion rate measurement would then be a characteristic of soil fabric per se.

This investigation is a continuation of the work initiated by Brandt (2, 5). A simplified and less expensive apparatus as well as silver electrodes are used to measure dissolved oxygen concentration in soil systems in this study.

II. LITERATURE REVIEW

A. Polarographic Determination of Oxygen

The dissolved oxygen content of electrolyte solutions has been determined by polarographic methods since the work of Heyrovsky in 1924 (7). Dropping mercury electrodes are used in many studies for measuring oxygen concentration in various liquid media (9). Karsten (8) first applied the dropping mercury electrode in studying oxygen content in soil solution. He used six different soils of widely varied texture and organic matter. At a certain potential, the only substance in the soil that was reduced at the electrode was oxygen.

Substitution of the platinum microelectrode for the dropping mercury electrode has been common in several fields of research (9). Lemon and Erickson (13) introduced the use of the platinum microelectrode to the field of soil science by measuring the oxygen diffusion rate in soils. From then on, many studies have been done on oxygen diffusion rate and plant response.

An oscilloscopic polarographic microelectrode technique using a bare platinum wire has been developed by Brandt (2) to measure oxygen concentration within the soil water films. The principle is the same as that for measuring oxygen diffusion rates with the platinum microelectrode, except that only very early portion of the time-current curve (the first second) is used. In this portion of the curve, oxygen diffusion to the electrodes can be considered to be linear to the cylindrical wire surface and the current proportional to the concentration of oxygen.

Brandt's (2, 5) procedure involved placing a -0.65 volt, 2 second square wave pulse to a 0.625 mm diameter silver wire which had been tygon coated except for the 4 mm tip. Current versus time curves were measured with an oscilloscope and recorded by a poloroid camera. The area under the curve between 0.1 and 0.4 second was measured as it is in this range of time that these electrodes give a constant and theoretical $i\sqrt{t}$. The electrodes are calibrated in 3% bentonite suspensions in 0.01 N Na₂SO₄ that are at equilibrium with various partial pressures of oxygen. This gives a straight line relation between oxygen concentration and the area under the curve.

B. Factors Affecting the Polarographic Measurement of Oxygen in Soil

The factors influencing the measurement of oxygen diffusion rate which have been discussed by Van Doren and Erickson (20) and Birkle et al. (1) will also affect the measurement of oxygen concentration, because both are measuring the oxygen diffusion current except different diffusion times are used. The factors which will be discussed here are some of the important ones.

1. Applied Voltage

Oxygen begins to be reduced at a potential of about -0.2 volts. As the negative potential is increased, the current increases. Lemon and Erickson (14) observed a plateau in the current-potential curve in the range of -0.6 to -0.8 volt when measurement was made in a soil-water suspension. Birkle et al. (1) studied the current-potential relation in unsaturated soil. As the 22-gauge electrodes were used, any potential between -0.55 and -0.75 volt could be used for oxygen diffusion rate measurement.

2. Electrical Resistance

In the electrolytic reduction of an uncharged substance (such as oxygen) it is necessary to have an inert

electrolyte in the system to provide electrical continuity. Van Doren (19) reported that electrical resistance, between the platinum microelectrode and the reference electrode, regulates the hydrogen overvoltage at applied potentials of 0.80 and 1.00 volts. Any factor which results in an excessive resistance between the reference cell and the metal wire electrode may become a limiting factor in the current flow and oxygen concentration measurements.

3. Wetting of the electrodes

A film of water must cover the electrode surface to provide electrical continuity with the body of the soil solution in order for the reduction of oxygen to occur. Only the area covered by a moisture film will participate in the This was termed "effective area" of the electrode reaction. by Van Doren and Erickson (20). The true area and effective area must be equal at all times in order that the correct oxygen concentration may be calculated from the measured The ability to recognize when these dimensions current. are not equal is probably the most difficult task in the operation of the apparatus and interpretation of the re-The relationship between moisture tension and texsults. ture of the soil influences the wetting of the electrode surface.

4. Temperature

The influence of temperature on the diffusion current is quite marked as the diffusion coefficient of oxygen changes 3 percent per degree centigrade in the vicinity of 25° C (17), the standard temperature chosen for polarographic work.

C. The Relation between Oxygen Concentration and Plant Roots

A theoretical approach to the relationship between dissolved oxygen and plant roots was presented in a sequence of papers by Lemon et al. (12, 15, 8, 3). They used the model of diffusion through a uniform cylindrical shell to calculate oxygen concentrations present at the surface of roots (C_r). Their calculations of C_r were used to predict whether oxygen availability at roots was optimal in accordance with known critical oxygen levels in solution.

Lemon (12) showed that the problems of oxygen supply in the soil and oxygen demand by plant roots are interdependent and cannot be theoretically separated. He pointed out that critical oxygen concentrations at root surfaces, C_r' , are those that reduce the concentration at the root axis to zero. Thus, oxygen sink strength in the root is a

hyperbolic function of increasing oxygen concentration until the dissolved oxygen concentration at the root surface is equal to C_r ' and then the uptake rate levels off at a maximum. Because this critical concentration must be maintained at root surfaces before aerobic metabolism predominates within roots, oxygen concentration at root surface, C_r , is of fundamental importance.

Further studies of Lemon and Wiegand (15) indicated that oxygen consumption rate of root tissues varies with the genetic background and the physiological age of the tissue. When oxygen is plentiful, the substrate supply at the reaction loci determines the reaction rate; if the oxygen concentration at the root surface is below the critical level, diffusion controls the rate of oxygen uptake.

D. PO₂ Gradients in Microenvironments

Currie (4) recognized that in naturally cohesive soils, all the microorganisms and most of the active root systems occur and respire within, rather than between, the crumbs. He presented oxygen profiles in respiring aggregates of different radii with given physical properties. Oxygen consumption rates for the whole soil body were

assumed to apply to individual crumbs within that body. He also assumed that oxygen was consumed at a uniform rate at all depths in aggregates and subsequently predicted that oxygen was deficient in the center of aggregates above a given diameter.

With the proper micro-technique, the model of uniform respiration could be tested against that of surfacial oxygen consumption. This same micro-technique might be used for detecting the pO_2 gradients in moisture films. In order to test that, the method must incorporate small electrode size with a technique for accurately determining electrode position. In this way it should be possible to relate variations in microbial activity to position-dependent variations in oxygen availability.

III. PROCEDURE

A. Theory

Under certain conditions the current resulting from the electrolytic reduction of oxygen at a metal electrode is governed solely by the rate at which oxygen diffuses to the electrode surface from the surrounding solution (14). The oxygen diffusion rate can therefore be calculated from steady-state diffusion currents with the mathematical model for linear diffusion given by Kothoff and Lingane (9) as obtained from Fick's First Law:

$$i_t = nFAf_{x=0,t} = nFAD \left(\frac{\partial C}{\partial x}\right)x=0,t$$
 (1)

where $i_{+} = current$ in amperes at time t in seconds,

n = number of electrodes used per molecule of oxygen
 electrolyzed
F = the Faraday, 96500 coulombs/equivalant
A = area of electrode in cm²
f_{x=0,t} = moles of oxygen diffusing to the electrode
 at time t in seconds
D = diffusion coefficient of oxygen in cm²/sec

C = concentration of oxygen in moles/ cc at a distance x cm from electrode surface t sec-onds after beginning diffusion.

By applying the differential equation for linear diffusion (Fick's Second Law), Kothoff and Lingane (9) expressed equation 1 as:

$$i_t = nFAC \sqrt{\frac{D}{\pi t}}$$
 (2)

where C = initial uniform oxygen concentration.

At relatively short time oxygen diffusion to the electrodes can be considered to be linear to the cylindrical wire surface and the current proportional to the concentration of oxygen (2, 5). The oxygen concentration can therefore be calculated from the measured electric current by using equation 2.

B. The Apparatus

An oxygen diffusion meter was modified to measure oxygen concentration by adding a circuit closing device and a current recording device. A simplified schematic diagram of the instrumental hook-up used with these basic units is given in Figure 1.



Figure 1.--Schematic diagram of the apparatus

1. Oxygen Diffusion Meter

This portion of equipment is the same as that developed by Lemon and Erickson (14) and is commercially available.¹

Three different types of electrodes were used in the studies of choosing the best electrode for measurements. The electrodes were constructed by 22 gauge (0.6439 mm diameter) silver, gold, or platinum wire which had been tygon coated except for the 4 mm tip.

¹Dicks Machine Shop, Lansing, Michigan

A silver-silver chloride reference cell was used with KCl salt bridge and porous ceramic cup to make electrode contact with the soil or solution.

2. Timer and Switching Device

A switch and two different time relay delays^{\perp} were used to measure a delayed current flow period within the first half second after the beginning of the diffusion current. The switch activated both time delay relays. The first time delay relay applied the potential to the electrode and started the diffusion current and then cut off the potential. The period of activation by the first switch could be adjusted to 0.05 to 0.5 second. The second switch had a variable time delay (0 to 0.5 second) and a variable closing period (0 to 0.5 second). It was wired so that it would sample the diffusion current at between 0.1 and 0.3 or 0.5 seconds after the diffusion current began. This made it possible to avoid the first portion of the current which would include the charging as well as the electrode absorbed oxygen effects and select a portion of the diffusion current which would be

¹Airborne Accessories Co., Hillside, New Jersey

linear as used by Brandt (2, 5). The function of these switches is illustrated in the following diagram.

Switch _____ give signal to model 05 timer Model 05______ close the circuit of diffusion cell Model 08______ current go to recording device

The purpose of this part of the study was to select the best portion of current-time curve which gave better linear relationship between the diffusion current and the oxygen concentration of the tested medium. The timers used in the equipment had a time range of 0.5 second. Therefore, any time periods between 0 to 0.5 second could be compared.

3. Recording Device

The diffusion current changes very rapidly after its initiation and makes it impossible to determine the current manually. The photographic oscilliscopic technique of Brandt was expensive and unwieldy. This problem was solved by using a model 300 electrometer operational amplifier¹ which acted as an electrometer and converted the rapidly changing diffusion current occurring over a fraction of a second into a steady voltage across a capacitor. This voltage could be

¹Keithley Instruments, Cleveland, Ohio.

measured by a voltmeter by the selection of a capacitor of proper size.

The input current can be calculated from output voltage by using equation 3:

$$v_{out} = \frac{Q}{C_{fb}} = \frac{I_{in} t}{C_{fb}}$$
(3)

where, V is the output voltage in volts,

Q is the applied charge in coulombs I_{in} is the input current in amperes t is the time in seconds C_{fb} is the feedback capacitance in farads.

According to equation 3, the capacitance of the capacitor is related to (i) diffusion current at short time, (ii) range of voltmeter, and (iii) time period selected. Suppose the diffusion current for 3% bentonite suspension at air equilibrium at 0.2 second is 60 microamperes, maximum range of voltmeter is 1 volt, and time period is 0.1 to 0.3 second; then the capacitance calculated from equation 3 is 12 microfaras. The capacitor used in the equipment was a 15 microfarad oil-impregnated paper capacitor.

C. Materials and Methods

Measurements with the metal wire electrodes were generally made in the following standardized medium. Three grams of Wyoming bentonite were added to 100 grams of 0.01N KCl solution. The clay was dispersed thoroughly with a Waring blender and stored for future use. Gas mixtures of 0, 5, 10, 15, and 21% oxygen were flowed through gas dispersion tubes into the suspensions for 15 minutes to bring the suspensions to equilibrium prior to measurements.

In order to choose the proper applied potential in oxygen concentration studies, measurements were made at 0.05 volt intervals from 0.65 to 0.80 volt in the standardized suspensions.

The effect of resistance on the measurement of diffusion current was studied by connecting various resistors in series with reference cell and measuring the overall resistance with a Bouyoucos soil moisture meter (vacuum tube resistance meter).

In the study of the degree of moisture film coverage of the microelectrode, three different sizes of sands and natural soil cores from three different sites were used. Fritted disc funnels (Buchner type) were used to maintain different moisture tensions in sands and a tension table was used for soil cores.

The experiments were done in constant temperature room to eliminate the effect of temperature. Temperature in the room was controlled to $25\pm2^{\circ}C$.

D. Calculation of Oxygen Concentration

The result of the measurement is a voltage across a capacitor and is the integration and amplification of the diffusion current for the selected time period. This might be defined as "apparatus reading" which is in the units of volts.

The diffusion current is related to concentration of oxygen by equation 2. One can rearrange this equation as:

$$C = \frac{i_t \sqrt{i}}{nFA \sqrt{\frac{D}{\pi}}}$$
(4)

where n = 4,

F = 96487 columbs/equivalent $A = 0.08417 \text{ cm}^2$ $D = 2.33 \times 10^5 \text{ cm}^2/\text{sec in soil (3) or } 2.38 \times 10^5 \text{ cm}^2/\text{sec}$ in water (17).

 $\pi = 3.1416$

it = diffusion current at time t, which depends on the time period used, can be obtained from ap-paratus reading by equation 3. C = concentration of oxygen in mole per cc which can $be changed to the unit of ppm by multiplying a factor <math>32 \times 10^6$.

As the time period is 0.1 to 0.3 second, the average diffusion current within this period is equal to the diffusion current at time t:

$$t = \left(\frac{\sqrt{.1} + \sqrt{.3}}{2}\right)^2 = 1.94$$

Then the apparatus readings can be converted to charge, average diffusion current, and oxygen concentrations as shown in Table 1.

TABLE 1.--Calibration Table for Apparatus Readings and Charges, Average Diffusion Currents, and Calculated Oxygen Concentration

Apparatus	Charge,	Average Diffusion	Calculate Concent	Calculated Oxygen Concentration				
Volts	Micro- coulombs	Micro- amperes*	mole/cc	mqq				
0.1	1.5	7.5	3.8×10 ⁻⁸	1.2				
0.2	3.0	15.0	7.6	2.4				
0.3	4.5	22.5	11.4	3.6				
0.4	6.0	30.0	15.2	4.8				
0.5	7.5	37.5	19.0	6.0				
0.6	9.0	45.0	22.8	7.2				
0.7	10.5	52.5	26.6	8.4				
0.8	12.0	60.0	30.4	9.6				
0.9	13.5	67.5	34.2	10.8				

IV. RESULTS AND DISCUSSION

A. Choice of the Best Conditions for Measurement

1. Electrode

Metal wire electrodes are used in this study because with respect to oxygen movement they resemble plant roots. Their use makes it possible to measure the oxygen concentration within the soil crumb.

The results of the comparison of three kinds of metal wire electrodes are shown in Table 2.

Oxygen Concentration, %	0	5	10	15	21					
Types of Electrode	Charge, Micro-coulombs**									
Platinum	2.9*	5.4	7.5	9.9	13.2					
Gold	2.0	4.4	6.0	8.4	11.4					
Silver (used)	1.7	3.8	5.9	8.1	10.8					
Silver (new)	1.5	3.5	5.4	7.4	9.8					
Silver (pretreated)***	2.4	4.7	6.8	9.0	11.7					

TABLE 2.--Charge Measurements in 3% Bentonite Suspensions Using Different Types of Metal Wire Electrodes

*Each value is an average of 5 measurements, each measurement is an average of 3 electrodes of each type.

**Charges flowing between 0.1 and 0.3 seconds after the application of-0.65 volt.

***The pretreatment was to apply a -1.0 volts for 20 minutes and storing in 0.01 N KC1. Figure 2.--Relation between charge* measured and oxygen concentration in bentonite suspension using different types of metal wire electrodes.





Silver electrodes gave lower residual current reading and more linear relationship between oxygen concentration in the medium and measured electrical charge.

The reason for the lower residual current is that the silver surface is less reactive than the platinum and gold surfaces and gives better reproducibility (5). The silver electrodes are therefore used in the rest of the experiments.

Newly made silver electrodes produced less oxygen reduction current than those that were used (Table 2). The sensitivity of these electrodes increased after several times use and also increased markedly after a negative potential (-1.0 volt) had been applied with the electrodes stored in 0.01 N KCl for 20 minutes. This pretreatment of electrode was not applicable because it increased the residual current as well as increasing the sensitivity.

2. Applied Voltage

The results of measurement of oxygen concentration in 3% bentonite suspension with different applied potentials are presented in Table 3.

It is evident that the measured charges will depend upon the potential applied. Choosing one voltage to use in

TABLE 3.--Charge Measured from Standard Suspensions Using Various Applied Potentials including the Correlation excluding the Residual Current

Oxygen Concentration, %	0	5	10	15	21						
Applied Voltage,Volts	Charge, Micro-coulombs**										
-0.65	2.1*	4.4	6.6	8.7	11.2						
- 0.70	2.4	4.8	7.2	9.3	11.7						
-0.75	2.7	5.4	8.3	10.2	12.4						
-0.80	2.8	5.7	8.4	10.5	12.9						
Corrected for residual cu	irrent										
-0.65	0	2.3	4.5	6.6	9.1						
-0.70	0	2.4	4.8	6.9	9.3						
-0.75	0	2.7	5.6	7.5	9.7						
-0.80	0	2.9	5.6	7.7	10.1						

*Each value is an average of two measurements, each measurement is an average of ten electrodes.

**Charges flowing 0.1 and 0.3 second after the application of the potential.

all measurements is important for comparison of various results. It seems that the current-voltage curve reaches a plateau at -0.75 volt but some unknown reasons cause the charge vs oxygen percentage curve to bend downward at higher percentage. Since the best linearity was obtained from a potential of -0.65 volt, an applied voltage of -0.65 volt was then selected in the experiments.

It appears that oxygen is reduced at a less negative potential at the silver surface than at the platinum surface Figure 3.--The relationship between charge* measured and oxygen concentration in bentonite suspension using various applied potentials.



*Micro-coulombs flowing 0.1 and 0.3 second after the application of the potential.

(9). However, the fresh silver surface had a lower hydrogen overvoltage than the bright platinum surface, so the evolution of hydrogen also occurred at less negative potential on the silver surface. This probably is the reason that -0.65 volt is better than the greater negative potentials.

Another reason for selecting -0.65 volt as applied voltage was that many investigators had published results of measurement of oxygen diffusion rate made at -0.65 volt (14, 16) and there is no compelling reason to use another potential.

3. Time Period

Various time periods (from 0.1 to 0.3 second) are compared with charge that flowed using bentonite suspensions. The same principle was followed in selecting the best time period by testing linearity and minimizing residual current. As shown in Table 4 and Figure 4, any time period seemed suitable.

There is no theoretical reason for any time period being better fitable. For the purpose of convenience, a circuit closing time of 0.1 to 0.3 second was fixed on the device throughout the experiment.
Figure 4.--Relation between charge* that flowed and oxygen concentration in bentonite suspensions using different selected time period



*Micro-coulombs flowing during the time period after applying -0.65 volt.

Oxygen	Concentrat	ion,%	0	5	10	15	21
	Time						
Initi- ation	Termin- ation	Dura- tion		Charge,	Micro-c	COULOMDS**	
	Seconds						
0.10	0.40	0.30	2.7*	5.3	7.8	10.5	13.0
0.125	0.375	0.25	2.3	4.8	7.4	9.8	12.1
0.15	0.35	0.20	1.8	4.1	6.2	8.3	10.9
0.175	0.325	0.15	1.5	3.2	4.7	6.3	8.0
0.20	0.30	0.10	1.4	2.3	3.3	4.5	5.7

TABLE 4.--Charge Measured from Bentonite Suspension using Different Time Periods

*Each value is an average of twenty measurements by a single electrode.

**Charges flowing during the time period after applying -0.65
volt.

B. Limitations of the Measurements

1. Resistance of the Solution

Tables 5 and 6 summarize the data of an experiment designed to show the effect of resistance between reference cell and silver electrodes on the measured charges. At all concentrations, the resistance influenced the diffusion current. This probably is due to the limiting current-resistance product which is a function of the applied potential and the chemical e.m.f. of the two electrodes. However, there are

Resistan	ce, kilo-ohms	0.9	1.6	3.0	5.0	7.5	10.5
Oxygen Conc.%	Replicate		Charc	ge, Micro	-could	ombs**	
21	1	10.8*	11.0	11.1	9.7	8.3	6.9
	2	10.8	11.0	11.4	10.0	8.3	6.8
	3	10.9	11.7	12.5	11.2	9.5	7.5
		11.2	11.6	12.0	11.0	9.0	7.7
	Mean	10.9	<u>11.3</u>	11.8	10.5	8.8	7.2
		s ² =0.2	77 LS	SD.05 ^{=0.6}	LSI	0.01=0.	9
15	1	8.7	8.9	9.3	8.4	7.2	6.2
	2	8.3	8.6	9.2	8.7	7.5	6.3
	3	8.6	9.0	9.6	9.9	8.9	7.2
	4	8.1	8.6	9.3	9.2	8.1	6.9
	Mean	<u>8.4</u>	8.8	9.4	<u>9.1</u>	7.9	6.7
		s ² =0.	20 LS	^{SD} .05 ^{=0.5}	LSI	0.01 ⁼⁰ .	8
10	1	6.2	6.5	6.6	7.1	6.8	6.0
	2	6.0	6.2	6.6	6.9	6.5	5.7
	3	6.3	6.8	6.9	8.1	7.2	6.6
	4	5.8	6.0	6.9	7.4	6.6	5.8
	Mean	$\frac{6.1}{}$	<u>6.4</u>	6.8	7.4	6.8	6.0
		s ² =0.	15 LS	$SD_{.05} = 0.5$	LSI	 .01 ⁼⁰ .	8
5	1	4.4	4.5	5.0	5.4	5.1	4.8
	2	4.1	4.2	4.8	5.1	5.4	4.7
	3	4.2	4.4	4.5	5.6	5.9	5.3
	4	4.2	4.4	4.5	5.6	5.4	5.4
	Mean	4.2	4.4	4.7	5.4	5.5	_5.1
		$s^2 = 0$.	05 LS	 SD _{.05} =0.3	LSI	0.01 ⁼⁰ .	5
0	1	2.3	2.4	2.7	2.9	3.2	3.2
	2	1.9	2.1	2.3	2.6	3.0	3.2
	3	2.1	1.9	2.3	3.2	3.5	3.5
	4	2.1	2.1	2.1	2.6	3.2	3.0
	Mean	2.1	2.1	2.4	2.8	3.2	<u> 3.3</u>
		s ² =0.	05 LS	$5D_{.05} = 0.3$	LSI	0.01 ⁼⁰	5

TABLE 5.--Effect of Resistance on the Charge Readings from Bentonite Suspensions Adjusted to Various Oxygen Concentrations

*Each value is an average of ten electroce measurements. **Charges flowing 0.1 and 0.3 second after applying -0.65 volt.

Resistance	, kilo-ohms	1.8	2.6	3.4	5.5	8.0
Oxygen Conc.%	Replicate	Cha	arge, M	licro-co	oulombs	;**
21	1	12.0*	11.0	10.2	9.5	8.0
	2	11.1	10.0	9.9	9.3	7.8
	3	10.5	10.2	9.8	8.4	7.5
	Mean	11.2	10.4	10.0	9.1	7.8
		s ² =0.24	4 LSI		 B LSD	0.01=1.2
15	1	9.0	9.0	8.4	7.8	6.9
	2	8.6	8.4	8.4	7.8	7.1
	3	8.3	8.6	7.4	6.9	6.3
	Mean	8.6	8.7	8.1	7.5	6.8
		$s^2 = 0.2$	 21 LS	D.05 ⁼⁰	- <u></u> .7 LS	D.01 ^{=1.}
10	1	6.8	6.5	6.5	6.2	5.4
	2	6.8	6.9	6.9	6.2	5.6
	3	6.5	6.6	6.0	6.0	5.3
	Mean	<u>6.7</u>	6.7	6.5	6.1	5.4
		s ² =0.0	06 LS	$5D_{.05} = 0$.4 LS	$D_{.01} = 0$.
5	1	4.1	4.5	4.2	4.4	3.9
	2	4.7	4.8	5.0	4.4	4.1
	3	4.7	4.7	4.1	4.1	3.8
	Mean	4.5	4.7	4.4	4.3	3.9
		s ² =0.0	08 LS	D.05 ⁼⁰ .	.4 LS	D.01 ⁼⁰ .
0	1	2.3	2.3	2.0	2.1	2.1
	2	2.3	2.6	2.1	2.1	2.1
	3	2.6	2.6	2.1	2.4	2.4
	Mean	2.4	2.5	2.1	2.2	2.2
		$s^2 = 0.0$	 03 LS	^D .05 ⁼⁰ .	.3 LS	D _{.01} =0.

TABLE 6.--Effects of Resistance on the Charge Readings from 0.01 N KCl Solutions Adjusted to Various Oxygen Concentrations

*Each value is an average of ten electrode measurements. **Charges flowing 0.1 and 0.3 second after applying -0.65 volt. --No significant difference at 5% level. --No significant difference at 1% level. no significant differences between charge measured at resistances below 3 kiloohms from 3% bentonite suspension and below 3.4 kiloohms from 0.01N KCl solution when oxygen concentration was 21%. This limiting resistance became greater when oxygen concentration decreased. It seems that the oxygen concentration in the solution may influence the relationship between resistance and measured diffusion current. The explanation of the results of this experiment is not known at present, and further study is recommended.

For practical purposes, if a 10% error is acceptable in a soil measurement, the diffusion current could be considered resistance independent when resistance is below 5 kiloohms. The effects of resistance greater than 5 kiloohms should be considered influencing the diffusion current and any measurement made at resistance greater than that could have a large error.

2. Moisture Tension

In a discussion of limitations and errors involved with the platinum microelectrode method, Lemon and Erickson (14) indicated that the most serious limitation was the wetting of the electrode when making in situ measurements in the soil. In order to obtain quantitative measurements,

the area of the electrode must be known and it is essential to have the whole electrode surface covered by a moisture film. It is only when the entire electrode is wet that the total surface area functions as a reducing surface.

There is apparently a unique relationship between moisture tension and texture or pore size distribution which influences the wetting of the electrode surface. Tables 7 and 8 illustrate the behavior of oxygen diffusion currents in sands of various size as affected by moisture tension. There are no significant differences between the measured charge at moisture tensions up to 7 cm, 15 cm, and 30 cm in coarse, medium to fine, and very fine sand, respectively. The finer the sand, the greater the moisture tension required to rupture the liquid film wetting the electrode surface. The results of measured resistance between silver electrode and reference electrode show that resistance increased with increasing moisture tension. Above 7, 15, and 30 cm of tension in coarse, medium to fine, and very fine sand, the resistance increased sharply. These studies indicate that the effect of moisture tension on measured current is due to resistance caused by decreasing the moisture content in the medium and/or decreased effective surface of electrode.

Moisture Tensio	n, cm	0	5	6	7	8	9
Sands	Replicate	С	harge	, Micro	o-coul	ombs**	
Coarse	1	8 6*	83	78	74	4 5	3 2
1.0-0.5 mm	2	8.0	7.8	7.7	7.8	5.0	2.7
	3	7.8	8.3	8.4	8.1	5.7	3.8
	4	8.1	8.1	8.1	7.7	4.8	3.8
	- 5	8.6	8.0	8.1	8.3	5.4	3.2
	Mean	8.2	8.1	8.0	7.9	5.1	3.3
		s ² =0.	14	LSD 05	=0.4	LSD.01	=0.6
Moisture Tensio	n, cm.	0	5	10	15	17.5	20
Medium to fine	1	7.8	8.0	7.8	7.8	5.1	1.4
0.5-0.1 mm	2	8.0	8.1	8.7	7.7	4.7	1.4
	3	8.1	7.5	7.8	7.7	5.9	2.0
	4	7.8	7.5	7.7	8.0	4.4	3.3
	5	8.0	8.0	8.3	8.9	6.5	3.0
	Mean	7.9	7.8	8.1	8.0	5.3	2.2
		s ² =0.	31	LSD.05	=0.6	LSD.01	=0. 9
Moisture Tensio	n, cm	0	10	20	30	40	50
Very Fine	1	7.1	6.8	6.9	7.1	6.0	2.3
0.5-0.05 mm	2	8.3	7.8	8.0	8.0	5.7	3.8
	3	6.8	7.4	8.0	8.9	5.1	2.0
	4	8.1	8.9	9.2	7.2	4.8	1.7
	5	8.1	9.0	8.6	8.1	4.4	3.2
	Mean	7.7	8.0	8.1	7.9	5.2	2.6
		s ² =0.	60	LSD.05	=0.8	LSD.01	=1.2

TABLE 7.--Charge Measured at Various Moisture Tensions in Sands

*Each value is an average of ten electrodes measurements. **Charges flowing 0.1 and 0.3 second after applying -0.65 volt, residual currents are subtracted.

Moisture Tensio	n, cm	0	5	6	7	8	9
Sands	Replicate		Re	esista	nce, K	2	
Coarse	1	3.2	3.5	3.7	4.1	8.8	12.1
1.0-0.5 mm	2	3.1	3.2	3.4	3.7	8.8	11.0
	3	2.9	3.2	3.3	3.7	7.4	9.9
	4	2.7	3.0	3.6	3.7	7.5	14.2
	5	2.8	3.0	3.2	3.5	6.4	10.5
	Mean	2,9	3.2	3.4	3.8	7.8	11.5
	s ² =0.6	59	LSD.05	=0.90	LSD	.01 ^{=1.}	31
Moisture Tensio	n, cm	0	5	10	15	17.5	20
Medium to fine	1	3.1	3.2	3.7	4.3	6.3	14.3
0.5-0.1 mm	2	3.4	3.6	3.9	4.4	6.5	14.6
	3	2.9	3.7	3.8	4.2	8.5	13.5
	4	3.3	3.7	3.7	4.0	9.0	11.4
	5	2.7	2.7	3.2	3.8	6.1	12.2
	Mean	3.1	3.4	3.7	4.1	7.3	13.2
	s ² =0.6	59	LSD.05	=0.90	LSD	.01 ^{=1.}	31
Moisture Tensio	n, cm	0	10	20	30	40	50
Very Fine	1	3.4	3.4	3.9	4.6	7.0	12.6
0.25-0.05 mm	2	3.5	3.6	3.8	4.8	7.4	10.0
	3	2.9	3.8	4.1	4.1	7.5	14.2
	4	3.2	3.6	4.0	4.5	7.8	14.1
	5	3.2	3.6	3.8	4.4	7.2	11.3
	Mean	3.2	3.6	3.9	4.5	7.4	12.4
	s ² =0.5	59	LSD.05	=0.83	LSD	.01 ^{=1.}	21

TABLE 8.--Resistance Between Two Electrodes at Various Moisture Tensions in Sands

*Each value is an average of ten electrodes measurements.

The 5 kiloohms resistance limit coincides with the previous study of limiting resistance. As it is very difficult to determine whether the wetting of the electrode surface is complete or not, the measurement of resistance between two electrodes may be used as an indicator of the feasibility of making an oxygen concentration measurement with a bare wire electrode.

3. Measurements in the Soil Cores

Five natural soil cores were taken from each of three kinds of soil. The cores were saturated with tap water and then ten silver electrodes were inserted in the cores far enough to make the necessary measurement of oxygen concentration, diffusion rate and electrical resistance. After the electrodes were removed, the cores were placed on a 10 cm tension table for 48 hours and the measurements were made. This process was repeated until all measurements had been completed through 60 cm of water tension. The natural structure of the cores was undoubtedly altered by the introduction of fifty holes into each core, since the data were not to be used for comparison of soil structure, these alterations were not an important factor.

Moisture	Tension, cm	n O	10	20	40	60	Mean
Soil	Repli- cate		Cha	rge, Mi	cro-cou	lombs**	
Spinks	1	6.0*	9.1	10.5	11.7	12.0	9.9
sandy	2	10.0	10.3	11.7	7.5	12.1	10.3
loam	3	8.9	9.0	8.7	8.0	7.8	8.5
	4	9.6	8.9	9.9	10.8	9.2	9.7
	5	11.9	11.0	11.5	11.3	11.3	11.4
	Mean	9.3	9.7	10.5	9.9	10.5	10.0
		s ² =2.4	ŀ	LSD.0	5 ^{=1.6}	LSD.0	1=2.4
Hillsdale	e 1	6.0	6.6	6.3	5.3	5.0	5.8
sandy	2	7.8	7.8	7.7	5.7	8.1	7.4
loam	3	7.2	7.8	5.3	6.5	8.9	7.1
	4	7.2	7.7	7.6	7.7	8.6	7.9
	5	8.9	7.2	6.6	7.1	6.2	7.2
	Mean	7.5	7.4	6.7	6.5	7.4	7.1
		s ² =0.8	33	LSD.0	5 ^{=1.0}	LSD.0	1=1.5
Holt	1	8.6	8.7	9.3	9.5	8.7	9.0
sandy	2	8.7	8.0	7.4	10.4	10.3	9.0
loam	3	10.3	8.6	8.9	9.2	12.5	9.9
	4	8.0	8.6	9.2	11.2	8.7	9.1
	5	8.3	7.4	8.7	6.5	6.2	7.4
	Mean	8.8	8.3	8.7	9.4	9.3	8.9
		s ² =1.5	55	LSD.0	5=1.4	LSD.0	1=2.0

TABLE 9.--Charge Measurements in Natural Soil Cores as a Function of Moisture Stress

*Each value is an average of ten electrodes measurements. **Charges flowing 0.1 and 0.3 second after applying -0.65 volt, residual currents are subtracted.

Moisture	Tension, cm	0	10	20	40	60	Mean
Soil	Repli- cate			Resista	nce, K(C	
Spinks	1	4.1*	3.7	3.1	2.1	2.8	3.2
sandy	2	2.5	2.5	2.5	3.4	2.8	2.7
loam	3	4.5	4.1	4.8	4.6	3.4	4.3
	4	3.3	3.5	4.2	3.9	3.6	3.7
	5	2.8	3.1	3.3	3.5	2.7	3.1
	Mean	3.4	3.4	3.6	3.5	3.1	3.4
		s ² =0.	28	LSD.0	5 ^{=0.6}	LSD.0	1 ^{=0.8}
Hillsdale	e 1	7.1	6.2	6.1	7.3	6.1	6.6
sandy	2	5.5	5.7	5.5	6.2	4.7	5.5
loam	3	6.4	5.4	6.0	6.9	5.3	6.0
	4	5.7	5.8	6.1	5.7	5.0	5.7
	5	5.4	4.8	6.1	5.7	6.2	5.6
	Mean	6.0	5.6	6.0	6.4	5.5	5.9
		$s^{2}=0.$	23	LSD.0	5 ^{=0.5}	LSD.0	1=0.7
Holt	1	4.0	3.8	4.0	3.2	3.7	3.7
sandv	2	3.9	4.1	3.5	3.5	3.2	3.6
loam	3	3.6	3.4	4.0	4.8	2.9	3.7
	4	5.4	4.6	4.4	3.4	3.6	4.3
	5	3.6	3.8	3.9	5.2	5.1	4.3
	Mean	4.1	3.9	4.0	4.0	3.7	3.9
		$s^2 = 0$.	47	LSD.0	=0.8	LSD .0	1=1.1

TABLE 10.--Resistance Measurements in Natural Soil Cores as a Function of Moisture Stress

*Each value is an average of ten electrodes measurements.

Moisture	Tension,	cm O	10	20	40	60
Soil	Repli- cate	Oxygen	Diffusion	Rate,	x 10 ⁻⁸ gm/	cm ² /sec
Spinks	1	19.5*	16.0	20.7	78.0	76.4
sandy	2	17.7	21.2	42.5	82.6	81.5
loam	3	28.4	28.4	53.1	67.3	73.2
	4	16.4	33.4	79.8	84.5	88.5
	5	18.3	17.2	55.5	84.0	82.8
	Mean	20.1	23.2	50.3	79.5	80.5
Hillsdale	e 1	20.1	25.4	41.3	71.5	74.0
sandy	2	20.1	29.0	41.3	75.6	78.0
loam	3	15.4	13.6	44.3	64.5	79.3
	4	18.3	30.1	49.1	73.4	82.1
	5	20.7	26.0	57.8	65.6	65.0
	Mean	18.9	24.8	46.8	70.1	75.7
Holt	1	14.8	10.6	31.8	75.5	79.2
sandy	2	13.0	45.0	24.8	89.0	85.0
loam	3	33.3	23.3	40.1	79.7	74.0
	4	39.0	49.0	53.7	93.4	84.5
	5	14.8	17.7	47.3	70.3	69.2
	Mean	23.0	29.1	39.5	81.6	78.4

TABLE 11.--Oxygen Diffusion Rate Measurements in Natural Soil Cores as a Function of Moisture Stress

*Each value is an average of ten electrodes measurements.

The data shows there are no significant differences between measured current readings at all moisture tensions. This means that the moisture tension up to 60 cm is not a limiting factor for measurements on these three soils. But there is some difference in the current measured between three kinds of soil. It seems that the smaller the resistance of the soil the greater the measured current in these three soils. The resistance of Hillsdale sandy loam is greater than 5 kiloohms and the measured current is lower than normal. This resistance difference probably is not due to incompletely wetting of electrode surface but from a low conductivity of the soil solution.

It may be concluded that the method is more reliable over a wider range of tensions in fine soils if adequate supporting electrolyte is present. For soils containing little silt or clay, the validity of microelectrode measurements might be questionable at relatively low moisture tensions.

C. Precision and Accuracy

Variability Among Individual Silver Electrodes

Ten selected silver electrodes were put into air saturated 3% bentonite suspension and 0.01 N KCl solution and measurements of oxygen concentration were made. After the electrodes were removed, they were wiped with disposable paper tissues and put back into the media again and additional measurements were made.

The results of those measurements were analyzed statistically as shown in Tables 12 and 13.

The variability of the electrodes is due to slight differences arising in the manufacture of the electrodes. It is very difficult to make the electrodes with exactly the same surface area. All newly made electrodes should be tested both in air and nitrogen saturated bentonite suspension. The electrodes that give lower residual current in nitrogen saturated media and higher current in air saturated media should be chosen.

The variability among measurements is due to the sensitivity of the electrodes, the salt content of media and probably the variability due to timer, potentials, etc., in the circuitry.

In both the 3% bentonite suspension and 0.01 N KCl solution the coefficient of variability of measurements are about 2% which are considered small for this type of measurements. Therefore, the average of ten electrode measurements is a good estimation of oxygen concentration in the media.

2. Variability among Measurements on Different Dates

The same experiment as discussed before was repeated day by day. Results and statistical analyses are shown in Tables 14 and 15.

Elec	e- le l	2	3	4	5	6	7	8	9	10	Mean
Meas ure- ment	5 - - -			c	harge	, mic:	ro-coi	ulomb	5		
1 2 3 4 5	11.2 11.1 11.3 11.3 11.3	11.2 11.3 11.3 11.4 11.6	10.5 11.1 10.7 10.8 10.8	10.7 11.6 10.7 11.1 11.3	11.1 11.1 10.7 11.4 11.6	11.1 11.3 10.8 11.3 11.3	11.1 11.4 10.7 11.0 11.6	10.5 10.5 11.0 11.1 11.4	10.7 11.0 10.7 11.0 11.3	10.6 11.6 11.1 11.4 11.7	10.9 11.2 10.9 11.2 11.4
Mear	n 11.2	11.4	10.8	11.1	11.2	11.2	11.2	11.1	10.9	11.3	11.1
Α.	Analys Source Elect: Measu: E x M	sis o: e rodes rement	f var: ts 	iance 1f 9 4 36	ss 1:64 1.75 1.55	Ms 0:18 0.44 0.04	$\frac{5}{3}$ $\frac{1}{4}$ $\frac{1}{3}$	EM: $C = M$ $C = M$	5 ² o _E e o ² M	4	F 26** 3**
Β.	B. Estimated variances $\hat{\sigma}_{EM}^2 = 0.043$ $\hat{\sigma}_{M}^2 = 0.040$ $\hat{\sigma}_{E}^2 = 0.028$										
c.	Estimation $\hat{\sigma}_{\bar{\mathbf{X}}}^2 = \frac{1}{2}$	ated 2 <u>EM</u> + em	$\frac{\hat{\sigma}_{E}^{2}}{\frac{\sigma_{E}}{e}} +$	nce o ^2 ^o <u>M</u> m	f mea: w	n hen e	= 10	, m =	1	$\hat{\sigma}_{\bar{x}}^2 =$	0.047
D.	Coeff	icien	t of v	varia	bilit	Y					
	$S \sqrt{0.047}$										

TABLE 12.--Charges Measured in Bentonite Suspension with Ten Silver Microelectrodes

 $\frac{S}{\bar{x}} = \frac{\sqrt{0.047}}{11.1} = 1.9\%$

Elec trod	:- le 1	2	3	4	5	6	7	8	9	10	Mean
Meas ure- ment	. - .			C	narge	, Micı	:o-co	ulomb	S		
1 2 3 4 5 6 Mean	11.0 11.6 11.0 11.3 10.8 10.8	11.4 11.0 11.1 11.1 11.0 11.0 11.0	10.8 11.0 11.3 11.0 10.7 10.7	11.6 11.6 11.3 11.4 11.0 10.8	11.1 11.4 11.0 11.0 10.4 10.5	11.1 11.0 11.6 11.7 11.0 11.0 11.0	10.7 10.8 11.0 10.7 10.5 10.4	11.0 11.3 11.9 11.6 10.8 10.8	11.4 11.4 11.3 10.7 10.5	10.7 10.7 10.5 10.8 10.8 10.5	11.1 11.2 11.2 11.3 10.8 10.7
Α.	Analys <u>Source</u> Elect:	sis o: e rodes	f var:	iance <u>lf</u> 9	s <u>SS</u> 2.61	<u>MS</u> 0.29		EM	<u>s</u>		<u>F</u>
	Measu	remen	ts	5	2.61	0.52	2	σ _{EM} +	e σ _M ²	10.	5**
	E x M			45 : 	2.25	0.05	5	^о ем			
в.	Estima	ated v	varia	nces							
	$\hat{\sigma}_{EM}^2 =$	0.05			² м = (0.047		σ	$\frac{2}{E} = 0$.04	

TABLE 13.--Charge Measured in 0.01 N KCl Solution with Ten Silver Electrodes

 $\hat{\sigma}_{EM}^2 = 0.05$

C. Estimated variance of mean

$$\hat{\sigma}_{\overline{x}}^2 = \frac{\hat{\sigma}_{EM}^2}{em} + \frac{\hat{\sigma}_{E}^2}{e} + \frac{\hat{\sigma}_{M}^2}{m}$$
 when $e = 10$, $m = 1$ $\sigma_{\overline{x}}^2 = 0.056$

D. Coefficient of variability

$$\frac{s}{x} = \frac{\sqrt{0.056}}{11.0} = 2.2\%$$

^_

	Date	4/12	4/13	4/14	4/16	4/17	4/18	4/19	4/20	
M	easure ment	-		Charg	e, Mic	ro-cou	lombs*	*		
	1	10.4*	10.8	11.0	10.7	10.8	10.4	11.1	11.4	
	2	10.1	10.7	11.3	10.8	11.0	10.7	10.8	11.1	
	3	10.1	11.0	10.8	10.7	11.0	10.7	10.8	11.0	
	4	10.7	10.8	11.1	10.8	11.0	10.5	10.7	11.4	
	5	10.7	10.8	11.4	10.8	10.8	10.5	10.8	11.0	
	Mean	10.4	10.8	11.1	10.8	10.9	10.6	10.8	11.2	10.8

TABLE 14.--Charges Measured in Bentonite Suspension on Different Dates

*Each value is an average of ten electrodes measurments. **Charges flowing 0.1 to 0.3 second after applying -0.65 volt.

A. Analysis of variances

Source	<u>df</u>	<u>_\$S</u> _	MS	EMS	F
Among date	7	2.52	0.36	$\sigma_W^2 + d\sigma_A^2$	11**
Within date	32	1.06	0.033	σ <mark>2</mark> ₩	

B. Estimated variances

$$\hat{\sigma}_{W}^{2} = 0.033$$

 $\hat{\sigma}_{A}^{2} = 0.066$

Date	4/26	4/27	5/1	5/5	5/8	5/9	5/11	
Measurement		То	tal Ch	arge,	Micro-	coulom	bs**	
1	11.6*	11.9	10.5	11.8	10.7	11.1	11.6	
2	11.4	11.6	10.7	11.6	11.0	11.1	11.4	
3	11.6	11.3	9.9	11.3	10.7	11.3	10.8	
4	11.3	11.4	9.6	11.0	11.1	11.3	10.8	
5	11.5	11.0				10.8		
6						10.7		
Mean	11.5	11.4	10.2	11.4	10.9	11.1	11.2	11.

TABLE 15.--Charges Measured in 0.01 N KCl Solution on Different Dates

*Each value is an average of ten electrodes measurements.
**Charges flowing 0.1 to 0.3 second after applying -0.65 volt.

A. Analysis of variance

Source	<u>df</u>	<u>SS</u>	_MS_	EMS	F
Among date	6	5.81	0.97	$\sigma_{W}^{2} + c\sigma_{A}^{2}$	7.7**
Within date	25	3.15	0.13	σ <mark>2</mark> w	

B. Estimated variance

$$\hat{\sigma}_{W}^{2} = 0.13$$

 $\hat{\sigma}_{A}^{2} = 0.18$

Since the measurements were made on different dates, differences in temperature also might have affected the results. Oxygen solubility in aqueous solution decreases with the temperature while the diffusion coefficient of oxygen and rate of reaction increases. The decrease in the solubility of oxygen between 23° and 27° is about 1.9 percent per degree rise in temperature within the same temperature range in water (17).

The data shown in Tables 14 and 15 are the results of measurements which are influenced by all factors including electrodes, equipment, media and temperature, etc. However, the over-all standard deviations among dates are 0.26 and 0.42 microcoulombs in 3% bentonite suspension and 0.01 N KCl solution, respectively. The coefficients of variability are 2.4 and 3.8% which can be considered small for measurements in the soil. This variability might be lessened by standardizing electrodes before making measurements, controlling the condition of the equipment, etc. Therefore, it may be concluded that the results of measurements on different dates are comparable for oxygen concentration studies.

3. Variability of Measurements in Sand and Soil

The standard deviations of measurements of oxygen concentration in coarse, medium to fine and very fine sand at various moisture tensions are 0.38, 0.56, and 0.78 microcoulombs, respectively (Table 7). The corresponding coefficients of variability are 5%, 7%, and 10% with an average of 7%. As calculated from Table 9, the coefficients of variability among measurements in the soils at various moisture tensions are 15%, 13%, and 14% for Spinks sandy loam, Hillsdale sandy loam, and Holt sandy loam, respectively.

Those measurements were not made within the same day. All variables discussed in sections 1 and 2 might be included in the variability discussed here.

When measuring in the sand and soil, the microelectrodes become scraped and rescraped upon repeated insertions into the sand and soil which will change the surface properties of the electrodes, and the dimensions of the silver wire may become changed due to repeated bending of the wire.

It may also be noticed in Tables 7 and 9 that, in general, as the moisture tension increases the range in charge readings increases. Such behavior is indicative of

the differential drainage of pores in the sand and soil at the lower tensions, increasing the heterogeneity of the system. It may be concluded that the often large variability among measurements is not due to erratic behavior of the microelectrodes, but is a measure of the actual heterogeneity of the soil system with respect to the silver microelectrode. Variability in the micro-conditions of the soil also among microelectrodes has been recognized as a sampling problem in obtaining representative microelectrode readings. However, even at various moisture tensions, the standard deviation of the sample population of measurements in the soil is about ten percent. This is probably as much precision as could be expected for measurements in heterogeneous soil systems.

4. Accuracy of Measurements

The oxygen concentrations in the media which are calculated from microelectrode readings in Tables 2 to 6 by equations 3 and 4 are shown in Table 16. After residual values were subtracted from each correspondent value, the calculated oxygen concentrations became similar.

The solubility of oxygen is a linear function of its partial pressure and at 1 atmosphere and 25[°]C, it is

Oxygen P	artial Pressu	0	5	10	15	21	
Source of Data	Medium	Kind of Result	Oxygen	conc	entra	tion,	ppm
a	Water	Known	0	2.0	4.0	6.0	8.3
Table 2	bentonite suspension	calculated*	1.4	3.0	4.7	6.5	8.6
Table 3 Table 4 Table 5 Table 6	" " 0.01 N KC1		1.7 1.4 1.7 1.7	3.5 3.3 3.4 3.5	5.2 5.0 5.1 5.2	6.9 6.6 6.8 6.9	9.0 8.7 9.1 9.1
Table 2	bentonite suspension	residual current subtracted	0	1.6	3.3	5.1	7.2
Table 3 Table 4 Table 5 Table 6	" " 0.01 N KC1		0 0 0 0	1.8 1.9 1.7 1.8	3.5 3.6 3.4 3.5	5.2 5.2 5.1 5.2	7.3 7.3 7.4 7.4

1.9 3.8 5.8 8.3

6.0 8.3

8.3

8.3

8.3

5.9

6.0

5.8

4.0

4.0

3.8

3.8

2.0

2.0

1.9

1.9

0

0

0

0

TAB	LE 16O:	xygen Concer	ntrations	in	Bentonite	Suspension	and
KCl	Solution	Calculated	with Lin	ear	Diffusion	Theory and	Cali-
		brated	by Stand	ard	Curves		

Table 2

Table 3

Table 4

Table 5

Table 6

bentonite

...

..

...

0.01 N KC1

^a"Handbook of Chemistry and Physics," 32nd Ed., pp. 1478. *Measured values calculated by equations 3 and 4.

****Calculated** values subtracted by correspondent residual values.

***Calibrated by standard curves (Figures 5 and 6).

suspension calibrated*** 0

8.3 ppm in pure water. In electrolyte solution the solubility is smaller to an extent dependent on the ionic strength (9). Therefore, the oxygen concentrations in bentonite suspension and KCl solution are smaller than that in pure water. The data shown in Table 16 substantiate this assumption.

The microelectrode readings depend upon the resistance between silver electrode and reference cell. Theoretical calculation of oxygen concentration can not apply when the resistance approaches the limiting value of 5 kiloohms. A standard curve can therefore be used for calibrating the oxygen concentrations in different media at various resistances. Figures 5 and 6 are the standard curves, which are drawn by using the data shown in Tables 5 and 6, for 3% bentonite suspension and 0.01 N KCl solution with resistance ranges of 1 to 10 and 2 to 8 kiloohms, respectively. When these curves were used in calibrating the data in Tables 2 to 6, the oxygen concentrations in different media tecome identical to the known values in water.

The results of calculation and calibration of oxygen concentration measurements in the soils (data in table 9) are shown in Table 17.

The results from calculations are not so meaningful as those from calibrations because the resistances in soils

Figure 5.--Standard curves of oxygen concentration in bentonite suspension vs charge readingstat different resistances**



*Micro-coulombs flowing 0.1 to 0.3 second after applying 0.65 volt.

**Data from Table 5.

Figure 6.--Standard curves of oxygen concentration in 0.01 N KCl solution vs charge readings* at different resistances**



*Micro-coulombs flowing 0.1 to 0.3 second after applying -0.65 volt.

**Data from Table 6.

TABLE 17.--Average Oxygen Concentrations in Soils as Calculated with Linear Diffusion Theory and Calibrated by Standard Curves

	Oxygen Concer	Resistance.		
S011	Calculated*	Calibrated**	kΩ	
Spinks sandy loam	8.0 ± 0.24	8.6	3.4 ± 0.11	
Hillsdale sandy loam	5.6 ± 0.05	8.7	5.9 ± 0.10	
Holt sandy loam	7.1 ± 0.20	8.6	3.9 ± 0.14	

*Calculated by equations 3 and 4.

**Calibrated by standard curves for 3% bentonite suspension
 (Figure 5).

are too high for calculation. The oxygen concentrations calibrated by standard curves for bentonite suspension are higher than those in standardized medium. This is because the solubility of oxygen in the soil solution is smaller than that in the water and perhaps the bentonite suspension.

This fairly high degree of accuracy illustrates that the silver microelectrode technique could be used to make quantitative estimations of oxygen concentrations in the soil.

D. Errors

1. Errors from Silver Microelectrodes

The newly made electrodes will not give the same readings even if they were made the same size and length.

This is due to the difference in surface condition of silver wire. Treatments during manufacture which preoxidize or pre-reduce the silver surface will give higher or lower readings for a period and then drop or increase to normal.

When the electrodes have been left in the soil for a long period of time a change in the silver surface--probably a chemical deposit--will occur that changes the electrode reaction. This poisoning effect had been studied by Van Doren (18) and Letey et al. (16). The data indicate that poisoning can be prevented by removing the electrodes from the soil and reinserting them. But if one wants to sample a more nearly true environment, the electrode should be left in the soil for a few minutes. The silver surface is more chemical reactive than platinum surface; therefore, poisoning would be a more important factor influencing measurement by using silver electrode and the time in the soil should be limited.

Pretreatments of electrodes also cause the errors in measurements. Electrodes which were stored in distilled water cause less error than those stored in the atmosphere because gases such as H_2S will react with silver surface and then decrease the active electrode surface area. These errors can be lessened by standardizing electrodes in the

laboratory, discarding erratic ones, and cleaning the silver surfaces daily before making in situ measurements.

2. Errors from Reference Electrode

As discussed in Chapter IV, measurements depend upon resistance between silver electrodes and reference electrode. Therefore poor contact at the KCl bridge-soil junction causes error which might be overcome by wetting the soil around that area. Moreover, distance between the reference electrode and the silver electrodes will affect the measurements. To overcome this difficulty, the silver electrodes should be put into soil with equal distance to the reference electrode. And this distance must not be too long wherever the resistance is approaching the limiting value of five kiloohms.

After the reference electrode has been inserted into the soil, KCl will diffuse through the porous ceramic cup to the outside solution and then increase the salt content of soil solution and decrease the resistance between two electrodes. This error can be lessened by changing the saturated KCl solution after a certain period of time.

E. Suggestions

- After electrode has been inserted into the medium to be measured, a few minutes are needed for the electrode surfaces to become equilibrated with the surroundings. This procedure produces less erratic and more precise results.
- 2. As shown in Tables 5 and 6, the resistances affected the measurements in KCl solution and bentonite suspension differently. The explanation of these results is not known at present, and further study is recommended.
- 3. When the reference cell is inserted into the soil, the saturated KCl diffused out and the resistance of soil solution decreased. This flow of salt solution into soil might be reduced by filling the ceramic cup with KCl-saturated agar.
- 4. A further research is recommended on studying the reliability of the method in fine textured soils over a wider range of moisture tensions.

F. Conclusion

In view of the fact that no substances have been found to interfere in the measurement of oxygen concentration in soil suspensions with silver microelectrode, it is believed that if the electrode is completely wet (which can be determined by making a resistance measurement) by the moisture in the soil, the microelectrode can be used to measure oxygen concentrations in the soil in situ. If this measurement can be made successfully, it is possible to determine biological demand for oxygen through the soil fabric and correct the oxygen diffusion measurements so that the oxygen diffusion rates will reflect the structure of the soil per se without the confounding influence of biological oxygen sinks.

V. SUMMARY

1. A modified microelectrode technique was developed to measure oxygen concentration in the soil solution within the root environment.

2. The oxygen diffusion currents at relatively short time (0.1 to 0.3 second) are measured by an electrometer operational amplifier. The apparatus reading can be converted to the oxygen concentration in the medium by applying linear diffusion theory.

3. Electrical resistance between the silver and reference electrodes up to 5 kiloohms has no effect on the concentration measurement using an applied voltage of -0.65 volt. When higher resistance was presented in the soil, a standard curve was successfully used to calibrate the oxygen concentration.

4. It is imperative that the microelectrode be used only when the soil moisture content is sufficient to maintain a moisture film on the entire silver surface. This range of moisture tension depends upon soil texture and pore size relations. The preliminary investigations on this matter suggest that for sandy soils the electrode can

be successfully used at moisture tensions up to 60 cm. This is not a problem in dry conditions in that aeration is not a limiting factor.

5. The coefficient of variability of the ten electrode measurements in soil is about 13%, this is quite satisfactory for the determination of oxygen concentration in the heterogenous soil system. Nevertheless, it is necessary always to standardize the electrodes before in situ measurements.

6. The silver microelectrode method of measuring soil oxygen concentration has several advantages over other methods:

- Microelectrodes simulating plant roots makes it possible to measure the oxygen concentrations in microregion.
- Inexpensive, total cost of materials required for the apparatus is approximately \$600.
- c. Portable, total weight is less than 100 pounds and the power supplied by D.C. batteries.
- Rapid response, all ten electrode readings can be made within a minute.

These advantages make it a valuable tool for field studies.

7. The measurement of oxygen concentration with the silver microelectrode should assist in these types of investigations.

- a. To determine the critical oxygen concentration on root surface to insure an adequate supply throughout the tissue.
- b. Rates of oxygen consumption by the biological respiration can be determined by a microelectrode measurement of the time rate of decrease of oxygen concentration in a sealed container of soil.
- c. Provide oxygen concentration data which can be used to correct the oxygen diffusion measurements so that the oxygen diffusion rate will reflect structure of the soil per se without the confounding influence of biological oxygen sinks.

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