

FIELD ADAPTATION OF OXYGEN DIFFUSION
MEASUREMENTS WITH THE PLATINUM
MICROELECTRODE

Thesis for the Degree of M. S.
MICHIGAN STATE UNIVERSITY
David Miller Van Doren, Jr.
1955

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WITH THE PLATINUM MICROELECTRODE

By

DAVID MILLER VAN DOREN, JR.

A THESIS

**Submitted to the School of Graduate Studies of Michigan
State University of Agriculture and Applied Science
in partial fulfillment of the requirements
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MASTER OF SCIENCE

Department of Soil Science

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THESIS

ACKNOWLEDGMENT

The author wishes to sincerely thank Dr. A. E. Erickson for his guidance and assistance given throughout this research project. Dr. Erickson gave freely of his knowledge and time and provided the necessary equipment to carry this investigation to a successful completion. Special appreciation is also extended to the author's wife, Janet, for her valuable aid in editing and typing this paper.

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Approved: R. L. Cook

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ABSTRACT

FIELD ADAPTATION OF OXYGEN DIFFUSION MEASUREMENTS
WITH THE PLATINUM MICROELECTRODE

A method of evaluating soil aeration and subsequently soil structure by measuring oxygen diffusion with the platinum microelectrode is presented and adapted for use under field conditions. A theoretical parameter for comparing the structures of different soils is developed. Laboratory experiments performed verify the use of the parameter and standardize the diffusion measurements. The final equation to be used for comparison of field physical conditions is:

$$S \propto \frac{i_t \theta}{C^{1.3}}$$

where i_t is the diffusion current, $C^{1.3}$ is the initial uniform oxygen content of the soil solution, θ is the moisture content of the soil in percent by weight, and S is a structure factor dependent upon the spacial arrangement of soil solids, pore size distribution and the distribution of water in the pores.

Field measurements made on several soil treatments in an attempt to measure structural differences between various cultural treatments show no significant differences in structure. It is assumed that these differences, if present, are slight. Tillage practices are followed with good success throughout the first three months of the growing season, illustrating the effect of tillage and rainfall on soil structure. The future of this

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measurement of soil physical conditions is discussed.

David M. Van Doren, Jr.

TABLE OF CONTENTS

	Page Number
1. Introduction - - - - -	1
2. Theory - - - - -	5
3. Apparatus- - - - -	13
a. Manufacture of Platinum Micro-electrodes - - - - -	14
b. Manufacture of the Electrode Control Box- - - - -	17
c. Manufacture of the Standard Reference Electrode- - - - -	17
d. Assembly of Apparatus- - - - -	24
e. Operation of Apparatus - - - - -	24
4. Laboratory - - - - -	27
a. Polarogram with the Stationary Platinum Microelectrode- - - - -	27
b. Determination of Moisture Film on the Platinum Microelectrode- - - - -	30
5. Field Experiments- - - - -	38
a. Ferden Field Experiments, Chesaning, Michigan- - - - -	38
b. Horst Farm Experiments, Akron, Michigan - - - - -	42
c. Studies on Cropping Rotations - 1955 - - - - -	44
6. Summary and Conclusions- - - - -	52
7. Bibliography - - - - -	54

INDEX OF FIGURES

	Page Number
Figure 1 Diagram of Completed Microelectrode	15
Figure 2 Microelectrodes in Various Stages of Construction - - - - -	16
Figure 3 Microelectrode Control Box- - - - -	18
Figure 4 Wiring Diagram for Microelectrode Control Box - - - - -	20
Figure 5 Standard Silver-Silver Chloride Reference Electrode - - - - -	22
Figure 6 Sample Electrical Circuit for a Single Microelectrode - - - - -	23
Figure 7 Assembly of Apparatus for Field Measurement of Oxygen Diffusion with the Platinum Microelectrode - - - - -	25
Figure 8 Polarographic Determination of Oxygen Diffusion in 0.1 N Potassium Chloride with a Stationary Platinum Microelectrode- - - - -	29
Figure 9 Log $i_{t\theta}$ Versus Log C for Natural Cores - - - - -	34a

INDEX OF TABLES

		Page Number
Table I	Legend for Microelectrode Control Box Figures - - - - -	19
Table II	Values of $\frac{1t\theta}{C}$ Calculated for Several Natural Cores at Various Moisture Tensions - - - - -	32
Table III	Initial Readings (C) in Microamps for Several Natural Cores at Various Moisture Tensions - - - -	34
Table IV	Slopes for Curves of Log $1t\theta$ Versus Log C - - - - -	35
Table V	Values of $\frac{1t\theta}{Cl.3}$ Calculated for Several Natural Cores at Various Moisture Tensions - - - - -	36
Table VI	Results of Oxygen Diffusion Measurements on Soil Conditioner Plots, September 10, 1954 - - - -	40
Table VII	Results of Oxygen Diffusion Measurements on Horst Organic Matter Plots, 1955 - - - - -	43
Table VIII	Average of Structure Factor $\frac{1t\theta}{Cl.3}$ for Six Days on Cash Crop Rotations, 1955 - - - - -	45
Table IX	Seasonal Variation of Soil Structure $\left(\frac{1t\theta}{Cl.3}\right)$ as Affected by Cultural Practices and Rainfall- - - -	48
Table X	Comparison of Structure of Plow Layer and Sub-plow Layer in Cash Crop Rotations, 1955- - - - -	50

INTRODUCTION

Soil structure and physical edaphology have been extensively studied by soil scientists for many years. A thorough understanding of these soil conditions as well as other soil factors will make possible the production of larger, better quality crops from the land now available for cultivation.

Many methods of measuring various phases of soil structure, in both the field and laboratory, have been proposed. Soil structure has been observed with a microscope (2). It has been characterized by certain physical properties of the soil such as aggregate stability, size distribution of aggregates, bulk density and pore size distribution. It has been characterized by functional relationships such as permeability to water and air, gaseous diffusion, and by measuring the rigidity of the soil. The different methods of measuring or characterizing soil structure and its relation to plant growth are much too numerous to describe in this paper. A few of the major advantages and disadvantages of these methods will be discussed later.

In selecting a type of measurement suitable for characterization of physical conditions and their relationships to plant growth in one operation, the

problem was approached from a functional point of view. What naturally occurring process is a function of soil structure and is also very much related to plant growth? Certainly soil aeration is such a process. Secondly, what naturally occurring process would best characterize soil aeration? The movement of a gas through a concentration gradient, preferably caused by a plant, is such a process.

The diffusion of oxygen toward an actively respiring root has been chosen as the best single characterization of soil aeration and therefore soil structure. This measurement will not predict the stress the soil structure will be able to withstand without being altered, the length of time that it will remain in its present state or its resistance to root elongation. However, it will give a reliable estimate of what the present structure is, not piece by piece, but integrated as it affects the plant.

Instead of using a plant root as such, a small piece of platinum wire is substituted for the root. The oxygen at the surface of the platinum is removed by electrical means much as the oxygen at the surface of a similar sized root is removed by respiration. This causes a concentration gradient of oxygen between the surface of the platinum wire (plant root) and the main body of the soil atmosphere. The gas then tends

to diffuse from the region of greater concentration to that of lesser concentration of oxygen. The rate at which this diffusion can occur is dependent upon the concentration of oxygen in the soil atmosphere, the moisture content of the soil, and the obstruction to flow of the gas by the soil particles. This latter process is due to what is called soil structure because it is affected not only by the size distribution of these particles, but also by the spacial arrangement of the primary particles with each other. Therefore, the method of measuring oxygen diffusion with a platinum microelectrode as developed by Lemon (6) has been chosen to try to characterize soil physical conditions in situ.

It might be of interest to note some of the advantages and disadvantages of this method as compared to other methods. As stated previously this measurement will not indicate the stability or longevity of the present structure nor will it indicate individual phases of soil structure. However, this method will give an indirect measure of particle arrangement. Unlike many other measurements it can be made in situ, thereby obviating the need for collecting "representative" soil samples. It is a rapid method that gives a good single measure of physical edaphology. It is a measure of a natural process and is a result of the entire aspect of soil structure. The major disadvantage

characteristic of this measurement is the fact that a large sample (a field) is being measured by a micro method. If enough measurements are taken, however, this objection may be dispensed with.

This method of measuring oxygen diffusion is not completely untried, having been used by several other investigators. Archibald (1) has used the platinum microelectrode to measure the effect of soil aeration on the germination of oats and sugar beets. Wiersma and Mortland (13) used this technique to measure the effects of aeration on sugar beet growth and correlated aeration with response to peroxide fertilization. Several papers have been written and not yet published in which the platinum microelectrode was used to evaluate the effect of various manipulations of the soil on soil aeration and subsequent plant growth.

After this brief introduction to the concept involved, it seems advisable to look into the actual theory of the operation, introduce the equipment involved, and finally utilize this method of characterizing soil structure in the field.

THEORY

This method of measuring oxygen diffusion with the platinum microelectrode was developed by Lemon (6) and Lemon and Erickson (7,8).

When oxygen is removed from a small volume of the soil atmosphere, oxygen will diffuse from the surrounding volume to replace the gas removed. This removal of oxygen is accomplished by the reduction of oxygen at a bright platinum wire cathode.

Applying the principle of polarography, Lemon used a potential of -0.8 volt between the platinum microelectrode and a saturated calomel reference electrode to produce the limiting diffusion current of oxygen. At this potential, assuming that no substance other than oxygen is involved in the reaction at the microelectrode, the current flowing through the circuit is directly proportional to the quantity of oxygen diffusing to the surface of the microelectrode. However, one restriction must be made. The surface of the microelectrode must be covered by a water film for reduction to take place.

Kolthoff and Lingane (5) have applied Fick's Law of Diffusion to this type of measurement.

$$(1) \quad i_t = nFAf_{x=0,t} = nFAD \left(\frac{dC}{dx} \right)_{x=0,t}$$

where i_t = the current in microamps at time t .

n = the number of electrons involved in the reaction at the microelectrode with each oxygen molecule.

F = Faraday (96,500 coulombs).

$f_{x=0,t}$ = flux at the electrode surface.

A = area of the microelectrode in square centimeters.

D = diffusion coefficient of oxygen in square centimeters per second.

C = original uniform concentration of oxygen.

x = distance from the electrode surface in centimeters.

Assuming that the residual current due to ionic flow is very small, as it is in the soil, the entire current is a result of the reduction of oxygen at the microelectrode. Lemon has shown that the limiting diffusion current is reached in three to five minutes. Therefore the value of t used in this paper is five minutes. The value of n is either two or four depending upon whether hydrogen peroxide or water is the reduction product of oxygen at the microelectrode. This problem has not as yet been solved.

At a constant potential and constant electrode size, n , F and A are constants. The diffusion current, i_t , is then proportional to D and $\left(\frac{dC}{dx} \right)_{x=0,t}$. The greater the original concentration of oxygen, the greater the concentration gradient from the body of the soil atmosphere to the electrode surface, where the concentration of oxygen is essentially zero, and the greater the diffusion current. The diffusion coefficient of oxygen

depends upon the nature of the gas itself and upon the characteristics of the soil which impede the movement of the gas to the microelectrode. Since the nature of the gas is constant at a given temperature, the variation in D between locations in the soil is due to properties of the soil. These properties are essentially soil structure and soil moisture.

Fick's Law may be simplified to show the variables influencing the diffusion current for any situation in the soil.

$$(2) \quad i_t = KD \left(\frac{\partial C}{\partial x} \right)_{x=0, t}$$

where $K = nFA$, and D , C and x have the same meaning as before.

Kolthoff and Lingane analyze the factors influencing the diffusion coefficient, D :

$$(3) \quad D = \frac{RT}{N} \zeta_\xi$$

where R = molar gas constant.

T = absolute temperature.

N = Avagadro's number.

ζ_ξ = mobility of oxygen through the soil.

According to Kolthoff and Lingane, the diffusion coefficient of a molecule depends upon the characteristics of the molecule (in this case oxygen gas), the medium in which the movement takes place, and if the medium is aqueous, upon its ionic strength. For the range of salt concentrations in most soils and the accuracy with which the oxygen diffusion measurements can be obtained, this slight dependence upon ionic

strength may be neglected. The factors influencing $\mathcal{D}_i$ are just the characteristics of the molecule and the medium.

The medium consists of the three phases of the soil - soil air, soil water, and soil solids. Comparison of data from various tables shows that the mobility of oxygen is much greater in air than in an aqueous solution. Under a given set of soil physical conditions as the moisture content of the soil increases, it is logical to assume that the rate of diffusion decreases due to the effective reduction of the mobility of the oxygen. Therefore:

$$(4) \quad \mathcal{D}_i \propto \frac{1}{\theta^b}$$

where θ = soil moisture content in percent by weight.

b = exponent, assumed equal to one for the present.

Also, the mobility of oxygen is dependent upon the physical impedance offered by the soil solids.

$$(5) \quad \mathcal{D}_i \propto S$$

where S may be defined as a soil structure variable consisting of the mechanical impedance to oxygen diffusion due to the arrangement of soil particles and the pore size distribution and subsequent distribution of water in the pores.

As the impedance to oxygen diffusion increases, S decreases. Relying upon present conventions, as S decreases the desirability of the structure decreases. Combining equations (4) and (5):

$$(6) \quad j_z \propto \frac{S}{\theta}$$

$$\text{and (7)} \quad j_z = k \frac{S}{\theta}$$

where k is a proportionality constant depending upon the characteristics of the gas, oxygen, as related to its mobility through air, aqueous solutions, and across air-water interfaces, and is independent of soil physical conditions.

Combining equations (3) and (7):

$$(8) \quad D = \frac{RT}{N} k \frac{S}{\theta}$$

$$\text{or (9)} \quad D = K' \frac{S}{\theta}$$

$$\text{where } K' = \frac{RTk}{N}$$

Combining equations (2) and (9) yields:

$$(10) \quad i_t = KK' \frac{S}{\theta} \left(\frac{\partial C}{\partial X} \right)_{X=0, t}$$

It follows from equation (10) that if a measure of θ and $\left(\frac{\partial C}{\partial X} \right)_{X=0, t}$ can be obtained and K and K' evaluated for a particular set of conditions, the parameter of soil structure, S , can be determined by measuring the diffusion current, i_t . K can be calculated from n , F and A , but K' as yet cannot be calculated because the absolute value for k has not been obtained. Therefore, equation (10) can be altered to:

$$(11) \quad i_t \propto \frac{S}{\theta} \left(\frac{\partial C}{\partial X} \right)_{X=0, t}$$

Rearranging:

$$(12) \quad S \propto \frac{i_t \theta}{\left(\frac{\partial C}{\partial X} \right)_{X=0, t}}$$

Knowing i_t , θ , and $\left(\frac{\partial C}{\partial X} \right)_{X=0, t}$ different soils may be compared with each other on a qualitative or comparative basis using equation (12).

The diffusion current, i_t , is measured in microamps and θ in percent by weight. The remaining factor $\left(\frac{\partial C}{\partial x}\right)_{x=0,t}$ has not been measured quantitatively. A method is being developed using a measure of the current flow at $t = 0$ to determine the original concentration of oxygen in the soil in equilibrium with the surface of the microelectrode. The method may be summarized in a few sentences. When measuring oxygen diffusion at the microelectrode the first increment of current flow from $t = 0$ to $t = \frac{1}{\infty}$ is due to the concentration of oxygen at the surface of the microelectrode. This concentration should be a measure of that throughout the rest of the system. The initial flow is recorded as the farthest point of swing of the microammeter needle. However, this reading is affected by the surface adsorption of oxygen by the platinum and the characteristics of the microammeter. These latter factors affecting the initial swing should be the same for each microelectrode provided the electrodes are similar as to construction and history and the ammeter is stable and does not shift with time. Therefore, this measurement of the original oxygen concentration, which will hereafter be referred to as the "initial reading", can be used in a comparative manner in equation (12).

Using the initial reading as such to compare soil structure, its relationship to $\left(\frac{\partial C}{\partial x}\right)_{x=0,t}$ can be shown as

follows:

- a. When $t = 0$, the concentration of oxygen in the soil atmosphere is proportional to the initial reading, C .
- b. If $t = 5$ minutes in every case and the electrode is a constant size, x is defined. (Lemon evaluated $x = 5$ millimeters.)
- c. Therefore, $\left(\frac{\partial C}{\partial x}\right)_{x=0,t} \propto \frac{\text{initial reading}}{5 \text{ mm}}$
- d. or, $\left(\frac{\partial C}{\partial x}\right)_{x=0,t} = K'_c \frac{C}{5 \text{ mm}}$
where K'_c is the proportionality constant dependent upon the adsorption of oxygen on the platinum wire.
- e. or, $\left(\frac{\partial C}{\partial x}\right)_{x=0,t} = K_c C$
where $K_c = \frac{K'_c}{5 \text{ mm}}$

Therefore, C can be substituted for $\left(\frac{\partial C}{\partial x}\right)_{x=0,t}$ in equation (12) yielding equation (13).

$$(13) \quad S \propto \frac{i_t \theta}{C}$$

where i_t and C are measured in microamps and θ in percent. The parameter, S , is dimensionless and can be used to compare the structure of different soils and locations.

In summary, the parameter, S , includes the physical variables (1) arrangement of soil particles, (2) pore size distribution, and (3) the distribution of water in the pores, all of which contribute to the physical impedance of the soil to oxygen diffusion. Equation

(13) is valid provided the following are experimentally held constant: A , T , t , and the applied potential. If these are constant, x and k will be constant, and n , F , R and N are always constant for soil conditions. By following carefully the prescribed procedure in the field or laboratory, these conditions can be maintained, with the exception of constant temperature. Errors introduced here are small because of the small variations in soil temperatures during the growing season. Therefore, reasonably accurate results may be obtained.

APPARATUS*

Use of microelectrodes to characterize the physical properties of an entire field requires specially designed equipment. The microelectrodes must be small enough to simulate plant rootlets and be of such a size and shape that they will not alter the physical properties of the region in which they are inserted into the soil. They must also be strong enough to withstand a good deal of punishment, and cheap enough to manufacture if there is considerable breakage.

Since the electrodes are micro in nature, they will encounter a wide variety of conditions, even in a soil with fairly uniform physical characteristics. If a large enough number of measurements are taken, however, a statistically significant average of these various locations may be calculated. This average will effectively characterize the entire system known as soil structure for the field under consideration. For this purpose an electrode control box was designed to enable the operator to take ten measurements in little more time than it takes to make a single measurement.

Finally, the standard reference electrode must be large enough to withstand continuous current flow

*All of the apparatus described here was developed by Dr. A. E. Erickson of the Michigan State University Agricultural Experiment Station.

without becoming polarized, and must be sturdy enough to withstand considerable shaking and jarring.

Manufacture of Platinum Microelectrodes.

A 10 inch length of 20 gauge copper wire is fused with 6 to 8 millimeters of 22 gauge pure platinum wire. The wire is then placed in a piece of glass tubing 9 inches long and 5 millimeters in diameter. One end of this glass tubing has been previously drawn to a taper and almost sealed. The platinum wire is placed at the tapered end of the tubing with 2-3 millimeters of platinum exposed. A liquid plastic material (Castolite) is drawn up into the glass tubing through the tapered end by placing suction at the opposite end. When the desired height of plastic is drawn up into the tube, the suction is removed and the end containing the platinum wire is pushed gently, but firmly, into a small piece of cork to seal it and prevent the plastic from draining out of the glass tube. After allowing the plastic to set in a 60°C oven for at least 48 hours, the glass tubing is chipped away from the plastic. Enough plastic is removed from the platinum so that exactly 4 millimeters of the metal is exposed. A sketch of the microelectrode is shown in Figure 1. The microelectrode in various stages of construction is illustrated in Figure 2.

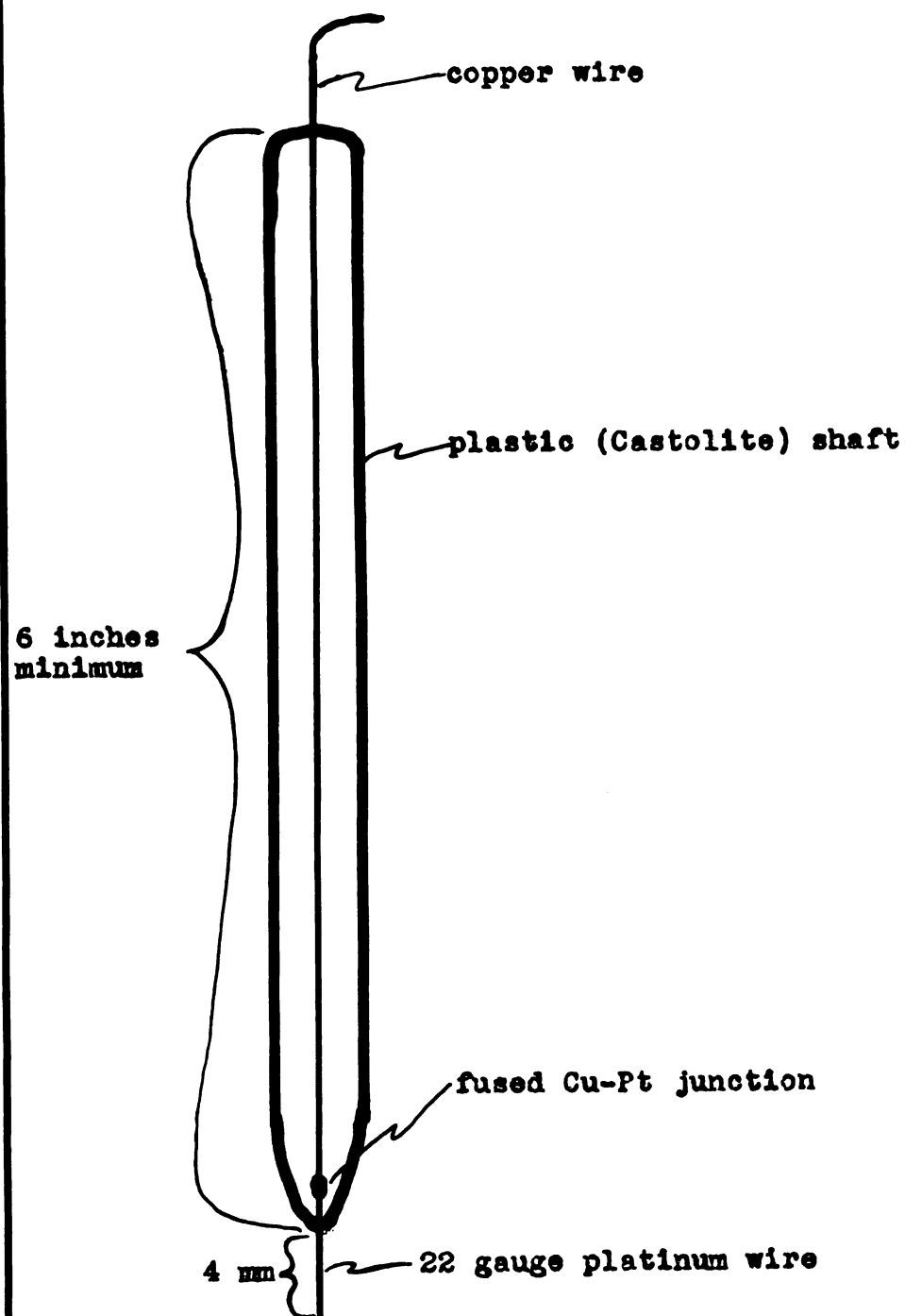


FIGURE 1: Diagram of Completed Microelectrode

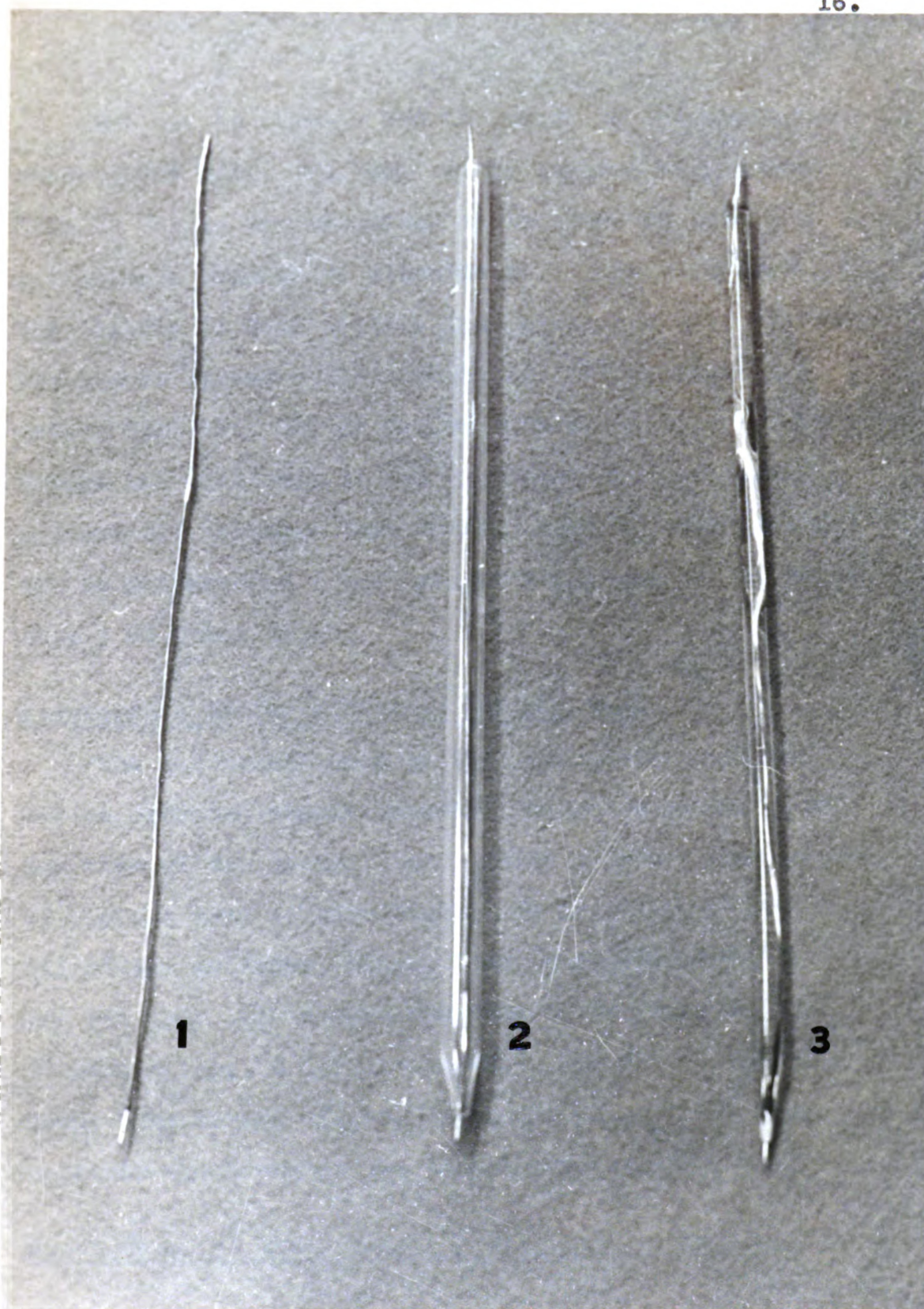


FIGURE 2: Microelectrodes in Various Stages of Construction
1. Copper-platinum wires fused.
2. Fused wires inside glass tubing.
3. Completed microelectrode.

The use of plastic for the shaft of the electrode works quite well. The tip can be tapered with a metal file to enable the electrode to be inserted into the soil with a minimum of disturbance of the structure. The plastic is less brittle than glass and will withstand some stress without breaking. If breakage does occur, the shaft can be mended with masking tape. Even though the electrode is fairly sturdy and resilient, appreciable breakage does occur. However, the electrodes can be produced on a mass production basis for approximately 35 cents apiece.

Manufacture of the Electrode Control Box.

The box is designed so that ten microelectrodes may be operated simultaneously. Figure 3 presents the top view of the control box. Table I is an explanation of symbols used in this figure and in Figures 4 and 6. All of the switches, plugs, leads and microammeters are set in a lightweight aluminum instrument chassis 17 inches long, 9 1/2 inches wide, and 2 1/4 inches deep. The wiring diagram in Figure 4 shows the connections which enable the control box to operate.

Manufacture of the Standard Reference Electrode.

The saturated silver-silver chloride reference electrode was decided upon as the type most likely

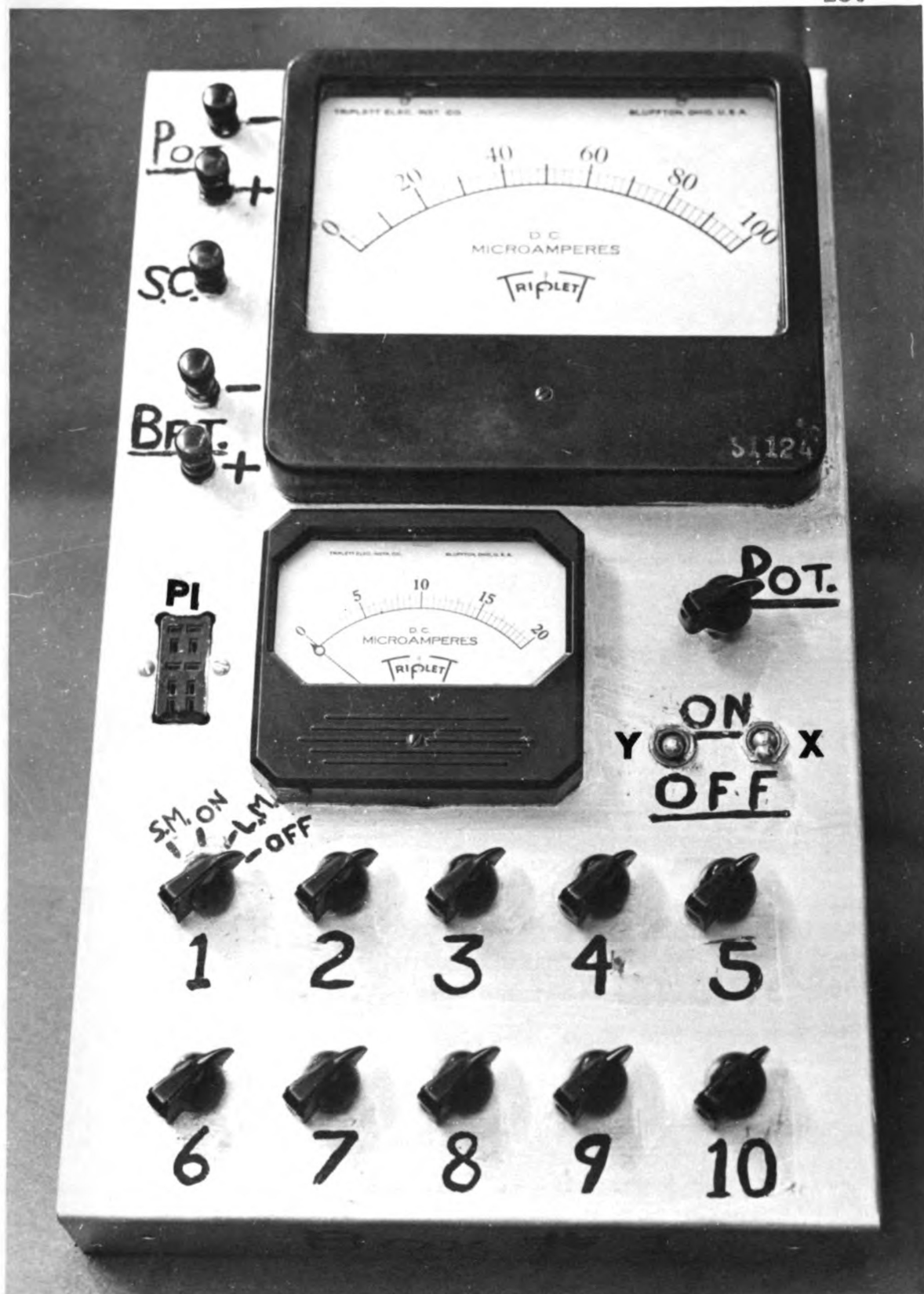


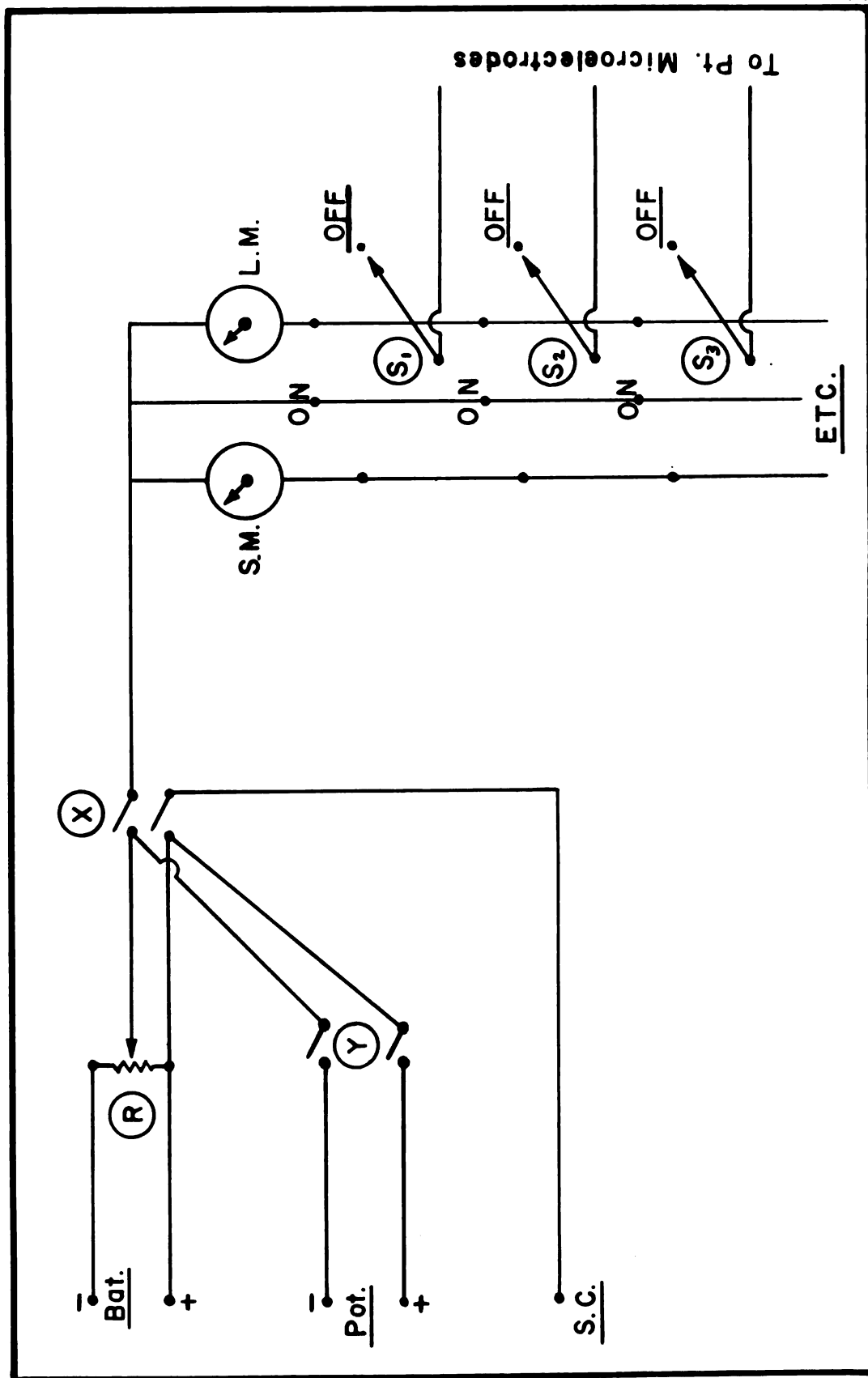
FIGURE 3: Microelectrode Control Box

TABLE I

Legend for Microelectrode Control Box Figures

- Pl - 10 hole plug for connecting 10 electrodes to the circuit simultaneously.
- BAT. + - positive terminal of the 2 volt wet cell battery.
- BAT. - - negative terminal of the 2 volt wet cell battery.
- POT. + and - - connection for a voltmeter to measure voltage applied between the standard cell and the microelectrode.
- S.C. - saturated silver-silver chloride standard cell terminal.
- R - rheostat for regulating the potential applied from the battery.
- X - double pole-single throw switch to connect battery to circuit.
- Y - double pole-single throw switch to allow measurement of the applied voltage with a voltmeter.
- S_n - 5 position rotary shorting switch for connecting an electrode to the large microammeter plus the electrical circuit (designated by L.M. next to switch), to only the electrical circuit (designated by ON next to switch), or to the small ammeter plus the electrical circuit (designated by S.M. next to switch).
- L.M. - large microammeter, range of 0-100 microamps.
- S.M. - small microammeter, range of 0-20 microamps.

FIGURE 4: Wiring Diagram for Microelectrode Control Box



to withstand rigorous field conditions and still operate correctly. A 50 inch length of pure silver foil 4 inches wide is accordioned into a plastic food container 8 inches high and 4 inches square. A small strip of silver, still attached to the main body of the metal, is led through a slit in the plastic case and sealed with Epon VI adhesive (Shell Chemical Corporation). A short piece of glass tubing is sealed into another side of the plastic case so that a length is exposed both inside and outside the case. The cell is charged by passing current through the cell containing approximately 0.1 N hydrochloric acid. A large platinum gauze is used as one electrode and the silver acts as the other. Silver chloride is plated out onto the surface of the silver foil as the silver is oxidized to silver, valence plus 1, by the current. The cell is then rinsed out and filled with saturated potassium chloride. A piece of Tygon plastic tubing is attached between the glass tubing sealed into the plastic case and a porous clay cup. This acts as the salt bridge to the soil. A pinch clamp is used to close off this contact when desired. Two views of the completed standard cell are presented in Figure 5.

The electrical circuit is shown in Figure 6. The potential of -0.8 volt, as measured with a voltmeter, is applied between the platinum microelectrode and



FIGURE 5: Standard Silver-Silver Chloride Reference Electrode, Side View

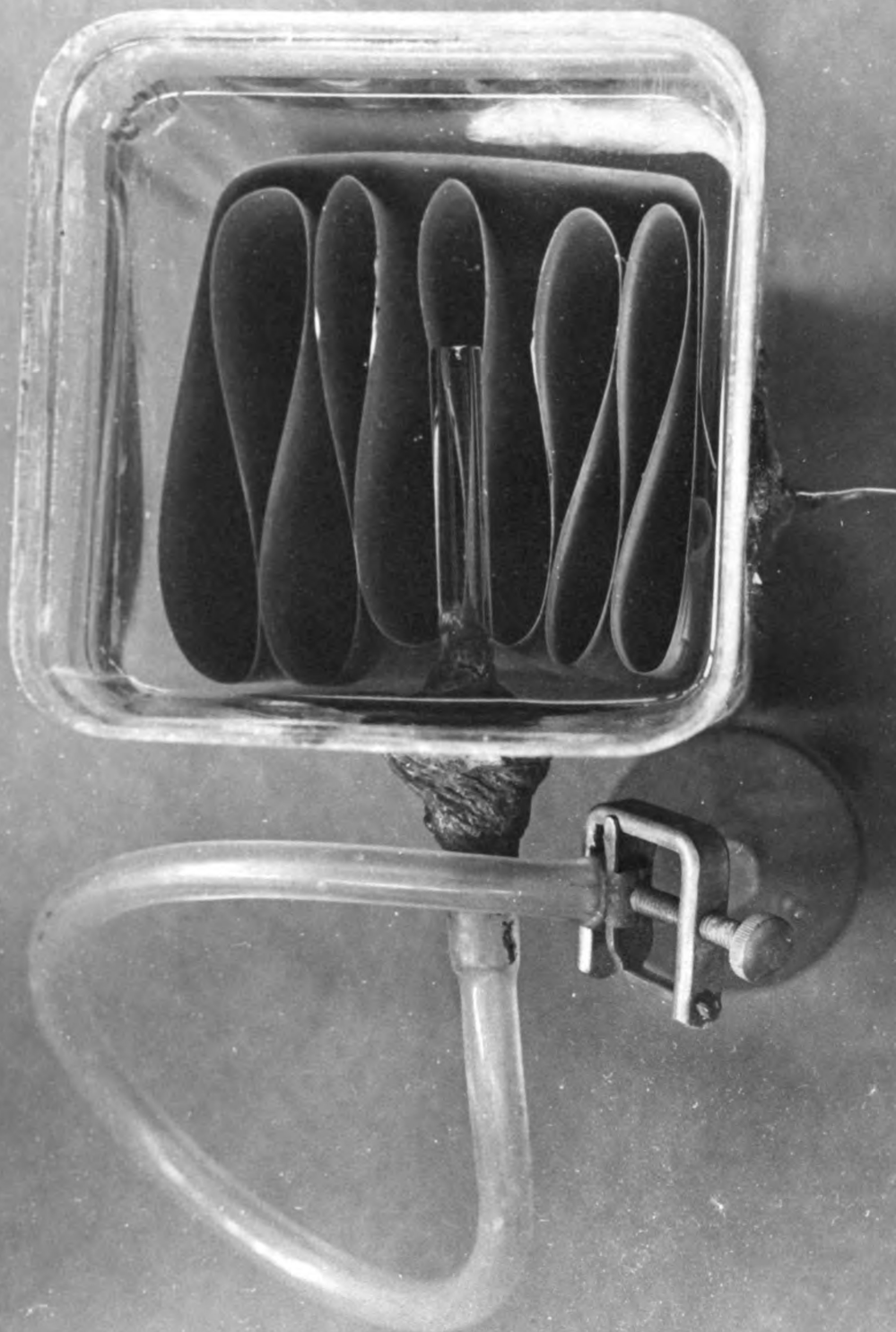
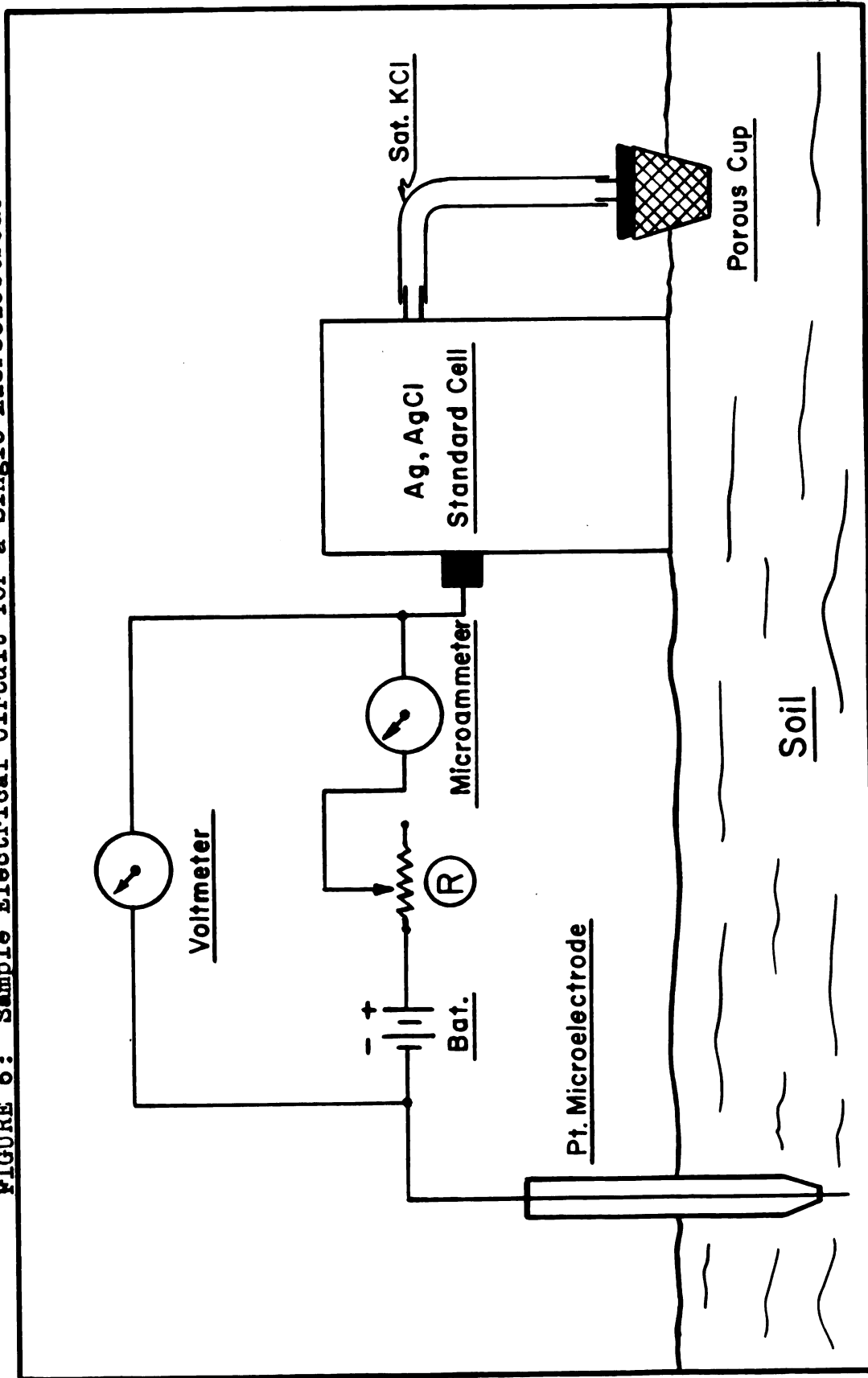


FIGURE 5: Standard Silver-Silver Chloride Reference Electrode, Top View

FIGURE 6: Sample Electrical Circuit for a Single Microelectrode



the standard cell by the battery. Oxygen is reduced at the surface of the platinum, and current flows through the above ground circuit, through the standard cell into the ground. The salts in the soil complete the electrical circuit between the porous cup and the platinum microelectrode.

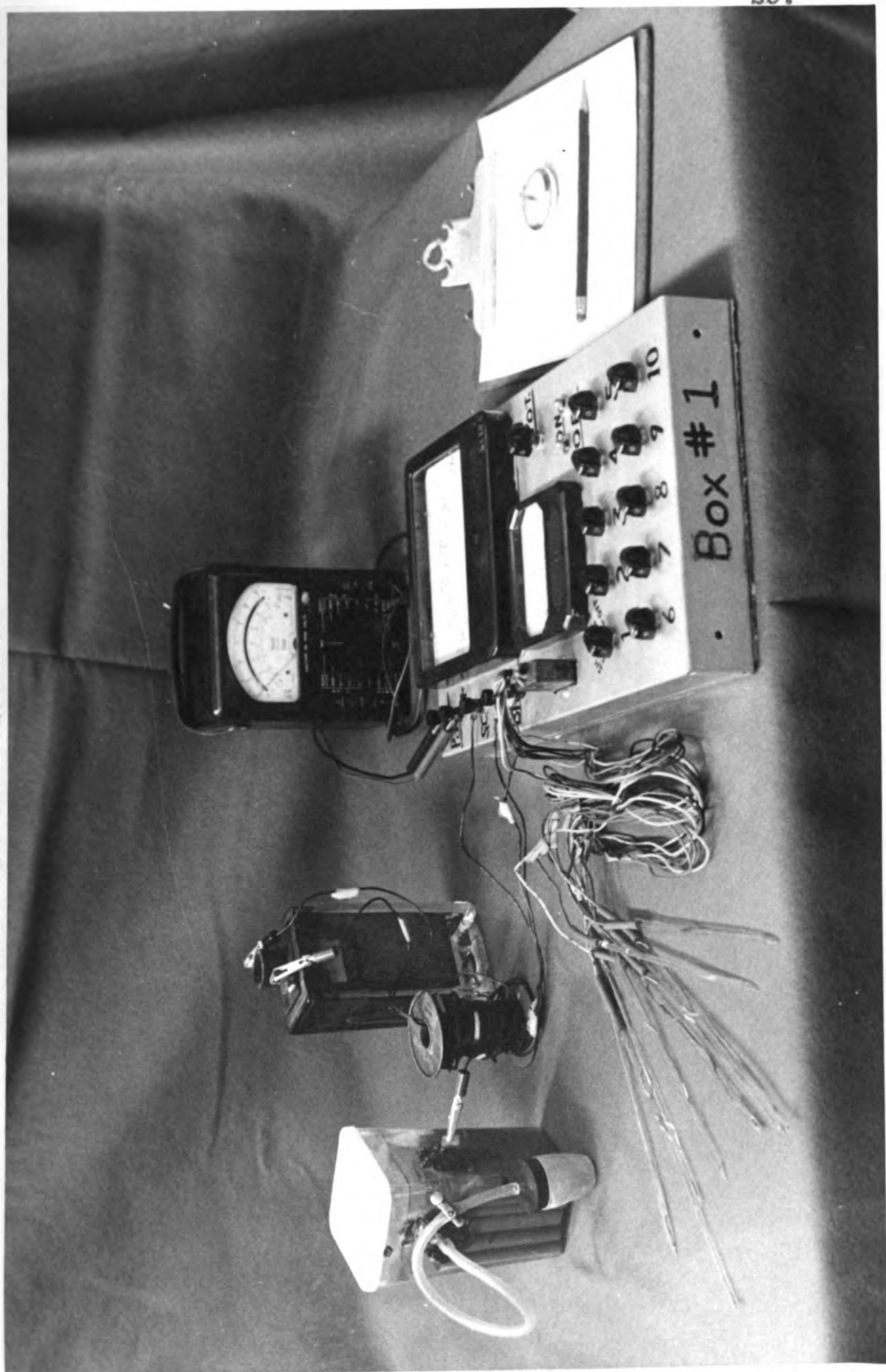
Assembly of the Apparatus.

The terminals of a 2 volt wet cell battery are connected with the appropriate terminals of the control box. An alligator clip is attached to the strip of silver protruding from the reference cell and a lead is attached to the S.C. terminal on the control box. Ten electrodes are soldered to 5 foot lengths of insulated wire and these wires are soldered to a male plug which is inserted into the 10 hole plug (P1) on the control box. The entire apparatus, as assembled, is shown in Figure 7.

Operation.

The two switches, X and Y, are turned on and the rheostat, R, is adjusted so that the potential between the standard cell and the platinum microelectrodes is exactly -0.8 volt. The porous clay cup is inserted into the soil, the soil wetted with more potassium chloride if necessary, and the screw clamp opened to permit electrical contact with the soil. The microelectrodes

**FIGURE 7: Assembly of Apparatus for Field Measurement of Oxygen Diffusion
with the Platinum Microelectrode**



are pushed approximately 4 inches into the soil and the measurements are ready to be taken.

A stopwatch is started and the first switch, S_1 , is turned to L.M. The farthest point of swing of the needle is recorded as the initial reading and the switch is turned to ON. This process is repeated rapidly for the other 9 switches, allowing only enough time between readings to permit the meter needle to come to rest at zero after the meter is disconnected from the circuit. At the end of 5 minutes, switch S_1 is turned to S.M. and the reading is recorded as the 5 minutes reading, or i_t , and the switch turned back to ON. This process is repeated rapidly for the remaining switches. All switches, S_n , X and Y, are then turned off, the electrodes removed from the soil, replaced at a different location and the entire process repeated with the exception of setting the rheostat. If the battery potential is constant with time, the rheostat need only be checked periodically to be sure that it has not been changed accidentally.

Using this apparatus, ten diffusion readings of 5 minute duration and the initial measure of oxygen concentration for each can be taken in about 6 minutes, saving a great deal of time and allowing more measurements to be taken during a day's work.

LABORATORY

Before taking the microelectrodes into the field several problems had to be resolved.

Polarogram with the Stationary Platinum Microelectrode.

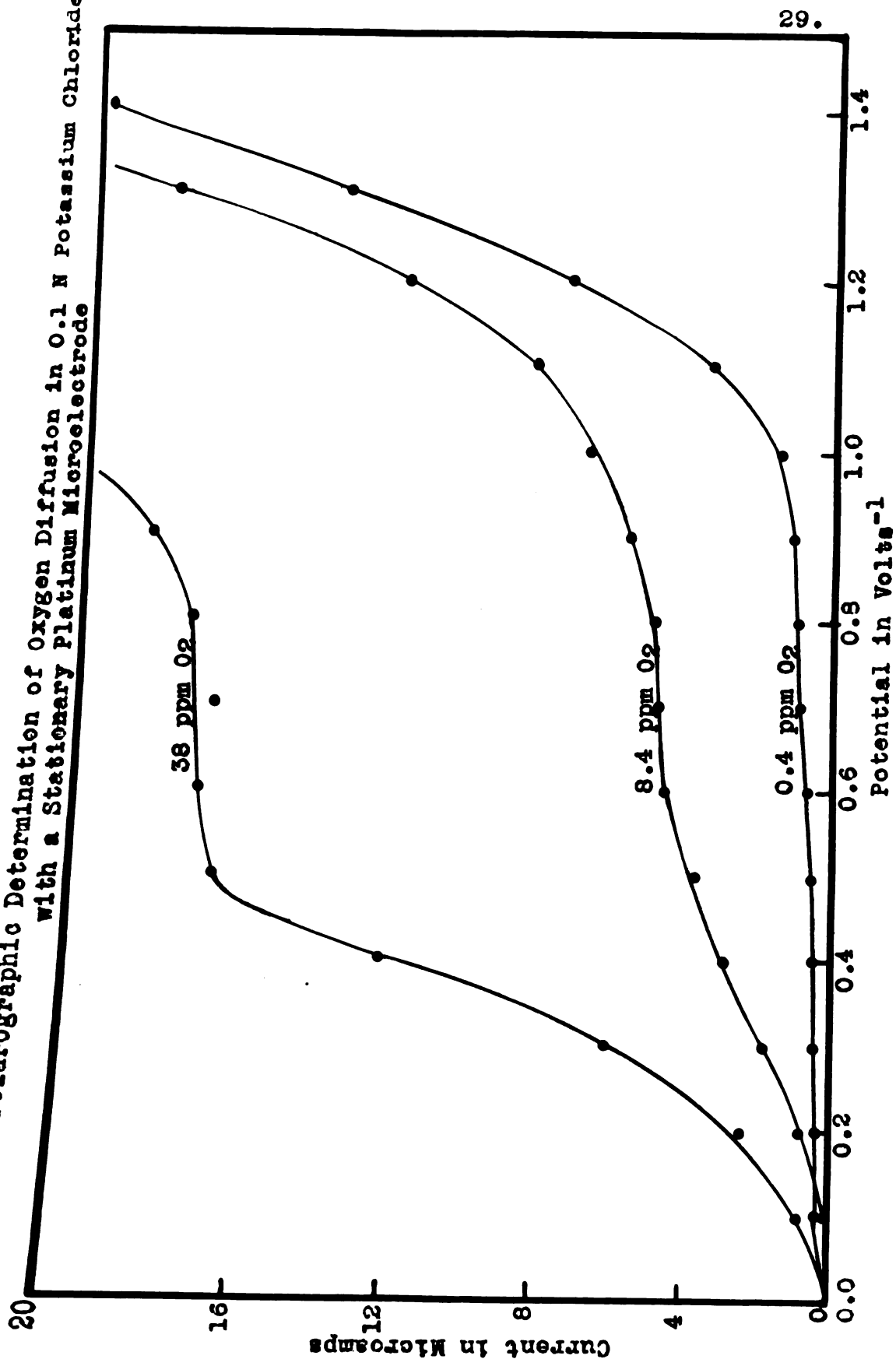
Doubts had arisen that a polarogram could be made properly with a stationary platinum microelectrode. It was argued that eddy currents would be set up at the electrode due to the formation of water at the surface of the platinum, and that these currents would cause varying diffusion rates of oxygen to the electrode. A laboratory experiment was set up to discover if this were actually the case.

A container was built which could be completely closed off to the atmosphere. A dilute solution of potassium chloride was introduced and gas of known oxygen content bubbled through the solution until the solution and gas in the chamber were of the same oxygen content as the bubbled gas. A platinum microelectrode and potassium chloride contact to a saturated calomel electrode had previously been placed in the solution. The solution was stirred with a magnetic stirrer for 1 minute, allowed to stand for 5 minutes, and the proper potential applied for 1 minute. The diffusion current was read at the end of that time. The potential was then removed and the process repeated at a different

potential. Potentials of -0.1 to -1.4 volt were applied and solutions of 0.4, 8.4 and 38 parts per million oxygen were measured. The polarograms are plotted in Figure 8. At the end of 1 minute the microammeter showed the current to be steady, and it is assumed that eddy currents, if produced, had no effect on the measurement of diffusion.

Lemon and Erickson (8) published a graph similar to that in Figure 8 with the exception that the solution was a 1:1 soil to water suspension of Brookston clay loam. The "plateau" regions of the curves of the 1:1 suspension occurred between -0.7 and -0.8 volt. These same potentials lie on the plateaus of the curves in Figure 8, confirming the use of -0.8 volt as that potential which produces the limiting current. It is logical to assume that if these two types of polarograms can be determined without disturbing effects of eddy currents, the same type of polarogram could be determined in the soil where resistance to such currents would be greater than in a soil-water suspension or in a water solution. In no case during all the field measurements was there any evidence of eddy currents. More or less violent fluctuation in diffusion current was observed when the control box was wetted by rain and shorted to the ground. In this case the measurements were of no value anyway.

FIGURE 8: Polarographic Determination of Oxygen Diffusion in 0.1 N Potassium Chloride with a Stationary Platinum Microelectrode



Determination of Moisture Film on the Platinum Micro-electrode.

One of the limitations of this determination is that the platinum microelectrode must be completely covered with a moisture film in order to operate as a reducing surface for oxygen. If it were not so completely covered, the effective size of the electrode would be reduced, causing differences in size between electrodes. Equation (13) would then no longer be valid. Another laboratory experiment was set up to evaluate the moisture stress necessary to rupture the complete moisture film surrounding the microelectrode.

Natural cores of the top 3 inches of several types of soil were taken during 1954. These cores were saturated with water and placed on pF tables to obtain the desired moisture tensions. After the cores had come to equilibrium they were removed from the tables and placed on a moist porous plate. Three electrodes were placed in each core and the potassium chloride bridge connected to the porous plate to complete the circuit. The initial reading was taken and the diffusion current was recorded after 5 minutes. For moisture tensions greater than 60 centimeters of water, a pressure cooker was used. The weight of the core was recorded after each reading and after all the oxygen diffusion measurements were taken the core was oven dried at 105°C. The moisture

content in percent by weight was calculated for each core at the various moisture tensions.

According to equation (13): $S \propto \frac{1t\theta}{C}$. Relating this equation to equation (10) and e., page 11, equation (14) is obtained.

$$(14) \quad SKK'K_c = \frac{1t\theta}{C}$$

where $K = nFA$ and K' and K_c have the same meaning as before.

$$\text{or (14a)} \quad SK'K_0nF = \frac{1t\theta}{C} \times \frac{1}{A}$$

It is assumed that n , F and A were all constants when the proportionality constant K was introduced. After the moisture film on the platinum microelectrode has burst, as soil moisture comes under successively greater stress, this film will shrink in area, effectively reducing the operating size of the electrode, A .

In order to maintain the equality of equation (14a), assuming constant S in each core, $\frac{1t\theta}{C}$ must decrease as A diminishes. Or, if A remains constant, $\frac{1t\theta}{C}$ must remain constant. To find out if this is true, $\frac{1t\theta}{C}$ has been calculated at each moisture tension for the different cores and is reported in Table II.

In many cases the values were quite uniform until the large change in moisture tension from 60 to 342 centimeters. Then a marked increase in the $\frac{1t\theta}{C}$ value was observed. This was quite unexpected and indicated that some variable not previously evaluated had caused this value to increase instead of remain constant or to decrease.

TABLE II

Values of $\frac{10^6}{C}$ Calculated for Several Natural Cores
At Various Moisture Tensions

Cores	Moisture Tension in Centimeters of Water									
	10	20	30	40	60	342	513	1026		
Conover-66 (Heavy Loam)	1.7	1.4	1.5	1.8	2.7	1.7	1.5	1.9		
Brookston-67 (Heavy Loam)	2.8	1.8	2.0	2.2	2.3	3.0	3.0	4.4		
Marinesco-74 (Sandy)	3.9	4.3	5.2	5.3	4.5	5.8	4.9	4.6		
Marinesco-77 (Loamy Sand)	5.1	4.9	4.4	4.9	5.4	9.6	9.1	7.8		
× Selkirk-69 (Clay)	1.6	1.9	1.7	2.7	3.9	5.3	5.4	5.8		
× Pickford-72 (Clay)	4.0	4.3	3.1	4.3	5.3	10.1	13.1	14.1		
Skane-80 (Sandy Loam)	2.7	1.8	2.7	3.2	4.7	4.1	3.7	4.0		
× Munising-86 (Sandy Loam)	2.3	3.9	4.5	5.3	7.7	8.2	9.1	7.8		

A comparison of the initial readings in Table III with the $\frac{i_t \theta}{C}$ values given in Table II shows that the large increase in the latter value is accompanied by a large increase in initial reading. It seems reasonable that these two large increases may be related to one another. It may be postulated that as the increased oxygen content at the surface of the microelectrode causes a larger and larger initial reading, the inertia of the microammeter has a greater effect upon the reading. In other words, as the needle deflection increases, or tends to increase, the inertia inherent to the microammeter reduces the reading to a greater extent. The following procedure was used to discover if this were actually the case.

Let equation (14) be changed so that the term C has an exponent, a. This exponent is due entirely to the characteristics of the microammeter and could be termed the microammeter correction factor.

$$(14b) \quad SKK'K_c = \frac{i_t \theta}{C^a}$$

$$\text{Then (15) } \log i_t \theta = a \log C + \log SKK'K_c$$

Equation (15) is that of a straight line with a the slope and $\log SKK'K_c$ the intercept. $\log i_t \theta$ versus $\log C$ was plotted for all the cores and a typical example is shown in Figure 9. The slopes for all the curves are recorded in Table IV.

TABLE III

Initial Readings (C) in Microamps for Several Natural Cores
at Various Moisture Tensions

Cores	Moisture Tensions in Centimeters of Water									
	<u>10</u>	<u>20</u>	<u>30</u>	<u>40</u>	<u>60</u>	<u>342</u>	<u>513</u>	<u>1026</u>		
Conover - 66	12	17	22	21	18	83	100	93		
Brookston - 67	6	9	8	9	17	56	62	65		
Marinesco - 74	11	8	16	17	17	49	53	86		
Marinesco - 77	19	22	28	30	37	82	80	81		
Selkirk - 69	20	23	22	17	32	74	69	66		
Pickford - 72	17	13	18	19	23	81	46	46		
Skanee - 80	11	18	15	21	20	81	74	73		
Munising - 86	4	13	18	18	22	83	74	76		

34a.
FIGURE 9: $\log i_{t\theta}$ Versus $\log C$ for Natural Cores

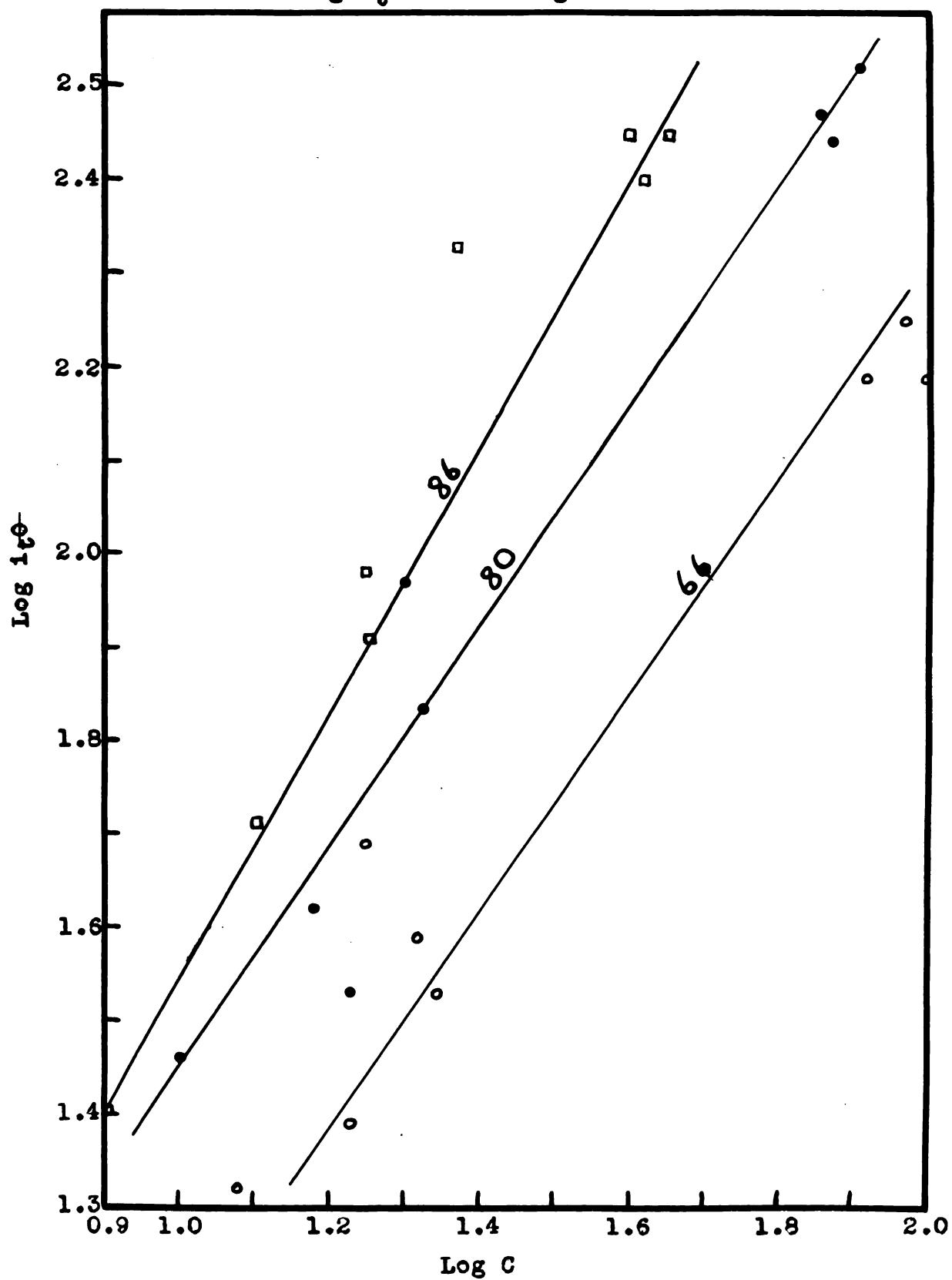


TABLE IV: Slopes for Curves of Log $\frac{1}{C} \theta$ Versus Log C

<u>Core Number</u>	<u>Slope</u>
66	1.17
67	1.20
74	1.08
77	1.20
69	1.46
72	1.43
80	1.21
86	1.44
Average	1.3

The average slope of all lines was 1.3. This value was selected for a and $\frac{1}{C} \theta$ was calculated for all cores at each moisture tension and recorded in Table V. It is evident that if this value is constant for each core, the effective surface, A , of the microelectrode is constant. In other words, as the moisture tension increases, if $\frac{1}{C} \theta$ remains constant, then the moisture film is intact on the surface of the microelectrode and is no longer a limitation to field application. As can be seen in Table V, the values are relatively constant for each core, except for the Marinesco, number 74, which gave a downward trend indicative of a shrinking moisture film. This soil is the sandiest of the eight studied and this fact may explain why the moisture film started to shrink prior to 1 atmosphere tension.

There are several reasons why the values in Table V are only relatively constant. Up to 60 centimeters tension the cores were not covered so that evaporation may have caused some discrepancies with the observed

TABLE V
Values of $\frac{10}{Cl.3}$ Calculated for Several Natural Cores
at Various Moisture Tensions

Cores	Moisture Tensions in Centimeters of Water							
	<u>10</u>	<u>20</u>	<u>30</u>	<u>40</u>	<u>60</u>	<u>342</u>	<u>513</u>	<u>1026</u>
Conover - 66	0.8	0.6	0.6	0.7	1.2	0.5	0.4	0.5
Brookston - 67	1.7	1.0	1.1	1.2	1.0	0.9	1.5	1.3
Marinesco - 74	1.9	2.3	2.3	2.2	1.9	1.8	1.5	1.2
Marinesco - 77	2.1	2.0	1.6	1.8	1.8	2.6	2.5	2.1
Selkirk - 69	0.7	0.8	0.7	1.1	1.4	1.5	1.5	1.6
Pickford - 72	1.7	2.0	1.2	1.8	2.1	2.1	4.8	3.8
Skanee - 80	1.3	0.8	1.2	1.4	1.9	1.1	1.0	1.0
Munising - 86	1.5	1.8	1.8	2.2	3.1	2.2	2.5	2.4

moisture data. Also, the microelectrodes were left in place and some poisoning of the platinum may have occurred. For tensions above 60 centimeters of water, the cores were placed in pressure cookers. To do this the microelectrodes had to be removed and could be replaced only after the cores were taken from the cookers to be measured. Many holes were thereby dug in the core where the electrodes had been. This could cause variation in S and therefore in $\frac{1_t \theta}{Cl.3}$, but the accuracy is sufficient to validate the reasoning throughout this paper.

In conclusion it may be stated that over a wide range of soils a moisture tension as high as 1 atmosphere and probably higher will maintain a complete moisture film on the surface of the platinum microelectrode.

As a sidelight to this study the data were analyzed to see if the exponent on θ should be a value other than unity. Correlations between 1_t and θ were calculated. In no case was the coefficient of correlation less than -0.83 indicating a linear relationship between 1_t and θ . Therefore, if the exponent on 1_t is unity, the exponent on θ must also be unity.

Equation (13) may now be written in final form to be used to analyze data from field work.

$$(16) \quad S \propto \frac{1_t \theta}{Cl.3}$$

FIELD EXPERIMENTS

Now that the theory of oxygen diffusion measurements has been developed, a parameter for measuring and comparing soil structures introduced, and equipment both sensitive and sturdy constructed, the apparatus is ready to be taken into the field.

Perden Field Experiments, Chesaning, Michigan.

The first field study was completed in 1954 on a series of plots designed to study the effects of soil conditioners on structure and plant growth. The plots are 21 feet square and are laid out at random on an acre of flat Brookston clay loam. The treatments studied, with four replicates of each, are as follows:

1. Check
2. IBMA (2000 pounds/acre)
5. IBMA (250 pounds/acre)
10. Crude Abeidic Acid (3000 pounds/acre)
14. VAMA (1000 pounds/acre)
17. Lignin Sulfate (15,000 pounds/acre)

Pea beans were grown and harvested, with the weight of the beans per plot recorded at harvest time.

Only one set of the oxygen diffusion measurements can be of any use because only on this particular day were moisture samples taken. At the same time oxygen diffusion as measured with the nitrogen filled tube developed by Raney (9) was performed to supplement the diffusion measured with the platinum microelectrode.

The comparative data are given in Table VI.

The data obtained with the Raney tubes cannot be used to characterize structure because they do not take into account the oxygen level of the soil atmosphere and the soil moisture content. They are used as a soil aeration factor and can be compared with the diffusion reading, i_t , a comparable factor obtained with the microelectrodes. Such a comparison yields absolutely no significant results or correlation. This can be explained on the basis of what the two methods for measuring oxygen diffusion actually determine. The Raney tubes are macro in size and measure the diffusion through large pores, cracks and worm holes. These plots were very dry and large cracks existed in the surface. Measurements of this nature under such conditions may yield data not indicative of the entire aeration condition of the soil. On the other hand, the microelectrodes will not function if they happen to be placed in such a crack or void. They operate when surrounded by soil particles and a complete moisture film. In such surroundings, they measure diffusion through the smaller pores, as affected by the supply of oxygen which can be circulated through the larger pores and cracks. Therefore, these measurements are believed to be a more accurate measure of the whole soil aeration than that obtained with the Raney tubes.

TABLE VI

Results of Oxygen Diffusion Measurements
on Soil Conditioner Plots, September 10, 1954

Plot	Bean Yield pounds/plot	Microelectrode Measurements		Raney Tube Measurements	
		i_t microamps	$\frac{i\theta}{Cl.3}$ (Structure)	$\frac{i\theta}{Cl.3}$ (Aeration)	D/D ₀ (Aeration)
2 A	13.5	1.10	25.6		0.569
2 B	12.4	1.10	14.4		0.697
14 B	11.9	1.07	15.6		0.593
10 A	11.0	1.02	22.8		0.719
17 A	11.2	0.93	18.4		--
5 A	12.0	0.92	14.8		0.838
1 A	12.3	0.91	11.2		0.664
14 A	8.0	0.77	22.0		0.718

Correlation between $\frac{i\theta}{Cl.3}$ and crop yield: Students t = -0.3564

Correlation between D/D₀ and crop yield: Students t = -0.0263

As can be noted from Table VI there is no significant correlation between the structure factor, $\frac{1.0}{0.1.3}$, and bean yields. It is evident that if the data are valid, neither structure nor soil aeration were the limiting factor to plant growth this season. It is believed that soil moisture was that limiting factor. Soil moisture measurements show moisture percentages as low as 13.5 percent, below the wilting point.

The fact that moisture content was so low brings out the possibility that the moisture film on the platinum microelectrodes may not have been complete, causing errors in the observed values and invalidating the structure parameter. This is the admitted weakness of this measurement, that at such low moisture contents the platinum microelectrodes will not function properly as a measure of oxygen diffusion. But under these conditions, a measure of soil aeration is meaningless because soil aeration is not a limiting factor to plant growth. Also, structure is no longer limiting to plant growth. If a measure of structure is still desired at this time, other methods will have to be applied. However, by the time structure is again an influence on plant growth, it will have changed from what it was when measured by these other methods, and the platinum microelectrodes can again be used as the device for measuring soil structure.

Horst Farm Experiments, Akron, Michigan.

Two separate rotation experiments were studied in 1955. One of these was a rotation designed to study the results of several methods of adding organic matter to the soil. The crops grown were row crops and small grains in alternate years, and those treatments studied for this paper were:

1. Sweet clover every 2 years.
 2. Both manure and sweet clover every 2 years.
 3. Manure every 2 years.
 4. Check, no organic matter additions.
 5. Sweet clover every 4 years.
- Sugar beets were grown in 1955.

Oxygen diffusion measurements were made on two separate occasions using both the platinum microelectrodes and the Raney tubes. These data are presented in Table VII.

Again, an analysis of the data shows little, if any, significant difference in structure between treatments. The structure parameter shows more variability between replicates than between treatments, indicating that conditions were quite favorable for the maintenance of good structure or these rotations have little effect upon structure.

One interesting observation may be made. Except in three cases, the structure factor for each plot was practically the same for both measurements. This agreement, in spite of variation of diffusion measurements, i_t , and moisture contents between the two days, indicates

TABLE VII

Results of Oxygen Diffusion Measurements on

Horst Organic Matter Plots, 1955

Rotation	Plot No.	Platinum Microelectrodes				Raney Tubes	
		1t, microamps		1t ² Cl.3		D/D ₀	
		5/26/55	6/15/55	5/26/55	6/15/55	5/26/55*	6/15/55
Sweet clover every 2 years	18	7.2	8.7	0.79	0.77	--	--
	26	7.4	7.3	0.68	0.59	0.970	0.574
Both manure and sweet clover	20	6.9	--	0.64	--	--	--
every 2 years	28	6.9	7.2	0.59	0.64	0.950	0.473
	33	7.7	7.9	0.61	0.58	--	--
	44	--	8.2	--	0.54	--	--
Manure every 2 years	15	6.8	8.2	0.63	0.74	--	--
	29	6.7	6.4	0.55	0.54	0.772	0.451
Check	16	7.0	7.6	0.63	0.57	--	0.469
	27	8.8	7.7	0.68	0.63	0.794	0.463
	39	8.6	8.8	0.73	0.65	--	--
	48	--	7.0	--	0.46	--	--
Sweet clover every 4 years	17	5.9	--	0.49	--	--	--
	30	6.7	--	0.61	--	0.792	--
	37	7.7	--	0.61	--	--	--

*Erratic data on this date and results probably not valid.

that the structure had not changed appreciably. Since no cultural practices occurred in the interum between sampling dates, and only one very light shower fell during that time, there was little if any tendency for structure to be changed. Therefore, the agreement of the data indicates the validity of the factor, $\frac{10}{01.3}$.

Studies on Cropping Rotations - 1955.

The other study made in 1955 was on rotations at the Ferden farm designed to show the differences in crop yield strictly on the basis of the result of the rotations. These are five year rotations of: (1) corn, sugar beets, barley and 2 years alfalfa-brome mixture, (2) sugar beets, corn, barley and 2 years alfalfa-brome and (6) corn, sugar beets, barley, beans and wheat. Each year each rotation is replicated 4 times so there are 20 plots for each rotation. Only the sugar beet and corn plots of these three rotations were measured.

A great many measurements were made during the first three months of the growing season. All of the plots studied were not measured on the same day so that direct comparison of all the data would not be satisfactory. Therefore, the data from 6 days in which all the corn plots were measured are averaged. Similarly, the data are averaged for 6 days in which all the sugar beets were measured. These data are reported in Table VIII.

Table VIII
 Average of Structure Factor $\frac{1+t_0}{C1.3}$ for Six Days
 on Cash Crop Rotations, 1955

<u>Sugar Beets</u>				
<u>Rotation</u>	<u>Replicates</u>			
	<u>B 1</u>	<u>B 2</u>	<u>B 3</u>	<u>B 4</u>
1	1.10	1.06	0.99	0.97
2	1.10	1.00	0.74	0.76
6	1.01	1.06	0.98	0.83

<u>Corn</u>		
<u>Rotation</u>	<u>Replicates</u>	
	<u>B 1</u>	<u>B 2</u>
1	0.87	1.06
2	1.07	1.03
6	1.14	1.00

It should be noted that the plots run north to south in order from replicates 1 to replicates 4. The plots become sandier moving from north to south, and the structure is visibly poorer on the southern side of the plots. This structural gradation is evident from the data in Table VIII and is due to soil differences and not necessarily to differences due to rotations.

All in all there is very little difference in structure between the soils in the three different rotations. The reason is fairly obvious. At no time this year has more than 0.76 inch of rain fallen in one day, and the rains that have fallen have been very gentle. The plots were worked at optimum moisture conditions for tillage, and there was no reason for a poorer structure to develop on some plots than on others just on the basis of cropping practices. Oxygen diffusion was determined with Raney tubes, but few data were accumulated and the data obtained showed no significant differences in aeration between rotations.

It might be of interest to follow the structure of some of these plots as measured with the platinum micro-electrode through the first 3 months of the growing season. Admittedly these were selected plots on the basis of the data obtained. All of the plots did not follow the same pattern with rainfall and cultural practices, and this behavior is difficult to explain.

The data not reported were not all erratic, because there were indications of seasonal trends, but there were many deviations from the season pattern. The explanation which seems most logical is that a field will not have uniform structure throughout, but will vary within certain limits. Whether or not this variation in structure caused the variation in the structure factor can only be speculated at the present time.

In Table IX are shown the $\frac{1.6}{1.3}$ values and dates when the measurements were taken for several plots, plus the dates of cultivation and the accumulation of rainfall between measurement dates. From this table the seasonal variations of soil structure can be followed.

All the plots had a given structure at the starting point, May 6. The structure factor in rotation 1 plots was low and did not change appreciably until the plots were plowed and planted. The structure factor for rotation 6 soil was a little better to start with, but decreased as the rains came and became about equal to that of rotation 1 before plowing. Three weeks after planting and just after several light rains the soils were measured again and showed an increase in the structure factor due to the once over tillage used in planting the corn. Following this measurement the corn was spiked. This was followed two days later by a half inch of rain. The structure measurements after this cultivation and

TABLE IX

Seasonal Variation of Soil Structure $\left(\frac{1+\theta}{\theta 1.3}\right)$ as Affected
by Cultural Practices and Rainfall

Cash Crop Rotation Plots - Corn - 1955

Date	Rainfall and Cultivation	Rotation 1 in 3rd year alfalfa-brome		Rotation 6 in wheat stubble	
		<u>1-A-B1</u>	<u>1-D-B2</u>	<u>6-A-B1</u>	<u>6-D-B2</u>
4/6/55		0.78	1.04	1.16	1.16
4/19	0.76 in. rainfall				
4/22		0.62	0.82	0.88	0.79
4/24-25	0.66 in. rainfall accumulated				
4/27		0.63	0.81	0.66	0.73
4/29		0.60	0.94	0.88	0.94
5/3	Plowed and planted		1.28		0.80
5/24-25	0.81 in. rainfall accumulated				
5/25		1.00	1.18	1.12	1.26
5/27	Spiked corn				
5/29	0.50 in. rainfall				
6/1		0.94	1.10	1.36	0.85
6/3	Cultivated corn				
6/7-11	1.10 in. rainfall accumulated				
6/13		0.76	1.08	1.10	0.96
6/15	Cultivated corn				
6/23		1.10	1.17	1.21	1.00

rain showed a decrease in structure in all but one plot. It may be noted that this cultivation had no beneficial effects on soil aeration or structure and the only benefit, if any, was the control of weeds.

The corn was cultivated two days after the last measurement, and the cultivation was again followed by rain. Measurements of structure two days after the rain showed a continued general decrease in the structure factor. However, between the next cultivation and the last measurement on June 23, there was no rainfall and the structure in all cases showed some improvement, presumably due to the cultivation.

No general conclusions can be drawn from this analysis of data because the data were selected on the basis of the results, but there is introduced a possible application of the platinum microelectrode measurements of oxygen diffusion for determining the effects of various forms of cultivation on soil structure.

One more study was made on the sugar beet soil in the cash crop rotations which was designed to compare structure in the plow layer with that below the plow layer. Measurements were made at the surface and 10 to 12 inches below the surface. The results are presented in Table X. In every case the sub-plow layer structure was considerably poorer than the surface structure, which may be expected on the basis of the cultural practices

TABLE X

Comparison of Structure of Plow Layer and Sub-plow Layer
in Cash Crop Rotations, 1955

<u>Rotation</u>	<u>Replication</u>	<u>Date</u>	$\frac{1\text{t}\theta}{\text{Cl.3}}$ 4 inches deep	$\frac{1\text{t}\theta}{\text{Cl.3}}$ 10-12 inches deep
1	1	5/13/55 5/18	1.12 1.31	0.41 0.45
1	2	5/13 5/18	1.11 1.25	0.50 0.72
1	3	5/18	1.33	0.43
1	4	5/18	0.95	0.37
6	1	5/13 5/18	1.62 0.98	0.53 0.46
6	2	5/13 5/18	0.90 1.02	0.53 0.49
6	3	5/18	1.06	0.44
6	4	5/18	0.83	0.45

followed in this experiment. Of the 4 plots in which 2 measurements were made the results of the 2 sub-plow layer measurements are in close agreement with but one exception. This again tends to confirm the validity and accuracy of the $\frac{1t\theta}{cl.3}$ structure parameter.

SUMMARY AND CONCLUSIONS

The method of measuring oxygen diffusion in the soil with the platinum microelectrode as developed by Lemon is refined, both as to procedure and equipment, and is adapted to field work. The theory of Lemon and Lemon and Erickson is expanded, yielding a factor called the structure parameter. Field measurements with the platinum microelectrode are analyzed and discussed.

The laboratory and field data presented in this paper indicate the validity and usefulness of the method and its application. Much work has been done to improve equipment and measurement techniques, and much more work remains to be done. For the sake of quantitative evaluation of oxygen diffusion as related to soil physical conditions, the mobility of oxygen through the soil, water and across soil-water interfaces should be evaluated and the initial reading calibrated in terms of actual units of oxygen concentration in the soil. Also, the exact effect of ionic strength of the soil solution and of soil temperature on diffusion should be determined.

With the development of quantitative oxygen diffusion measurements and the absolute evaluation of soil factors influencing the diffusion, an unlimited field for application of this technique unfolds. Factors affecting soil

structure, such as tillage, cropping systems, incorporation of organic matter and meteorological phenomenon can be evaluated in situ as they occur. Critical aeration values for plants can be determined, both as to duration and severity. With further development of this measurement of oxygen diffusion, valuable contributions to the fields of soil physics and crop production appear imminent.

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