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MEASURING SOIL AERATION

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MEASURING SOIL AERATION

The complexity of the interactions of soil air with the soil environment and with plant roots is such that although there are many indicators of soil aeration status, each reflecting particular aspects of it, none of them adequately describes the whole of the phenomenon. The indicators currently in use are air-filled porosity, air permeability, gas diffusion coefficient, respiration rate, soil air composition, oxygen diffusion rate (ODR), redox potential, and some further indicators employing chemical and biological procedures.

All these methods are briefly described below. Because work on methods never ceases and none of the methods is as yet ultimate and ideal, no recommendation of, or preference for, particular methods will be given here but only a presentation of the measurement principle and the related literature.

I. AIR-FILLED POROSITY

Determining the air-filled porosity is the oldest and the simplest method of assessing soil aeration status. It is reasonable to assume that an air content above 0.25 m^3m^{-3} is sufficient for good aeration. In the range of 0.10 to 0.25 m^3m^{-3} aeration may be deficient under some conditions while values below 0.10 m^3m^{-3} characterize decidedly deficient aeration. Air-filled porosity is usually calculated from knowledge of the actual moisture content, the bulk density of the soil and the density of its solid phase; these values being determined by well-known methods which will not be described here.

A more rapid determination can be made by the use of air pycnometers; numerous models being described in the literature. Some of these are portable and can be used directly in field, their readings being unaffected by variations in atmospheric pressure.

II. SOIL AIR COMPOSITION

Soil air analysis comprises determination of such components as O_2, CO_2, C_2H_4, CH_4, N_2O, and H_2 and sometimes NH_3, NO, and NO_2. Obviously not all these gases are determined in every situation. Sometimes determination of only one component, e.g., O_2 or CO_2, is sufficient.

1. Oxygen

The oldest analytical methods are volumetric techniques based on absorption in sodium anthraquinone-β-sulfonate. Modification of these methods made possible microanalysis of samples as small as 0.5 to 0.001 cm^3 for O_2 and CO_2. These laborious methods have been replaced by more modern and rapid techniques.

Paramagnetic oxygen analyzers are based on the principle that oxygen is the only gas attracted by a magnetic field. They require a rather large air sample usually more than 50 cm^3 to flush the internal chamber containing the magnetic balance. Portable paramagnetic analyzers can be used directly in field. More complicated high precision O_2 analyzers can only be used in the laboratory for measuring respiration by continuous air flow procedures or for analysis of air samples brought from field.

Polarographic membrane covered sensors are very convenient in use as they require relatively small air samples (up to 10 cm^3) which can be analyzed in the field with the portable oxygen meters. The water condensation effects encountered when the O_2 sensors were buried in the soil for continuous O_2 monitoring have been eliminated by a double membrane system. The drawback of the polarographic sensors is the variability of the calibration and frequent recalibration is required. A miniaturized version of the membrane covered electrode has been applied to measure O_2 gradients over distances below 1 mm.

Gas chromatography is a modern technique allowing small air samples of the order of several cubic millimeters to be analyzed accurately in a matter of minutes. For chromatographic separation of oxygen, the common practice is to use molecular sieve 5 A column at room temperature.

Katharometers providing a detection limit of 75 cm^3m^{-3} and an ultrasonic detector with a detection limit of 1 cm^3m^{-3} have been used for oxygen detection in gas chromatography.

Oxygen dissolved in water can be detected in 10 mm^3 samples on a column with Porapak® T (for H_2O absorption) and molecular sieve 5 A column with the use of an electron capture detector.

A determination of oxygen in soil air by mass spectrometry has also been described. It should be mentioned that this method can be applied both in the laboratory and in field conditions.

2. Carbon Dioxide

Older analytical methods for carbon dioxide determinations in soil air samples were based on absorption in alkali solutions.

The microanalytical techniques can be used with samples as small as 0.5 to 0.001 cm^3 while in macrotechniques samples of several cubic centimeters are used.

Gas chromatography is at present commonly used for carbon dioxide determination in small samples of air. The columns are filled with Porapak® Q. Katharometers provide a detection limit of 20 cm^3m^{-3} while ultrasonic detectors and helium ionization detectors have at least a tenfold sensitivity advantage over katharometers with detection limits of the order of 1 cm^3m^{-3}.

Other methods which can be used for CO_2 analysis in soil air employ membrane covered glass electrodes or katharometers, mass spectrometers, and infrared analyzers.

3. Ethylene

Ethylene is most conveniently analyzed by gas chromatography with flame ionization detectors providing a limit of detection of 0.02 cm^3m^{-3} and even 0.005 cm^3m^{-3}. Other detectors, e.g., helium ionization, are less sensitive.

Ethylene can be separated from atmospheric gases on Porapak® Q columns.

Separation of ethylene from other light hydrocarbons can be accomplished by utilizing a combination of columns with alumina F1, Porapak® P, and Molecular Sieve® 13X or a column of alumina deactivated with sodium iodide.

4. Methane

Methane is determined by gas chromatography with the use of Porapak® Q, alumina deactivated with sodium iodide, or Molecular Sieve® 5 A columns. Flame ionization detectors with a detection limit of 0.02 cm^3m^{-3}, ultrasonic detectors with a detection limit of about 1 cm^3m^{-3}, or helium ionization detectors with similar sensitivity can be used. The detection limit using a katharometer is about 20 cm^3m^{-3}.

5. Nitrogenous Gases

Gaseous nitrogen is separated from oxygen on a column with Molecular Sieve® 5 A at room temperature or with Porapak® Q at the temperature of a dry ice-acetone bath.

Nitrous oxide is readily determined by gas chromatography with the use of columns with Porapak® Q, Porapak® R, or Molecular Sieve® 5 A.

With the use of a katharometer, a detection of 1 cm^3m^{-3} of N_2O in air is possible, while with a helium ionization detector or an electron capture detector, concentrations of N_2O as low as 0.1 cm³m⁻³ can be detected. Atmospheric air usually contains about 0.3 cm³m⁻³ of nitrous oxide.

Methods of gas chromatography for NO determination with the use of Molecular Sieve 5 A and Porapak Q have also been reported. They are, however, only suitable for gas analysis in closed systems free of oxygen, and have not been applied to soil atmosphere analysis.

6. Hydrogen

Hydrogen can be determined by gas chromatography on a column with Porapak Q or Molecular Sieve 5 A with the use of a helium ionization detector or an ultrasonic detector. The detection limit is of about 1 cm³m⁻³ with either detector.

7. Hydrogen Sulfide

Hydrogen sulfide in soil air can be determined by gas chromatography on Porapak Q with the use of a helium ionization detector.

III. OXYGEN DIFFUSION RATE (ODR)

A. Principle of the Method

The method of ODR measurement consists of amperometric measurement of electric current intensity corresponding to oxygen reduction on a platinum cathode placed in the soil and negatively polarized with respect to a saturated calomel electrode or silver chloride electrode. This was first proposed by Lemon and Erickson in 1952 and since that date it has been treated in numerous publications.

When a negative voltage within the range 0.2 to 0.8 V with respect to the saturated calomel electrode is applied to the platinum electrode placed in the soil the current initially decreases with time but stabilizes after a few minutes (cf. Figure 1).

By plotting this "limiting" current, corresponding to the attainment of a quasistationary state (after 4 or 5 min) vs. gradually increasing applied voltage two essentially different types of current voltage characteristics may be obtained (cf. Figure 2).

In a saturated soil or its suspension an increase in current intensity is observed, then a "plateau" range corresponding to oxygen reduction is reached and thereafter a steep increase in the current intensity, due to commencement of hydrogen reduction, is observed (see Figure 2 and also Figure 3). The plateau range usually lies within −0.4 to −0.7 V vs. the saturated calomel electrode, although there may be some changes depending on the soil pH. In particular, under acid conditions the plateau values are shifted to the left.

In unsaturated soils, however, there is no plateau at all (cf. curve 3 in Figure 2 and curves 2, 5, 6, 9, 10 in Figure 3). This is a serious deficiency of the method and its principle must be a matter of question.

The process of oxygen reduction on the electrode surface according to the McIntyre is as follows, in the pH range 5 to 12:

$$O_2 + 2H_2O + 4e \rightarrow 4\,OH^- \qquad (5)$$

and

$$O_2 + 4H^+ + 4e \rightarrow 2\,H_2O \qquad (6)$$

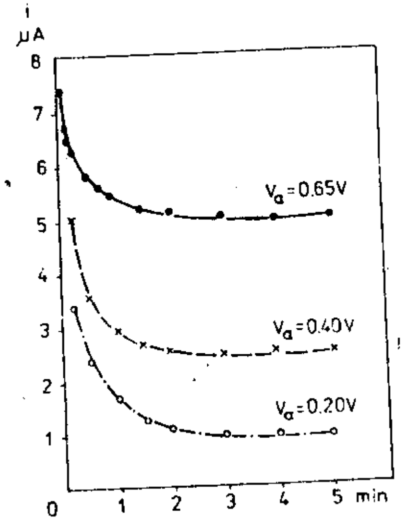

FIGURE 1. Current time curves obtained by polarizing 0.5 × 4 mm platinum electrode with a constant applied voltage V_a vs. saturated calomel electrode. The electrode placed in unsaturated sandy loam soil.

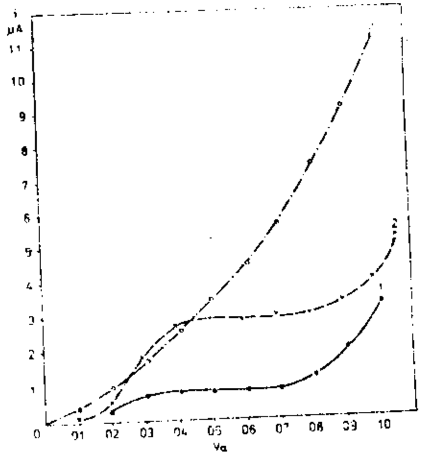

FIGURE 2. Current-applied voltage characteristics of a platinum electrode in (1) saturated sandy loam soil, (2) stirred soil suspension, and (3) unsaturated sandy loam soil.

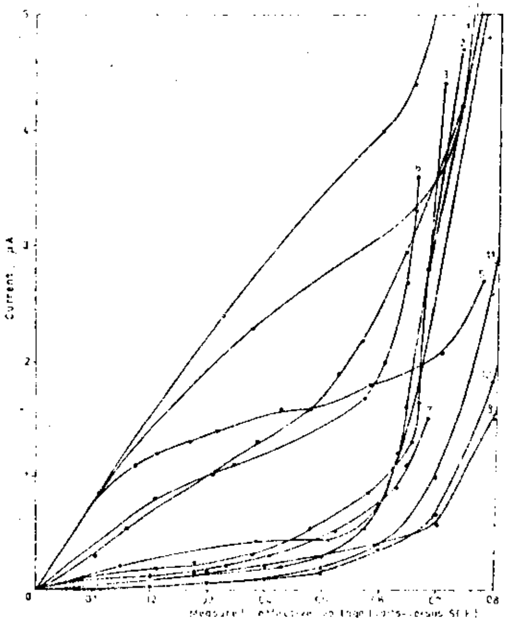

FIGURE 5 Current-effective voltage characteristics for 12 different soils (curves 1, 3, 4, 7, 8, 11, and 12 — soils of moisture tension within 0.25 to 2.5 kPa; curves 2, 5, and 6 — soils of moisture tension from 3 to 10 kPa; curves 9 and 10 — soils of moisture tension 12 to 60 kPa)

at pH <5.

Thus, independently of pH, reduction of one oxygen molecule is connected with uptake of four electrons. Current intensity is described as follows:

$$i = n\,F\,A\,f_i \tag{7}$$

where i = current intensity in amperes, n = 4 — number of equivalents per mole of oxygen, F = the Faraday (= 96,500 C per equivalent) A = electrode area in square meters, f_i = oxygen flux in moles $m^{-2}s^{-1}$

Oxygen flux f_i can be calculated as follows:

$$f_i = \frac{i}{n\,F\,A} \tag{8}$$

Expressing f_i in SI units ($\mu g\ m^{-2}s^{-1}$) and denoting it as ODR we obtain:

$$ODR[\mu g\ m^{-2}s^{-1}] = \frac{M\,i}{n\,F\,A} = 8.29 \cdot 10^{-5}\,\frac{i\ [\mu A]}{A\ [m^2]} \tag{9}$$

where M is the molecular weight of O_2 (32 g mol^{-1}).

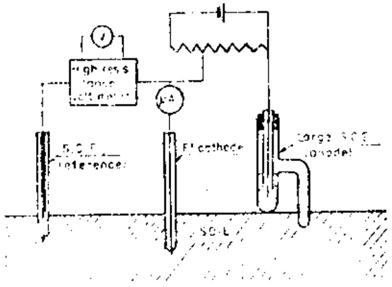

FIGURE 4. A scheme of the system allowing for measurement of applied and effective voltage during ODR measurement.

A comprehensive review on the ODR method has been given by McIntyre. He lists several types of electrode polarization that are likely to occur during ODR measurement viz. resistance polarization, electrolyte transport polarization, activation polarization, concentration polarization, and reaction polarization.

The resistance polarization arises from the voltage drop (V_R) across the resistance of the cathode-soil-anode system (R) due to the flow of current i, and, according to Ohm's law:

$$V_R = i\,R \tag{10}$$

Thus the effective voltage of reduction (V_e) is lower than the applied voltage (V_a) by the value of V_R, i.e.,

$$V_e = V_a - i\,R \tag{11}$$

The resistance R of the path in the soil is of order of one to several tens of kilohms giving, at current intensities of several microamperes, a voltage drop of as much as 0.2 to 0.4 V, i.e., more than half of the applied voltage.

Several methods have been proposed in order to eliminate resistance polarization. The most convenient method is the application of an independent (noncurrent) reference electrode to monitor the effective reduction voltage using a voltmeter having a high input resistance ($>10^{10}\Omega$). The scheme of such a system is shown in Figure 4. The original method used by Lemon and Erickson did not contain the "noncurrent" reference electrode and high resistance voltmeter. The current intensity and thus the resistance polarization are negligible in the second (monitor) circuit.

Electrolyte transport polarization V_A arises from accumulation of hydroxide ions on the cathode surface due to inadequate removal of these ions from the electrode. This polarization is a cause of some overvoltage V_A in addition to that necessary to perform the reaction of oxygen reduction.

Activation polarization is the result of an insufficient reaction rate at the electrode surface. This causes the current to be controlled by the rate of reaction and not by the flux of oxygen. The presence of activation polarization is manifested by a nonlinear increase of current with increase in oxygen concentration.

Concentration polarization is caused by low reactant concentration at high current densities. The degree of polarization increases with voltage until the concentration at the electrode reaches zero. In this situation the reaction rate is completely diffusion-controlled and the diffusion current is obtained.

Reaction polarization may be involved when a chemical reaction precedes or succeeds the electrochemical one. This is likely to occur during catalytic decomposition of H_2O_2 which is an intermediate in O_2 reduction to H_2O.

In the ideal case only concentration polarization and resistance polarization should occur while the other types should be eliminated. The resistance polarization is unavoidable but its contribution can be assessed either by calculation or by direct measurements as shown in Figure 4. This permits the measurement to be performed with a constant known effective voltage.

However, the absence of the polarographic plateau, which is never seen in tests with unsaturated soils, implies that besides concentration polarization activation polarization and electrolyte transport polarization are probably present. The presence of activation polarization is indicated by the nonlinear current-oxygen concentration dependence found by many authors.

The possibility of eliminating electrolyte transport polarization has been considered and discussed by Stępniewski. No satisfactory way of eliminating undesired polarizations and thus obtaining a plateau in unsaturated soils has been found as yet.

Despite these numerous limitations and uncertainties, ODR is at present still the best index of potential oxygen availability for plant roots in the soil.

B. Equipment

The first forms of apparatus used for ODR measurements in soil did not allow for the effective voltage to be controlled. However, they enabled a constant voltage to be applied to many platinum electrodes and measurement of the individual currents.

Some subsequent arrangements permitting the measurement of soil resistance and correction of the applied voltage according to Equation (11) of this chapter have been described. Also some devices for automated measurements have been reported.

The method providing automatic control of the effective electrode voltage was described by Malicki and Walczak.

Platinum cathodes, usually several simultaneously, are used for ODR measurement. They are constructed of 10 mm Pt wire in length with diameters in the range of 0.4 to 1.2 mm but most commonly about 0.5 mm. This wire is connected to a copper cable and mounted in a sheath which may be glass, plastic, or metal allowing some 4 to 5 mm of bare Pt wire to project. In the case of a glass sheath the attachment may be made by fusion or with special adhesives, e.g., epoxy resins, which are also suitable for plastic materials and metals. To minimize the physical effects of electrode insertion in the soil it is desirable to make the electrode sheath as thin as possible. However, it is not easy to construct electrodes thinner than 3 mm. The measurement time is usually 4 to 5 min, permitting quasistationary conditions to be achieved.

It is recommended that the electrodes are inserted into the soil immediately before the measurement; leaving the electrodes in the soil may cause a decrease of the readings obtained with them. This phenomenon, sometimes called "poisoning" of the electrodes has been observed by several authors but its mechanism has not been explained satisfactorily.

It was suggested that precipitation of some compounds such as carbonates or hydroxides may occur due to OH formation at the electrode surface. Electrode cleaning by washing and abrasion removes the "poisoning" effect. Between the measurements electrodes can be kept in air.

As reference electrodes, saturated calomel electrodes or silver chloride electrodes have been used. In the original Lemon and Erickson system the reference electrode is also the anode through which a current of up to some tens of microamperes flows. Because of this, large electrodes of special construction with a surface of mercury (in the case of calomel electrodes) or of silver covered with silver chloride, which have an area of several square centimeters, are used to preserve a constant potential despite the flow of current. In the system described by Gawlik et al. and shown in Figure 4, a copper or brass rod can be used as the current carrying anode while the second "noncurrent" reference electrode can be a standard calomel one as commonly used for pH measurements.

It should be pointed out that ODR measurement is reliable only when the entire electrode surface is wetted. The ODR value, normally increasing with soil moisture, decrease sharply below a certain moisture content corresponding to break up of the water film covering the platinum surface. Thus, for proper interpretation of ODR changes in a particular soil in the field, the relationship between ODR and moisture content should be checked. The apparent values of ODR corresponding to the moisture interval at which continuity of moisture films on the platinum cathode disappears should be discarded as artificial. Usually the moisture range for reliable ODR measurements corresponds to a moisture tension up to 50 to 100 kPa.

IV REDOX POTENTIAL

Redox potential in soil is measured with bright platinum electrodes of different shapes and sizes, their potential being measured with respect to a saturated calomel electrode. As the measuring device, a high input resistance voltmeter is used. This requirement is fulfilled by all modern portable pH-meters which have an input resistance of 10^{10} to 10^{12} Ω.

Some authors reported a phenomenon of "poisoning" the Pt electrodes during redox measurement but this phenomenon is not so evident as in ODR measurement. Some authors obtained good records of the variation in redox potential in the soil over a long period by leaving the electrodes in the soil.

It should be added that use of the same electrodes immediately after ODR measurements causes the redox potential values indicated to be less than the true values. This is due to negative polarization of the electrodes which should not be used for redox measurements. The duration of this polarization after effect, in the case of an electrode left in the soil, is more than 24 hr. Reinserting the electrode decreases the magnitude and duration of the effect. The exact conditions of the disappearance of this effect have not been described. It should be mentioned that some authors recommend short polarization of the electrode (3 min with a voltage about 600 mV) before the measurement in order to shorten the time of reaching equilibrium potential.

The range of moisture contents in which reliable redox potential measurements are possible is wider than for ODR as partial electrode moistening is sufficient for the electrode to acquire the potential of the soil.

The redox potential values with respect to a standard hydrogen electrode are calculated by adding the reference electrode potential. The potential of a saturated calomel electrode is 254, 251, 247, and 244 mV at temperatures 10, 15, 20, and 25°C, respectively.

Redox potential is the best measure of soil reduction processes in waterlogged soil and in conditions of oxygen exhaustion in the soil when other indicators such as ODR or O_2 content are insensitive and of little value.

Devices and facilities for continuous multiple measurements of redox potential have been described. Some of them are coupled with simultaneous ODR measurements.

The problem of measuring of the redox potential and its maintenance on a desired level in soil suspensions has been discussed by Patrick et al. and in soil cores by Patrick and Henderson.