

REPEATABILITY OF MEASUREMENTS OF THE POTENTIAL OXYGEN FLUX DENSITY IN THE SOIL BY THE VOLTAMPEROMETRIC METHOD

A. Bieganowski

Institute of Agrophysics, Polish Academy of Sciences
Doświadczalna 4, 20-290 Lublin 27, P.O. Box 201, Poland

A b s t r a c t. Influence of the measuring procedure on the repeatability of measurement of the potential oxygen flux density in the soil has been presented. Five measuring procedures were applied: measurements taken one directly after another, reinstallation of the electrode after each measurement, reinstallation of the electrode after each measurement with a simultaneous mechanical cleaning of surfaces, measurements with 15-min breaks between consecutive measurements, measurements with electrochemical "cleaning" of the electrode surface.

The OFD value was determined by a voltamperometric method using a tri-electrode measuring system. It was found out that the best repeatability can be obtained by repeating the measurement with 15-min (or longer) time intervals.

K e y w o r d s: soil aeration measurement, Oxygen Flux Density (OFD), Oxygen Diffusion Rate (ODR).

INTRODUCTION

The problem of platinum electrode "poisoning" during Lemmon and Erickson's amperometric ODR measurements [8,10,11] was discussed a lot of times. Already Laitinen and Kolthoff [9] reported that the oxygen half-wave potential on platinum depends on the way the electrode was prepared for the measurements. The same effect was noticed by Sawyer and Interrante [19]. Oden [16] found out that at some reaction values, ferric and aluminium oxides together with other colloids can get sorbed at the platinum surface. Moreover, with strong alkaline reaction of the soil, carbonates can be deposited on the electrode. Taking the above phenomena into account, a term "poisoning" was introduced for the cathode (platinum). It is understood as changes on the cathode surface that most probably result from the deposits of previous reactions [4].

A large group of researchers is of the opinion that while preparing the cathode for the measurements, it is enough to clean it delicately with abrasive paper [7,15, 17] or that inserting and removing the cathode from the soil is sufficient to remove deposits from its surface [1,7].

Black and Buchanan [5] observed small difference between the results obtained from the electrodes oxidised for a certain period of time, and the results from the electrodes that were mechanically cleaned. Rickman *et al.* [18] were of the opinion that cathode preparation for work by its immersion into nitrogen acid without mechanical cleaning of its surface is enough to refresh (oxidise) its surface.

Callebaut *et al.* [6] found out that the most suitable cleaning of the electrodes is electrochemical. They applied 4.5 V in the circuit that consisted of a platinum electrode, 0.1 M HCl solution and a carbon electrode. The process of electrochemical cleaning lasted for 2 min (the above authors did not give any information whether platinum was a negative or a positive electrode in the circuit). The electrode prepared in such a way, was then stored in the distilled water to avoid formation of oxides on its surface.

Some authors wanted to make sure whether the platinum surface had been sufficiently cleaned by the preparation procedures applied, and measured electrode potential in relation to the control electrode in a specific electrolyte [6,17].

However, there are no reports on the problem of the conditions of the electrode surface as reflected in the results of voltamperometric measurements of the oxygen flux density in the soil.

Therefore, the aim of the present research was to answer the question how the platinum electrode preparation procedures influence the shape of voltamperometric curves and repeatability of the potential oxygen flux density (OFD).

MATERIALS AND METHODS

Study material

Soil samples were prepared from the soil material described in Table 1. Soil material was wetted with distilled water. One sample was wetted to the saturation state (0.30 g g^{-1}). Moisture content of the second sample - the unsaturated one (0.24 g g^{-1}) was chosen in the way that enabled to achieve a quasi plateau area in the voltamperometric curve [20].

The wetted soil material was placed in the PCV containers $10 \times 10 \times 7$ cm in size in such a way as to obtain samples with uniform density.

Table 1. Some properties of the soil material studied

Site	Soil type (FAO)	Horizon	Depth (cm)	ρ_s (Mg m ⁻³)	Granulometric composition (%)			C _{org} (%)
					sand 1-0.1 mm	silt 0.1-0.02 mm	clay <0.02 mm	
Czesła- wice	Orthic Luvisol	Ck	140-160	2.48	0	68	32	0.34

Method

The measurements were carried out using a specially designed and constructed, digitally controlled voltamperometer [13]. The rate of changes in the cathode potential was equal to 4 mV s⁻¹ [3]. Voltamperometric curves were recorded by the polarisation of the indicator electrode in the potential range from 0 to -1200 mV.

The measurements were carried out in the tri-electrode system [14]. The indicator electrode was a Pt wire with the diameter of 0.5 mm and the length of 10 mm, and the circuit closing electrode (counter electrode) was a wire made of stainless steel with the diameter of 3 mm and the length of 70 mm. The reference electrode was a saturated calomel electrode.

Measuring procedures

The measurements were carried out following five procedures, i.e.:

1. Measurements taking place one after another. The platinum electrode was installed in the soil sample and then consecutive voltamperometric curves were recorded. Time intervals between consecutive measurements were about 10 s and were caused by the shortage of instruments.

2. Reinstallation of the electrode before each measurement. The platinum electrode was installed in the soil sample, and then the voltamperometric curve was recorded. Before the next measurement, the electrode was taken out of the soil sample and installed in another place. Only after the electrode had been installed again in the new place, the next measurement was taken.

3. Reinstallation of the electrode before each measurement with a simultaneous mechanical cleaning of the surface. This procedure was the same as the one described above. The only difference was a delicate cleaning of the platinum surface with abrasive paper.

4. Measurement with the 15-min intervals between consecutive repetitions

(this procedure was similar to the procedure No. 1, the only difference was that between the consecutive measurements there was a 15-min interval).

5. Measurements with electrochemical “cleaning” of the surface. The indicator electrode was negatively polarised at the rate of 4 mV s^{-1} in the range between $0 \div -1200 \text{ mV}$ recording the voltamperometric curve [2]. After the process had been finished, the electrode was left for 15 min to allow for the reconstruction of the electrochemical balance of the system. Then, the electrode was polarised with positive potential at the same rate in the range between $0 \div 1200 \text{ mV}$. After the process of positive polarisation had been finished, another 15 min was given to reestablish the balance. Positive electrode polarisation was a procedure of electrochemical cleaning of its surface. The next measurement was then taken with the electrode prepared in the above way. Figure 1 presents the lay-out of this procedure.

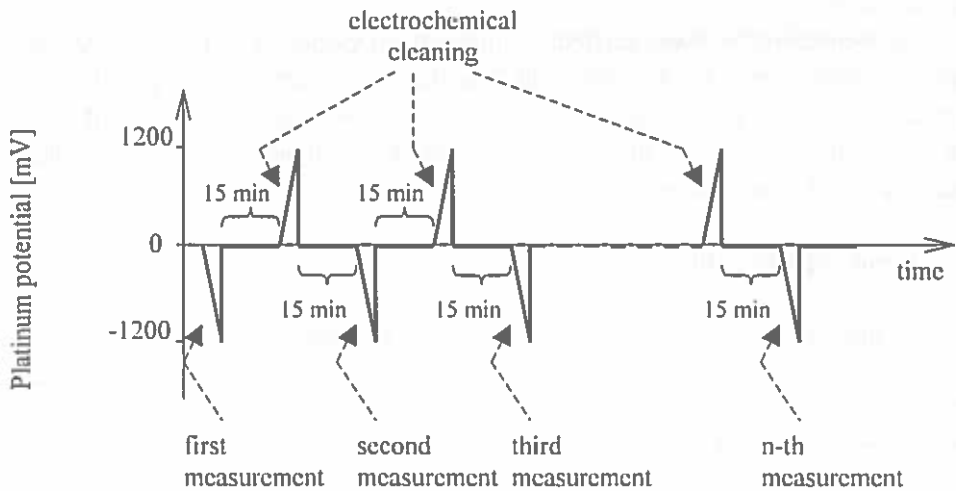


Fig. 1. The scheme of electrochemical cleaning of the electrode surface.

Calculation of the oxygen flux density

Oxygen flux density in the soil was calculated according to the voltamperometric method [12] in the potential range of $0 \div -700 \text{ mV}$, marking the obtained value with the OFD symbol (Oxygen Flux Density). The value of integral was averaged from seven repetitions.

RESULTS AND DISCUSSION

Figure 2 presents voltamperometric curves and the OFD values calculated on the basis of the curves obtained in the soil sample saturated with water (0.30 g g^{-1}). Similar results were obtained for the second moisture level of the studied soil (0.24 g g^{-1}). The graphs given in Fig. 2 should be treated as examples.

Figure 3 presents averages OFD levels and standard deviations related to them for both moisture level of the soil samples.

In the case of recordings carried out one directly following another (procedure 1 - Fig. 1A1), it can be clearly seen that the shape of the first recorded curve is considerably different from the shapes of the next curves. Positive values of the oxygen reducing current are most probably caused by the inability of the system to get rid of the deposits that remained on the electrode surface during previous measurements. In such conditions, a cell is formed with the electromotive force that is difficult to assess. Discharging of this cell (removing deposits from its surface) initiates current flow in the direction opposite to the current that is generated during reduction of the molecular oxygen on the platinum cathode. In this situation, the current measured by the measuring circuit is the sum of two currents with opposite directions. It is impossible to assess individual elements of this current in the conditions of the present experiment. The positive value of the current is the reason for the negative integral value in the range between 0 ÷ -700 mV . Assuming this negative value of the integral for the calculation, we would arrive at a negative OFD value (taking into consideration the physical sense of OFD - density of the oxygen flux - its value was not calculated on the basis of the curves that were registered directly one after another, and hence there is no OFD value for this measuring procedure in Figs 2 and 3).

While analysing the curves recorded with the procedures that called for the electrode reinstallation - procedures 2 and 3, it could be observed that there was a bigger "scatter" than in the case of curves recorded with the one-time electrode installation in the sample. Relatively high values of standard deviation confirm this observation (Figs 3A and 3B). The reason for such a phenomenon could be lack of repeatability of the soil-electrode system geometry.

The shape analysis of voltamperometric curves recorded for the procedure No. 4 (Fig. 2D1) as well as the changes in the OFD values in consecutive repetitions (Fig. 2D2) leads to the conclusion that in the conditions of experiment 2, the first recordings are different from the next, i.e. the current value for a given electrode potential had higher values. Basing on the above observations, the first and the

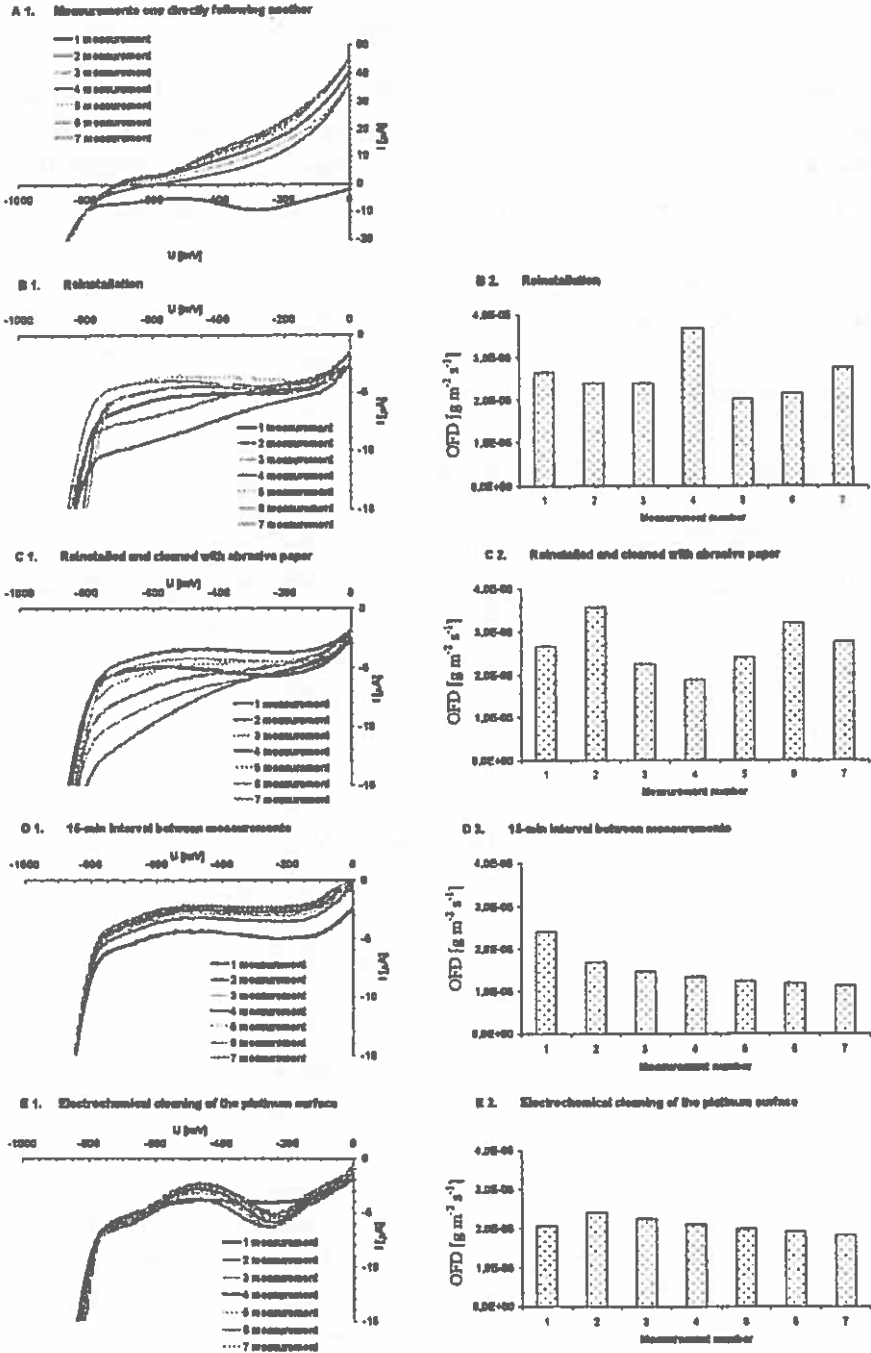


Fig. 2. Voltammetric curves obtained for saturated (0.30 g g^{-1}) silty soil sample.

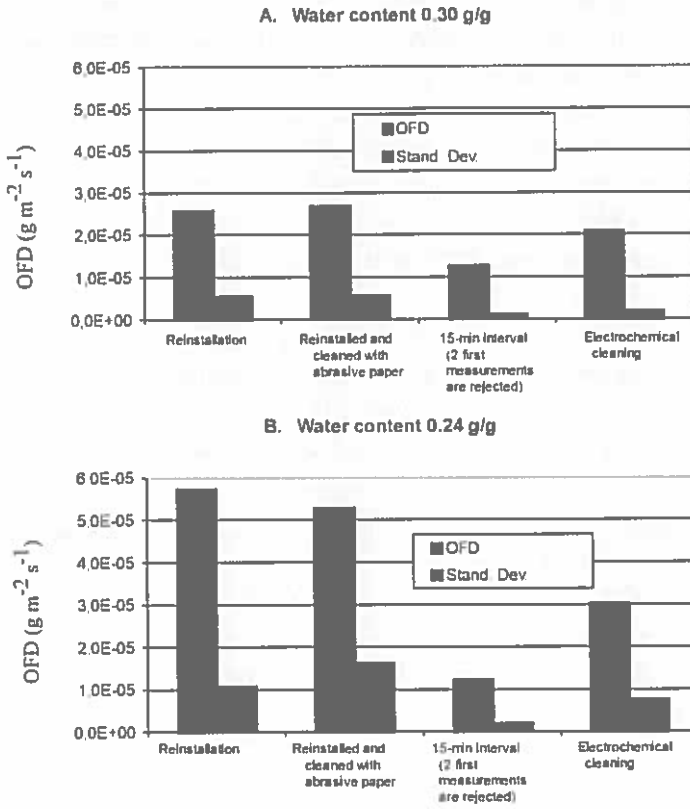


Fig. 3. Averaging values of OFD and standard deviation obtained for soil samples having different moisture.

second values were rejected in the calculation of the averaged OFD value. It resulted in decreasing standard deviation from 4.43×10^{-6} to 1.31×10^{-6} for the moisture levels of 0.30 g g^{-1} and from 8.19×10^{-6} to 2.02×10^{-6} for the moisture level of 0.24 g g^{-1} . Figs 3A and 3B present averaged values from 5 repetitions after 2 first measurements had been rejected.

The reason for the increased OFD values in the first two measurements when applying the fourth measuring procedure, can also be the lack of balance in the measuring system. Only after the first two runs, the system reaches the state of balance so that the following curves show good repeatability.

A phenomenon similar to the measuring procedure with 15-min intervals could be observed when electrochemical cleaning of the platinum surface was

applied - measuring procedure No. 5. Also in this case the two first measurements (and especially the first one) are different from next one with good repeatability (Fig. 2E1). However, the analysis of the same figure shows that the voltamperometric curves in the potential range between -150+-600 mV, at which the predominant reactions at the platinum cathode is reduction of molecular oxygen and the current limited by oxygen diffusion should reach a constant value different from the expected shape. It could be observed that the maximum appeared at the potential of about -250 mV and the minimum at the potential of about -480 mV.

The reason for such a shape of the voltamperometric curve, i.e. the maximum that appears on the curve, can be the oxygen generated during the process of electrochemical cleaning. As can be seen in Fig. 1, after recording the curve at negative polarisation of the platinum electrode (platinum is then a cathode in the measuring system), positive polarisation of the this electrode takes place (and during the process of cleaning it is an anode). Assumption for such a measuring procedure was application of the electric field with such a direction that increases deposit removal rate from the electrode surface. Nevertheless, since the applied potential exceeded the value at which water electrolysis takes place during the process of electrochemical cleaning, a following reaction could have taken place on the platinum surface:



Oxygen generated during this reaction was deposited on the platinum and saturated its closest neighbourhood. At the next measurement (negative platinum polarisation), the aeration conditions were completely changed when compared to the depth of the solution. Hence, the current flowing in the circuit in the beginning of the process of platinum electrode polarisation was caused by the reduction of oxygen generated during the reversed polarisation. When the oxygen "supplied" in such a way was used up, the current decreased to the value that was limited by the diffusion of molecular oxygen to the electrode. This observation was further confirmed by the comparable values of the current at the potential of -480 mV when the measurements were carried out according to the procedures 4 and 5. When the moisture level of the soil sample was 0.30 g g^{-1} , the above values increased to, respectively, $3.0 \text{ }\mu\text{A}$ and $2.8 \text{ }\mu\text{A}$, and for the moisture of 0.24 g g^{-1} , they were, respectively, $5.1 \text{ }\mu\text{A}$ and $3.2 \text{ }\mu\text{A}$.

CONCLUSION

Measurements should be repeated without disturbing electrode installation with intervals not shorter than 15 min.

REFERENCES

1. **Armstrong W.**: The relationship between oxidation-reduction potentials and oxygen-diffusion levels in some waterlogged organic soils. *J. Soil Sci.*, 18, 27-34, 1967.
2. **Bieganowski A.**: Ocena mikrodyfuzji tlenu w glebie na podstawie krzywej voltamperometrycznej redukcji tlenu. Rozprawa doktorska. Instytut Agrofizyki PAN, Lublin, 1997.
3. **Bieganowski A., Malicki M.A.**: The problem of the Pt cathode driving potential change velocity in the chronovoltammetric measurement of soil oxygen diffusivity. *Proc. Int. Conf. "Role of Soil in Functioning of Ecosystems"*. PTGleb-IA PAN - UMCS, Lublin, Poland, 1999.
4. **Birkle D.E., Letey J., Stolzy L.H., Szuszkiewicz T.E.**: Measurements of oxygen diffusion rates with the platinum microelectrode. II. Factors influencing the measurement. *Hilgardia*, 35, 555-566, 1964.
5. **Black J.D.F., Buchanan A.S.**: Polarographic reduction of oxygen at platinum surface in relation to the measurement of oxygen flux in soils. *Australian J. Chemistry*, 19, 2169-2174, 1966.
6. **Callebaut F., Balcaen M., Gabriels D., De Boodt M.**: Data acquisition system for field determination of redox potential, oxygen diffusion rate and soil electrical resistance. *Med. Fac. Landbouw, Rijksuniv. Gent*, 45(1), 15-29, 1980.
7. **Carnell R., Anderson M.A.**: A technique for extensive field measurement of soil anaerobism by rusting of steel rods. *Forestry*, 59, 129-140, 1986.
8. **Gliński J., Stępniewski W.**: *Soil Aeration and its Role for Plants*. CRC Press Inc., Florida, USA, 1985.
9. **Laitinen H.A., Kolthoff I.M.**: Voltammetry with stationary microelectrodes of platinum wire. *J. Am. Chem. Soc.*, 62, 1061-1079, 1940.
10. **Lemon E.R., Erickson A.E.**: The measurement of oxygen diffusion in the soil with Platinum microelectrode. *Soil Sci. Soc. Am. Proc.*, 16, 160-163, 1952.
11. **Lemon E.R., Erickson A.E.**: Principle of the platinum microelectrode as a method of characterizing soil aeration. *Soil Sci.*, 79, 383-392, 1955.
12. **Malicki M.A., Bieganowski A.**: Chronovoltammetric determination of oxygen flux density in the soil. *Int. Agrophysics*, 13, 273-281, 1999.
13. **Malicki M.A., Kotliński J., Bieganowski A.**: A setup for automatic recording of the current-voltage relationship in the electrodes-soil system as applied for estimation of the soil oxygen microdiffusion. 6th Int. Conf. on Agrophysics. IA PAN Lublin, Poland, 1997.
14. **Malicki M., Walczak R.**: A gauge of the redox potential and the oxygen diffusion rate in the soil, with an automatic regulation of cathode potential. *Zesz. Probl. Post. Nauk Roln.*, 220, 447-451, 1983.
15. **Mc Intyre D.S.**: The platinum microelectrode method for soil aeration measurement. *Adv. Agron.*, 22, 235-283, 1970.
16. **Oden S.**: Electrometric methods for oxygen studies in water and soil. IV. Fundamental problems involved with the design and use of oxygen diffusion electrodes. *Grundforbatring*, 3, 117-210, 1962.
17. **Rankin J.M., Sumner M.E.**: Oxygen flux measurement in unsaturated soils. *Soil Sci. Soc. Am. Proc.*, 42, 869-873, 1978.
18. **Rickman R.W., Letey J., Aubertin G.M., Stolzy L.H.**: Platinum microelectrode poisoning factors. *Soil Sci. Soc. Am. Proc.*, 32, 204-208, 1968.

19. **Sawyer D.T., Interrante L.V.:** Electrochemistry of dissolved gases. II. Reduction of oxygen at platinum, palladium, nickel and other metal electrodes. *J. Electroanalytical Chem.*, 2, 310-327, 1961.
20. **Stępniewski W.S.:** The usefulness of the tip-point micro electrode in the measurement of ODR in soil. *Roczn. Glebozn.*, 30, 15-23, 1979.