

Determination of the integration range in voltammetric measurements of oxygen flux in the soil with the use of two- and three-electrode systems*

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Received August 25, 2004; accepted September 30, 2004

Abstract. This paper presents the methodological aspects of the measurement of oxygen flux in the soil by voltammetric method with the use of three- (with potentiostat) and two-electrode systems. The studies were performed on artificially prepared samples of Polish mineral soils. It was found that the averaged limits of the integration range (quasiplateau) in voltammetric measurements of the potential oxygen flux in the soil, obtained for measured soil samples of Polish mineral soils investigated, were: $-460 \div -700$ mV for the three-electrode system and $-1260 \div -1600$ mV for the two-electrode system. The OFD values obtained with the use of voltammetric method follow the lognormal distribution. Uncertainty of the results obtained with the use of the three-electrode system is smaller than for the two-electrode system. However, this does not make it impossible to use the two-electrode system, especially for measurements in compacted soils, where installation of the electrode in glass body is a technical problem and in the aspect of simultaneous measurements of OFD and soil water content by TDR technology with the same probe.

Key words: soil aeration, soil oxygen flux density, ODR

INTRODUCTION

Oxygen conditions in the soil, along with the water content and the availability of nutrients, are one of the most important factors stimulating the growth of roots and, correspondingly, the development of the whole plants (Gliński and Stępniewski, 1985; ISO 15709:2002). From many quantities characterizing the soil aeration, the most important are the oxygen concentration and the oxygen flux that can flow in specific conditions in a given soil. Especially the latter parameter seems to be important, because it enables simultaneous evaluation of the

availability and the speed of replenishment of oxygen used in the plant roots (Bieganski and Malicki, 2002).

Determination of the potential oxygen flux in the soil is possible, among others, with the use of the voltammetric method. It consists in the registration of the current-voltage curve *ie* the dependence between the current and the potential on the cathode, $I(U)$. When the oxygen flux magnitude is limited by the diffusivity of the medium, which manifests itself in the occurrence of the plateau area in $I(U)$ dependence (in fact the plateau never occurs because nearly always there is a slope in this dependence and it is accepted to use the term of quasiplateau), the calculated integer of the function $I(U)$ in the quasiplateau area is converted into the oxygen flux in the soil (Malicki and Bieganski, 1999). The quantity determined this way is called OFD (oxygen flux density).

The application of the voltammetric method was an improvement of previously realized amperometric measurements of the potential oxygen flux in the soil. The amperometric method, proposed by Lemon and Erickson in the 50-ies of the twentieth century, consisted in the measurement of the current applied to a two-electrode measuring system. The measuring electrode was a polarized platinum cathode (usually with the voltage of -650 mV) and the circuit was closed by a saturated calomel electrode, NEK. The amperometric method was called ODR (oxygen diffusion rate) (Lemon and Erickson, 1952; 1955).

The measurement in the two-electrode system did not enable the control of the real cathode potential in relation to the soil solution because in measuring conditions the decrease of potential related to changes of soil water content was not determined (soil water content decrease causes an increase of the electrical resistance) (Malicki 1990).

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*This paper was partly realized within the framework of the research project No. 6 P06B 027 20 financed by Polish State Committee for Scientific Research in the years 2001-2003.

This problem was solved by Malicki and Walczak (1983) by introducing into the measuring set an additional, current-free circuit of potentiostat, which made it possible to precisely control the cathode potential. However, this approach causes the necessity to incorporate an additional electrode to the measuring set. Consequently, it is necessary to install in the soil a platinum cathode, an anode (made of a conductor of the first kind) and the reference electrode *eg* NEK. This solution, proper from the point of view of the merits, is inconvenient, especially, in compacted soils where installation of the electrodes on a specified level can sometimes be a technical problem. Another complication arises due to the necessity of installing the NEK as close to the platinum cathode as possible. It can, consequently, cause a disturbance of the medium studied, because a relatively thick ending of the NEK presses the soil and leads to a change of the oxygen diffusion coefficient in the soil.

The use of the potentiostat system in the amperometric measurements is a necessity, whereas the use of the voltammetric method gives a chance to abandon the three-electrode measuring set and, what is even more important, it seems that there is a chance to avoid the need to use the reference electrode (NEK or a chlorosilver electrode), the maintenance of which is difficult and dangerous. This possibility comes from the chance of verification of the potential ranges at which the plateau occurs for each individual measurement.

The aim of this paper is to determine, in saturated and nearly saturated mineral soils, the ranges of the potential (for two- and three-electrode set with a potentiostat) at which a quasiplateau occurs on the current-voltage curve.

MATERIAL AND METHOD

The studies were performed on soil material taken from the soils specified in the Soil Samples Bank Representing Mineral Soils of Poland (Gliński *et al.*, 1991). The description of the selected properties of the soil material studied is presented in Table 1.

The collected soil material was dried at room temperature to reach the air dry state. Then, the soil aggregates were crumbled by a hammer and the lot was screened through a sieve with 2 mm mesh.

The soil material prepared in this way was wetted with distilled water. By mixing it carefully, the saturation state was obtained. The saturated soil material was placed in small portions in plastic pots (having the diameter of about 6 cm and the height of about 9 cm). When filling the pots, special care was taken to assure the maximum possible homogeneity of the bulk density. For each soil material the saturated samples were prepared, as well as two samples having water contents close to the saturation (a total of 76 soil samples).

The current-voltage curves were registered with a voltammeter produced by ForTest, applying three- and two-electrode sets of electrodes.

The three-electrode set consisted of a platinum cathode (platinum wire – purity 3n, diameter of 0.5 mm, length of 10 mm, sunk in a glass pipe), a steel anode (stainless steel wire, diameter of 2 mm and length of 40 mm) and a reference electrode which was a saturated calomel electrode (NEK). The potential of the cathode was controlled by the system of potentiostat (Malicki and Walczak, 1983).

The two-electrode set consisted of two identical platinum electrodes – platinum wire, having purity of 3n, diameter of 0.5 mm, length of 10 mm, sunk in a glass pipe. One of these electrodes was the cathode and the other – the anode.

Taking into consideration the lack of repeatability of the results obtained during succeeding replications under single-time installation of electrodes (Bieganowski, 2003), the analysis of the impact of the range of integration on the obtained values of the potential oxygen flux in soil was performed on the basis of the first, registered for a given installation of the electrodes, current-voltage curve.

In both cases (two- and three-electrode systems) the registration of current-voltage curves was conducted under the rate of the change of cathode potential equal to 4 mV s^{-1} .

RESULTS AND DISCUSSION

The choice of the integration range can be done in different ways. The most objective way seems to be an individual analysis of each of the current-voltage curves obtained and, basing on the results of this analysis, determination of the upper and lower borders of the plateau area. It is equivalent to determination of the integration range.

Unfortunately, in spite of the fact that the measurements were conducted in the artificially prepared saturated and nearly saturated soil samples and it would be expected that for each measurement the quasiplateau of the $I(U)$ dependence should occur, the identification of the quasiplateau was possible only in 42 cases for the three-electrode system and in 28 cases for the two-electrode system (it is difficult to explain unambiguously at this stage of the investigation why in the remaining cases the quasiplateau did not occur). The averaging of the lower and upper limit of plateau area for these cases allowed to determine the integration ranges: $-460 \text{ mV} \div -700 \text{ mV}$ for the three-electrode system and $-1260 \div -1600 \text{ mV}$ for the two-electrode system.

The lack of quasiplateau in the $I(U)$ dependence made us look for a way of determination of the borders of the integration ranges. On the basis of experience resulting from the realization of a large number of measurements (including other experiments), arbitrary ranges were

Table 1. Description of the investigated soil samples

Soils	Number in Bank of Soil of Soil Samples*	Symbol of soil formation	Place of sampling	Granulometric composition (%; dia in mm)		
				2-0.02	0.02-0.002	<0.002
Brown soils	553	Bli	Sady com. Skierbieszów	50	40	10
(Cambisols)	568	Bli	Majdan Skierbieszowski com. Skierbieszów	58	31	11
	569	Bli	Majdan Skierbieszowski com. Skierbieszów	71	25	4
	570	Bli	Kol. Lipna Nowa com. Skierbieszów	62	27	11
	591	Bpłg	Rogalin com. Horodło	70	27	3
	604	Bps.pl	Wólka Kątna com. Markuszów	96	3	1
	605	Bps.pl	Wólka Kątna com. Markuszów	95	4	1
	607	Bps:pl	Bobowisko com. Markuszów	95	4	1
	611	Bps:pl	Kol. Olempin com. Markuszów	94	5	1
Chernozems	586	Cli	Hostynne com. Werbkowice	59	30	11
(Haplic Phaeozems)	601	Cli	Kol. Hostynne com. Werbkowice	60	34	6
	619	Cli	Sahryń com. Werbkowice	86	13	1
	621	Clz	Sahryń gm. Werbkowice	63	32	5
	622	Cli	Terebin com. Werbkowice	60	34	6
	623	Cli	Terebin com. Werbkowice	60	29	11
Alluvial soil (Dystric Fluvisol)	593	Fglp.pli	Kośmin com. Żyrzyn	86	12	2
Muck soil (Terric Histosol)	606	Mps.pl	Wólka Kątna com. Markuszów	97	2	1
Grey brown podzolics	594	Apłp.gs	Osówka com. Niemce	77	21	2
(Haplic Luvisols)	597	Apgm.gl	Dęba com. Kurów	95	4	1
Rendzinas	557	Rcgc	Bezek com. Chełm	61	21	18
(Rendzic Leptisols)	560	Rcglp:gc	Chojno Nowe com. Siedliszcze	85	13	2
	562	Rbgp.gs	Chojno Nowe com. Siedliszcze	49	35	16
	565	Rcgl.gs	Okszów com. Chełm	78	17	5
	556	Rbgl.gs	Okszów com. Chełm	91	8	1
Black soil (Mollic Gleysol)	613	Dpli.płg	Późóg Nowy com. Końskowola	79	20	1

*Gliński *et al.*, 1991.

adopted for both sets of electrodes, and the OFD values were determined for them (Table 2).

When looking for the value which can be regarded as a reference level for the evaluation of the integration range in case of the three-electrode system, it is possible to use the

values of the oxygen flux density in the soil calculated for the potential of -650 mV, in reference to NEK (J (-650 mV) in Table 2). This value is most frequently accepted for polarization of platinum cathode in amperometric measurements of ODR (Bieganowski, 2003).

Table 2. Arbitrary established integration ranges for the three- and two-electrode systems.

Set of electrodes	Integration ranges (mV)					
Three-electrode	0 ÷ -650	0 ÷ -800	-500 ÷ -650	-650 ÷ -800	-250 ÷ -650	ODR J(-650)
Two-electrode	0 ÷ -1300	0 ÷ -1700	-500 ÷ -1300	-800 ÷ -1400	-800 ÷ -1600	-1200 ÷ -1500 -1200 ÷ -1750

The first step that enables further interpretation of the results obtained is specifying which distribution are the results obtained subject to. The test of fitting the distribution, carried out in Statistica (v.6.1) under the significance level of 0.05 for all the integration levels for both sets of electrodes (two- and three-electrode sets), showed that obtained values of OFD follow the lognormal distribution.

Figure 1 presents the interrelation between the values of ODR and the OFD values calculated for the common integration range (-460 mV ÷ -700 mV) and the OFD values calculated for the integration ranges subjectively set for each measurement. Table 3 contains the equations and respective determination coefficients for the interrelation of OFD calculated for all the integration ranges.

The analysis of the results presented in Table 3 leads to the conclusion that the highest determination coefficient (0.963) was obtained for the common integration range (-460 ÷ -700 mV). This would confirm the assumed procedure of determination of the upper and lower limit of the quasiplateau. However, it should be thought over why the determination coefficient determined subjectively and

individually for each curve of a specific quasiplateau had such a small value (0.765).

In the case of the two-electrode system there is no possibility to determine the reference value analogically as for the three-electrode system. In the three-electrode system the potential of the platinum cathode is controlled by the potentiostat. In the two-electrode system there is no control of the actual cathode potential. Only the voltage applied to the electrodes is known. Thus, the actual potential that is accumulated at particular electrodes is unknown. There are also no premises which would enable to accept any of the integration ranges as a better one than others and to treat it as a reference level.

Therefore, using the experience obtained for the three-electrode system, a similar procedure of determination of a common range was established:

1. Individual evaluation of each curve and subjective determination of the quasiplateau area.
2. From the data achieved in item 1, the calculation of the mean value of the lower limit of the quasiplateau – the value of -1260 mV was obtained.

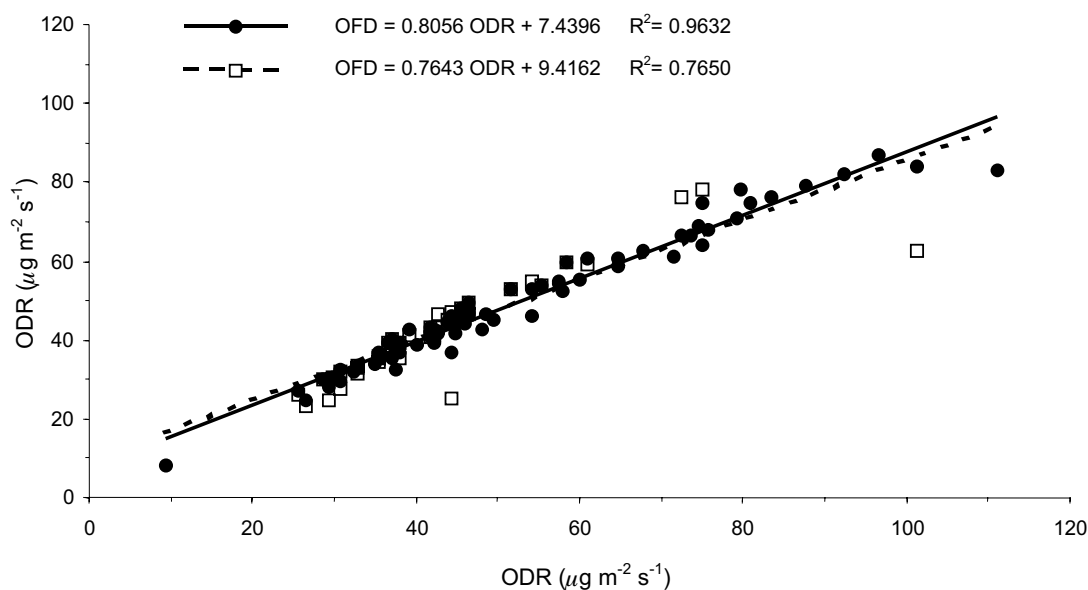


Fig. 1. Comparison of the values of potential density of oxygen flux calculated by voltammetric method (OFD) with the values of potential density of oxygen flux calculated by amperometric method (ODR). Both measurements were performed with the use of the three-electrode system; black filled circles – the OFD values calculated for the common integration range (-460 ÷ -700 mV); empty squares – the OFD values calculated for the subjectively appointed for each measurement integration ranges - if it was possible to identify the quasiplateau area.

Table 3. Three-electrode system. Equations describing interrelations between OFD calculated for assumed integration ranges and ODR calculated for the potential of -650 mV

Range of potentials accepted for integration during OFD calculations (mV)	Interrelation equations	Determination coefficient (R^2)
0 ÷ -650	OFD = 0.47 ODR + 10.77	0.643
0 ÷ -800	OFD = 0.67 ODR + 6.33	0.846
-500 ÷ -650	OFD = 0.75 ODR + 9.61	0.921
-650 ÷ -800	OFD = 1.51 ODR - 12.59	0.790
-250 ÷ -650	OFD = 0.59 ODR + 13.13	0.712
OFD calculated for subjectively established integration range	OFD = 0.76 ODR + 9.42	0.765
OFD calculated for common integration range (-460 ÷ -700)	OFD = 0.81 ODR + 7.44	0.963

3. From the data achieved in item 1, the calculation of the mean value of the upper limit of the quasiplateau area – the value of -1600 mV was obtained.

4. Accepting the averaged limits of the quasiplateau area obtained in items 2 and 3 as the limits of integration

5. On the basis of the integration limits determined in item 4, determination of OFD.

Assuming the values of OFD calculated for a common integration range as a reference level, the interrelation with OFD calculated for the other integration ranges was determined. The equations obtained and the respective determination coefficients are presented in Table 4.

The analysis of the data contained in Table 4 leads to the conclusion that the highest correlation occurred between the OFD values calculated for the common integration range (-1200 ÷ -1600 mV) and for the range of -1200 ÷ -1750 mV. As it was in the case of measurements with the use of the three-electrode system, it is puzzling that the determination coefficient had a small value (0.3388) when determining the interrelation between the OFD values assumed as a reference level and the OFD values calculated individually for each current-voltage curve.

The analysis of the determination coefficients for the measurements obtained with the use of the three- (Table 3) and two-electrode (Table 4) systems should not be treated as an equivalent source of information. In the case of measurements conducted with the three-electrode system in the system of potentiostat it is possible to speak about a reference value which was made objective and is defined as a value of the potential oxygen flux calculated for the cathode potential of -650 mV. In the case of measurements conducted with the use of the two-electrode system there is not such a reference value and it is not surprising that the correlation of results is high for similar integration ranges because in both cases the same dependences of $I(U)$ were integrated. Therefore, the determination coefficients presented in Table 4 can be treated only as one of the measures of uncertainty of OFD measurement with the voltammetric method.

Another way of evaluation of the uncertainty of measurements conducted with the use of both sets of electrodes can be the calculation of the deviation for OFD values calculated for all the integration ranges. In both cases the values of standard deviations were calculated for OFD

Table 4. Three-electrode system. Equations describing interrelations between OFD calculated for assumed integration ranges and OFD calculated for common integration range (-1260 -1600 mV)

Range of potentials accepted for integration during OFD calculations (mV)	Interrelation equations	Determination coefficient (R^2)
0 ÷ -1300	OFD = 0.2529 OFD _{common integration range} + 3.2844	0.2888
0 ÷ -1700	OFD = 0.4733 OFD _{common integration range} + 2.0593	0.7652
-500 ÷ -1300	OFD = 0.4098 OFD _{common integration range} + 2.2537	0.3451
-800 ÷ -1400	OFD = 0.5831 OFD _{common integration range} + 1.1261	0.4874
-800 ÷ -1600	OFD = 0.7198 OFD _{common integration range} + 0.7645	0.7849
-1200 ÷ -1500	OFD = 0.8469 OFD _{common integration range} + 0.4464	0.8849
-1200 ÷ -1750	OFD = 1.1860 OFD _{common integration range} - 2.5858	0.9559
OFD calculated for subjectively established integration range	OFD = 0.8292 OFD _{common integration range} + 9.3714	0.3388

attained for arbitrary assumed integration ranges, OFD determined for a common integration range and, if it was applied, for OFD calculated under individually determined ranges of integration. The results of standard deviations are shown in Table 5.

Table 5. Standard deviations calculated for the three- and two-electrode systems for all the integration ranges

	Three-electrode system	Two-electrode system
Maximum value of standard deviation	64.92	21.08
Minimum values of standard deviation	1.89	2.65
Mean value of standard deviation	10.56	7.00
Mean value of OFD ($\text{mg m}^{-2} \text{s}^{-1}$)	46.37	19.01

The theoretical analysis of the assumptions of electrochemical methods for the determination of the potential oxygen flux in the soil enables to put forward a thesis that this measurement can be burdened with high uncertainty resulting from heterogeneity of the granulometric distribution, the water content and oxygen conditions, *etc.* Therefore it is difficult to compare the standard deviation values of OFD when the OFD values differ themselves significantly. The solution of this problem can be the comparison of the variation coefficients defined as the ratio of the standard deviation value to the mean value. The results of the analysis of the variation coefficients are presented in Table 6.

Summarizing the data contained in Table 6 it should be stated that the measurement with the use of the three-electrode system is characterized by smaller uncertainty.

Table 6. The ratio of standard deviation calculated for OFD values obtained from all the integration ranges to OFD calculated for the common integration range as a measure of uncertainty of voltammetric measurements of potential oxygen flux in soil

	Three-electrode system	Two-electrode system
Maximum value of variation coefficients	0.71	0.77
Minimum values of variability coefficients	0.04	0.15
Mean value of variation coefficients	0.21	0.37

CONCLUSIONS

1. The averaged limits of the integration range (quasiplateau) in voltammetric measurements of the potential oxygen flux in the soil, obtained for the saturated and close to saturation, artificially prepared soil samples of the Polish mineral soils studied in this paper are:

- i) $-460 \div -700$ mV for the three-electrode system,
- ii) $-1260 \div -1600$ mV for the two-electrode system.

2. The OFD values obtained with the use of the voltammetric method follow the lognormal distribution

3. The uncertainty of the results obtained with the use of the three-electrode system is smaller than under the use of the two-electrode system. However, it does not enable the use of the two-electrode system, especially:

- i) in the situation of measurements in compacted soils, where installation of the electrode being in the glass body is a technical problem,
- ii) in the aspect of conducting with this probe simultaneous measurements of OFD and the soil water content by TDR.

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