

Determination of the background current in electrochemical measurements of oxygen flux density in organic soils

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Abstract. The aims of this paper were: to state if the soluble substances contained in organic or organic-mineral soils can reduce in the same range of potentials as oxygen, falsifying (revaluing) the results of the potential oxygen flux density derived using amperometric and/or voltamperometric methods; to evaluate a correction which would enable one to eliminate this systematic error. The conclusions which are stated in the paper are: the voltamperometric method of oxygen flux density (OFD) measurements in organic soils enables one to obtain more reproducible results than the amperometric (ODR) method; as far as the values of the current obtained with the two methods can be interpreted in terms of potential oxygen flux density in soil, the obtained results are expressed by the relation: ODR (result from amperometric method) ≈ 2 OFD (result from voltamperometric method); the contribution of the background current in the value of the potential oxygen flux density, determined with the use of the voltamperometric method is smaller than that obtained with the amperometric method; the corrections, taking into account the background current in organic and mineral-organic soils which should be subtracted from derived values of the potential oxygen flux density in the soil are: 10.8 for ODR and 5.5 $\text{g m}^{-2} \text{s}^{-1}$ for OFD; the results obtained both with amperometric and voltamperometric methods should be treated rather as an indicator, indicating the oxidation status of the soil, than as a real meter of the amount of oxygen available for the plant roots.

Key words: oxygen flux density in the soil measurements, ODR, OFD

INTRODUCTION

The electrochemical measurement of potential oxygen flux density in soil can be performed using amperometric (Lemon and Erickson, 1952; 1955) and voltamperometric (Bieganski, 1997; Malicki and Bieganski, 1999) methods.

The amperometric method proposed by Lemon and Erickson consists in the measurement of the current under

the voltage applied to a two-electrode measuring system. This voltage is usually -650 mV in respect to a saturated calomel electrode. Under such an approach the real potential of the cathode in relation to the soil solution is not known, due to the decrease of the voltage, caused at the very last by the soil electrical resistance which is difficult to evaluate and which depends among other things on the soil water content. In 1983 Malicki and Walczak improved the measurement, introducing a three-electrode system with the use of a potentiostat (Malicki and Walczak, 1983) which made it possible to precisely control the cathode potential.

The voltamperometric method is based on the interpretation of the curve of the dependence between the cathode potential (U) and the current (J). Under such an approach, the problem of precise determination of the cathode potential starts to be insignificant and besides, the analysis of the curve enables one to reject the results which cannot be interpreted in terms of potential oxygen flux density, e.g., because of the soil overdrying (Malicki and Bieganski, 1999). It is especially important during the measurements performed under field conditions.

To distinguish the results obtained by the two electrochemical methods, those obtained with the amperometric method were denoted in the paper as ODR (oxygen diffusion rate) whereas the results obtained with voltamperometric method were denoted as OFD (oxygen flux density) (Malicki and Bieganski, 1999).

Both methods are based on the same assumption: the only substance that is reduced on the platinum cathode in the settled range of potentials is the molecular oxygen. It means that other components of the solution, in a given range of potentials, do not depolarize the cathode. In the case when this assumption is not fulfilled, the current measured in the

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circuit would be a sum of the reduction currents of molecular oxygen and another substance. It would lead to an overestimation of the potential density of the oxygen flux.

In practice, the situation when nothing except the oxygen reduces on the cathode, never occurs. A proof of this is the occurrence of the so called residual current. However, if the residual current is sufficiently small, it can be omitted without adding to the measurement a significant source of uncertainty.

The aim of this paper was to state if the soluble substances contained in the organic or organic-mineral soils (often suffering from the problem of insufficient aeration) can reduce in the same range of potentials as the oxygen, falsifying (revaluing) the results of the potential oxygen flux density derived using amperometric and/or voltamperometric methods. The aim of the paper was to evaluate a correction which would enable one to eliminate this systematic error.

MATERIAL AND METHOD

The selectivity of the reaction of the molecular oxygen reduction can be investigated in deoxidized water extracts of organic and mineral-organic soils. Under the lack of a substance depolarizing the cathode, the current value (in the range of potentials not exceeding the liminal value, under which the reduction of hydrogen ions begins during the water electrolysis) is small and comparable with the residual current value obtained in the deoxidized KCl solution (the selection of the KCl solution was caused by the fact that neither potassium nor chloride ions react within the considered range of potentials). Because the investigations were performed in the water extracts, it was possible to obtain easily reproducible measurement conditions.

The extracts were prepared as follows: approximately 200 g (as recalculated to the dry mass) of a newly taken soil formation of chosen organic or mineral-organic soil was flooded with distilled water to obtain the mixture volume of about 1 dm³. The obtained mixture was being shaken for one hour and then left for sedimentation for 48 h. The limpid extract was poured (through a cable release) from above the sediment.

The soil material was selected this way that to represent the majority of organic and mineral-organic soils, characteristic for Poland. The description of the soil material is presented in Table 1.

The obtained extracts were poured into a specially prepared glass utensil of a spherical shape. This utensil had two gas inlets (in the bottom and in the top) and one outlet (in the upper part).

The extract was vented by passing, from the bottom of the utensil, 1000 cm³ of nitrogen per minute (oxygen content 8 ppm) for 30 min. The time of deaeration was chosen experimentally. Then the nitrogen inlet was closed from the bottom of the utensil and the nitrogen was directed through

the upper inlet. This procedure made the atmosphere above the extract free of oxygen. The flow of the nitrogen above the extract was limited to 50 cm³ min⁻¹, what for the utensil's capacity of about 1 dcm³ did not cause its mixing. The measurement started 30 min after the end of deaeration.

To evaluate the impact of the presence of the substances dissolved in the extracts on the measured value of the current in the system, the voltamperometric curves were registered in deaerated solutions of potassium chloride. The solutions were prepared by dissolving the potassium chloride in distilled water and waiting for it to reach the ambient temperature. The conductivity values of five prepared KCl solutions were chosen in such a way so as to be in the range of the soil extracts conductivity. The procedure of KCl deaeration was the same as in the case of the soil extracts.

The current passing in the deaerated soil extracts and KCl solutions can be considered as a background of the measurement. To allow evaluation of the participation of the background current in the total value of the potential oxygen flux density, the measurements in the maximally aerated extracts were carried out after the series of the measurements in deaerated extracts. The aeration was done with the air, compressed in the cylinder. The procedure of aeration was the same as the procedure of deaeration.

The voltamperometric curves were registered in five repetitions with the use of a voltamperometer, constructed by Easy Test Ltd. Firm, equipped with the three-electrode measuring system with a potentiostat (Malicki and Walczak, 1983). The electrodes worked in two circuits. The current circuit enabled to register the reduction current of molecular oxygen and consisted of a cathode (Pt wire, 10 mm long, 0.5 mm diameter) and an anode (stainless steel wire, 50 mm long, 3 mm diameter). The current-free circuit, which enabled one to control the potential of the cathode, consisted of a platinum cathode and a saturated calomel electrode (SCE) as a reference electrode.

The rate of changes of the potential was 4 mV s⁻¹ in the range from 0 mV to -1200 mV (in relation to SCE).

For the calculation of ODR, the values of the current read from the voltamperometric curves under the potential of -650 mV (in respect to SCE) were used. The OFD values were calculated for an arbitrarily assumed integration range: -250 ÷ -650 mV. The reason that the integration ranges were assumed arbitrarily was, that there was no oxygen wave (deaerated solutions) on the voltamperometric curve and resulting inability to determine a quasiplateau area. A motivation for the assumed integration range was the fact, that in case of the molecular oxygen appearance in the electrolyte, the so called oxygen wave, i.e., the range of potentials in which the quasiplateau of the J(U) dependence occurs, is contained directly in this range, i.e., -250 ÷ -650 mV (Malicki, 1990). Because the voltamperometric method consists in determination of an integral of J(U) function and then in referring the obtained value to the time of

Table 1. Description of studied soil materials from organic and mineral-organic soils (Okruszko, 1976)

No.	Description of the soil material	Decomposition degree	Soil type	Place of sampling	Depth of sampling (cm)	Ash content (g g ⁻¹)
1	Sedge peat strongly silted up	R ₃	Gt11	Grzędy	5–15	77.15
2	Proper sedge peat	R ₃	Gt21	Grzędy	5–15	23.99
3	Mud formation		Gm11	Budne	10–20	83.06
4	Mud formation		Pmm	Budne	15–25	23.47
5	Proper hypnum-moss peat	R ₁	Mt1aa	Kosiły	30–50	6.30
6	Proper rush-reed peat	R ₂	MtIIbb	Modzelówka	40–50	14.68
7	Proper sedge peat	R ₂	PtIbb	Canal Łęg-Kapie	40–50	11.36
8	Proper rush peat	R ₃	MtIIcb	Grzędy Jegrznia	30–50	13.28
9	Proper oloess peat	R ₃	MtIIcc	Biebrza	30–50	14.39
10	Proper sedge peat	R ₃	MtIcb	Grzędy Studzienka	7–15	11.91
11	Peaty muck (Z ₁) from proper peat		Mt1aa	Kosiły	10–20	14.23
12	Humic muck (Z ₂) from proper peat		MtIIcc	Biebrza	7–15	13.76
13	Proper muck (Z ₃) from proper peat		MtIIcc	Biebrza	7–15	16.45
14	Proper muck Z ₃ (coke muck) from proper peat		MtIIcb	Modzelówka	10–20	23.92
15	Muck formation		Me11	Biebrza	5–15	89.14
16	Muck formation		Me11	Biebrza	5–15	89.81
17	Proper rush peat	R ₃	MtIIbb	Sosnowica	80–130	15.78
18	Mixed gythia (mineral-organic)		MtIIbb	Sosnowica	200–250	44.82
19	Mineral-humic formation from black degraded soil		D21	Sosnowica	5–15	94.80
20	Mineral-organic formation from black mucky soil		D21	Sosnowica	5–15	88.20

The soil samples Nos 1–16 were taken in the area of Biebrza National Park, the soil samples Nos 17–20 were taken in the area of Lublin Polesie. R₁–R₃ – increasing decomposition from 1 to 3.

measurement, the selection of the integration range is not a critical parameter, from the point of view of the results' reliability (Bieganowski, 1997). The same procedure was used both for the soil extracts and KCl solutions.

RESULTS AND DISCUSSION

Relation between ODR and OFD

The mean values of ODR and OFD obtained in the deaerated soil extracts and KCl solutions are presented in Fig. 1 whereas the averaged values for all the soil extracts and KCl solutions in Table 2.

Through the analysis of the data in Table 2, both quantities, ODR and OFD, characterizing the potential oxygen flux density in the soil can be compared. It is seen

that the amperometric (ODR) measurement gives higher values than the voltamperometric (OFD) measurement. The dependence ODR(OFD) is presented in Fig. 2.

The advantage of the voltamperometric method over the amperometric method lies in the possibility of review and rejection of the results which are not suitable for the interpretation in terms of potential oxygen flux density. The base for the rejection is the analysis of a shape of a voltamperometric curve. If the shape of the curve strays from the expected one, it should not be interpreted.

The use of the mentioned possibility is responsible for the omission of the results in Fig. 2, obtained for the extract of the rush peat from Sosnowica (extract No. 17 in Table 1 and Fig. 1). The reason for a different shape of the voltamperometric curve could be an adsorption on the electrode surface of the chemical substances, contained in the extract

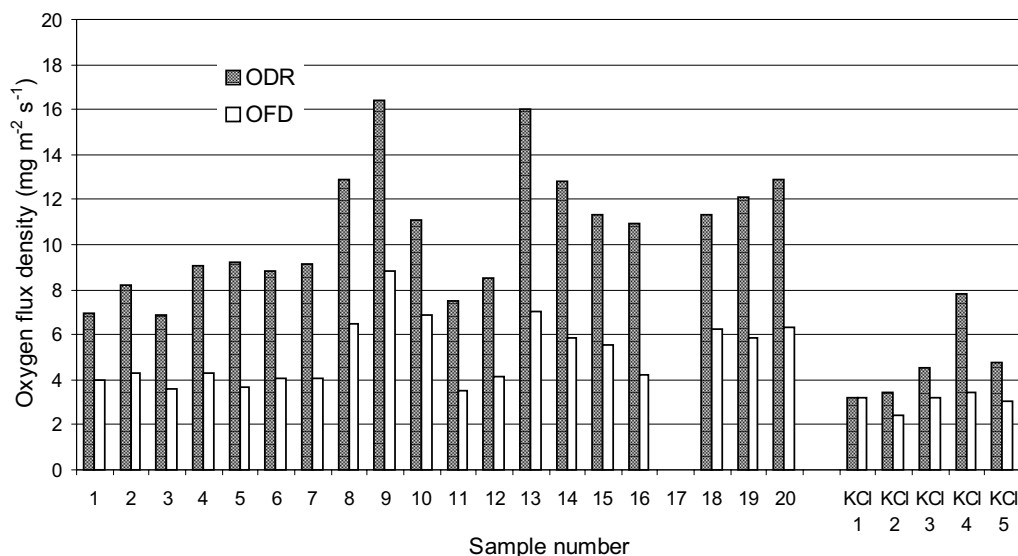


Fig. 1. ODR and OFD values obtained in deaerated soil extracts and KCl solutions. The numbers under the columns correspond with the numbers of extracts in Table 1.

Table 2. Mean values of ODR and OFD for the extracts and KCl solutions

Measure	ODR	OFD
	(g m ⁻² s ⁻¹)	
Mean value for soil extract	10.8	5.5
Standard deviation for soil extract	2.8	2.1
Mean value for KCl solution	4.8	3.1
Standard deviation for KCl solution	1.8	0.4

or being the effect of an electrode reaction. To eliminate this phenomenon, the electrode was rubbed with glass-paper and immersed for three minutes in the concentrated nitrous acid after the measurements in a discussed extract.

An important conclusion resulting from the analysis of Table 2 is a statement that both for the soil extracts and KCl solutions the dispersion of the OFD values is smaller than of the ODR values. It can be testified by the smaller values of the standard deviation for the results obtained by the volt-ampometric method.

The slope (2.036) as well as the offset value (-0.029) of the straight line fitted to the dependence between ODR and OFD for the investigated soil extracts are in good correlation with the parameters of an analogical straight line obtained by Malicki and Bieganski (1999) for three mineral soils

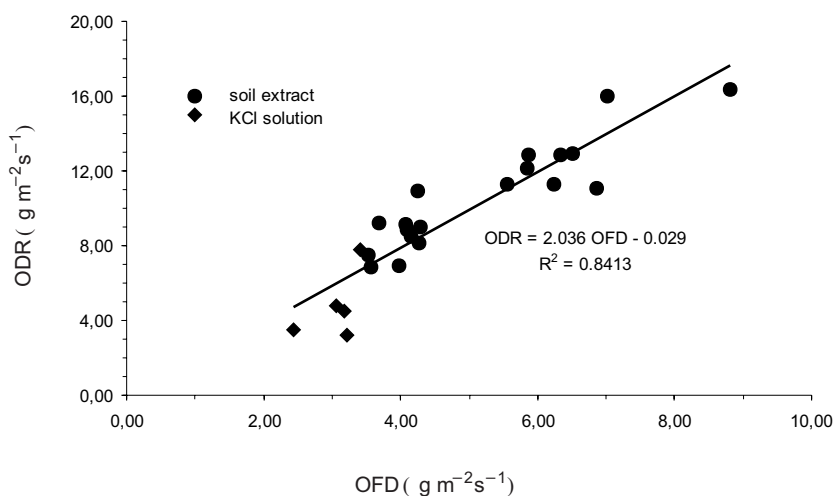


Fig. 2. The dependence between ODR and OFD obtained for the studied soil extracts and KCl solutions.

and one peat-muck soil -1.93 and -5.73×10^{-10} , respectively. However, the correlation coefficient is smaller than in the case of the soils. For the investigated extracts it was 0.8413 , whereas for the mentioned soils it was 0.9495 .

Comparison of ODR and OFD in soil extracts and KCl solutions

The ODR values obtained for deaerated soil extracts ranged from 6.9 to $16.4 \text{ g m}^{-2} \text{ s}^{-1}$ (Fig. 1) with mean value $10.8 \text{ g m}^{-2} \text{ s}^{-1}$ (Table 2), while those for the deaerated KCl solutions – from 3.2 to $7.8 \text{ g m}^{-2} \text{ s}^{-1}$ (Fig. 1) with mean value $1.8 \text{ g m}^{-2} \text{ s}^{-1}$ (Table 2).

The OFD values in deaerated soil extracts ranged from 3.5 to $8.8 \text{ g m}^{-2} \text{ s}^{-1}$ (Fig. 1) with a mean value $5.5 \text{ g m}^{-2} \text{ s}^{-1}$ (Table 2), whereas those in deaerated KCl solutions from 2.4 to $3.4 \text{ g m}^{-2} \text{ s}^{-1}$ (Fig. 1) with a mean value $3.1 \text{ g m}^{-2} \text{ s}^{-1}$ (Table 2).

It results from the data presented in Fig. 1 that for the majority of cases, the values obtained in KCl solutions were smaller than in the soil extracts. And although, the statistical analysis cannot be a base for a rejection of the thesis about the equality of means for the extracts and KCl solutions (t-student test under the confidence level 0.05), it can be stated, considering the obtained results, that there are dissolved substances in the soil extracts which can reduce simultaneously with the molecular oxygen (for the range of potentials applied in the studies). It is proved by a higher mean of the currents registered under lack of oxygen in the extracts compared to KCl solutions.

To answer the question, to what extent the described above phenomenon decreases the reliability of the electrochemical measurement of the oxygen flux density in soil, the contribution of the background current (a current in deaerated extracts) in the values of the current for completely aerated extracts has to be determined.

In Table 3, the results are presented obtained in maximally aerated soil extracts and KCl solutions. It results from the presented data that contrary to the case of the deaerated solutions, the mean values obtained for KCl solu-

tions were higher than the values obtained for the soil extracts. At the moment there is a lack of premises to recognize this phenomenon as important from a physical point of view. Therefore these results can indicate the amount of the method's noise.

When calculating the contribution of the background current in completely aerated electrolytes the following coefficients were obtained:

- for the extracts: 0.19 for ODR measurements and 0.09 for OFD measurements,
- for KCl solutions: 0.08 for ODR measurements and 0.05 for OFD measurements.

It results from the above data, that both for the soil extracts and KCl solutions, the voltamperometric method gives the results charged with smaller error.

It can be assumed that ODR and OFD values obtained for the soil extracts and deaerated solutions appoint a systematic error that is made during the measurements performed on organic soils. This error changes depending on the chemical composition of the soil.

At the moment there are no data which would enable one to connect the background current with the occurrence of specific chemical substances. It is expected, that even if such data were available, in most cases the quantitative-qualitative analysis of organic soils would not be performed simultaneously with the studies of the potential oxygen flux density, due to the costs and time consumption. Therefore, the elimination of this systematic error can be based on the algorithm considering its statistical parameters.

The consequence of such an approach will be assuming the values presented in Table 2 as corrections to the measurements performed in the extracts of organic soils and KCl solutions. The correction value should be subtracted from each obtained result. The assumed algorithm can mean that a negative value of the potential oxygen flux density is obtained. In such a case a zero value of the potential oxygen flux density should be assumed.

The question arises whether the values of the correction, presented in Table 2 can be applied to the measurements realized not only in extracts but also in the organic soils. Taking into consideration the way of preparation of the samples in the investigations of the extracts there can be a positive answer.

The measurements of potential oxygen flux density are performed in saturated or nearly saturated soils because only in this case the deficit of oxygen available for the rooting system can occur. In such a situation nearly all the space between soil particles is filled with soil solution. Therefore, the mineral and organic substances available in the soil get into the liquid phase, dissolving in it. The method of samples preparation was elaborated this way that to let the highest elution of these substances from the soil. Therefore the background current measured in the soil extracts can be treated as representative for the soils.

Table 3. ODR and OFD values obtained in maximally aerated soil extracts and KCl solutions

Measure	Soil extract		KCl solution	
	ODR	OFD	ODR	OFD
	($\text{g m}^{-2} \text{ s}^{-1}$)			
Maximum	77.9	76.0	61.2	69.8
Minimum	46.4	51.7	54.2	58.6
Mean	56.8	59.3	57.6	65.8
Standard deviation	9.3	6.4	2.6	4.6

The methodology and the results presented in this paper are not easily comparable with earlier literature reports referring to this subject.

To show the selectivity of the amperometric method, Lemon and Erickson (1955) presented the dependence between the current passing in the circuit and the oxygen concentration in the air above the soil sediment. According to their expectation, the current value was proportional to this concentration. Similar results were obtained by Birkle *et al.* (1964).

Karsten (1939) was engaged in the studies of oxygen reduction in the soil sediment with the use of dropping mercury electrode (DME). He investigated six different soils in a broad range of grain size distribution and content of organic matter and did not find, in the voltage range of the oxygen reduction, any other substances which would reduce simultaneously with it.

Van Doren and Erickson (1966) discussed the problem of a simultaneous reduction of substances, different than oxygen. According to their results, the simultaneous reduction with the molecular oxygen is possible for: Co^{3+} , Cu^{2+} , Fe^{3+} , Mn^{2+} and Mo^{4+} . From the above mentioned cations only manganese and iron can be present in a dissolved form in the soil solution, however their concentration is so small that the current of their reduction can be omitted. The authors noticed that some organic substances such as unsaturated acids, nitro compounds, nitrogen compounds and organic peroxides, can influence the value of the reduction current.

Armstrong (1967) investigated completely deaerated soil samples and stated, that for different peat soils, the residual current, resulting from the reduction of substances other than oxygen, differs slightly. He postulated that to obtain an absolute value of the oxygen reduction current, a background resulting from the residual current should be subtracted. However, he did not give a method which would enable to determination of the background current.

Summing up, the majority of authors find the condition of selectivity of the reaction taking place on a platinum cathode under its potential -0.65 V as practically fulfilled (Gliński and Stepniewski, 1985). However, the information can be found in some reports, that some organic substances such as unsaturated acids, nitro compounds, nitrogen compounds, organic peroxides or humus substances can reduce simultaneously with oxygen (Fiedler *et al.*, 1976; Van Doren and Erickson, 1966).

CONCLUSIONS

1. The voltamperometric (OFD) method of oxygen flux density measurements in organinic soils enables one to obtain more reproducible results than the amperometric (ODR) method.

2. As far as the values of the current obtained with the two methods can be interpreted in terms of potential oxygen flux density in soil, the obtained results are expressed by the relation: $\text{ODR} \approx 2 \text{ OFD}$.

3. The contribution of the background current in the value of the potential oxygen flux density, determined with the use of the voltamperometric method is smaller than this obtained with the amperometric method.

4. The corrections, taking into account the background current in organic and mineral-organic soils which should be subtracted from derived values of the potential oxygen flux density in the soil are: $10.8 \text{ g m}^{-2} \text{ s}^{-1}$ for ODR and $5.5 \text{ g m}^{-2} \text{ s}^{-1}$ for OFD.

5. The results obtained both with amperometric and voltamperometric methods should be treated rather as an indicator, informing about the oxidation status of the soil, than as a real measure of the amount of oxygen available for the plant roots.

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