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### Simultaneous measurement of oxygen flux and salinity of the water saturated mineral soils\*

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A b s t r a c t. This paper presents a possibility current-voltage curve interpretation, registered in the saturated soil, in categories of soil salinity evaluation. A quantity containing the information about the salinity is electric conductivity of the soil. This conductivity can be evaluated by the analysis of the slope of a straight line, fitted into the part of the current-voltage curve, which is responsible for the reduction of hydrogen ions during the electrolysis of the water contained in the soil.

It gives a chance to evaluate simultaneously the oxygen flux density and the soil salinity in conditions of maximum humidity, i.e., in a situation, when the availability of oxygen is minimum and it can be a limitation of the plant growth and when the mobility of ions, dissolved in the soil solution is maximum.

K e y w o r d s: soil salinity, soil oxygen, flux density, ODR, OFD

### INTRODUCTION

The mineral substances, available for the roots in the soil are an important source of plants' supply with necessary nutrients. The evaluation of the abundance of the soil in these substances is relatively simple, however, in majority of cases it consists in taking a sample and analyzing it in laboratory. Such an approach preclude automatic recording with processing of electrical signals and causes the increase of expenses of the studies as well as elongation of the time, needed to obtain the results.

In the context of development of the precision agriculture, the need exists to elaborate and improve the methods, which will be able to provide quick and cheap information even at the cost of decrease of the precision.

The measurement of soil salinity by determination of soil conductivity does not provide the information, which ions are available in the soil, however, it enables to determine a summary index, giving information about the availability of mineral substances (Malicki *et al.*, 1998).

A factor, equally important as the availability of mineral substances, which determines the plant growth is the availability of molecular oxygen for roots. This parameter can be characterized by electrochemically determined quantities: in amperometric measurement of ODR (oxygen diffusion rate) (Lemon and Erickson, 1952; 1955; Gliński and Stępniewski, 1985; Malicki, 1990) and in voltammetric measurement of OFD (oxygen flux density) (Malicki and Bieganowski, 1999).

The voltammetric method of the evaluation of the oxygen availability for plant roots consists in interpretation of the current-voltage curve in the range of potential values for which a predominant reaction occurring on the platinum cathode is the reduction of the molecular oxygen (Malicki and Bieganowski, 1999).

A possibility of simultaneous evaluation of salinity and aeration (understood as a potential flux of oxygen in the soil) was secured till now by performing two independent measurements.

The aim of this paper is to show, that the interpretation of the current-voltage curve (the same as in the measurements of the soil aeration) in the range of potentials in which the reduction of hydrogen ions occurs, can provide additional information about the conductivity/salinity of the medium. Therefore, a simultaneous evaluation of both parameters, which characterize the soil environment, will be possible, just by performing one measurement.

### MATERIAL AND METHOD

The investigation was performed on a soil material, taken from mineral soils contained in the Bank of Soil Samples Representing Polish Mineral Soils (Gliński *et al.*,

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1991). The description of features of the studied soil material is presented in Table 1.

The collected soil material was dried in the room temperature until obtaining the air-dry state. Then, the soil aggregates were crumbled with a hammer and screened through a sieve having the mesh of 2 mm. The soil material, prepared this way was wetted with the distilled water. By mixing it carefully, the saturation state was obtained for each material. The saturated soil material was placed at small portions in plastic pots (having the diameter of about 6 cm and the height of about 9 cm). When filling the pots a special care was taken to assure a maximum

Т	a b l	l e	1. Descri	ption of	the inv	estigated	soil s	amples
						0		1

Soil	Number	Symbol	Pleace of soil sample uptake	FAO		
	in Bank of Soil Samples*	of soil formation		sand 2–0.02	silt 0.02–0.002	clay <0.002
Brown soil	553	Bli	Sady com. Skierbieszów	50	41	10
(Cambisol)	568	Bli	Majdan Skierbieszowski com. Skierbieszów	58	30	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
	594	Apłp. gs	Osówka com. Niemce	77	21	2
	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
Chernozem	586	Cli	Hostynne com. Werbkowice	59	30	11
(Haplic Phaeozem)	601	Cli	Kol. Hostynne com. Werbkowice	60	35	6
	619	Cli	Sahryń com. Werbkowice	86	12	1
	621	Clz	Sahryń gm. Werbkowice	63	31	5
	622	Cli	Terebin com. Werbkowice	60	34	6
	623	Cli	Terebin com. Werbkowice	60	29	11
Alluvial soil (Dystric Fluvisol)	593	Fglp.płi	Kośmin com. Żyrzyn	86	12	2
Muck soil (Terric Histosol)	606	Mps.pl	Wólka Kątna com. Markuszów	97	2	1
Grey brown podzolic (Haplic Luvisol)	597	Apgm.gl	Dęba com. Kurów	95	4	1
Rendzina	597	Rcgc	Bezek com. Chełm	61	21	18
(Rendzic Leptisol)	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	Dpłi.płg	Pożóg Nowy com. Końskowola	79	20	1

\*Gliński et al., 1991.

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possible homogeneity of the bulk density. The water contents referring to the weight, determined using gravimetric method, of the soil samples obtained this way are put together in Table 2.

The measurement of the conductivity of the soil samples (as a mean of expressing the soil salinity) was performed with the LOM instrument of Easy Test Ltd. (Easy Test). The obtained values of conductivity are included in Table 2.

The current-voltage curve was registered with ForTest voltammeter, using a three-electrode system of the potentiostat (Malicki and Walczak, 1983).

in a glass pipe), steel anode (stainless steel wire, 40 mm long, diameter of 2 mm) and a reference electrode, which was a saturated calomel electrode (SCE).

The measurements were taken in six repetitions under the speed of the cathode potential changes equal to  $4 \text{ mV s}^{-1}$ . The break of 15 min between consecutive measurements was applied to enable a recreation of the electrochemical equilibrium of the system (Bieganowski, 2000).

# RESULTS AND DISCUSSION

The set of electrodes consisted of a platinum cathode (Pt ple wire – purity 3n, diameter of 0.5 mm, length of 10 mm, sunk Fig

Exemplary current-voltage curves, obtained for a sample of the brown soil (No. 569 – Table 1), are presented in Fig. 1. Similar curves were obtained for each soil sample.

T a ble 2. Soil water contents, electrical conductivities of investigated soil samples and the slopes of the straight lines and determination coefficients of the fitted straight lines

Soil type	Number in Bank of Soil Samples	Soil water content (g g <sup>-1</sup> )	Electrical conductivity (S m <sup>-1</sup> )	Slope a	R <sup>2</sup>
Brown soil	553	0.489	0.078	0.40	0.9933
(Cambisol)	568	0.467	0.012	0.18	0.9997
	569	0.470	0.017	0.28	0.9996
	570	0.494	0.033	0.40	0.9982
	591	0.475	0.035	0.46	0.9960
	594	0.423	0.018	0.27	0.9989
	604	0.358	0.006	0.06	0.9988
	605	0.373	0.010	0.09	0.9978
	607	0.389	0.011	0.11	0.9953
	611	0.367	0.010	0.10	0.9968
Chernozem	586	0.511	0.028	0.33	0.9990
(Haplic Phaeozem)	601	0.468	0.018	0.26	0.9982
· • /	619	0.600	0.074	0.61	0.9984
	621	0.479	0.027	0.45	0.9964
	622	0.489	0.101	0.74	0.9959
	623	0.484	0.025	0.35	0.9966
Alluvial soil (Dystric Fluvisol)	593	0.438	0.016	0.23	0.9991
Muck soil (Haplic Histosol)	606	0.419	0.013	0.15	0.9982
Grey brown podzolic (Haplic Luvisol)	597	0.384	0.015	0.20	0.9992
Rendzina	557	0.487	0.090	0.57	0.9818
(Rendzic Leptisol)	560	0.410	0.017	0.27	0.9997
	562	0.545	0.052	0.58	0.9984
	565	0.579	0.036	0.48	0.9966
	556	0.368	0.009	0.13	0.9980
Black soil (Mollic Gleysol)	613	0.426	0.021	0.26	0.9985

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Fig. 1. Exemplary current-voltage curves, obtained for a sample of the brown soil (No. 569 – Table 1).

The analysis of the curves, presented in Fig. 1, leads to the conclusion that in the range of the potential values under which the electrolysis of water takes place (below -800mV), a linear decrease of the current with the decrease of the potential can be noticed. This conclusion is not a surprise and has been described in literature concerning the electrochemistry of solutions. However, an attempt to use the above phenomenon to interpret the conductivity of the soil solution (soil salinity) encounters a specific for this environment methodical problem. The value of the potential, under which the reduction of hydrogen ions during the electrolysis of water start to dominate (in Fig. 1 it is assigned as threshold potential) can change and it depends between other on the soil reaction and its water content (Bieganowski, 1999; Bieganowski and Wolińska, 2001). Therefore, it becomes important to choose the range of potentials, in which it can be assumed that the relation I(U) is linear.

On the base of the analysis of all the current-voltage curves obtained in the described experiment and the experience gained under registration of the curves for other soils, the range of potentials, in which a straight was fitted into the relation I(U), was assumed arbitrary. The upper limit of this range was a potential, under which the current intensity exceeded the value of -50 A. The lower limit of the potentials range depended on the experimentally determined lower limit of the voltammeter dynamic range (the



Fig. 2. Interdependence between the slopes of the fitted straight lines and the electrical conductivity of the soil samples.

range of the measured currents, in which a characteristic of the voltammeter preserved linearity) – in the experiment, it was -100 A.

The range of the potentials, in which the corresponding current values from 6 repetitions were averaged and successively, a straight line was fitted, is presented in Fig. 1.

The values of the slopes of the straight lines, fitted according to the presented above procedure and corresponding coefficients of determination, are presented in Table 2.

Figure 2 presents the interdependence between the slopes of the fitted straight lines and the electrical conductivity of the soil samples. A logarithmic functional relation, determined on this base (a =  $0.2255 \ln (\sigma) + 1.1715$  under R<sup>2</sup> = 0.8984), is very close to the analytical dependence determined for solutions (a =  $0.2154 \ln (\sigma) + 1.0607$  under R<sup>2</sup> = 0.9257) (Bieganowski, 2003). A lower value of the coefficient of determination in the soils is caused by smaller homogeneity (e.g., of bulk density and water content) of the samples and therefore, by smaller reproducibility of the measuring environment.

Further studies are predicted, which would enable to determine if and how the soil water content modifies the obtained dependence, and consequently, if this method makes it possible to evaluate the salinity of unsaturated soils.

### CONCLUSION

The interpretation of the current-voltage curve in the range of the potentials corresponding to the electrolysis of the soil water enables to obtain the information concerning the electrical conductivity of the saturated soil.

It gives a chance to evaluate simultaneously the oxygen flux densities and the soil salinity in conditions of maximum humidity, i.e., in situation, when the availability of oxygen is minimum and can be a limitation of the plant growth and when the mobility of ions, dissolved in the soil solution is maximum.

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