

ODR MODIFICATIONS BY THE STORING CONDITIONS OF SOIL SAMPLES

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A b s t r a c t. ODR was calculated for the soil water extracts prepared from freshly taken soil, wet soil stored in plastic bags and air dry soil. ODR in KCl solution was used as reference.

ODR recorded for the extracts obtained from freshly taken soil was lower than for the extracts prepared from the stored soil samples. This indicates that for ODR measurements fresh soil should be investigated.

K e y w o r d s: oxygen diffusion rate (ODR), soil aeration, soil samples storage.

N o m e n c l a t u r e: Amperometry – an electrochemical method for the determination of an electroactive substance concentration; Θ - dry matter water content [g g^{-1}]; σ – conductivity [S m^{-1}]; ODR – Oxygen Diffusion Rate [$\text{g m}^{-2} \text{s}^{-1}$]; SCE – Saturated Calomel Electrode; S_0 – ratio of ODR in deaerated soil water extracts to ODR in deaerated potassium chloride solution; S_1 - ratio of ODR in aerated soil water extracts to ODR in aerated potassium chloride solution.

INTRODUCTION

While investigating oxygen diffusion rate (ODR) in the soil using amperometry [9,10], we come across the problem whether reduction of other than oxygen substances at the cathode exerts any influence [1,13]. This problem is especially important in the organic soils [4]. There are different ways to examine these phenomena [3,7,9].

The most suitable approach is registration of current – voltage curves in the

de-aerated soil water extracts [2]. ODR (with the dimension of oxygen flux density) depends on the diffusion coefficient and the concentration gradient according to the first Fick's law. The diffusion coefficient of any substance in the soil depends on the moisture and geometrical configuration of soil particles in the vicinity of the electrode. A choice of soil water extracts levelled out the influence of diffusion coefficient. The concentration gradient in the vicinity of the electrode appears because the platinum electrode is an annihilator for any substance, which can get reduced in the applied potential. The presence of molecular oxygen in the extract evokes the current in the electrical circuit when the platinum cathode is polarised in the range of -300 – -650 mV (versus SCE). The absence of oxygen in the extract results in no current, unless another depolarizer is present. Application of soil water extracts is based on the assumption that chemical compounds, which are electroactive in the soil solution pass to the extract. It means that the chemical composition of the extract is representative of the soil solution. It can be concluded that when the current in the extract is about zero, there is not any depolarizer.

Shape of the current – voltage curve in the soil water extract may depend on the way the extract was prepared. It is possible that extracts prepared from fresh soil do not show presence of other reducers beside oxygen, but extracts prepared from the same stored soil has one. Another problem arises from the way of soil storage. There are different ways of soil storage in the laboratory practice. Some investigators store wet soil in plastic bags and other store air dry soil depending on its further use.

Taking into account the amperometric purposes it should be examined if the way of soil storage influences increase in the reducers' level (for instance, because of microbiological activity, or specific aeration). The aim of this paper is to compare ODR values in the soil water extracts for differently stored soils. This will allow to choose the best soil storage method as regards ODR measurements in laboratory conditions.

MATERIALS AND METHOD

Soils

The experiment was conducted on muck formations taken from the surface layer of two post bog peat fen soils located in Sosnowica (the Region of Lublin Polesie). The soils represent Terric Histosols and one of them, according to the Polish Classification System, was classified as peat-muck soil weakly mucked (MtI), the second as peat-muck soil medium mucked (MtII). Both investigated soil materials belong to peaty-muck formations (Z1); one of them is formed from

moss-sedge peats (MtI), the other from tall-sedge peats (MtII), with the ash content of 0.225 g g^{-1} and 0.227 g g^{-1} , respectively.

In the investigated soils, two stages of the soil forming process on fens after their dewatering can be distinguished. They are typical and dominant in the hydrogenic sites in the Lublin Polesie Region. Peat-muck soils are the most often used for agricultural as meadows and pastures [14]. Hence, they are used for the investigations of anaerobiosis [5,6,8]. The results obtained for these two soils can be treated as reliable for other organic soils used in agriculture.

Extracts

Three kinds of soil water extracts were prepared from both soils:

- extracts from freshly taken soils;
- extracts from wet soils stored in plastic bags for 3 years;
- extract from air dried soil.

All the extracts were prepared according to the same procedure. The amount of soil which was taken for extract preparation was recalculated to 100 g of air dried soil. This amount of soil was then supplemented with 1 dm^3 of distilled water. The suspension obtained was shaken for 1 h and left for 24 h. After 24 h the suspension was shaken for 1 hour once again. Then the mixture was left for 48 hours. The extract from the above sediment was decanted. Data concerning extracts are shown in Table 1.

Amperometer

Table 1. Potassium chloride solution ($\sigma = 0.02 \text{ S m}^{-1}$) was used to compare ODR with ODR in soil water extracts

Soil	Storage mode	θ of sample (g g^{-1})	pH	σ (S m^{-1})
MtI	Fresh	3.17	6.53	0.005
	Wet - stored in plastic bag	4.00	5.67	0.072
	Air dry	-	6.43	0.022
MtII	Fresh	2.45	5.98	0.015
	Wet - stored in plastic bag	2.92	4.58	0.128
	Air dry	-	5.94	0.015

Three-electrode amperometer was used [11]. There were two electrical circuits in the amperometer. A current circuit, which serves to determine the current of oxygen molecule reduction, consist of a cathode (10 mm long and 0.5 mm diameter platinum wire) and an anode (20 mm long 1.5 mm diameter silver wire). The voltage circuit, controlling the cathode potential, consists of a platinum cathode and a small size saturated calomel electrode (SCE). Both circuits were closed by the soil water extract.

Procedure of measurement

The extracts were saturated with nitrogen. Amount of oxygen in the nitrogen was 0.8 ppm. The gas was passed through the extract for 30 min. ($1000 \text{ cm}^3 \text{ min}^{-1}$) and then directed to the space above the extract ($500 \text{ cm}^3 \text{ min}^{-1}$). There was a small overpressure in the vessel all the time to avoid penetration of atmospheric gasses. The same procedure was carried out for air saturation.

To avoid "poisoning" of the Pt electrode [12], the procedure of electrocleaning was proposed. Before the main measurements the "zero" curve was recorded (cathode potential changed from 0 to -1500 mV vs SCE). Fifteen-minute breaks were applied. The curve with inverted polarisation of the electrodes was recorded, then (cathode potential changed from 0 to $+1500 \text{ mV vs SCE}$). The next 15 minute break was applied. The electrode prepared in this way was ready for measurements. A similar procedure of electrode cleaning was repeated (after the measurement: 15 minutes of waiting; positive polarisation of the platinum; next 15 minutes of awaiting). Changes in the platinum potential during measurements were in the range of $0 \pm 1500 \text{ mV}$.

Calculations

The oxygen diffusion rate (ODR) was calculated for the potential of -650 mV vs SCE [10].

RESULTS AND DISCUSSION

Current voltage curves for muck formation from Mtl and MtlI peat-muck soils are shown at Figs 1 and 2. Deaerated and aerated conditions are presented at Fig A and B, respectively.

The calculated ODR values are shown at Fig. 3. Deaerated and aerated conditions are presented at Fig A and B, respectively.

Current - voltage curves recorded in the deaerated KCl solution are situated below the curves recorded in the deaerated soil water extracts (Fig. 1A and 2A). Curves for the extracts prepared from air dry muck formations show a wave in the potential range of $-500 \pm 700 \text{ mV}$. It can be caused by the reduction of any substances formed during drying and wetting. The same conclusion can be drawn from the current values of the extracts prepared from fresh and stored - wet muck in spite of lack a "classical" voltametric wave, because the current values are higher than the values for the KCl solution. The above arguments can be proved by the results shown in Fig. 3A, where ODR for the KCl solution is the lowest.

The value S_0 is defined as the ratio of ODR in deaerated soil water extract to

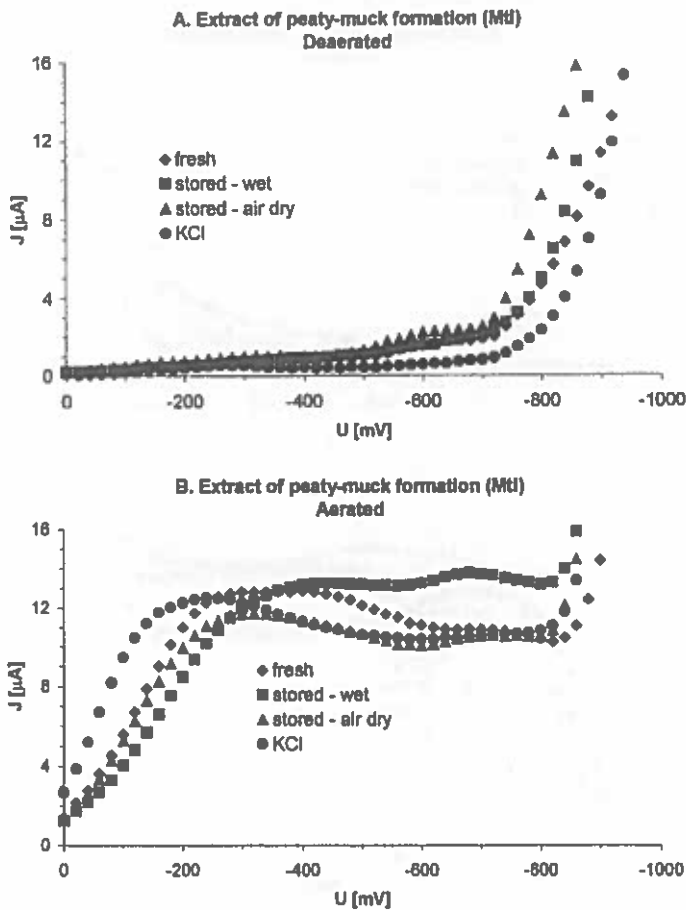


Fig. 1. Current-voltage curves for deaerated and aerated muck water extracts of MtI soil.

ODR in deaerated potassium chloride solution - Eq.(1).

$$S_0 = \frac{ODR_{\text{deaerated extract}}}{ODR_{\text{deaerated KCl solution}}} \tag{1}$$

It indicates that, S_0 shows how many times ODR in the extract is higher than ODR in the KCl solution.

S_1 is an analogous value for aerated extracts and KCl solution - Eq.(2).

$$S_0 = \frac{ODR_{\text{deaerated extract}}}{ODR_{\text{deaerated KCl solution}}} \tag{2}$$

S_0 and S_1 are shown in Table 2.

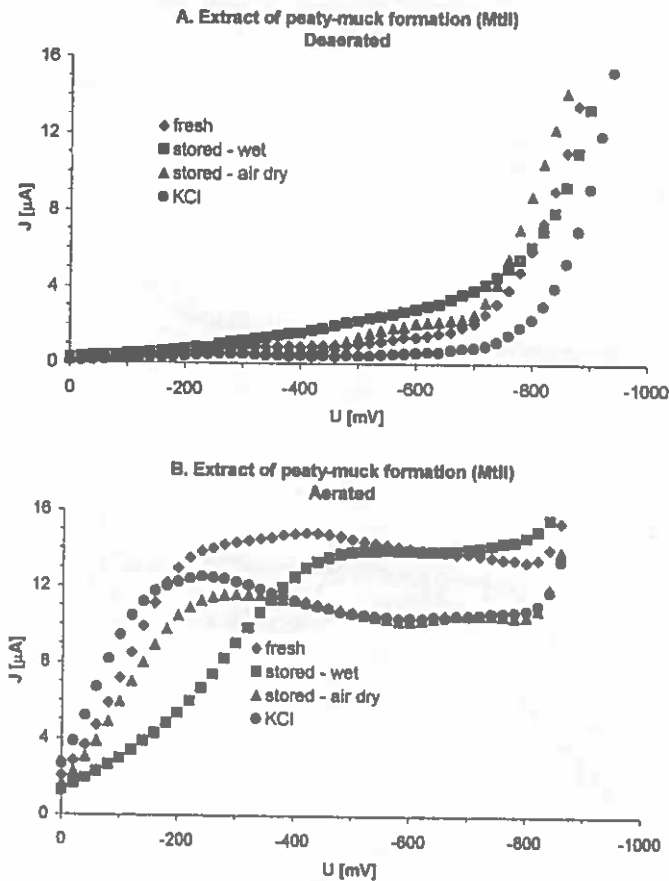


Fig. 2. Current-voltage curves for deaerated and aerated muck water extracts of MtII soil.

Table 2. The ratio of ODR in soil water extracts to ODR in potassium chloride solution

ODR ratio	KCl solution	Extract MtI			Extract MtII		
		fresh	stored-wet	stored air dry	fresh	stored-wet	stored air dry
S_0	1.00	2.70	2.70	3.55	2.50	4.85	3.40
S_1	1.00	1.05	1.31	0.99	1.33	1.34	1.00

The S_0 values are similar for the extracts prepared from fresh soils (2.70 and 2.50, respectively). S_0 is the lowest for the extracts prepared from fresh soils. Values for the extracts prepared from air dry soils were higher but comparable (3.55 and 3.4). The S_0 value for the extract prepared from MtII wet-stored soil was the highest. It can be related to the highest value of conductivity in this extract.

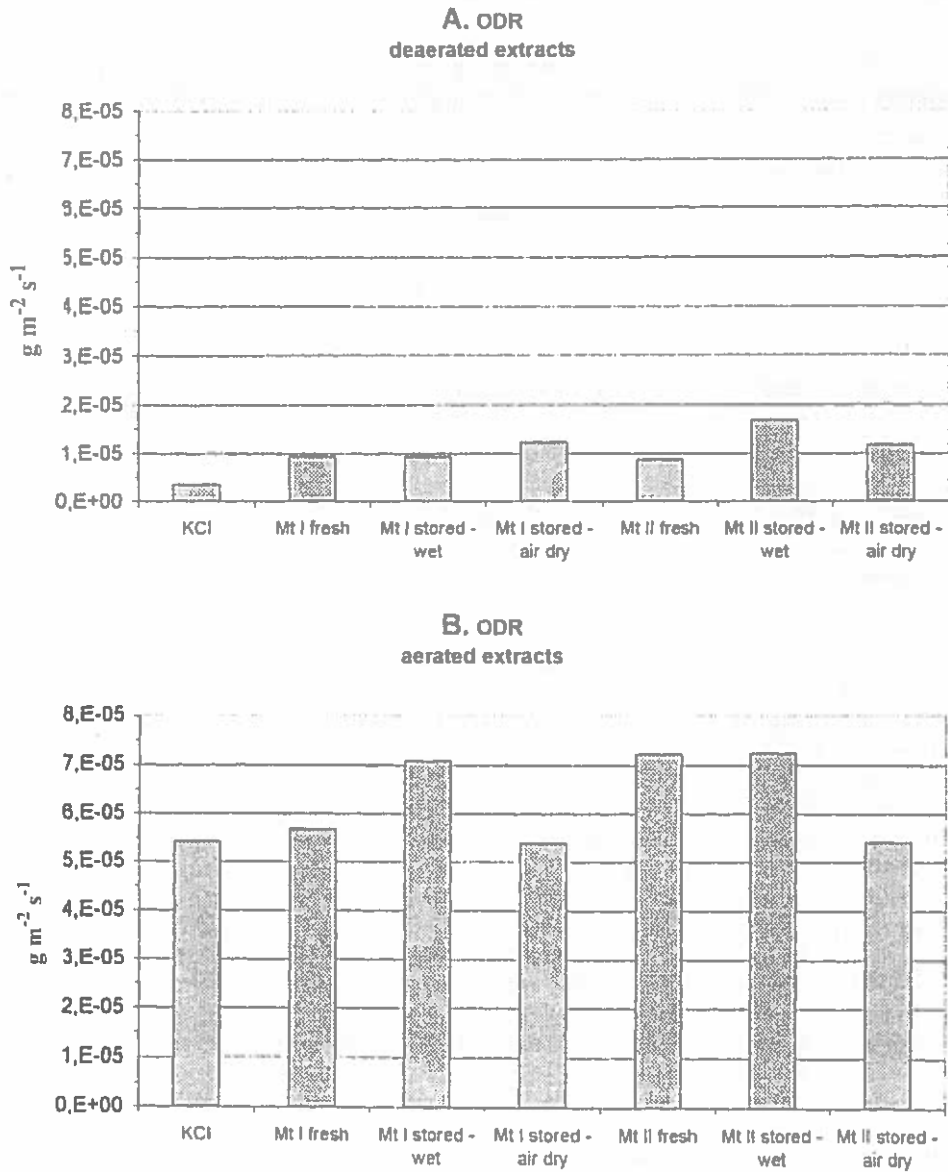


Fig. 3. ODR data obtained for muck formation from the investigated soils.

The S_1 values are significantly lower than S_0 . It can be explained by the fact that "parasite" reduction at the cathode has less influence on the total current in the aerated solution.

Attention should be paid to the ratio of S_0 Mtl to S_0 MtII and S_1 Mtl to S_1 MtII for different storage methods, respectively. In most cases this ratio is close to 1. The highest difference is for the deaerated extract prepared from wet stored soil sample (0.56).

The ODR ratio in deaerated extracts to ODR in aerated extracts is in the range of $0.12 \div 0.23$. The same ratio for KCl solution is 0.06.

CONCLUSION

When investigating fresh soil, an amperometric method should be applied, because current of reduction in the deaerated soil solution is the lowest for a fresh soil sample.

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