

THE MEASUREMENT OF DISSOLVED OXYGEN TODAY
– TRADITION AND TOPICALITY

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Today, the determination of the dissolved oxygen content of natural waters is practically an essential duty whenever background data is collected for investigations of a hydrobiological, ecological, and nature or environmental protection viewpoint. If the method by which the measurements are carried out is concerned, it can be stated that the 120 year old, classical Winkler-method is inevitable even today. However the development of hydroecological sciences have laid claim to such expectations that the necessity of in situ oxygen determinations have become increasingly important. In our work we present the survival of the traditional Winkler-method in the present practice, we review all those viewpoints which have facilitated the widespread application of in situ oxygen determinations as well as the methods of all the measurements that are presently regularly applied in the investigations of natural waters.

Key words: dissolved oxygen determination, stratification, dynamic daily and seasonal changes

INTRODUCTION

It has been well-known for a long time now that processes leading to chemical balance happen differently in water layers which contain oxygen and which do not. From among these, the formation of methane, sulphydric acid, and ammonia as well as the evolving of phosphates and humic compounds are also well studied in detail also (FELFÖLDY 1981, SCHWOERBEL 1977, TIPPING & WOOF 1983). The decrease of dissolved oxygen content can result in the increase of free carbon dioxide, moreover in such way that the quantitative relations of O₂–CO₂ change as the mirror images of each other (DÉVAI *et al.* 1970). As the consequence of all these effects, the composition of the benthic community can change first, and can transform for shorter or longer periods, during which first of all anaerobic bacteria become dominant first of all. In the beginning, different escaping reactions of the members of the macrofauna can be observed and dramatic kills can occur at the end (JØRGENSEN 1980).

In the case of standing waters, especially in deep lakes and sea bays, the changes in oxygen content follow a vertical gradient and are usually strongly related to the formation of thermal or salt stratification. However, the laws of deep

lakes can only be adapted to shallow standing waters by implementing considerable changes or not at all since they mix repeatedly in every year, like the majority of the standing waters in Hungary, and in their case, generally we can not speak about stable stratification. Nevertheless, in certain circumstances distinct stratification can occur in these water bodies as well, moreover the margin of the layer with low oxygen content can emerge into the water body from the benthic layer for as long a period as several weeks. Usually this stratification can not be observed in water courses. Oxygen and carbon dioxide are closely related in photosynthesis and community respiration. Oxygen participates in many fundamental chemical and biological reactions. The dissolved oxygen is consumed in respiration by both plants and animals and is produced by plants during the photosynthesis when light and nutrients are available. The short- and long term variations in dissolved oxygen of waters are a good measure of the trophic state of all aquatic habitats where water birds live and feed. When the dissolved oxygen decreases to a low level it causes a change in the redox state and solubility of metals and some nutrients. Organic matter from natural sources or domestic and industrial wastes also may also result in depletion of dissolved oxygen. When these anthropogenic processes take place most aquatic organisms and water birds perish or are replaced by a few specialized organisms tolerant of the lack of dissolved oxygen. All these processes have a critical effect on the condition of existence of aerobic organisms among the water birds and consequently on the changes of water quality (CARLSON 1977, WILCOCK *et al.* 1995, PLISNIER 1999).

MEASUREMENT METHODS AND STRATEGIES OF THE PRESENT

Winkler-method proved to be so abiding that it is frequently used in the water investigational practice of the accredited laboratories nowadays too. This primarily is possible because the Hungarian Standards Institution scores it as an accredited method, and has given it the reference number of the MSZ ISO 5813:1992 number (<http://www.mszt.hu>). This method is applicable during the laboratory investigations in every cases in which no more than three months have elapsed between the sampling, the fixation of dissolved oxygen in the form of precipitation and the laboratory processing. It can be used also as a reliable standardizing method during the calibration of every kind of instruments, by which the dissolved oxygen content is to be determined in situ. The Winkler-method nowadays, accordingly to the development of the in situ measurement techniques, as the standardizing method is ever more important.

In the methodology of the ecological water qualification (DÉVAI *et al.* 1999), the description of the characteristics of the oxygen balance belongs to the group of dynamic variables, in this way emphasizing that the dissolved oxygen content measured in one moment of time is only a temporary value, and can change at any time. This variability is supported by numerous studies about the waters of Hungary as well (BÁRDOSI *et al.* 2000, DÉVAI *et al.* 2001).

Besides these, it also must be considered that in addition to the temporary changes in standing waters, there are significantly varied oxygen conditions in different water depths. Oxygen balance is also affected by the location of the investigation: an open water body or a water body that is covered by stands of plants; moreover even the cover and species composition of the stands are also significant (RYBAK 1998).

To serve the professional demands, manufacturers produce a remarkably wide supply of in situ oxygen content determining equipments at present. The working principle of these is homologous in that a potential generator creates a constant potential between two electrodes and the oxygen reduces to hydroxyl ions on an electrode (cathode) made of precious metal (generally gold). Simultaneously oxidation goes on the anode (generally silver). The reduction of the oxygen results in a limitation in the strength of the electrodes, in this way the cell current is in direct proportion to the dissolved oxygen concentration. The electrodes are separated from the water to be measured by an oxygen permeable membrane that prevents other oxidizable ions to contact the electrodes. Since both the reaction of the cathode and of the anode requires alkaline environment, an alkaline buffer solution (e.g. hydrobromide) is placed on the inner side of the membrane, which provides constant pH value for a long time, in this way ensuring the reliable functionality of the equipment in the long run.

Beyond the general working principle, in the case of the individual equipments, there can be significant differences, which come out in the level of the service provided and naturally in the prices of the equipments. Even the simplest in situ dissolved oxygen determining equipments contain built-in thermometer head and by utilizing its measurements the value of oxygen saturation (%) can be read directly from the equipment or it can also be calculated. The joint measurement of water temperature, dissolved oxygen content and oxygen saturation is important because the differences in the temperature of the surface water layers and that of near the basin can lead to a stable thermal gradient. Because of the temperature dependent density anomaly of the water, 1 °C temperature increase between 24–25 °C results in thirty times bigger density change than between 4–5 °C (UHLMANN 1975). Therefore in the higher temperature range, so in summer, a vertical decrease of a few °C is enough to the formation of a stable thermal stratification. In this state, the mixing

up of the water and the water exchange between the layers are prevented. All these facilitate the formation of oxygen stratification even in shallow standing waters for a shorter or longer period.

The simplest extra service is equipment that can be purchased with cables of different lengths for deep (layer) measurements or with a sensor head that is equipped with a depth sensor of cm precision. The exactness of the measurements is significantly enhanced in standing waters if near to the oxygen permeable membrane there is a drift producing blade, because the getting of the dissolved oxygen gas through the membrane is more uniform. Of course, this aid hasn't got any importance in water courses. In the case of equipments providing more complex services, there are more sensors on the same head, which are suitable to the in situ measurement of other water quality indicators too (pH, conductivity, redox potential, salt content etc.). The equipments of the highest quality are able to measure even 15–30 water quality indicators in situ. Usually these also have such a computerised background that the measurements can be programmed in optional time intervals, the measured data can be stored and after the field work they can be transported to PC.

The structure of the measurement strategy to be applied should be adjusted to the level of the available equipment, but generally the following considerations should be followed. In standing waters, the measurement of the surface oxygen content only is never enough; rather the whole water column should always be investigated. The most widely applied method is that the measurements are carried out in every 25 cm from the surface until the bottom. In water courses, because of the turbulent flows, usually there isn't significant difference between the dissolved oxygen content of the surface and near bottom layers. For the tracking of the temporary changes, it must be considered that in the dissolved oxygen content of waters – depending on their trophic state and temperature change – usually significant daily changes can be detected. In Hungary, the dissolved oxygen content of waters reaches its maximum in the early afternoon hours, while its minimum is at sunrise. In oligotrophic waters, the difference between the maximum and the minimum can be hardly detected many times, while in eutrophic waters it can be quite remarkable (DÉVAI *et al.* 1970). For the precise measurement of the daily changes of the oxygen content 24 hour measurement series can be suggested, during which the actual oxygen values are recorded in every two hours. In the evaluation of the data, the daily changes of the oxygen content can be given by the O₂ index (DÉVAI *et al.* 1992). If it is not possible, then the measurement of the day maximum and night minimum can be suggested and if only one measurement is possible in a day, then it should be attempted to be during the period of the day maximum. Beside the daily changes, because of the climate in Hungary, significant seasonal changes

also can be detected in our waters. Naturally, the detection of the seasonal changes is more successful, the more frequent the measurements are, but so that we can state anything about the whole year, at least six measurements (February, April, May, June, August, October) should be made (DÉVAI *et al.* 1999). The fundamental work of two Hungarian hydrochemists and, at the same time, hydrobiologists, WINKLER and MAUCHA, made possible the fast and exact determination of dissolved oxygen in freshwaters.

CASE STUDIES

In 1997, we carried out measurements with a WTW COMBIBOX 750 type oxygen sensor suitable for depth measurement. The seasonal changes of oxygen saturation (%) was followed in the backwater of Boroszló-kerti-Holt-Tisza in winter (25–26th of February), in spring (8–9th of April), in early summer (12–13th of May), in middle summer (23–24th of June), in late summer (4–5th of August) and in autumn (14–15th of October) (Fig. 1). The measurements were performed at the deepest location of the basin, every 2 hours for 24 hours in every 2 hours from every 25 cm layer in each case. In the diagram, the data depth of 25, 100, 175 and 300 cm are represented. In winter – under ice 28 cm thick – in the perpendicular above the deepest location, the whole water column was anaerobic, therefore the data of oxygen saturation from February was not interpretable. On the other hand, the situation in spring is completely different. The oxygen saturation of the water column is good in its full depth. By early summer, the vertical differences begin to show up. A significant difference emerges between the 25 water layers on the surface and on the bottom. Near the surface, oversaturation is typical all day, while the layer near the bottom often runs out of oxygen completely, but only about 5% of the whole water body can be considered as anaerobic. In summer, the water column divides into two distinct layers: the upper with high oxygen level and the lower with moderate or low oxygen level. In this situation about 34% of the whole water body is oxygen free. In late summer, all the different water layers have a specific oxygen profile. From the surface towards the bottom, the quantity of the dissolved oxygen steadily decreases. The whole anaerobic water body is 22%. In autumn, the curves displayed in the diagram begin to become convergent again. The oxygen free state of the layer near the bottom ceases and the whole water body above it is characterised by good oxygen saturation.

In 2004, the in situ measurements were carried out by a portable multi-parameter water quality monitoring system (DataSonde4a and MiniSonde4a sensors with Survayor4a display unit manufactured by Hydrolab Co.). Figure 2 shows the

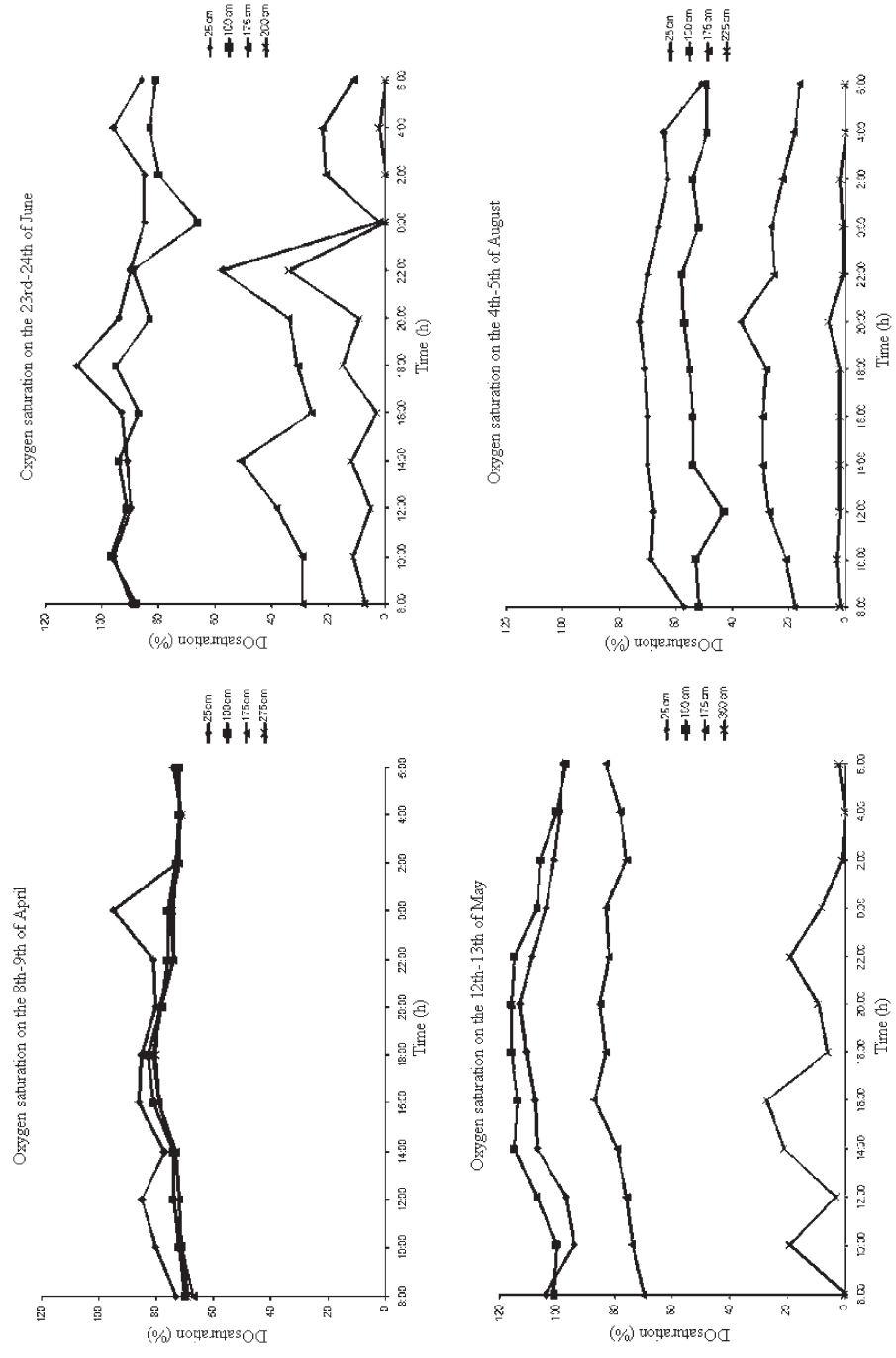


Fig. 1. Seasonal changes of oxygen saturation in the backwater of Boroszló-kerti-Holt-Tisza in 1997.

changes of the dissolved oxygen content of the open water bodies of the four backwaters of the lowland reservoir of River Tisza (Hordódi-Holt-Tisza, Szartos, Nagy-Morotva, Háromágú) from every 25 cm layer related to the depth, in three typical times of the year. In July, the vegetation period was in its full flourishing state, in September the decay of the large quantities of the plant stands was very in-

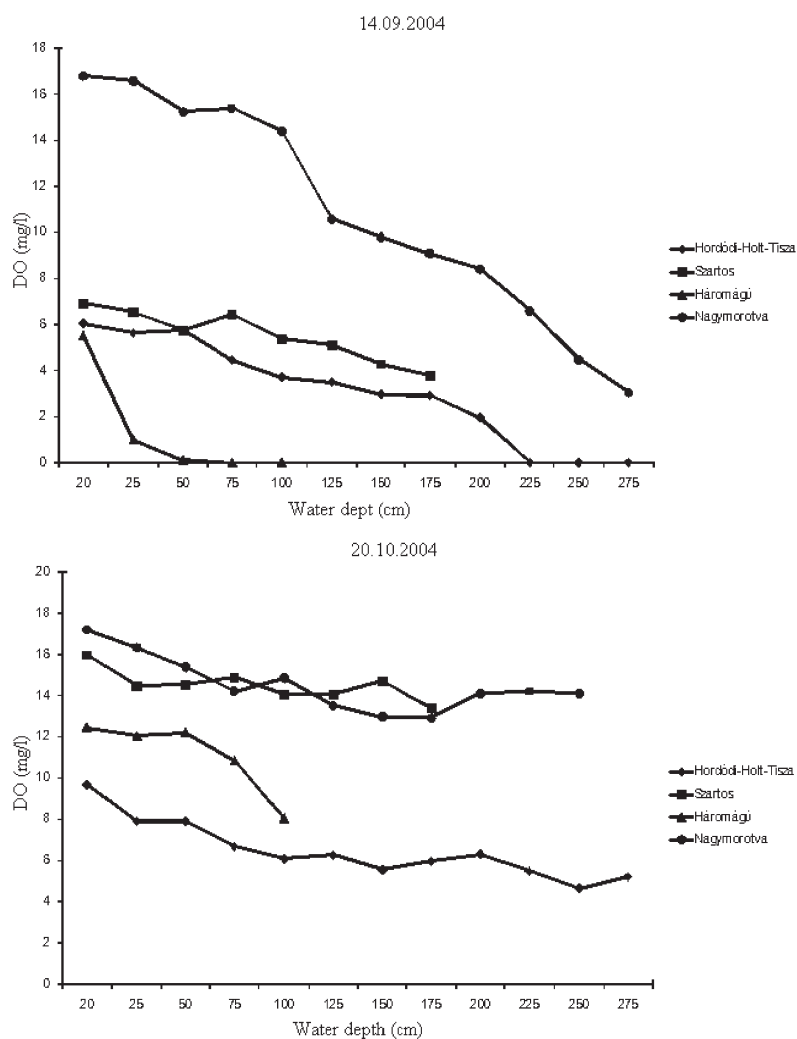


Fig. 2. The changes of dissolved oxygen content measured in the different backwaters of the lowland reservoir of River Tisza (Hordódi-Holt-Tisza, Szartos, Nagy-Morotva, Háromágú) in relation to water depth, during three typical period of the vegetation period. (The measurements were carried out in all cases in the open water body of the deepest location in the basin.)

tense, while by October the decay was practically finished. If the three measurements are compared considering the oxygen conditions, October is the optimal, while September is the most unfavourable. If the different backwaters are compared then it is clear from the diagram that a good oxygen supply characterises Szartos and Nagymorotva during the whole period of the investigations. However the oxygen supply of Hordódi-Holt-Tisza and Háromágú can not at all be considered so good, since in September in the case of Háromágú there are anaerobic conditions even at 50 cm, but at the same time in the case of Hordódi-Holt-Tisza also the dissolved oxygen is used up at the depth of 225 cm.

SUMMARY

Winkler-method was published in 1888 and it is important even today. In Hungary the determination of dissolved oxygen in water by iodimetric method – under the number MSZ ISO 5813:1992 – is the accredited laboratory method of water quality investigations. It is also an acknowledged application when it is used for the measurement precision checking or calibration of very different equipments suitable for in situ dissolved oxygen determination. Thus it can be stated that the dissolved oxygen determination method developed by LAJOS WINKLER and introduced in the hydrobiology by REZSŐ MAUCHA is a very reliable laboratory method and not seldom used in the aquatic ecology after 120 years from that time when it was developed.

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