

CONTINUOUS MEASUREMENTS OF DISSOLVED OXYGEN IN WATER CULTURE BY A SELF-CALIBRATING MONITOR

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Abstract—Description is given of the construction and the use of a self-calibrating oxygen system (SCOS). The probe is suitable for installation and *in situ* monitoring oxygen concentration in hydrophobics and other water bodies. Data illustrative of its use are presented and discussed.

INTRODUCTION

The theory of oxygen uptake by the root systems of plants grown in water culture has been described by the model of Ben-Asher *et al.* (1980). In this work it was found that the availability of oxygen is one of the main variables that effects the success of water culture. Its importance is especially pronounced when dealing with deep, large volumed liquid cultures. Under these conditions the exchange of oxygen between the atmosphere and the water body is limited only to the water atmosphere interface. Therefore, most of the root volume develops beyond the naturally aerated layer and must be artificially aerated. In order to maintain an aerated environment for the root zone it is helpful to follow the oxygen concentration continuously. The purpose of this study was to develop a self calibrating oxygen monitor for continuous measurements in water culture.

Membrane covered voltammetric sensors (sometimes referred to as "polarographic sensors" although the electroanalytical method is clearly voltammetry) for dissolved oxygen determination have found acceptance in a wide range of scientific and industrial applications. Among the many advantages of these sensors over the classical Winkler titration is the fact that they produce an electrical signal that can be continuously recorded or fed to an automatic control system. Experience has shown, however, that continuous operation of such sensors is often limited to relatively short periods. This is particularly evident when the test solution is dirty and contains large amount of suspended material as is often the case in experimental and commercial water culture systems. Accumulation of dirt and grit on the surface of the electrode, reduces the sensitivity and may eventually introduce large errors. The sensitivity (slope) error is usually more important than the base line ("dark current") error which is mainly due to instability of the electronic circuitry. In the present study we attempted to overcome the problem of sensitivity decrease by introducing the feature of self-calibration in a dissolved oxygen monitoring system designed for water culture applications.

Membrane covered dissolved oxygen (DO) sensors respond to the partial pressure of O₂ in solution (Mancy *et al.*, 1962; Ben-Yaakov, 1979, 1980).

Assuming that the partial pressure of O₂ at the sensor's cathode is zero the sensor current, I_s, is related to the partial pressure of O₂ in the test solution by:

$$I_s = \frac{K_i pO_2}{\frac{1}{P_{EL}} + \frac{1}{P_M} + \frac{1}{P_S}} \quad (1)$$

where

pO₂ = partial pressure of O₂ in solution

P_S = O₂ permeability of solution layer adjacent to membrane

P_M = O₂ permeability of membrane

P_{EL} = O₂ permeability of electrolyte film present between membrane and cathode.

K_i = a proportionality constant relating O₂ flux to the cathode's current.

The response of the DO sensor in air (gas phase) is similar to the response in solution except that the liquid film adjacent to the membrane is absent; i.e. 1/P_S = 0. Hence, the sensor's current in the gas phase for a given pO₂ is always higher than the response in solution with the same pO₂.

Accumulation of dirt on the surface of the membrane is equivalent to a change (decrease) in the permeability of the membrane. Due to this and the inherent "aging" of the electrode the response of DO sensors is observed to decrease with time. The drift in response can be tracked and corrected for by recalibrating the electrode in a solution of known pO₂. Alternately, the sensor can be calibrated in air (gas phase) with a constant pO₂ provided that the difference between gas and solution responses is taken into account. Normal open space air can be considered to have a constant pO₂ for all practical purposes. Such a calibration procedure is acceptable only if the variations of the "dark current" (i.e. the base line for zero pO₂) are relatively small as was the case in the present study.

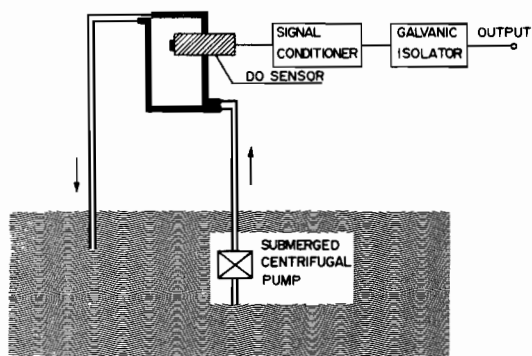


Fig. 1. Schematic diagram of flow-through cell and electronics.

INSTRUMENT DESIGN

The sensor used in the present study is similar in design to the membrane covered electrodes described earlier (Ben-Yaakov, 1979a,b, 1980). It comprises a gold cathode, a silver anode and a teflon membrane separating the internal electrolyte (2M KCl) from the test solution.

The current output of the sensor is fed to a temperature compensating current-to-voltage converter (Graem *et al.*, 1971) which is built around a commercial operational amplifier (RCA CA3130) with a thermistor in the feedback loop. The thermistor (Fenwal UUT 43J1) was chosen to provide temperature independent reading of pO_2 (Mancy *et al.*, 1962; Briggs & Viney, 1964).

The sensor was mounted in a flow-through cell (Fig. 1) through which the solution was circulated by a submerged centrifugal pump. The flow through cell design is such (Fig. 1) that it will empty when the circulation pump is stopped. This feature is applied during the autocalibration phase in which air (gas phase) is used as a pO_2 standard. Especially designed self-adjusting electronic circuitry is activated during the autocalibration stage to adjust the over all gain of the instrument so that the output reading will reach the desired level. The gain is then left constant until the next autocalibration cycle.

EXPERIMENTAL

A terminated tomato variety (*Solanum lycopersicum* L. var. *naama*) was used as an "oxygen consumer" which caused changes in oxygen concentration. Ten days old seedlings were transplanted into a stirred nutrient solution culture. The system consists of three channels (3 m long each) covered with polyethylene to prevent deep drainage into the soil. A Hogland type nutrient solution was pumped from one channel to another through connecting pipes. Oxygen was added continuously at an injection point and its concentration was measured at the remotest place from it. This way it was possible to detect the lowest concentration along the system. At the start of an experiment, aeration was stopped which caused depletion of oxygen with time. When the concentration reached its lowest value aeration started again to flow the increase in oxygen concentration.

For comparison between the designed DO monitor and commercially available manual DO analyser, all the measurements were followed with samples of oxygen concentration by MBK (Beer Sheva, Israel) DO Analyser. The above comparison was made either within the experimental nutrient solution or alternatively in a 3% sodium sulfite solution to follow the response time of each sensor and the signal at zero oxygen concentration.

The temperature response of the uncompensated and temperature compensated sensors was obtained by reading the sensor's current at various temperatures when placed in air saturated solution. Air saturation was ensured by continuously bubbling air through the solution.

RESULTS AND DISCUSSION

Temperature dependence of the uncompensated sensor response (Fig. 2) was found to follow the theoretical relationship. As matching between the sensor and thermistor constants is not perfect, the compensated sensor is slightly overcompensated. This was not deemed to be of concern since the self calibration feature of the system ensures proper calibration for any temperature. The temperature compensation obtained was considered sufficient for correcting the small temperature changes in between autocalibration cycles. During autocalibration, the reading in air (gas phase) is set to 108% taking thereby into account the difference between the sensor's reading in air and solution.

Figure 3 depicts a set of experiments at which oxygen changes with time were recorded. The vertical lines which appear every four hours on the chart,

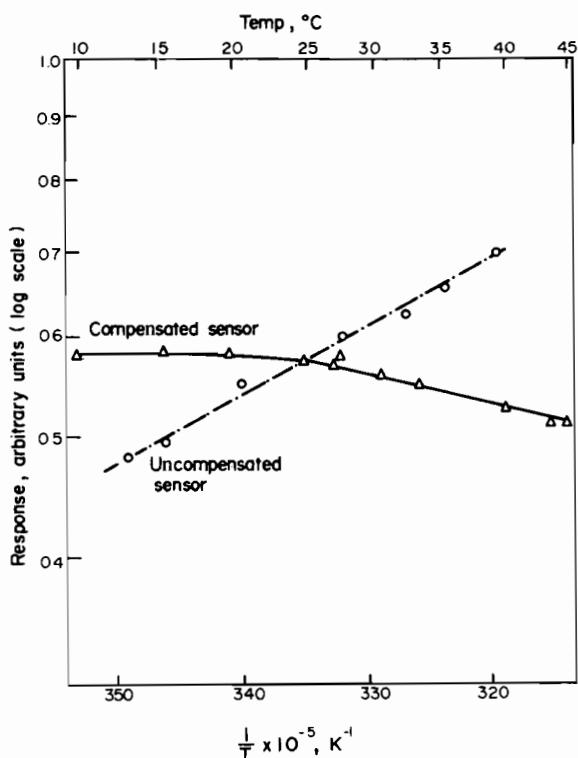


Fig. 2. Temperature response of uncompensated and compensated DO sensor at constant pO_2 .

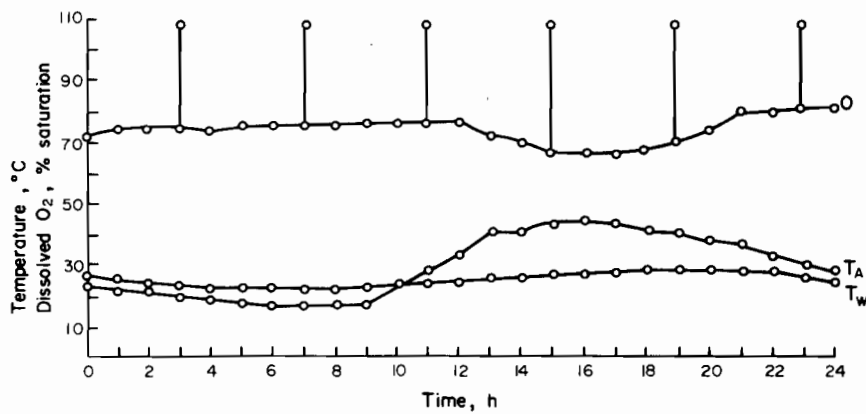


Fig. 3. Typical record obtained by present autocalibrating DO monitoring system. Vertical lines correspond to air self-calibration cycles.

indicate the calibrating period. From this figure it is clear that the calibrating period (4 min) takes only 1.7% of the total measuring time and therefore does not disturb the continuous readings significantly.

Although air injection was constant during the experiment of Fig. 3, oxygen level in solution was not maintained constant. Relatively large changes are noticed between the 12th and 20th hour of the experiment at which time the percent of dissolved oxygen saturation dropped by about 10%. The drop which occurred during day hours is correlated with a relatively large difference between air and solution temperatures (T_A and T_W respectively). This could reflect an increase in oxygen uptake by the root system during day time, reducing the pO_2 from about 75 to about 65% saturation. Another possible cause for a decrease in DO during day time is perhaps the lower efficiency of aeration by hot air (45°C) as compared to aeration by the colder air (20°C) which prevail in the greenhouse during night (Fig. 3). Further studies are required to identify the parameters which control DO concentration in the hydroponic channels and assess the effect of DO decrease of the plants' growth.

Calibration of the system against a manual DO analyser (Fig. 4) reveals a linear relationship between the two readings except that the self-calibrating system seems to suffer from a relatively large "dark current". This problem is evident when examining the response of the sensor in sodium sulfite solution (Fig. 5). Base line correction must therefore be applied to the reading of the self-calibrating system to obtain accurate readings. Figure 5 also reveals that the transient response of the system is exponential with a time constant of 8 s which is ample for the present application.

The scatter in the intercalibration curve of Fig. 4 is typical of field DO measurements and represent sampling and calibration error of the manual DO analyzer, variability of solution flow rate past the DO sensor of the manual DO analyzer and possibly other sources of error. The scatter is in contrast to the rela-

tively smooth calibration curve which is obtained under laboratory condition when the two sensors are placed in a beaker and the solution is stirred at a constant rate. The calibration curve of Fig. 4 sets the realistic accuracy of the present field DO measurements to about 0.5 mg l^{-1} which is acceptable for the intended application. Since the long term stability of the "dark current" was found to be better (about $\pm 0.2 \text{ mg l}^{-1}$) automatic correction of the base line drift was deemed unnecessary. Furthermore, no special effort was made to zero the baseline reading since data reduction will eventually be carried out by an on line computer that will take care of all required corrections.

The present configuration of the flow cell permit rapid and simple maintenance of the DO sensor. The

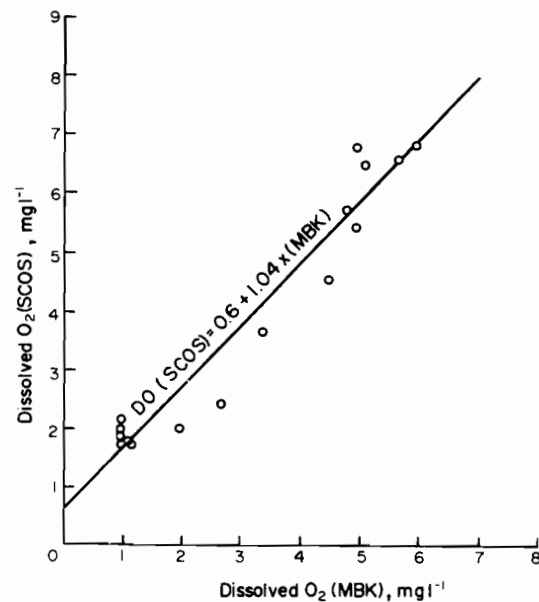


Fig. 4. Calibration curve of self-calibrating oxygen system (SCOS) against a manual DO analyzer (MBK, Beer Sheva, Israel).

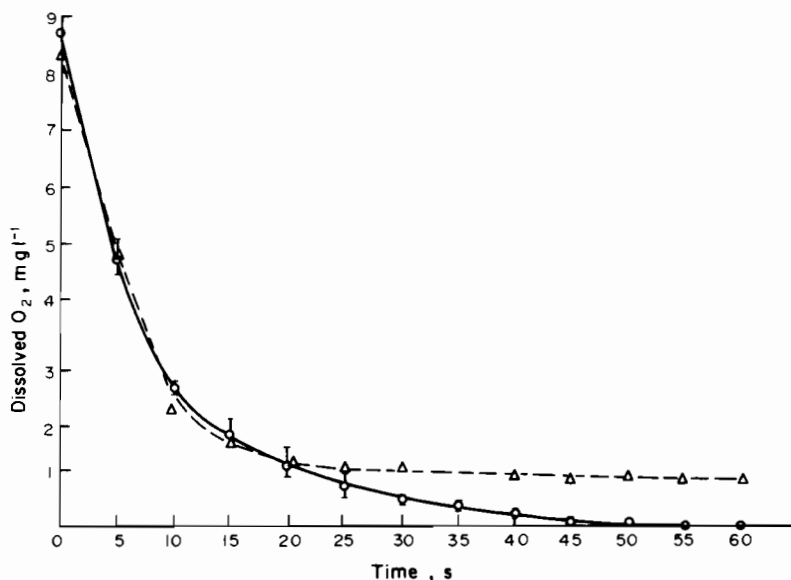


Fig. 5. Transient response of self calibrating DO system (broken line) and manual DO (analyzer) solid line, when transferred from air saturated solution to sulfite solution.

maintenance routine included cleaning of the sensor's head by fresh water once a month and replacement of membrane and internal solution every 3 months. A more intensive maintenance schedule may be necessary when monitoring highly eutrophic solutions due to biological growth on the surfaces.

CONCLUDING REMARKS

The SCOS (self calibrating oxygen) sensor can be used to continuously determine aeration conditions of hydroponics and other water bodies. Our experience has shown that application of this or a similar system is important for both research and commercial maintenance of water environments. The membrane-covered voltammetric sensor, the associated flow-through cell and electronics form a reliable and stable measuring system which automatically compensate for the effect of time and temperature on the output. The SCOS is especially useful for monitoring DO concentration in deep, large volumed water culture. It is used currently to optimize growth conditions for hydroponic plants.

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