

A PORTABLE DISSOLVED OXYGEN ANALY-
ZER FOR THE FISH FARMING INDUSTRY

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INTRODUCTION

Dissolved oxygen (DO) content is one of the most important parameters of natural, industrial and waste water. As oxygen is vital to all highly developed organisms, monitoring and control of DO is of economic necessity for the fish farming industry. The classical method of DO analysis, Winkler titration, is cumbersome, time consuming and requires special skills for successful execution, and therefore no longer adequate for the fish farmer who has to cultivate large and often remotely located fish ponds.

Ideally, a DO analyzer for fish farming applications should have the following characteristics

1. Reliable
2. Simple to operate
3. Simple to calibrate
4. Simple to maintain
5. Sturdy
6. Light weight

Most of the commercial DO analyzers meet only some of these requirements. As a result, fish farmers often undergo frustrating experiences when attempting to operate commercial analyzers originally designed for field operation.

The purpose of this paper is to describe the design and operation of a DO analyzer designed by the author. In cooperation with U. Rappaport of the Ministry of Agriculture, Ginosar and S. Sarig of the Laboratory for Research of Fish Diseases, Nir David, it was conceived and developed to meet the special requirements of the fish farming industry. A second objective is to discuss the various aspects of DO measurement and in particular, the problems encountered when applying a membrane covered DO sensor.

THEORETICAL BACKGROUND

DO Parameters

An aqueous solution in contact with a gas phase of a given partial pressure of O_2 (pO_2) will attain, at equilibrium, a partial pressure pO_2' equal to the partial pressure in the gas phase (Fig. 1). The relationship $pO_2' = pO_2$ is independent of the temperature and salinity of the solution and expresses the equivalence of O_2 activity (in the thermodynamic sense) in the aqueous phase, in equilibrium with the gas phase.

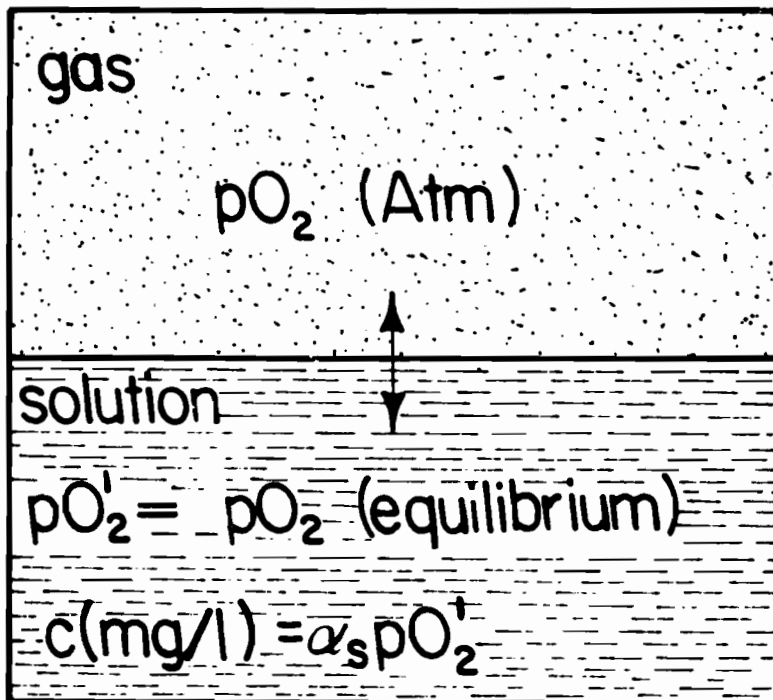


Fig. 1. Basic parameters of DO content.

- pO_2 = partial pressure of O_2 in the gas phase.
- pO_2' = partial pressure of O_2 in the liquid phase.
- α_s = solubility of oxygen.
- C = concentration of DO.

The total amount of oxygen that will dissolve in solution depends on oxygen solubility α_s , which is a function of both the temperature and the ionic composition of the solution (type and quantity of dissolved salts). The water's oxygen

content is measured in units of $\frac{\text{Weight of DO}}{\text{Unit weight of solution}}$ (mg/gr, ppm),

$\frac{\text{Weight of DO}}{\text{Unit volume of solution}}$ (mg/l) or $\frac{\text{Weight of DO}}{\text{Unit volume of solution}}$ (ml/l). In the

latter case, the O_2 content is referred to the standard state (STP) that is, the volume that DO will occupy when maintained at 1 Atm. pressure and 0°C . In the fish farming industry, DO content is usually measured in ppm (mg/gr) or mg/l which, are interchangeable, for fresh water.

Another means of expressing DO content is in units of percent air saturation actually, a measure of pO_2 and hence of O_2 activity in the water. The partial pressure pO_2' of a 100% air saturated solution is, therefore, equal to the partial pressure of oxygen in air. Since air contains about 21% O_2 by volume, the partial pressure of O_2 in air (and of a 100% air saturated solution) is about 0.21 Atm. This is true provided the total atmospheric pressure is 1 Atm. (760 mmHg). If not, a proportional correction must be made in order to allow for variations in barometric pressure. The total amount of oxygen dissolved in a 100% air saturated solution as a function of temperature is presented in Table 1. It is evident from these data that the temperature effect is rather large and amounts to approximately 2%/°C at 25°C. The salinity effect is relatively smaller. It amounts to about 6%/gr/l sea salt, (Weiss, 1970).

TABLE 1. O_2 Solubility in fresh water as a function of temperature.

°C	5	6	7	8	9	10	11	12	13	14
mg/l	12.8	12.5	12.1	11.9	11.6	11.3	11.1	10.8	10.6	10.4
°C	15	16	17	18	19	20	21	22	23	24
mg/l	10.2	10.0	9.7	9.5	9.4	9.2	9.0	8.8	8.7	8.5
°C	25	26	27	28	29	30	31	32	33	34
mg/l	8.4	8.2	8.1	7.9	7.8	7.6	7.5	7.4	7.3	7.2
°C	35	36	37	38	39	40	41	42	43	44
mg/l	7.1	7.0	6.9	6.8	6.7	6.6	6.5	6.4	6.3	6.2

Membrane Covered DO Sensors

Membrane covered DO probes have gained wide acceptance in a wide range of research and industrial applications (Hoare, 1968). The most practical sensors are the so called polarographic devices (the proper term is voltametric) which follow the concepts of Clark's design (Clark et al, 1975). In the basic configuration (Fig. 2), the sensor is comprised of a pair of electrodes immersed in an electrolyte solution separated from the tested solution by a gas (O_2) permeable membrane. Oxygen diffusing across the membrane is reduced at the surface of a noble metal found at the cathode. The electric current thus generated is proportional to the pO_2 at the surface of the membrane and to the Membrane's permeability to oxygen. Since permeability is a function of temperature, the response of the uncompensated DO sensor is highly temperature dependent even at constant pO_2 . Another temperature effect, the temperature dependence of O_2 solubility, must also be taken into account if the DO analyzer is required to read in concentration units (mg/l or ppm).

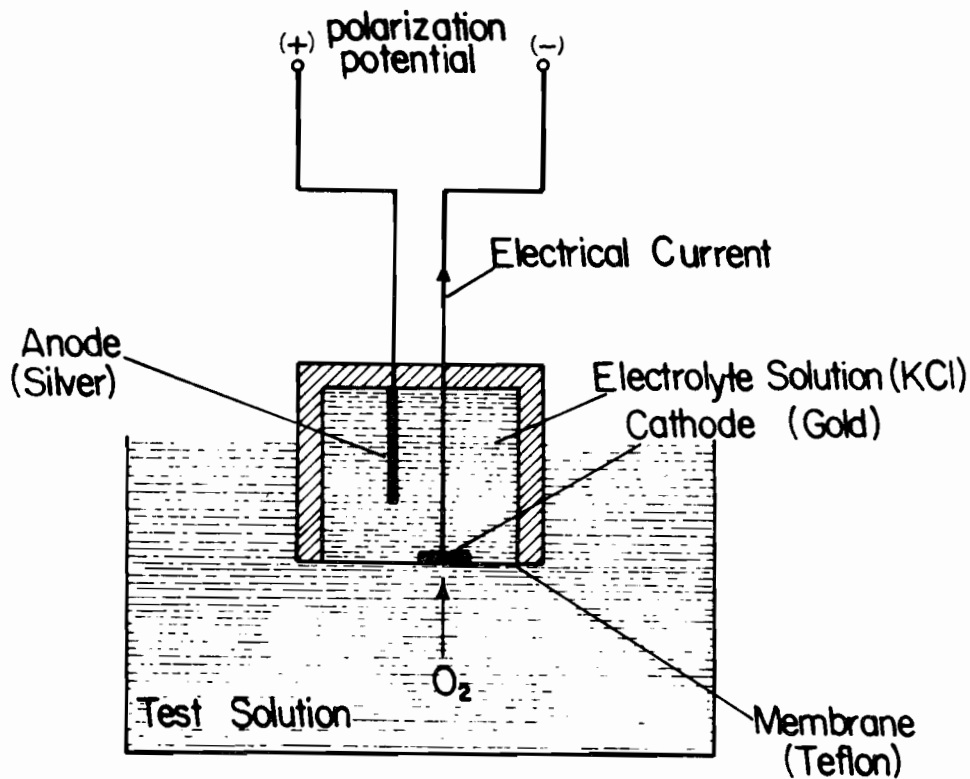


Fig. 2. Basic configuration of a membrane covered DO sensor.

Another major problem associated with the conventional membrane-covered sensor is its flow sensitivity. This stems from the fact that the sensor consumes oxygen and will therefore, register a low DO concentration if the removed oxygen is not replenished by a certain flow of solution past the sensor.

The requirement for flow or stirring in the application of DO sensors is a major disadvantage of conventional devices. It calls for a pump or other stirring mechanism if an accurate and stable reading is to be obtained. This difficulty has been largely overcome in the design of the present sensor.

DESIGN DETAILS

An expanded view of the DO sensor used in the design of the analyzer is shown in Fig. 3. It consists of a plastic body in which a gold cathode is cast, and a coiled silver wire which serves as the anode. Oxygen is reduced at the cathode according to the general reaction: $\frac{1}{2}O_2 + H_2O + e \rightarrow 2OH^-$ and the chloride ion (of the KCl in solution) is oxidized at the anode to form solid silver chloride: $Cl^- + Ag^0 \rightarrow AgCl^0 + e$

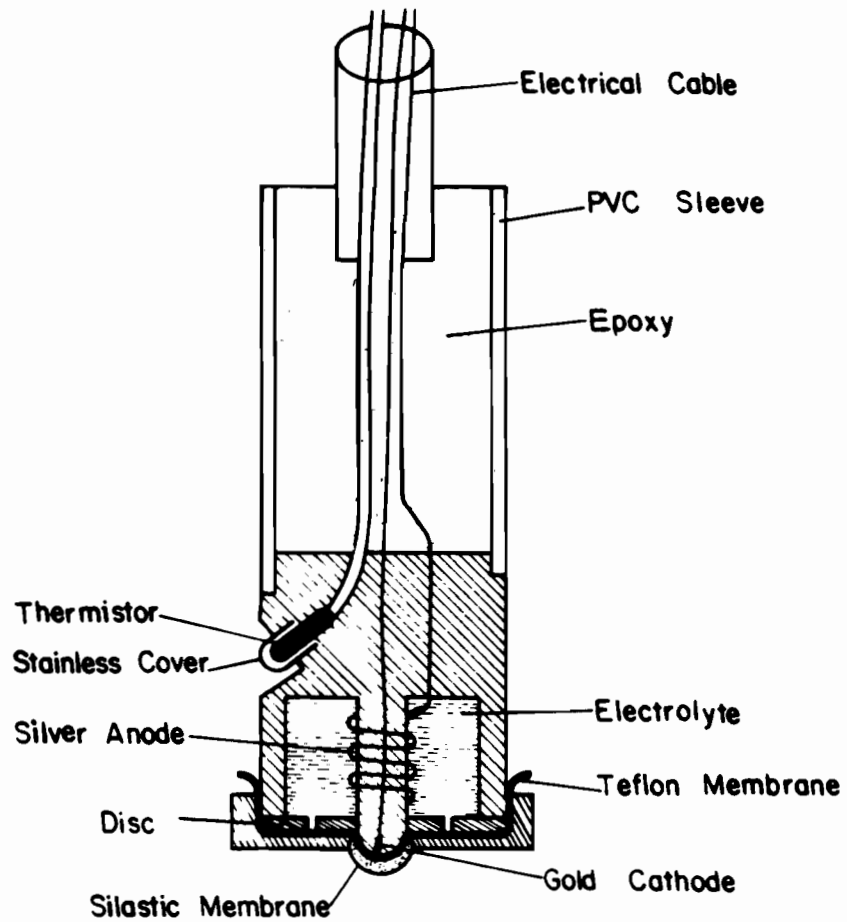
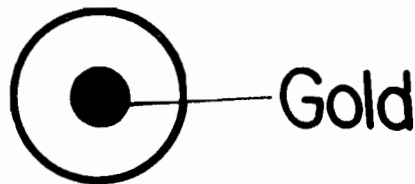


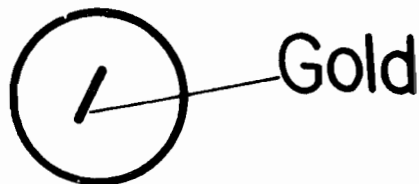
Fig. 3. The DO sensor used in the design of the DO Analyzer.

The electric current is thus proportional to the amount of oxygen reaching the surface of the cathode. This amount depends on pO_2 in solution and on the permeability of the membrane to oxygen.

The sensor (Fig. 3) employs two membranes, one made of Teflon, the other of silicone rubber (Silastic). The composite membrane in conjunction with the physical configuration of the cathode serves to markedly reduce the flow sensitivity of the sensor. This is achieved by reducing the oxygen consumption per unit area of the active membrane surface.



(a)



(b)

Fig. 4. Disc (a) and line (b) shaped cathode configuration. The present sensor uses a line cathode to reduce flow sensitivity.

Oxygen consumption is decreased by using a line-shaped cathode (Fig. 4b) rather than the conventional disc-shaped cathode (Fig. 4a). The line cathode may be considered an elongated "point cathode" which spreads oxygen consumption over a relatively wide area due to a large "edge effect". Further reduction of O_2 consumption per unit area is achieved by using the extra Silastic membrane on top of the Teflon membrane. Since Silastic is highly permeable to oxygen (about 60 times more than Teflon), the additional membrane serves to further funnel oxygen consumption from a much larger area. As a result, oxygen consumption per unit area is even lower than that for the line cathode with the Teflon membrane.

Temperature effects are compensated for by incorporation of a thermistor into the sensor. The thermistor, in conjunction with the electronic circuitry, automatically compensates for all temperature effects and produces a corrected reading in concentration units (ppm). The thermistor is also used for direct temperature measurements.

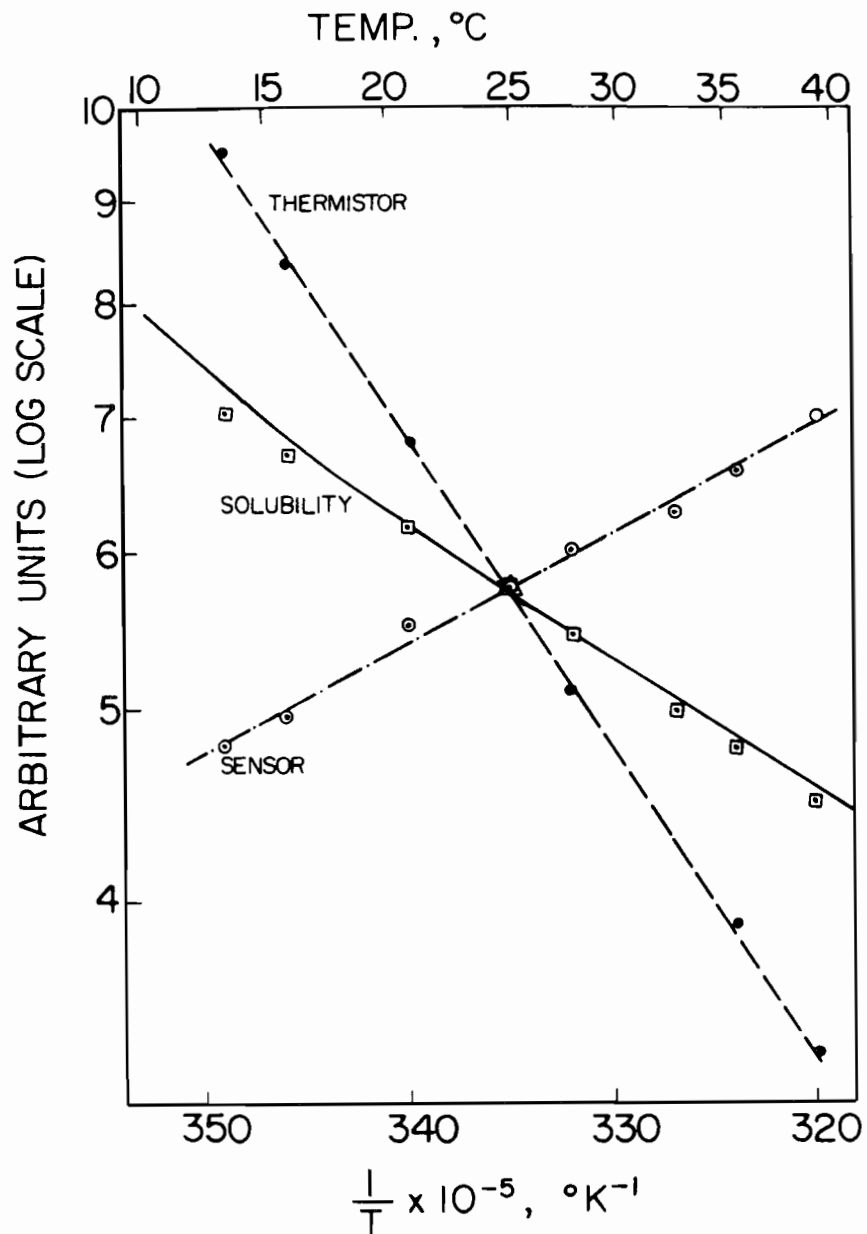


Fig. 5. **Major temperature dependence data.** Open circles — response of uncompensated DO sensor when exposed to a constant $p\text{O}_2$ level. Filled circles — response of thermistor. Squares — response of compensated DO sensor when exposed to a constant $p\text{O}_2$ level. Solid line — theoretical response based on O_2 solubility data.

PERFORMANCE

Major temperature dependence data are summarized in Fig. 5. The open circles depict the response of the uncompensated sensor when exposed to a constant pO_2 level. Filled circles depict the thermistor's response and the squares depict the response of the compensated sensor when exposed to a constant pO_2 level. The solid line is the theoretical response, based on O_2 solubility data.

The experimental data in Fig. 5 suggest that the maximum error attributable to temperature is less than 3% in the $12^\circ C$ — $40^\circ C$ range. This is the expected maximum error that will be encountered when the sensor is calibrated at a temperature different than that of the reading.

Flow sensitivity was tested in a 500 ml beaker by measuring the change in reading between an adequately stirred solution and an unstirred one. The difference was found to be about 3%. It should be pointed out though, that even in an unstirred solution there is a certain flow due to eddy diffusion currents.

APPLICATIONS

The electronic circuit of the analyzer was built into a small (16×9 cm \times 8.5 cm height) steel case and maintained in a pouch carried around the neck during measurements (Fig. 6). The instruments panel (Fig. 7) contains a panel meter, a selector switch for all functions a CALIBRATE control for calibration and a push button for testing the internal battery. The instrument includes three scales : two oxygen scales (0—5 ppm, 0—25 ppm) and a temperature scale 0— $50^\circ C$.

A unique feature of the instrument is the ability to calibrate it in air (the gas phase). This is made possible by the very low oxygen consumption which not only reduces flow sensitivity but also results in almost identical readings in air and in air saturated solution. Hence, calibration may be achieved by simply holding the sensor in air and setting the meter to the required reading with the CALIBRATE control. The low flow sensitivity of the sensor simplifies field operation as no pumps or stirrers are required.

Two years of field experience with this DO analyzer have proved highly favorable suggesting that the present DO analyzer better meets the special requirements of the fish farming industry than do other analyzers.

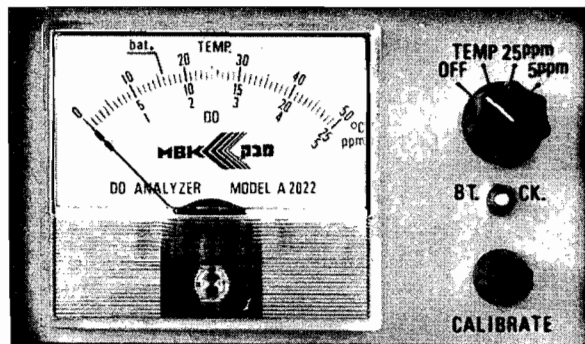


Fig. 6. Front panel of DO Analyzer.



Fig. 7. Method used to carry DO Analyzer while conducting field measurements.

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