# Engineering Notes (Marine Systems)

## In Situ Oxygen and Carbon Dioxide Sensors for Oceanography

A. Edward Wheeler*
*Beckman Instruments, Inc., Fullerton, Calif.*

As a result of the development of fixed and mobile platforms that may serve as undersea laboratories, considerable interest has been evidenced in in situ instrumentation for measurement of the various chemical and physical parameters of the sea water. Such platforms include submersible craft, such as the bathyscaph *Trieste*, manned underwater laboratories such as envisaged in later phases of the Man-in-the-Sea project, as well as fixed and movable buoy installations. Instrumentation of this type will provide information quickly and accurately, frequently more accurately than could be obtained by conventional laboratory analyses of samples brought to the surface, hence removed from the environment and subjected to changes in pressure and temperature that could largely affect the measurements, particularly those of the dissolved gases. Another advantage to be gained is the possibility of obtaining continuous vertical profiles of the parameters which may be measured. The most frequently requested determination is that of dissolved oxygen, with measurement of carbon dioxide next in demand. Sensory equipment for these determinations has been developed during recent months, under contracts from the U. S. Naval Electronics Laboratory, for research work planned by the Deep Submergence Group.

### Dissolved Oxygen Measuring System

The polarographic oxygen sensor (Fig. 1) has been used successfully for a number of years for measuring the partial pressure of oxygen in the atmosphere, as well as for various industrial monitoring purposes. More recently, specialized sensors have been developed for determining the amount of dissolved $O_2$ in aqueous solutions, again expressed in terms of partial pressure, usually as mm Hg. Specialized units for continuous flow determinations have been developed. Two factors, however, have previously precluded the application of sensory equipment of this type to in situ oceanographic measurements. The more obvious is the extreme pressure to which such equipment must be subjected; this has presented severe difficulties because of the basis of operation of the sensor itself, i.e., passage of $O_2$ through a thin, permeable membrane. A second factor that has proven to be critical is the sensitivity of previously developed units to the flow of water past the sensor.

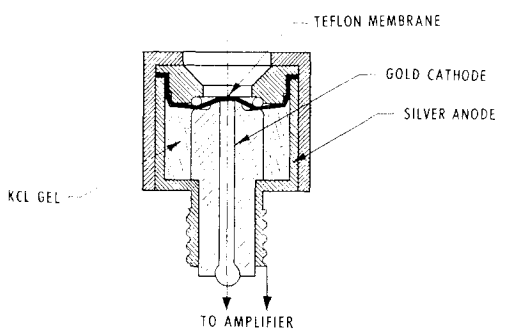


**Fig. 1 Simple oxygen sensor.**

This sensor comprises a pair of electrodes (usually a silver anode and a platinum or gold cathode) mounted in a housing made of nonconducting material and surrounded by an electrolytic agent retained by an oxygen-permeable thin membrane, with potential of somewhat less than 1 v applied across the electrodes. As oxygen diffuses through the membrane, a current flow results, the magnitude of which is directly proportional to the amount of oxygen passing through the membrane. This in turn is directly proportional to the partial pressure of oxygen to which the sensor is exposed. The reaction at the cathode is

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

and that at the anode is

$$4Ag + 4Cl^- \rightarrow 4AgCl + 4e^-$$

With other metals used for the electrodes, and other electrolyte materials, the second equation will reflect these ions, obviously, but the reaction at the cathode will be essentially the same. Since $O_2$ is actually removed from solution by the reaction, in effect consumed by the sensor itself, unstable operation will result unless the flow of water past the sensor is maintained at an appreciable rate, or unless the consumption of oxygen can be minimized. Oxygen consumption may be controlled by selecting a membrane with considerably lower permeability, but at the expense of the output signal produced.

A flexible diaphragm is used to equalize the internal and external pressure and seal the sensor from water. A silicone compound appeared to be attractive, but permeability could not be controlled adequately. After much experimentation, a dual membrane technique was selected. The membrane itself, stretched across the electrodes, was retained by a silicone cap with heavy sides and having a thin film circular window covering the membrane. This technique provided the means for pressure equalization, membrane retention, and sealing as well. Figure 2 is a simplified sectional view of the system finally developed, the film and membrane thickness drawn to an exaggerated scale for the purpose of clarity. Pressure equalization is achieved by means of several apertures in the cylindrical silver anode across which the silicone cap is stretched. The internal cavity is filled with the gel-type electrolyte. Since the external pressure is transmitted via

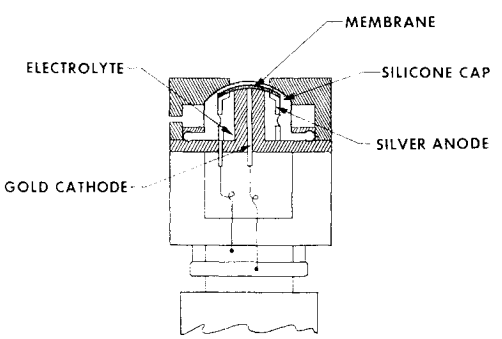


**Fig. 2 Dissolved oxygen sensor sectional view.**

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* Project Engineer.

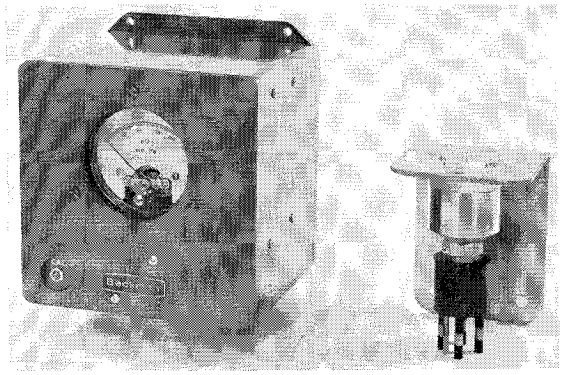

**Fig. 3 In situ dissolved oxygen system.**

the membrane to this electrolyte, the internal and external pressures on the membrane are equalized.

Design of suitable electronic circuitry for the system presented several major problems, in addition to the requirement for the amplification of a very weak signal. The system was to operate from a d.c. power supply, with a nominal voltage of 24 v, but with a possible variation between 20 and 26 v, necessitating a precise regulator circuit. Another requirement was the electrical isolation of the entire system from the electrical system of the *Trieste*, since any interaction could produce spurious signals due to a "third electrode" effect.

The dissolved oxygen sensor incorporates a standard bulkhead-type connector of a type suitable for underwater use, providing a convenient plug-in unit. The sensor was originally designed for operation at depths as great as 4000 ft and has been checked operationally at pressures equivalent to 6000 ft. Range of measurement is from zero oxygen to a partial pressure of 180 mm Hg; saturation at sea level under normal conditions is approximately 170 mm Hg, thus the range is inclusive. Temperature range is from 0° to ± 30°C, fully compensated by means of a selected thermistor incorporated into the sensor body, with suitable circuitry in the amplifier. The complete system is shown in Fig. 3.

### Dissolved Carbon Dioxide Measuring System

Several years ago an electrochemical carbon dioxide sensor was developed for the purpose of monitoring $CO_2$ in the atmosphere of manned space capsules. This sensor, although not suitable for measurement of dissolved $CO_2$, demonstrated the feasibility of electrochemical determination, and preliminary testing indicated that measurements in aqueous solutions would be practicable. The system design for the dissolved $CO_2$ system is somewhat different from that of the previously described oxygen measuring system, the sensor and electronics both mounted in a pressure housing, with a remote indicating unit. Determination of $CO_2$ by the electrochemical techniques is made by measurement of pH changes induced by the $CO_2$, an indirect but effective method. The sensor consists of a glass electrode, sensitive to pH, and a reference electrode, both enclosed within a single housing and surrounded by a gel electrolyte. The electrolyte is contained by a membrane, permeable to $CO_2$, stretched tightly across the sensory portion

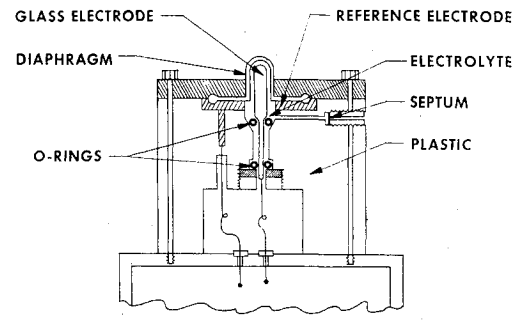


**Fig. 4 Dissolved carbon dioxide sensor sectional view.**

of the glass bulb; electrical contact between the two electrodes is maintained by the electrolyte. As $CO_2$ diffuses through the membrane, it reacts in the electrolyte as follows:

$$H_2O + CO_2 \rightleftarrows H_2CO_3 \rightleftarrows H^+ + HCO_3^-$$

Changes in the concentration of dissociated hydrogen ions in the electrolyte are detected as changes in pH, causing variations in the potential developed, proportional to the log of the concentration of $CO_2$ in the solution.

Although the glass electrode, because of the essentially spherical shape and the pressure resistance of the glass, presented no great difficulties in the development of a sensor operable at pressures of somewhat in excess of 2000 psi, it was necessary to provide a means of equalizing the pressures on the membrane. To maintain the high sensitivity required for the oceanographic sensor, the volume of electrolyte was minimized, and a resilient septum utilized for pressure equalization. A sectional view of the $CO_2$ sensor is shown in Fig. 4. The high impedance circuitry requires either that the sensor be placed very close to the amplifier (within a few inches), or that a preamplifier be incorporated into the sensory unit. The most practical method for the *Trieste* application was to encase the amplifier in a pressure housing, attach the sensor to the housing, and make electrical connections directly from the sensor to the amplifier via glass seal feed-through connectors. In order to protect the electronics against water damage due to accidental flooding resulting from accidental damage to the glass electrode, the entire housing, including the glass-sealed connectors, is designed to withstand the maximum rated operating pressure.

The range of measurement for the initial prototype unit was from 0.07 to 0.7 mm Hg, dissolved $CO_2$. Since the output from this type of sensor is approximately proportional to the log of the $CO_2$ concentration, a range of measurement in excess of one decade can be obtained only at the expense of precision readout at the lower end of the scale. Should a higher range be determined desirable, it would be possible either to provide a second measurement range, or expand the scale with a corresponding slight increase in readout precision. Temperature compensation through the range of 0° to 30°C is obtained by means of a thermistor mounted near the sensing element, with compensatory circuitry mounted near the sensing element.