

AN ELECTRICAL OXYGEN-TEMPERATURE METER FOR FISHERY BIOLOGISTS



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Through a score of bureaus and offices the Department has responsibility for the use and management of millions of acres of federally owned lands; administers mining and mineral leasing on a sizable area of additional lands; irrigates reclaimed lands in the West; manages giant hydroelectric power systems; administers grazing and forestry programs on federally owned range and commercial forest lands; protects fish and wildlife resources; provides for conservation and development of outdoor recreation opportunities on a nationwide scale; conserves hundreds of vital scenic, historic, and park areas; conducts geologic research and surveys; encourages mineral exploration and conducts mineral research; promotes mine safety; conducts saline water research; administers oil import programs; operates helium plants and the Alaska Railroad; is responsible for the welfare of many thousands of people in the Territories of the United States; and exercises trusteeship for the well-being of additional hundreds of thousands of Indians, Aleuts, and Eskimos, as well as being charged with resource management of millions of acres of Indian-owned lands.

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METER FOR FISHERY BIOLOGISTS

By

Kermit E. Sneed and Harry K. Dupree

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By

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ABSTRACT

An oxygen-temperature meter, designed particularly for fishery biologists, was constructed and tested. The oxygen circuitry was modified from polarographic devices, and the temperature circuit consists of a Wheatstone bridge and thermistor system driven by a transistor controlled, constant current regulator.

The platinum, silver-silver oxide electrode pair was imbedded in epoxy and weighted for measurements in any depth of water. When covered with a plastic membrane, the electrode response is not influenced by mild acids, alkali, salts, or pollution that does not dissolve or grossly foul the membrane. The increased hydrostatic pressure due to depth did not appreciably affect the electrode's linear response.

The electrode is temperature sensitive and has a positive coefficient of 3 - 8 percent per degree Centigrade, varying with the size of the working electrode and the thickness of the plastic membrane.

Circuitry, method of construction and directions for operation are included.

The polarographer has been familiar with the typical wave form of oxygen since the advent of polarographic analysis in about 1920 (Lingane, 1958). The oxygen wave depends on the relationship between the current-voltage curve (fig. 1) obtained when the dropping mercury or platinum electrode is operated at variable voltages to a standard non-polarizable reference electrode, such as saturated calomel, silver-silver chloride, or silver-silver oxide. The potential at which the diffusion current remains relatively constant (the current-voltage plateau) serves to identify the chemical (since this relation is constant, depending on the particular electrode reaction) and the height (amount) of the diffusion current serves to identify the quantity of the chemical.

Early devices (Saila, 1955) for the determination of oxygen in natural waters consisted of bare electrodes which quickly became "poisoned" due to the plating of the electrode with other metallic ions in the water. At best these devices served only to compare oxygens in two or more samples of water and did not hold their calibration more than a few minutes. Too, they were highly movement dependent, requiring a rather large circulation of water past the electrode.

Better polarographic techniques for the determination of oxygen in natural waters, blood, urine, and other aqueous and non-aqueous solutions continued to be developed. Clark, Wolf, Granger, and Taylor (1953) investigated certain

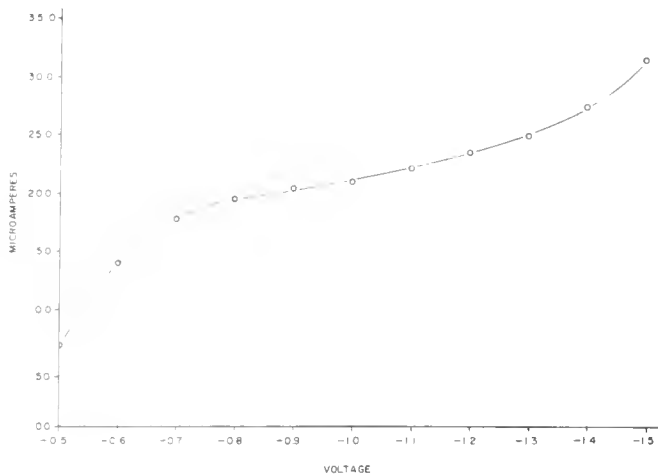


Figure 1:--The current-voltage wave of oxygen with a platinum working electrode, a silver-silver oxide reference electrode and potassium hydroxide electrolyte. The current-voltage plateau with KOH occurs between -0.75 and -1.15 volts.

plastic films to cover the electrodes and prevent "poisoning". These allowed continuous recording of oxygen over long periods of time. A symposium on the subject was held by the Federation of the American Society of Experimental Biology in 1957 and several specialists in the field summarized the existing knowledge and suggested new approaches. By this time the polyethylene covered electrode was in general use and was being used in blood and urine analyses.

Most of the techniques developed before 1959 were for laboratory analyses and employed microelectrodes, the current output of which was low and had to be amplified. Recently, several instruments of this type have appeared on the market and most of these are equipped with the Clark electrode or some modification of it. The great need for similar systems adapted for measurements in the aquatic environment led to the development of suitable electrodes (Carritt and Kanwisher, 1959; Kanwisher, 1959). These workers have shown that such electrodes respond linearly to oxygen tensions, are highly stable, very sensitive, have

rapid response, and are not influenced by pH, salts, most pollution, and changes in osmotic pressures.

The Carritt-Kanwisher system employs a large (1 - 2 centimeters) platinum disc for the working electrode and a pure silver tube (about 1 - 1 1/4 inches long and 3/4-inch in diameter) for the silver-silver oxide reference electrode. The electrodes are electrically insulated from each other by lucite or epoxy cement. The whole electrode assembly is covered by a polyethylene or Teflon membrane behind which is a 0.5N KOH electrolyte. A thermistor embedded with the electrode can serve both as a temperature measuring device or for partial temperature compensation of the electrode reaction, which is highly temperature sensitive (5 to 6 percent per degree centigrade). The mechanical details of construction of an electrode assembly similar to that of Carritt and Kanwisher are shown in figure 2.

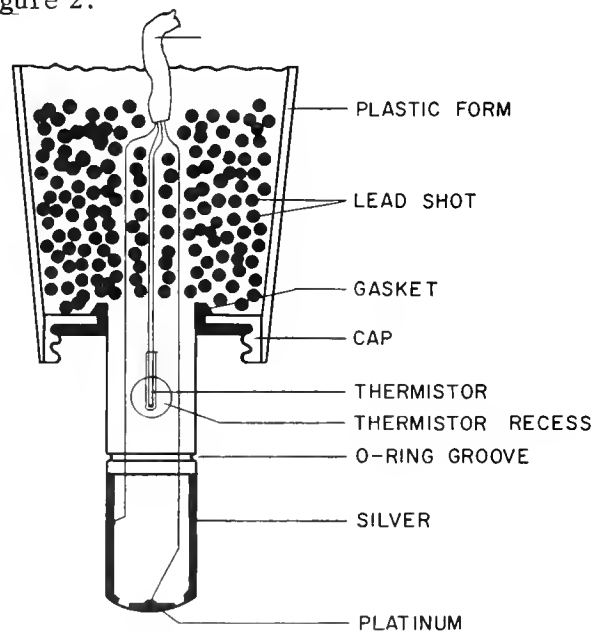


Figure 2:--Longitudinal section of oxygen-temperature electrode assembly suitably weighted for deepwater measurements.

Virtually none of the publications by electrochemists gives electrical circuitry (except in a theoretical way) that can be used by the average fishery biologist, who is usually unfamiliar with polarography. However, one company has developed an instrument, based

on the Carritt-Kanwisher data, which is designed for fishery biologists. Many biologists with small allotments cannot afford the expense of this instrument. Therefore, we developed circuitry and construction details for a home-made instrument which measures both oxygen and temperature and has manual temperature compensation.

The construction and operational details are given below, but for a more comprehensive discussion of polarographic electrodes of this and other types, one should consult the references cited in this paper. Only a minimum amount of theory is necessary to construct and operate the device described here.

THEORY

The polarographer is usually interested in the complete polarographic wave which is formed when an electrode pair is operated at various voltages differing from each other by about 0.1 volt. However, in the case of oxygen determination in content or tension, the fishery biologist is interested only in the amount of diffusion current. A steady diffusion current is established within a definite voltage range for various chemicals and this range is easily established; in fact, the data are already in the literature for most common elements and compounds. For oxygen, in 0.1 N KCl electrolyte with bare platinum vs. a silver-silver chloride electrode, the diffusion current plateau occurs between about -0.3 and -0.75 volts. With the plastic covered Carritt-Kanwisher electrode (in 0.5 N KOH electrolyte) the steady diffusion current occurs between -0.75 and -1.15 volts (fig. 1). Carritt and Kanwisher (1959) gave similar data and demonstrated (fig. 2, their paper) that the current-voltage curve shifted to the right (i.e. more negative) with increasing temperatures. Their data and ours indicate that the best operating voltage for water temperature from 4.5° C. - 30° C., with 0.5 N KOH as the electrolyte, is between -0.9 and -1.2 volts. Indeed, in actual practice any voltage within this range gives satisfactory results. The difference in diffusion current voltages in KCl and KOH probably depends on the pH of the electrolyte, changing the voltage at which decomposition currents of the electrolyte will occur.

The operational voltage on the cell in our instrument is established by the combination of resistors R-3 and R-4 (fig. 3, Schematic) which acts as a fixed voltage divider, since the complete polarographic wave is not wanted and a variable voltage is unnecessary. If a battery of 1.5 v. is selected and an operating voltage of -1.0 volt is desired, then: $1.0:0.5::R_4 : R_3$; therefore, R₄ and R₃ can have ohmic values that have the approximate ratio of 1: 0.5.

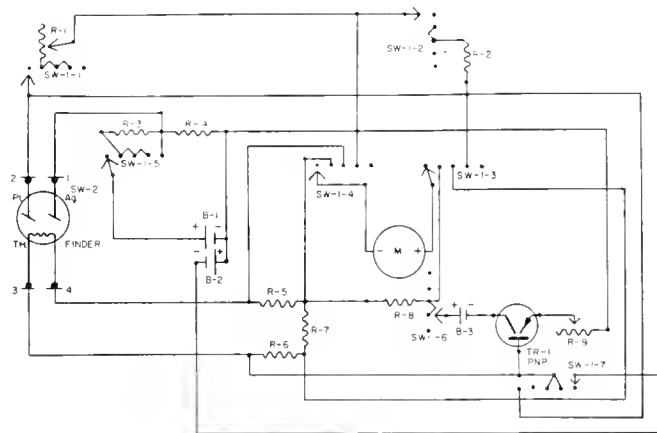


Figure 3:--Schematic diagram of the oxygen-temperature circuit.

In actual practice we use 1800 ohms for R₃ and 3600 ohms for R₄. One can install a 1.5 volt battery and operate at -1.0 v.; a 1.4 mercury battery and operate at -0.0 volts. Mercury batteries hold their voltages very well under load and continuous operation, and should be employed if possible. These batteries will maintain the calibration point for many hours or days, which eliminates the need of a variable voltage divider and attendant voltmeter circuit to check the operating voltage.

Bill of Materials

The following components and supplies are needed:

<u>Item</u>	<u>Approximate price</u>
SW 1-1-7 = 8 pole, 4 gang, miniature, 5 pos. wafer switch (phenolic)	\$ 3.12
B ₁ , B ₂ = 2 - ZM-9 mercury batteries, or equivalent	1.02
Battery holder, for above batteries	.38
B ₃ = Battery, 6 volt, Z4 or equivalent	.63
Battery holder, type 175	.24
M = 1 - 0-50 microammeter	16.76
Tr = 1 transistor 2N34, or equivalent	3.20
1 - Plug, 4 contact, Cannon XLR-4-12 C, or equivalent	1.20
1 - Socket, 4 contact, XLR-4-13	1.93
1 - Minibox 7 x 5 x 3 inches	1.78
R-1 = 1 - 10-turn micropot, Borg model 1111B, 5000 ohms, or equivalent	10.68
1 - Microdial for above, Model 1327, or equivalent	5.82
7 - Resistors, 1/2 watt, 5% Values:	1.68
R-6, 7 = 2 - 100 ohm	
R-8, = 1 - 10 ohm	
R-2, 3, 5 = 3 - 1800 ohm, or select R-5 (see text)	
R-4 = 1 - 3600 ohm	
R-9= 1 - 500 ohm wirewound potentiometer	1.12
Cable, 4 cond., any length desired about .10 per foot	
2 ft. - 9 wire cable, plastic covered	.20
1 - pure silver tube 1 inch long by 3/4 inch diameter	5.00
1 - piece of platinum foil about 1/2 inch square, approximately .004 inch thick. Priced according to market (about \$2 - \$3).	
3 tubes epoxy	3.00
Th = 1 - Thermistor, 1000 ohm at 25° C., Veco 31A11 or equivalent	2.85
2 - Small plastic baby bottles, 1 with cap and nipple	.40
Total	61.01

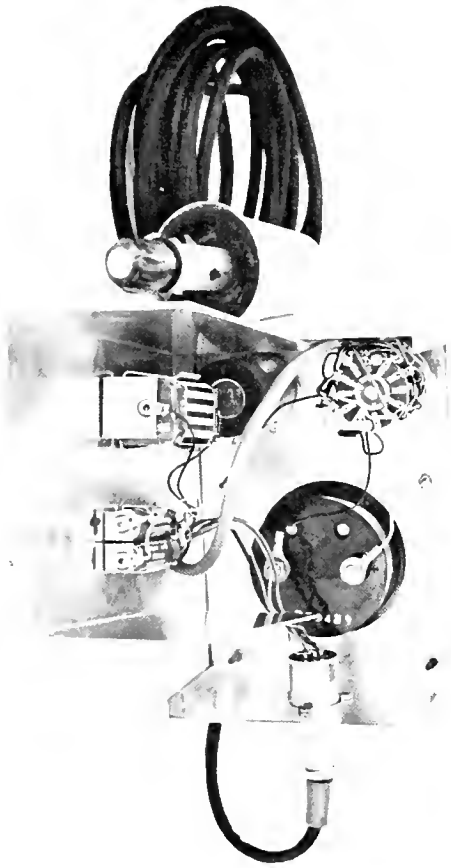
MOUNTING THE COMPONENTS

The instrument case (minibox) should be drilled to accommodate the switch, potentiometer R-9, potentiometer R-1 and its counter dial, and the meter as shown in Photograph 1. Follow the instructions included by the manufacturers for the switch, micropot and dial. The mounting of the meter and R-9 is obvious. Only the 1/2-inch hole for mounting the micropot and dial is critical.

After these major components are mounted on the cover plate, drill holes in the back plate and attach battery holders as shown in Photograph 2. Be sure to place the holders so that they do not interfere with other components when closing the case. The 4-way chassis plug for the electrode cable can be mounted on either end or side of case, depending on preference. The mounting and arrangement of components are not critical and can be done as preferred by the builder, within the limits of the space in the case.



Photograph 1:--View of complete oxygen-temperature meter.



Photograph 2:--Inside view of oxygen-temperature meter.

The wiring and lead dress are not critical, and the wires can be rat-nested or neatly arranged. All the resistors, except the micro-pot and wire-wound pot, can be mounted between the appropriate switch terminals. The transistor can be similarly soldered into the circuit by attachment to unused switch terminals, which make excellent tie-points. Caution: Avoid overheating the transistor. When soldering the leads, provide a heat sink; i.e. place pliers or a metal clip on the transistor lead between the solder joint and the body of the transistor. Pay particular attention to the arrangement of leads on the transistor and connect properly in the circuit. An error here will ruin the transistor. See figure 4 for proper identification of leads. Also, label the battery holders, plus and minus, so that the battery polarities will not be reversed when batteries are replaced. A reversed battery can ruin the transistor.

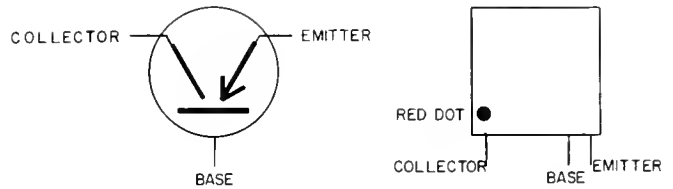


Figure 4:--Lead identification and schematic representation of transistor.

CONSTRUCTION OF THE ELECTRODE ASSEMBLY

The construction of the electrode may require some ingenuity on the part of the builder, but a description of some of the methods which we have used may be of benefit.

An empty 12-gauge shot gun shell is ideally suited for a mold for the epoxy since the 3/4-inch silver tube will fit inside the 12-gauge case. To prevent the epoxy from adhering to the paper, the inside of the shell should be coated with vaseline or similar material (mold release). A 6-inch length of wire should be soldered to the inside of the silver tube. Place the end of the silver tube in modeling clay and fill the tube with epoxy. Then drill a small hole (1/8-inch) through the center of the epoxy after it has hardened. Insert a wire through this hole and solder to the center of the platinum disc. This wire should be placed through the hole and fastened into position in the center of the silver tube in such a

manner that the platinum disc will stand above the edge of the silver tube about 1 or 2 millimeters (Fig. 2). A piece of scotch tape can then be wrapped around the tube to serve as a mold for the epoxy which holds the platinum disc in place and electrically insulates the electrodes. Care should be exercised in pouring this epoxy; do not get it on the platinum or silver. The working surface of the platinum disc can be covered with vaseline, so that any epoxy that is accidentally dropped on it can be easily removed. Do not put vaseline or mole release on any surfaces to be joined by epoxy. After this epoxy has hardened, file off all the excess so that the tip of the electrode will be smoothly rounded as illustrated in figure 2. This procedure will make an assembly which is about 2 1/2-inches long with the epoxy extending above the silver cylinder about 1 1/2-inches.

Now drill a hole (1/8-inch) somewhat off center into the epoxy to a depth of about one inch or about 1/2 or 3/4-inch above the top edge of the silver tube. Using a larger bit (3/8), drill from the outside (laterally) through the epoxy into this hole. This procedure forms a cavity about 3/8-inch in diameter to accommodate the tip of the thermistor which can be placed through the vertical hole and positioned in place with plasticine or modeling clay (in the 3/8-inch cavity, not in the vertical hole). The vertical hole should be filled with epoxy to hold the thermistor in place and insulate the leads. Make sure that the thermistor leads are not in contact with each other before pouring epoxy. When the epoxy has hardened, remove the clay from the cavity around the thermistor tip. It is important to have air-space completely around the tip of the thermistor so that water will circulate efficiently and completely to cause the thermistor to respond quickly to any change in water temperature.

The plastic baby bottle will have a nipple in the lid. This nipple should be cut away so that the outer portion remains as a gasket. The electrode assembly can be slipped through this rubber gasket. When the gasket is placed through the plastic cap, it will act as a seal to prevent the epoxy from running down the electrode surface. When the electrode assembly has been placed in the rubber gasket and lid, the four

leads in the cable should be soldered to the appropriate terminals, making certain that none of these four leads touch each other. The lid can then be placed in a small plastic mold (we used a small plastic glass with the bottom cut out) and cemented into place with epoxy. Some lead (shot) should be added to the epoxy at this point so that the electrode assembly will be heavy enough to straighten the cable in deep water.

A groove should be filed about 1/8-inch above the top edge of the silver tube to accommodate an O-ring which holds the polyethylene membrane in position. This can be done with a rat-tail file, and any irregularity smoothed with emery paper or steel wool.

When the electrode assembly is finished, plug it into the instrument case for polarization. Turn the switch to Polarization (Position 5) and place the electrode in a 0.5 N KOH solution and allow it to remain for about 30 seconds. It will turn black or dark brown. Additional instructions are given in the appendix.

HOW THE CIRCUIT WORKS

Temperature: There are five switch positions. The first (completely counter clockwise) is "Off", and no reading should be registered on the meter. The second is "Temperature Adjust". In this position the meter needle should move upscale and can be adjusted by resistor R-9. In this position the oxygen circuitry is also on, but the diffusion current is by-passed through R-2 which allows the electrode to begin equilibrating. The third position is "Oxygen Read". In this position the temperature circuitry is turned off and the output of the electrodes is switched to the meter. The fifth position is "Polarize". This position should never be used except when the electrode is bare and ready for polarization as in the instructions in the appendix.

Battery B-2 and B-3, variable resistor R-9, and the transistor Tr-1 form a constant current circuit to drive the Wheatstone bridge composed of R-5, R-6, R-7 and the thermistor. The output of the current to this bridge is measured in position two (T. Adj.) by the voltage drop across R-8. The change in resistance

of the thermistor with changing temperature (switch in "Temperature Read" position) will unbalance the bridge and the change of current can be read on the meter.

Oxygen: The voltage divider composed of R-3 and R-4 maintains a constant voltage on the platinum, silver-silver oxide electrode pair.

The molecular oxygen which will pass the membrane forms hydroxyl ions at the platinum surface. The OH ions diffuse through the electrolyte to the silver electrode where they release electrons that flow through the meter circuit, according to the following formula:



CALIBRATION OF THE TEMPERATURE SCALE

With the components listed in this paper the lowest temperature to which the instrument will respond will be about 10° C. which will be near zero microamperes on the meter. This lowest reading is controlled by resistor R-6 which is 1800 ohms, the approximate resistance of the thermistor at that temperature. If a lower (or higher) temperature reading is desired for zero microamperes, place the thermistor in a water bath at the temperature desired and with an ohmmeter determine its resistance. A resistor of this value (or near the value) substituted for R-6 will cause the zero microampere reading to correspond with that temperature. The upper range of temperatures will be determined by the setting of resistor R-9. To determine this setting, place the thermistor in water at the highest temperature desired. Adjust resistor R-9 until approximately full scale reading is obtained, with the selector switch set for "Temperature Read". Now switch to "Temperature Adjust" position and note the microampere reading. This is the voltage adjustment that should be maintained throughout all subsequent calibration procedures and for the final determination of temperatures, and this reading should be recorded and red-lined on the meter face.

In order to calibrate the instrument, only two temperatures are needed, one near the low end of the scale of temperatures, and another toward the high, say at 12° C. and 30° C. Place

the electrode in water so that the thermistor is covered, and stir the water vigorously to circulate it around the thermistor to assure thermal equilibrium. Turn switch to "Temperature Adjust" position and set the needle (with R-9) to indicate the microampere reading previously determined to give full scale deflection of the needle at highest temperature on scale. Switch to "Temperature Read" position. Note the microampere readings at these two temperatures. If these two temperatures are plotted on a graph against the corresponding microampere readings and a straight line is drawn between them, the line will pass through the proper microampere reading for other temperatures, as shown in figure 5. Now remove the cover from the meter and write the temperature readings on the face of the meter dial using proper drafting tools and water resistant ink. Be sure to red-line the voltage adjustment reading.

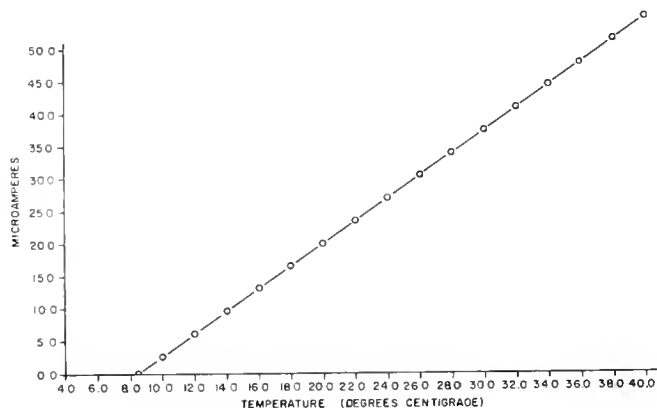


Figure 5:--Temperature plotted against microamperes for temperature calibration of the microammeter face.

CALIBRATION OF THE TEMPERATURE COMPENSATOR

The oxygen electrode is highly temperature sensitive, having a temperature coefficient in the order of 3 - 8 percent per degree C. This temperature coefficient varies both with the size

of the platinum electrode and the thickness of the plastic membrane over the electrode (figures 6 and 7). Theoretically, in a purely

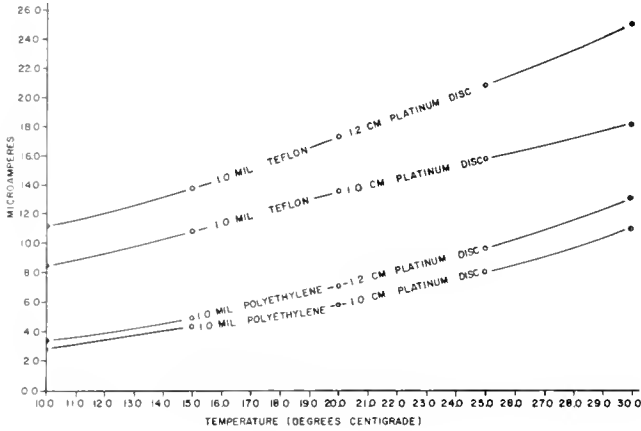


Figure 6:--Curves of the temperature coefficient of two platinum electrodes with diameters of 1 and 1.2 centimeters and covered with 1.0 mil Teflon or 1.0 mil polyethylene. The slope of the curve reflects the temperature coefficient and the height the relative output in microamperes.

diffusion controlled electrode system the temperature coefficient should be on the order of about 1 1/2 to 2 percent per degree C. (Lingane, 1958). With this electrode, it appears that the smaller the electrode the smaller the temperature coefficient, and the thinner the membrane the smaller the temperature coefficient (figures 6 and 7). Therefore, perhaps, if an infinitely small platinum electrode and an infinitely thin membrane were used, the temperature coefficient would be near the theoretical 1 1/2 or 2 percent due to diffusion alone. It is important, therefore, that once the temperature compensation curve has been determined for a particular membrane type that this kind of membrane be used in all future readings, or different temperature compensation curves may be determined for different membranes, for example, 1/2 mil Teflon, 1 mil Teflon, 1 mil polyethylene, etc.

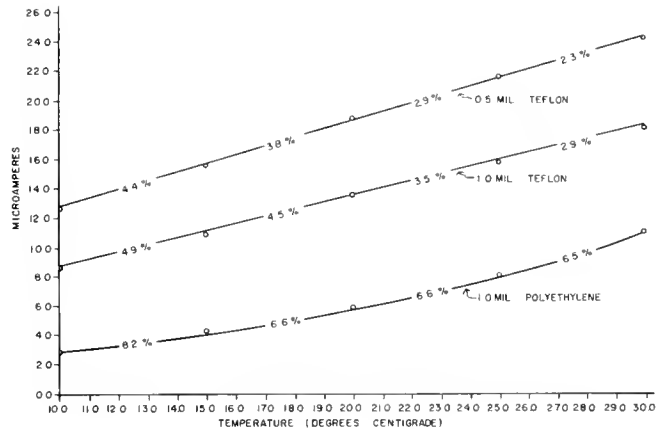


Figure 7:-- The temperature coefficients of a 1.0 centimeter diameter platinum electrode covered with three different membranes.

In order to calibrate the instrument, place it in water at the highest temperature expected to be encountered in natural waters or in the laboratory. The exact amount of oxygen in the water for calibration is unimportant; however, it is best that it be an amount that will not be supersaturated at the highest temperature, or it will go out of solution and form bubbles on the membrane. The proper oxygen content is most easily achieved by warming water above the high temperature (33° C.) and shaking off any excess oxygen, then place the electrode in this solution and cover with oil before lowering the temperature. When the electrode assembly is in place and a magnetic stirring rod is in position, cover the water with oil. The oil will limit oxygen diffusion during calibration. It is best to cool the water to the lowest temperature, say 10° C., and set the counter dial to 1000 and note the microampere reading at this point. By setting the counter dial to its highest resistance, one obtains the greatest sensitivity for any given membrane. Then warm the water by 1° C. intervals through the full range of temperatures; about 33° C. - 35° C. is high enough for warm-water fishery work. With each change of temperature the counter dial is changed so that the

reading in microamperes is always exactly the same as the first setting at 10° C. This procedure will give a series of counter-dial numbers which will correspond to the temperature of the water. In subsequent determinations, these numbers are set on the counter dial to correspond with the water temperature at the time of oxygen determination. Throughout the calibration period it is important that the stirring be sufficient to give the maximum read-out, and that this stirring be uniform throughout the duration of the calibration period. The magnetic stirrer is ideally suited for this purpose. When the temperature calibration curve is obtained, remove the electrode and wash any oil from the assembly with detergent. Remove the old membrane, prepare the electrode according to instructions and reassemble. The instrument is now ready for field or laboratory determinations of oxygen.

OTHER VARIABLES

In addition to being highly temperature sensitive, the electrode is slightly light sensitive, and the difference in light in the laboratory and bright sunlight may make a difference of 2 or 3 percent in oxygen determinations. This variable can be minimized by placing a dark-colored plastic baby bottle over the electrode assembly. A large hole should be cut in the bottom of the bottle and several small holes drilled in the "shoulder" of the bottle to permit circulation of water. This arrangement will also protect the membrane when the instrument is used in brush and rocks, or when it is lowered to the bottom mud in lakes or ponds.

The possibility that the electrode assembly would be pressure sensitive was also investigated. The instrument was taken to a lock-and-dam system and instrument readings were compared with Winkler determinations at various depths. The first series of determinations indicated variations in oxygen content due to stratification of water in the lock, but later the lock was drained and rapidly refilled to permit the passage of a barge. Temperature readings indicated that thermal equilibrium was established, and presumably chemical equilibrium as well. Table 1 lists the results of the test to a depth of 21 feet. Additional tests to a depth of 54 feet

Table 1:--A comparison between instrument readings and Winkler determinations of oxygen content in thermo-chemically equilibrated water obtained at various depths. The differences between Winkler determinations are probably within the limits of error of the method.

Depth (feet)	Temperature	Instrument Reading (microamperes)	Winkler Oxygen (Parts per million)
Surface	18.2	7.1	8.15
3	18.2	7.1	8.0
6	18.2	7.1	7.9
9	18.2	7.1	8.1
12	18.2	7.1	8.0
15	18.2	7.1	7.8
18	18.2	7.1	7.85
21	18.2	7.1	7.85

permitted the same conclusion -- that pressures due to depth did not appreciably influence oxygen determinations. This may only be true, however, if the electrode is properly constructed and the membrane is placed tightly over the platinum electrode. Then the pressure does not significantly alter the thickness of the membrane or the film of electrolyte behind it.

RESPONSE TIME

The response time of the electrode was checked with a recorder. Two beakers of water of the same temperature (24° C.) were placed on a magnetic stirrer. Sodium sulfite was added to one sample to remove the oxygen. The other water was saturated with oxygen. The electrode was placed in the zero-oxygen water and the recorder output was adjusted to zero. The recorder was adjusted to read 100 percent in the saturated water. The record is shown in Figure 8. The electrode output falls to zero within about three minutes, but of course will

adjust to smaller changes in proportionately less time. The response time from zero-oxygen to 8.5 ppm is about the same as the reverse, but about 99 percent of readout is achieved in approximately two minutes.

Undoubtedly, response time will depend upon type of membrane used, temperature, and rate of water circulation. In actual practice, when the instrument is employed in ponds, readings can be made at each depth in about one minute, as the change in oxygen from one depth to the next is usually small.

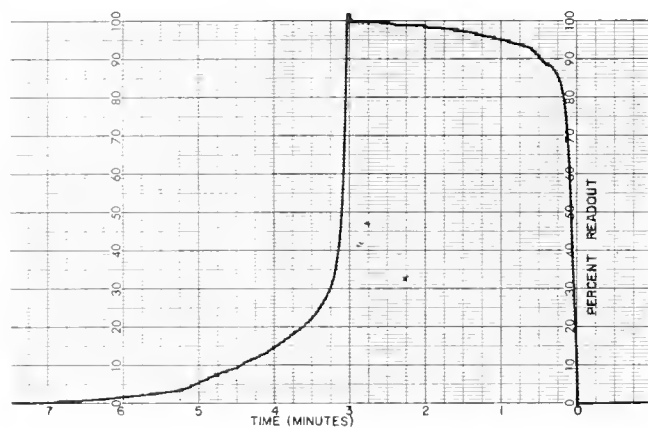


Figure 8:--Recording of the response time of the platinum-silver-silver oxide electrode covered with $\frac{1}{2}$ mil Teflon.

LITERATURE CITED

- American Physiological Society Symposium on Tissue Oxygen Tension.
1957. Federation Proceedings, Federation of American Society of Experimental Biology, vol. 16, no. 3, pp. 665-703.
- Carritt, Dayton E. and John W. Kanwisher
1959. An electrode system for measuring dissolved oxygen. Analytical Chemistry, vol. 31, no. 5, p. 9.
- Clark, L. C., R. Wolf, D. Granger, and A. Taylor.
1953. Continuous recording of blood oxygen tensions by polarography. Journal of Applied Physiology, vol. 6, pp. 189-193.
- Kanwisher, John.
1959. Polarographic oxygen electrodes. Limnology and Oceanography, vol. 4, no. 2, pp. 210-217.
- Lingane, James L.
1958. Electroanalytical Chemistry. second edition. Interscience Publishers, Inc., New York.
- Saila, Saul B.
1955. T-0₂, an instrument for the estimation of temperature and dissolved oxygen in natural waters. The Progressive Fish-Culturist, vol. 17, no. 4, pp. 162-165.

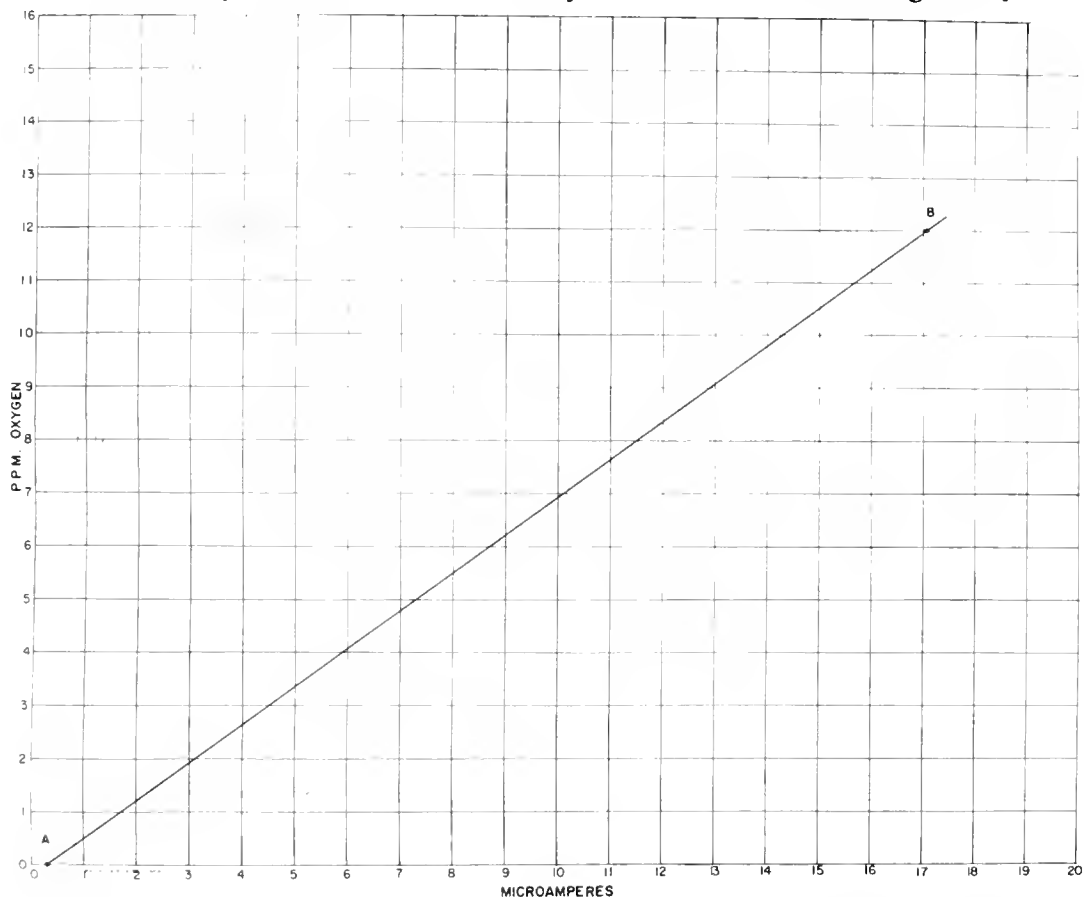
APPENDIX

Operation of Oxygen-Temperature Meter

1. Prepare a solution of 0.5N KOH. (28 grams plus distilled water to make 1 liter.)
2. Place about 100 cc. of this electrolyte in small glass jar and label "For Polarization". This solution may be saved and used several times. Discard when discoloration appears.
3. Clean the silver tube with very fine steel wool or emery cloth (#500) and rinse with alcohol or distilled water. Make sure electrode is free of steel wool or emery dust. The platinum disc will need only occasional cleaning. Do not sand it each time the silver is cleaned.
4. Place the electrode in the polarization solution and make sure the electrolyte completely covers the silver. Plug cable into socket. Turn switch to "Pol". Leave on until silver turns black or brown (about 30 - 60 seconds).
5. Turn switch to "Off" and remove electrode. Blot off excess KOH, but do not wipe. Allow electrode to dry 2 - 3 minutes.
6. Place a 4-inch square piece of the Teflon or polyethylene membrane in palm of hand and cup slightly. Place dime-size drop of 0.5N KOH (from stock, not that used for polarization) on the membrane. Place the electrode in drop and draw the membrane smoothly around all sides and up over the groove at top. Hold the electrode pointed down and place "0"-ring around end of electrode and roll or slide upward until it seats in "0"-groove.
7. Smooth the membrane again and trim off excess membrane above the "0"-ring.
8. Put the prepared electrode in water and turn switch to "O₂ Read" position. Leave on for 30 minutes - 1 hour to equilibrate.
9. Prepare saturated O₂ water (cool distilled water below room temperature) and aerate several hours; then warm it to room temperature and shake vigorously several times.
10. Place electrode in this standardized water and stir water or move electrode.
11. Turn switch to "Adj." and adjust needle to red line. Turn to "T. Read" and note temperature.
12. From the "Temperature compensation card" find the counter number corresponding to this temperature and set this number on the counter dial. This procedure compensates the electrode for temperature.
13. Turn switch to O₂ position and allow reading to become steady (about 1 - 2 minutes) stirring all the time. Record this reading (lower numbers on regular meter scale) for example 16.7 ua.
14. On saturation table find the ppm O₂ at the determined temperature. This is one point on a graph (see next paragraph).
15. Place electrode in small container of water (250 - 500 cc. or the storage bottle), add sodium sulfite (1 - 2 grams) and stir until needle indication stops going down (around 0.3 ua). This is Zero O₂ (the residual current), the second point on the graph. Draw straight line on graph (appendix figure) between these two points. Subsequent determinations of oxygen in unknown samples may be made by reference to this graph; i.e. by finding the ppm O₂ that corresponds with other meter readings.

Maintenance and Trouble Shooting

1. To test the instrument for proper function of the circuitry, unplug the electrode. Switch to "Adjust" position. There should be an upscale reading, adjustable with R-9. Switch to "T-Read" position. The meter should read below zero microamperes. No reading should result with switch on "O₂ Read" or "Polarize" positions.
2. With the electrode connected and the switch on "Adjust" position, the meter reading should be upscale and adjustable. On the "T. Read" position the meter reading should vary as the temperature of the thermistor. On "O₂ Read" an upscale reading will be present if the O₂ electrode is prepared with electrolyte and membrane. If uncovered and dry, no reading will be on the meter. If the platinum and silver are bridged by water or the tongue, an upscale reading will occur.
3. Batteries are long-lasting. Batteries 2 and 3 should be replaced if the meter will not adjust to the red line. Batteries 1 and 2 should be replaced if excessive time (4 - 5 minutes) is required for polarization.
4. Store electrode in water when not in use.
5. Turn switch to "O₂ Read" position and allow 30 minutes to equilibrate when the instrument has been turned to "Off" position. Leave on all day when instrument is being used periodically.



Appendix figure:--Example of oxygen calibration graph. Point A determined in water of known O₂ content. Point B in water with O₂ removed with excess sodium sulfite.

Appendix Table:--Dissolved oxygen saturation in distilled water exposed to 20.9 percent oxygen gas at various pressures and temperatures indicated

Alt. in ft.	0		1000		2000		3000		4000		5000		6000		7000		8000		9000		10000		12000		Alt. ft.							
	760	732	704	677	651	626	602	579	557	536	516	478	MM. Hg.	MM. Hg.	MM. Hg.	MM. Hg.	MM. Hg.	MM. Hg.	MM. Hg.	MM. Hg.	MM. Hg.	MM. Hg.	MM. Hg.	MM. Hg.	MM. Hg.	MM. Hg.	MM. Hg.	MM. Hg.				
0°C.	14.62	14.08	13.54	13.02	12.52	12.04	11.58	11.14	10.72	10.31	9.93	9.20	32° F.																			
1	14.23	13.71	13.18	12.68	12.19	11.72	11.27	10.84	10.43	10.04	9.66	8.95	33.8																			
2	13.84	13.33	12.82	12.33	11.86	11.40	10.96	10.54	10.14	9.76	9.40	8.70	35.6																			
3	13.48	12.98	12.49	12.01	11.55	11.10	10.68	10.27	9.88	9.51	9.15	8.48	37.4																			
4	13.13	12.65	12.16	11.70	11.25	10.82	10.40	10.00	9.62	9.26	8.91	8.27	39.2																			
5	12.80	12.33	11.86	11.40	10.96	10.54	10.14	9.75	9.38	9.03	8.70	8.05	41																			
6	12.48	12.02	11.56	11.12	10.69	10.28	9.89	9.51	9.15	8.80	8.47	7.85	42.8																			
7	12.17	11.72	11.27	10.84	10.42	10.02	9.64	9.27	8.92	8.58	8.26	7.65	44.6																			
8	11.87	11.43	11.00	10.57	10.17	9.78	9.40	9.04	8.70	8.37	8.06	7.47	46.4																			
9	11.59	11.16	10.74	10.32	9.93	9.55	9.18	8.83	8.49	8.17	7.87	7.29	48.2																			
10	11.33	10.91	10.49	10.09	9.71	9.33	8.97	8.63	8.30	7.99	7.69	7.13	50																			
11	11.08	10.67	10.26	9.87	9.49	9.13	8.78	8.44	8.12	7.82	7.52	6.97	51.8																			
12	10.83	10.43	10.03	9.65	9.28	8.92	8.58	8.25	7.94	7.64	7.35	6.81	53.6																			
13	10.60	10.21	9.82	9.44	9.08	8.73	8.40	8.08	7.77	7.48	7.20	6.67	55.4																			
14	10.37	9.99	9.61	9.24	8.88	8.54	8.21	7.90	7.60	7.31	7.04	6.52	57.2																			
15	10.15	9.78	9.40	9.04	8.69	8.36	8.04	7.73	7.44	7.16	6.89	6.38	59																			
16	9.95	9.58	9.22	8.86	8.52	8.20	7.88	7.58	7.29	7.02	6.76	6.26	60.8																			
17	9.74	9.38	9.02	8.68	8.34	8.02	7.72	7.42	7.14	6.87	6.61	6.13	62.6																			
18	9.54	9.19	8.84	8.50	8.17	7.86	7.56	7.27	6.99	6.72	6.48	6.00	64.4																			
19	9.35	9.01	8.66	8.33	8.01	7.70	7.41	7.12	6.85	6.60	6.35	5.88	66.2																			
20	9.17	8.83	8.49	8.17	7.86	7.55	7.26	6.99	6.72	6.47	6.23	5.77	68																			
21	8.99	8.66	8.33	8.01	7.70	7.41	7.12	6.85	6.59	6.34	6.10	5.65	69.8																			
22	8.83	8.50	8.18	7.87	7.56	7.27	6.99	6.73	6.47	6.23	5.99	5.55	71.6																			
23	8.68	8.36	8.04	7.73	7.44	7.15	6.88	6.61	6.36	6.12	5.89	5.46	73.4																			
24	8.53	8.22	7.90	7.60	7.31	7.03	6.75	6.50	6.25	6.02	5.79	5.36	75.2																			
25	8.38	8.07	7.76	7.46	7.18	6.90	6.64	6.38	6.14	5.91	5.69	5.26	77																			
26	8.22	7.92	7.61	7.32	7.04	6.77	6.51	6.26	6.02	5.80	5.59	5.17	78.8																			
27	8.07	7.77	7.48	7.19	6.91	6.65	6.39	6.15	5.91	5.70	5.48	5.08	80.6																			
28	7.92	7.63	7.34	7.06	6.78	6.52	6.27	6.03	5.80	5.59	5.38	4.98	82.4																			
29	7.77	7.48	7.20	6.92	6.66	6.40	6.15	5.92	5.69	5.48	5.28	4.89	84.2																			
30	7.63	7.35	7.07	6.80	6.54	6.28	6.04	5.81	5.59	5.38	5.18	4.80	86																			

Computed from Whipple and Whipple data as given on p. 153. Standard Water Analysis, American Public Health Assoc., 1936.

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