Version : 2.1
Date : 23-Feb-98
Author : MS

Model 93BF-DO
Dissolved Oxygen Transmitter

Congratulations !

You have purchased the latest in Instrumentation for Oxygen Data Logging. We hope that your new 93-BFDO will provide you with many years of reliable service.

This manual has extensive details. Please read carefully.

If at any stage we can be of assistance, please contact either your local TPS representative or the TPS factory in Brisbane.

TPS Pty Ltd. 4 Jamberoo St.,
Springwood, Brisbane,
Australia. 4127.

Phone : (07) 32 900 400
Fax : (07) 3808 4871

CONTENTS

1. Introduction

Oxygen to Frequency converter. The probes are fully isolated from the 12v DC supply galvanically. The 93BF-DO is designed to be used with YSI Oxygen probes, however the TPS ED500 may be used for % Saturation set-up.

NOMINAL : Specs: 0 - 20 ppM produces 0 - 10 Hz square wave.
SEE CONFIGURATION

Power : 12 v DC at less than 1.5 mA.
Regulator dropout 10 v nominal.
In practice about .7 mA is achieved.

2. Connections

Sensor connections…

Terminal No	Sensor Section	YSI Sensor	TPS ED500 Sensor
1	Cathode	Yellow	Blue
2	Anode	Green	Red
3	Common	Braid (covered with thick black or green heatshrink)	Braid (Clear)
4	ATC	Blue	No Connection
5	ATC	Red	No Connection

Power and Output Connections…

Terminal No	Description
6	Recorder +ve Signal out (see note below)
7	Recorder Common (***not*** isolated from sensor)
8	+12V DC Input (isolated from the sensor)
9	Common DC Input (isolated from the sensor)
10	No Connection
11	Pulse output Common (isolated from the sensor)
12	Pulse output Signal (isolated from the sensor)

3. Controls

Control	Position	Description
RV1	Lower Left	Set Span (Air Calibration)
RV2	Middle Trimmer	Zero Calibration
RV4	Top Trimmer	Set Vreg -3.7 volts (***FACTORY SET***)

NOTES:

- The Analog signal output on Pins 6/7 is High Impedance.
- Connection of a recorder of less than 1 Megohm Impedance will change output sensitivity of the frequency section.
- The Recorder outlet is NOT isolated from the Cell.
- Voltage is nominal 1.04v (+ve) at full scale.
- If the unit is modified or wet or covered in any potting material, warranty is void.

4. Configuration

Thus unit is covered for an input of __________ to __________ ppM

for an output of __________ to __________ Hertz

or __________ to __________ V DC

5. Oxygen Calibration

1. Turn the unit on with the Oxygen Sensor plugged in and allow 3 minutes or so polarization time. Look to see that the membrane over the end of the electrode is intact.

   Zero Adjustment:

2. This need ONLY be done after a membrane refit (and even then, only for confirmation purposes).

   NOTE: This following ZERO procedure can normally be left out.

   IF SO, GO ON TO STEP 4.....

3. Zero Adjustment Procedure:
   - Obtain a solution of 0.01 Molar Borax solution and add to 5 mL of this solution about 100 milligrams of sodium sulphite crystals. The solution may be stored for several hours if kept sealed.
   - Check the membrane. Replace if broken or wrinkled.
   - Fill a small beaker with the oxygen-free solution made above. Having turned on the unit for a few minutes before, to ensure that the cell is correctly polarized, place the cell in this oxygen-free solution.
   - The reading will fall slowly towards zero. Wait until the reading stops decreasing, then carefully adjust RV2 for exact zero. If this is impossible, then it is almost certainly due to ohmic leakage in the electrolyte resulting from a poorly sealed or fitted membrane. If this is the case, refit a new membrane.
   - Zero may well require 5 minutes, particularly if the sensor has just had a membrane refit.
   - For normal samples (50 - 100% saturation) a zero below 1 - 2 % is satisfactory.

   Span (Air) Calibration

4. Rinse and carefully dry the sensor tip and let it stabilize in air for a couple of minutes. Now set the RV1 control for a value from the calibration table on page xxx, which is determined by the AIR Temperature.

   For example "8.24 ppM. at 25oC.", set to 8.2.

   Repeat this "AIR CALIBRATION" as often as convenient.

5. Measure unknowns:
   - Stir steadily without bumping the sensor. The user may wish to apply Salinity Correction. This is because the meter reads Oxygen in terms of the partial pressure, and its reading is unaffected by salts. To get a correct reading for ppM compensated for salt, look up the table on page xxx.

     From the table (or formula) then, for example: "An 8.2 ppM (25oC) meter reading can be reported as 6.7 ppM in 33 ppK Salt Solution".

6. Dissolved Oxygen Electrode

The electrode used, is the amperometric type of Clark Electrode and is suitable for the measurement of oxygen pressures in the range 0 - 100 centimetres of mercury. While the probe actually reads partial pressure of oxygen, the circuit is calibrated to be read in percentage saturation or parts/million (Milligrams/litre). The operation of probes of the Clark type relies on the diffusion of oxygen through a suitable membrane into a constant environment of 0.1 molar potassium chloride. Measurements are best performed with a reasonable flow past the membrane. At sufficiently high flow rates, the oxygen current is totally independent of the flow (few cms./sec.). The cell must not be shaken however or unstable readings will result from electrolyte surge bringing new oxygen from the reservoir to the working cathode surface.

Operating Principle

The Clark oxygen electrode consists of a gold cathode and a silver/silver chloride anode, placed in an electrolyte solution. This solution is contained behind a plastic membrane. In this case the plastic is .025mm intermediate density polyethylene sheet. PTFE (teflon) can be supplied for special applications. It must be realised that using membranes of very different thicknesses will result in an error in the temperature compensation that is applied in the instrument for the membrane permeability. This coefficient (here +4.2%/oC at 25oC) is for this thickness polyethylene. A polarizing voltage of about 800 millivolts is applied between the two electrodes. The gold electrode is placed close to the membrane and because of the polarizing voltage, oxygen diffusing through the membrane will be reduced at the gold electrode.

$$\text{Equation: } 0_2 + 2H^+ + 2 \text{ electrons} \rightarrow H_2O_2$$

This reduction process will produce a current through the oxygen electrode. A load resistor (actually a thermistor in this case) situated in the electrode itself, converts this current into a voltage proportional to the oxygen partial pressure. The thermistor provided within the body of the electrode can have a temperature coefficient of -4.2%/oC. This gives an accurate temperature compensation for the temperature/permeability effect of the membrane to oxygen, over a range of +/- 20oC about a centre value of 25oC. Note this compensation is not for the solubility effects. A separate sensor also included achieves this.

7. Probe Maintenance

The membrane does not require replacement as long as it remains intact. If punctured or suspected of leaking around the edges, it must be replaced. The cap or ring is removed, the old membrane taken off. Make sure the reservoir is full with no bubbles by "pumping" gently on the side rubber membrane with a blunt instrument such as the top end of a pencil or biro. Add a few drops of electrolyte onto the gold cathode, until a "dome" of solution is formed. A new piece membrane material is pulled firmly over the end of the probe so there are no wrinkles close to the gold cathode. The cap or ring is carefully pushed into place. The excess membrane may be trimmed off with a razor blade. During this process the electrolyte will not normally drain out. If it is thought that the electrolyte may be contaminated or even used (it is actually consumed in the operation of the probe), then the probe may be washed out with distilled water. The gold surface must not be polished. Do not contaminate the gold cathode with oils etc from the skin by touching it.

The electrolyte is replaced with 0.1 molar KCl solution. No air bubbles should be present between the cathode and the membrane.

If the probe is washed off and put in fresh water, then, by viewing obliquely in a strong light, it is possible to see electrolyte "streaming" from the tip if it is leaking (even slowly). The effect is one of differential refractive index and is quite sensitive. Do not over-stretch.
If the response is low or reading overranged, fit a new membrane.

8. Importance of Correct Membrane Fitment

Addition to instruction leaflet for YSI 5739 Dissolved Oxygen Electrode

WARNING :
FAILURE TO READ THIS NOTE CAN RESULT IN DAMAGE TO YOUR NEW ELECTRODE:

The YSI 5739 dissolved electrode is shipped dry from the YSI factory. Before the electrodes are despatched from TPS, they are fully tested. Therefore the probe is already filled when you receive it, with a correctly fitted and tested membrane. This is part of the TPS Quality Control Program.

WHY is correct membrane fitting SO IMPORTANT...
There are two reasons why the membrane must form a perfect seal.

1. It stops the internal fluid leaking out and causing air bubbles to form behind the membrane.
2. Most important: It resists contamination from outside getting INTO the probe. Substances such as Sulphides will poison the Silver anode.
   (This is triangular-shaped piece behind the probe membrane.)

<u>HOW to fit the membrane correctly...</u>
Section "d." of the YSI "PROBE PREPARATION" instruction leaflet, enclosed with the YSI5739 sensor, says to stretch the membrane up and over the end of the probe.

This point cannot be overstated. The act of physically stretching the membrane is what forms the correct shape to seal the probe from the outside world. The "O" ring itself DOES NOT guarantee a correct seal of the probe membrane. It only helps to hold a correctly formed membrane in place.

The correct stretching technique will form a "CUP" shape in the membrane. Note that the membrane will stretch up to twice its original length without breaking. It is better to tend to over-stretch the membrane than not to form this "CUP" shape correctly.

It is also essential that the membrane is neatly trimmed off after fitting. If "scraps" of loose excess membrane are left behind the "o" ring, these can catch in the membrane protector thread as it is re-screwed, and pull on the end of membrane, opening the seal.

<u>HOW to check the membrane is fitted correctly...</u>
Remove the plastic "Humidity" bottle from the end of the electrode.
Rinse the electrode tip in distilled water and wipe it dry with tissues etc.
Hang the electrode up overnight in a dry place.

If the membrane seal is leaking, white crystals of Potassium Chloride will have formed under the edge of the membrane near the "o" ring, where the filling solution has leaked and crystallized. If these are visible, re-fit a new membrane and re-test.

<u>WHAT will happen if the membrane is not fitted correctly...</u>

The Silver anode will usually turn black when it is poisoned. When the anode is poisoned, the whole electrode is usually rendered unserviceable.

TPS may be able to re-furbish the electrode, but this is not certain.

1. Incorrect fitting of the membrane causes poisoning of the electrode.
2. Poisoning of the anode is NOT covered by warranty.

9. Probe Storage

The Oxygen probe should be kept moist when not in use to prevent the thin film of electrolyte behind the membrane from drying out. To achieve this, the probe can be stored with the tip in water.

10. Notes On Units Of Dissolved Oxygen

The terms "Oxygen Concentration" and "Oxygen Partial Pressure", frequently give rise to some confusion.

1. Oxygen Concentration is the absolute quantity of oxygen present per unit mass of the liquid.
2. Oxygen Partial Pressure is the pressure of the oxygen fraction of the total gas (dissolved gaseous).

In any one liquid system, Oxygen Concentration and Oxygen Partial Pressure are proportional. However, if the solubility of oxygen in the liquid should change owing to increased quantities of solutes, etc., then the ratio of the Concentration to the Partial Pressure must change. Thus, if one saturates distilled water and a 25% solution of Sodium Chloride with air at atmospheric pressure (>5oC) both solutions will have almost the same Oxygen Partial Pressure, namely 15.5 cms of mercury. However, the dissolved Oxygen Concentration parts per million (milligrams per litre) will be 8.4 in the distilled water, and 2.01 parts/ million (milligrams per litre) in the salt solution. This is a rather extreme example, as ocean water is only 3.6% It does however stress the importance of correct interpretation of salinity, etc.

If mass units (ppM) are used for measurement of Dissolved Oxygen, the temperature problem of relating the linear partial pressure reading of the probe, to the mass (ppM or mg/L) at different temperatures becomes more involved. As well, there is the mass variation due to dissolved salts (salinity correction). Therefore, the fully corrected instrument would need 3 correction systems…

(a) Membrane correction for temperature permeability effects.
(b) Solubility correction of D.O. with temperature, and, rather less importantly,
(c) Salinity correction of D.O. by weight (Salinity has no effect on pressure units readout).

In the 93BF-DO unit:
(a) is achieved AUTOMATICALLY.
(b) To provide the mass units (ppM) readout (so popular due to the Winkler process used in the past), the 93BFDO unit has Solubility Correction via an additional temperature sensor in the cell.
(c) Salinity correction is provided by the Salinity Correction Table.

The amount of Saturated Dissolved Oxygen (in ppM.) in pure water at each degree of temperature (0oC to 40oC) is shown.

The amount of Saturated Dissolved Oxygen (in ppM.) against the concentration of Sodium Chloride in sea water is also shown from 0oC to 30oC at every 1oC. 40 ppK NaCl contains 24.2 ppK chloride.

The following examples of standard conditions are especially worth noting, from the table…

(a) 15.5 cms. of Hg. (100% pressure saturation) is equivalent to 8.2 ppM. oxygen in pure water at 25oC for example.

(b) That this rises to 14.6 ppM. at 0oC and falls to 6.4 ppM. at 40oC.

(c) That 33 ppK. salinity causes this same 15.5 cms. Hg. to only have 6.7 ppM. DO at 25oC (for example) compared with 8.24 ppM in fresh water.

11. Velocity Past The Membrane

Workers have shown that the relationship between the diffusion current (oxygen current) and the external velocity of the liquid is expotential. Some workers using thicker membranes have shown even less dependence of the diffusion current on liquid velocity. Because of the expotential nature of the relationship, very considerable changes in velocity have to be made before noticing any change in the diffusing current once the flow is sufficiently high. Tests with this electrode have shown that flow rates above 0.2 litres/minute past the membrane give results indistinguishable from those with appreciably higher flow rates (5 litres/minute). Fluctuations in readings due to air bubbles passing through the membrane are, however, a different matter. With the type of electrode to be used with this instrument, very little changes in diffusion current are caused by altering the pH of the external environment. Pressure changes over a moderate range exerted on the membrane also cause no change. The probe is sealed by glands for total immersion to a few 1O's of metres.

12. Equilibrium Conditions

Whilst Saline Water has a lower ppM than does Fresh Water, it does not mean it necessarily has less oxygen, biologically available. Both have 100% Saturation (presuming no C.O.D., B.O.D. etc) because both are in partial pressure equilibrium with air. Any usage of oxygen is immediately supplied by the dissolving of more from air, to meet partial pressure equilibrium requirements. This is so for both saline and fresh water. The reporting of oxygen at a lower level (in ppM units) in the Salt Water is therefore QUITE MISLEADING! In closed systems, such as tanks, pipes and deep waters, equilibrium is not so readily available and the Salinity Effect gains the importance in the reporting of Dissolved Oxygen. It is suggested, unless such closed (or deep, low diffusion) systems are encountered, that Oxygen should be reported in % Saturation or ppM of equivalent Fresh Water.

13. Solubility of Oxygen in Water

Following is a table of Solubility of Oxygen in water exposed to water-saturated air, at 760mm Hg atmospheric pressure.

g/l Cl	0	4	8	16	20
ppK. NaCl	0	6.6	13.2	26.4	33
Temp (^{o}C)	Dissolved Oxygen - ppM (mg/L)				
0	14.57	13.91	13.26	11.94	11.29
1	4.17	13.54	12.90	11.63	11.00
2	13.79	13.18	12.56	11.33	10.72
3	13.43	12.83	12.24	11.05	10.45
4	13.08	12.50	11.93	10.78	10.20
5	12.74	12.19	11.63	10.52	9.96
6	12.42	11.88	11.34	10.27	9.73
7	12.11	11.59	11.07	10.03	9.51
8	11.81	11.31	10.81	9.80	9.30
9	11.53	11.04	10.56	9.58	9.09
10	11.26	10.79	10.31	9.37	8.90
11	10.99	10.54	10.08	9.17	8.72
12	10.74	10.30	9.86	8.98	8.54
13	10.50	10.07	9.65	8.79	8.37
14	10.27	9.86	9.44	8.62	8.20
15	10.05	9.65	9.25	8.45	8.04
16	9.83	9.44	9.06	8.28	7.89
17	9.63	9.25	8.87	8.12	7.74
18	9.43	9.06	8.70	7.97	7.60
19	9.24	8.88	8.53	7.82	7.46
20	9.06	8.71	8.36	7.67	7.32
21	8.88	8.54	8.20	7.53	7.19
22	8.71	8.38	8.05	7.39	7.06
23	8.55	8.22	7.90	7.25	6.93
24	8.39	8.07	7.76	7.12	6.80
25	8.24	7.93	7.61	6.99	6.68
26	8.09	7.78	7.47	6.86	6.55
27	7.95	7.64	7.34	6.73	6.42
28	7.81	7.51	7.21	6.60	6.30
29	7.68	7.38	7.07	6.47	6.17
30	7.55	7.25	6.95	6.34	6.04
31	7.42				
32	7.30				
33	7.18				
34	7.07				
35	6.95				
36	6.84				
37	6.73				
38	6.63				
39	6.52				
40	6.42				

<u>Salinity Correction, by Formula</u>

The corrected ppM value caused by salinity can be calculated as follows:

Salinity-corrected ppM = ppM x (1 - (0.005827 x Salinity in ppK))

14. Troubleshooting

READS TOO HIGH IN AIR:	Hole in plastic membrane- Re-Fit.
READS TOO LOW IN AIR:	Filling solution may need replacing.
READS NEAR ZERO IN AIR:	Check connections.
NOISY READINGS IN AIR:	Membrane not fitted smoothly- Re-Fit.
SLOW RESPONSE:	Membrane not fitted smoothly- Re-Fit.