Development of an Optimized Dissolved Oxygen Sensor for Oceanographic Profiling

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Sophisticated profiling of ocean salinity and temperature features began more than 30 years ago with the advent of electronic CTD (Conductivity, Temperature, Depth) instruments. Efforts to add dissolved oxygen (DO) to the suite of measured values began almost immediately; the goal was a fast, accurate, and stable sensor that would deliver oxygen data in a class with what had been achieved in salinity and temperature. Suitable DO sensors proved difficult to develop, but have now been achieved.

Where we have been

In past attempts to meet the needs of deep-ocean profiling, Sea-Bird and other CTD manufacturing companies re-packaged commercially available Clark electrodes. In these sensors, oxygen molecules diffuse through a membrane and are converted at a gold cathode to hydroxyl ions (OH^-). The rate of diffusion of oxygen molecules leads to a measurable electrical current that the sensor electronics converts to a voltage. The voltage signal is linear with partial pressure of oxygen. Taking temperature, salinity, and pressure into account, oxygen concentration can be calculated. These Clark sensors are very sensitive to pressure and temperature variations, slow responding, and unstable. Field calibration is needed but not easily performed. The poor behavior of DO sensors when profiling the dynamic ocean environment causes substantial discrepancies between downcast and upcast data. This has commonly been termed hysteresis.

Where we decided to go

Several intellectually interesting emerging technologies, especially those based on optical techniques, have offered promise of better results. On balance however, we doubted that sensors employing these different physical and chemical technologies would be any less susceptible to the problems exhibited by Clark cells, and we are sure that their use would introduce new problems. We believed that the Clark technology could be substantially improved by addressing weaknesses in its implementation. Accordingly, an R&D project was begun at Sea-Bird to identify the causes of the known problems with DO sensors and to develop solutions for each.

Problems with existing sensors

Sources of drift in previous Clark sensors include changes in membrane tension, depletion of electrolyte, impairment of the silver anode, plating of anode metal on the cathode, and the presence of chemical contaminants in the sensor's plastic body. Additionally, because of "polarization" effects, the sensors are slow to stabilize after power is applied.

Dynamic errors leading to apparent hysteresis are caused by response-time mismatch of the compensation temperature sensor to the time characteristic of the sensor's inherent temperature dependency, and are exacerbated by the large mass and slow thermal equilibration of existing sensors. Further errors are caused by inadequate control of flushing. Clark sensors are inherently flow sensitive and work poorly unless a pump is used to control the flow rate.

Membrane fouling also contributes to drift by altering the oxygen diffusion rate through the membrane, thus reducing sensitivity. Bio-fouling can be particularly troublesome because the living organisms either consume or create oxygen; the sensor becomes a micro environment in which oxygen levels cease to reflect ambient conditions.

Historically, sensor calibration by sensor manufacturers has been minimal. Typically, calibration was performed only at room temperature. The sensor was exposed to “zero” oxygen and a single up-scale value in air-saturated water, and offset and slope coefficients were calculated from the two readings. Although the Clark technology is essentially linear, the two-point calibration does not fully characterize the sensor’s response to oceanographic oxygen.

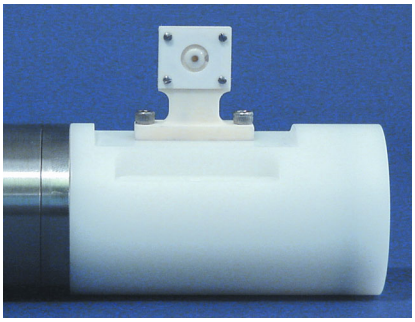
The path to a better DO sensor

The first task was to choose a material for the sensor. Plastics are inexpensive and easy to mold or machine, but do not possess the mechanical strength, stability, and good thermal properties needed for a successful sensor; alumina ceramic was chosen because it meets these needs. It can be diamond ground to tight dimensions and with good surface finishes. The finished parts are assembled using frit glass.

The new sensor’s flat “tombstone” shape permits the membrane to be precisely and permanently retained in a ceramic sandwich. Rapid consumption of the electrochemical constituents (anode and electrolyte) was addressed by increasing the volume of these components.

Polarization delay on power-up was eliminated by incorporating a non-hazardous five-year lithium battery inside the sensor. Temperature compensation problems were minimized by changes in the sensor materials and geometry. By making the sensor thin and flat and well ventilated by the flow, rapid equilibration was achieved; the high thermal conductivity of alumina ceramic minimizes equilibration time and the magnitude of internal temperature gradients. Placing the temperature compensation thermistor as close to the cathode and membrane as possible helped to ensure that the right temperature was measured at the right time. Sensitivity to the rate of flow across the membrane was carefully measured and a special plenum designed to direct the pump-controlled flow past the sensor in a predictable way; the plenum also provides effective mechanical protection for the membrane.

Fouling of the membrane surface by biological activity can be prevented by adding in-line poison cartridges before and after the plenum connections. These are most useful in moored applications where the pumped flow is intermittent and poisoning is effective between measurement periods. Membrane fouling is less problematic in profiling applications and thorough cleaning after use with a detergent is sufficient.



Close up of sensor head with plenum removed. Ceramic sensor head with Teflon covered aperture is visible. Cathode is visible through Teflon membrane. The large white cylinder to which the ceramic spar is attached is the reservoir containing the anode and electrolyte.

The entire sensor with high pressure housing for electronics and plenum attached. Water to be measured is pumped through the plenum past the sensor head. If needed, poison cylinders (not shown) can be added to the inlet and exhaust ports of the plenum.

A sophisticated automatic calibration system employing five oxygen concentration levels at two widely spaced temperatures was developed. Periodically standardized using Winkler titrations and gas standards, the new sensors are better characterized, calibrated more accurately, and their stability is better judged.

Eight SBE 43 sensors (in pumped pairs) are calibrated at one time in a computer-controlled bath.

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SENSOR SERIAL NUMBER = 0177
CALIBRATION DATE: 12-Nov-01r

SBE 43
OXYGEN CALIBRATION DATA

COEFFICIENTS:

Soc = 0.5041
Boc = 0.0000
Voffset = -0.4925

TCor = 0.0006
PCor = 1.350e-04

BATH OX ml/l	BATH TEMP (ITS-90 °C)	BATH SAL PSU	INSTRUMENT VOLTS	INST OX ml/l	RESIDUAL ml/l
1.42	25.00	0.06	0.982	1.44	0.02
1.53	5.00	0.07	0.829	1.52	-0.01
2.40	25.00	0.06	1.308	2.41	0.01
2.53	5.00	0.07	1.053	2.53	-0.01
3.39	25.00	0.06	1.643	3.40	0.00
3.56	5.00	0.07	1.279	3.55	-0.01
5.35	25.00	0.06	2.303	5.35	-0.00
5.55	5.00	0.07	1.726	5.56	0.01
7.27	25.00	0.06	2.953	7.26	-0.01
7.59	5.04	0.07	2.176	7.59	-0.00

V = voltage output from SBE-43
T = ocean temperature [°C] from CTD
S = ocean salinity [PSU] from CTD
P = ocean pressure [dbar] from CTD
Oxsat(T, S) = oxygen saturation [ml/l]
oxygen (ml/l) = (Soc * (V + Voffset)) * exp(Tcor * T) * Oxsat(T, S) * exp(Pcor * P)
Residual = instrument oxygen - bath oxygen

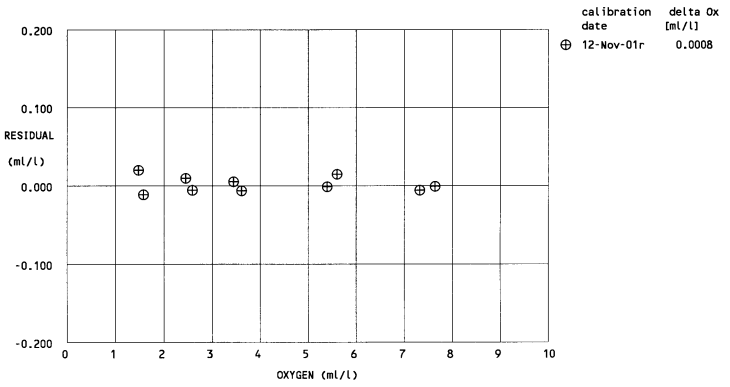

Figure 1. A typical calibration sheet showing calibration data and derived sensitivity, zero offset, and temperature correction factors. Included is a graphical plot of the residual differences between the sensor computed value and the measured bath oxygen levels. The oxygen levels in the bath are determined by Winkler titrations of bottle samples.

SBE 43 long-term stability is excellent. In Figure 2, repeated calibration of sensor s/n 112 shows the total drift in sensitivity over a 6-month period is less than 5%. Short-term fluctuations in sensitivity are less than 2%, and derive more from calibration uncertainty than sensor stability.

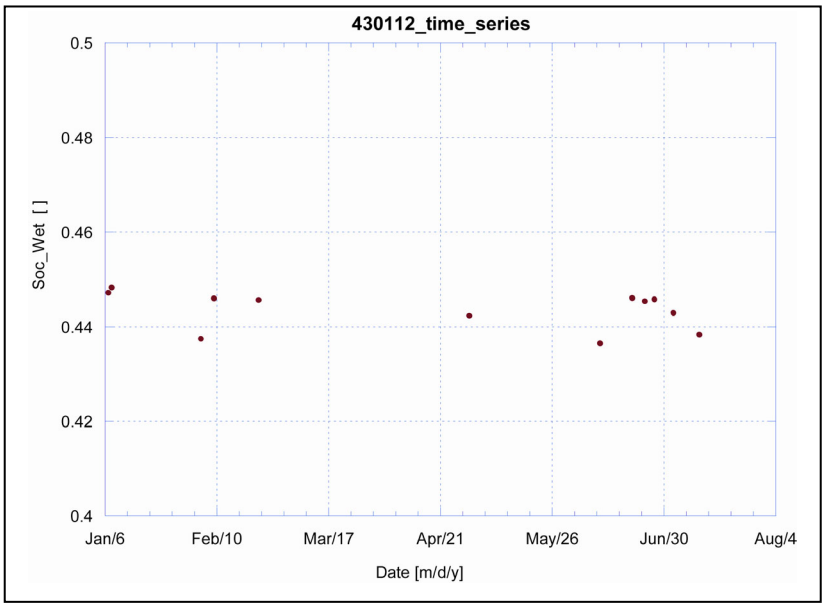

Figure 2. Processing the data from Clark type oxygen sensors started with equations developed in 1971 by Beckman Instruments Inc. for use with their MINOS® Dissolved Oxygen Meter. These equations were modified and formalized in 1985 by W. Brechner Owens and Robert C. Millard Jr. and are used within the oceanographic community to support Clark sensors of all types.
The equation for the SBE 43 is:
Oxygen =
*Soc * [V + offset] * Oxsat (T,S) * exp [Tcor*T + Pcor*P]*

Results

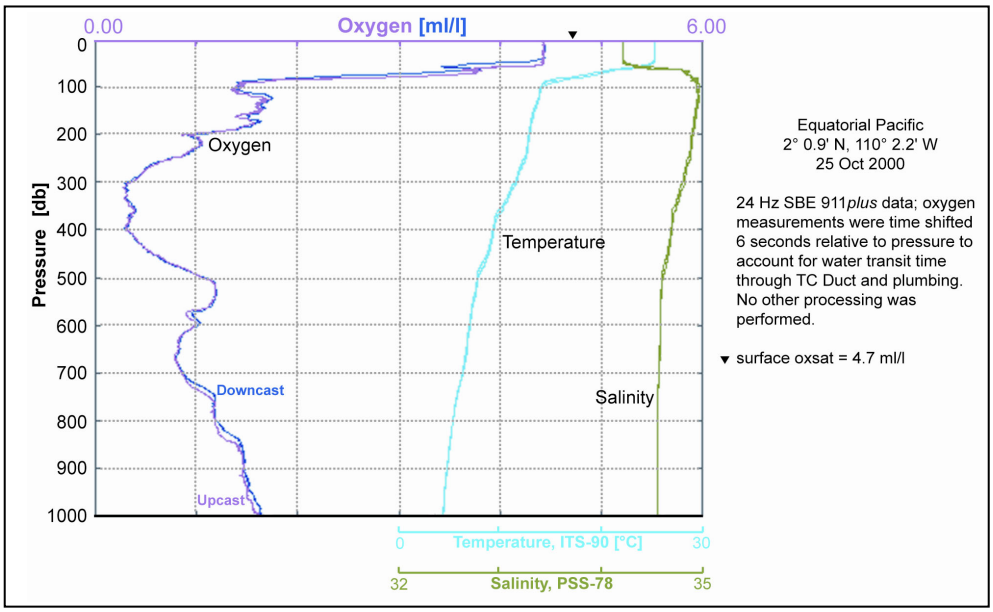

Figure 3. Profile of oxygen concentration obtained by researchers in the Equatorial Pacific Ocean.

The results in Figure 3 are typical for this new sensor using the standard processing equation in Figure 2. For this analysis, the oxygen data were shifted 6 seconds earlier in time to account for the transit time of the water in the plumbing, and for the response time of the sensor.

The good results obtained with the new SBE 43 sensor validate the Clark method *when it is well implemented.* Scientists are now collecting high quality oxygen profiles, over the duration of their cruise. Their accompanying Winkler titrations confirm the data quality, and for the first time, support the possibility of obtaining accurate oxygen data without doing titrations at sea.