Improvements to the SBE 43 Oxygen Calibration Algorithm

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Abstract

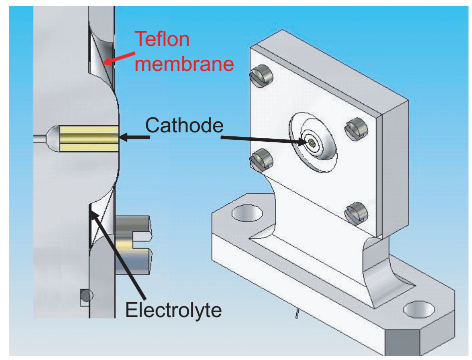
Efforts to refine the measurement of dissolved oxygen with Clark electrode polarographic sensors have yielded a greater understanding of the physics governing the sensor signal. A change in the Teflon membrane's oxygen permeability over the oceanographic temperature and pressure range alters the sensor's basic signal level and its time response. A new calibration algorithm improves the static temperature and pressure characterization, but also captures time dependent processes that control time constant and hysteresis. The corrections result in matching down and up profiles and a high conformance to Winkler titrated water samples.

Introduction

The SBE 43 characterization is approaching 1 micromolar error. It is optimized for profiling including dynamic temperature correction. The new algorithm offers better static characterizations as well as response and hysteresis corrections, permitting calibration of upcast or downcast data.

The SBE 43 offers:

- Electronic temperature compensation
  - More accurate cathode temperature
  - Automatic gain adjustment over temperature, preserving signal resolution
  - Accomplished with less phase error
- Better understanding of sensor physical properties
  - Better characterized static response
  - Correction for oxygen response time
  - Compensation of pressure-induced hysteresis
  - Improved moored and spot measurements



Calculating Dissolved Oxygen Concentration from Sensor Output Voltage

Dissolved oxygen concentration in ml/l is calculated from SBE 43 output voltage with the equation shown below. This equation is similar in form to Owens and Millard (1985), but with important changes to Tau, TCor, PCor, and OxSat. The functions that provide temperature compensation, time constant correction, and pressure compensation are discussed below.

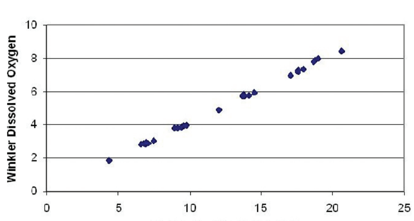
$$OX = \left(V + V_{offset} + \tau_{20} D_0 \left(e^{D_1 P + D_2 T} \right) \times \left(\frac{dV}{dt} \right) \right) \times Soc \times \left(1.0 + AT + BT^2 + CT^3 \right) \times OXSOL(T,S) \times e^{\left(\frac{EP}{K} \right)}$$

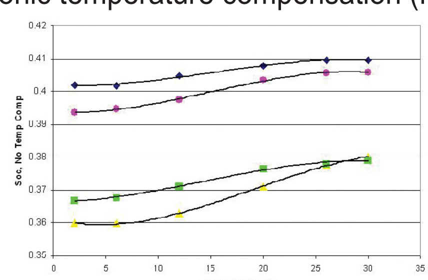
Where:

OX	CTD dissolved oxygen in ml/l	OXSOL	Oxygen solubility after Garcia and Gordon (1992)	dV/dt	Estimate of sensor output change over time
V	Sensor output in Volts	T	Temperature in degrees C	E	Compensation coefficient for pressure effect on membrane permeability (Atkinson et al, 1996)
V_{offset}	Sensor output offset voltage	S	Salinity in PSU	P	Pressure in decibars
Soc	Oxygen slope	τ_{20}	Sensor time constant at 20 deg C and 1 Atm	K	Temperature in Kelvin
A,B,C	Compensation coefficients for temperature effect on membrane permeability	D_0,D_1,D_2	Compensation coefficient for pressure effect on time constant		

Temperature Compensation

The SBE 43 electronics include a circuit for compensation of the effect of temperature on membrane permeability. The figure on the left shows sensor operation in a calibration bath over the temperature range of 2 to 28 degrees C and a dissolved oxygen range of 2 to 8.5 ml/l. The figure on the right shows the residual temperature effect, which remains after electronic temperature compensation (four sensors).



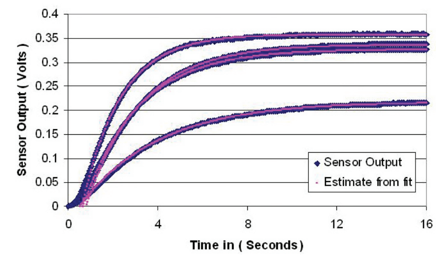


Characterization of Sensor Time Constant

The time constant of a polarographic oxygen sensor varies strongly with temperature and pressure. Characterization of the sensor time constant yields an improvement in dynamic accuracy and provides guidance in sampling protocols for moored deployments.

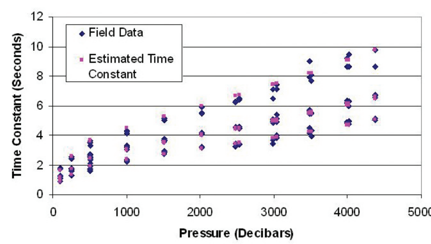
Measurement of Time Constant, In-Situ and in Laboratory

- Polarographic oxygen sensors consume oxygen, and thus require a flow of sample water past the cathode.
- Stopping the sample system pump halts water flow and allows a depleted oxygen layer to build over the cathode.
- Starting the CTD pumped flow again introduces a sharp step in oxygen from which the time constant can be computed.
- The process is repeated at several depths to accumulate a matrix of time response over a range of temperatures and pressures.
- The experiment is repeated at 1 atmosphere in a temperature-controlled bath to confirm the temperature model.
- Amplitude, step start time, and time constant are determined by a statistical fitting routine.
- Sensor output voltage is normalized.
- This figure shows data from four sensors, collected at 500 db and 6.6 deg C. The responses are clean exponential rises.



Field Results

Time constants or Tau measured at the HOT site in Hawaii are plotted versus pressure in this figure for each of four sensors.



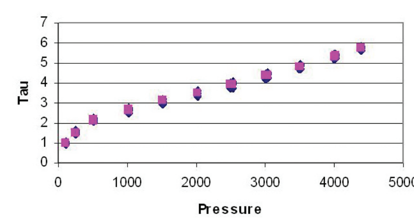
The shape of this curve can be characterized by a combination of two exponentials, one a function of P and the other a function of T, as in the equation below.

$$Tau = \tau_{20} \times D_0 \times e^{(D_1 \times P + D_2 \times T)}$$

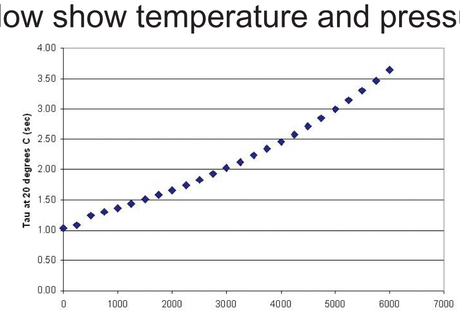
Where:

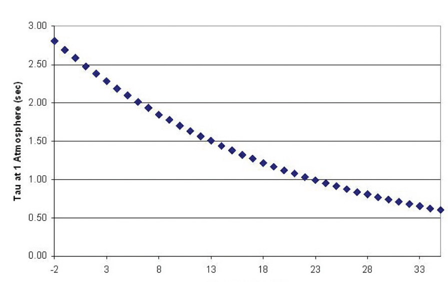
P	Pressure [dbars]	τ_{20}	Time constant measured at 20 degrees C 1 Atm
T	Temperature [deg C]	D_0, D_1, D_2	Statistical coefficients

Time constants for four sensors measured at eleven different depths provide assessments over a wide range of temperature and pressure. The data for four sensors in the figure at right collapse to a common curve when normalized by each sensor's time constant at 1 Atm pressure and 20 deg C (τ_{20}) via the equation above.

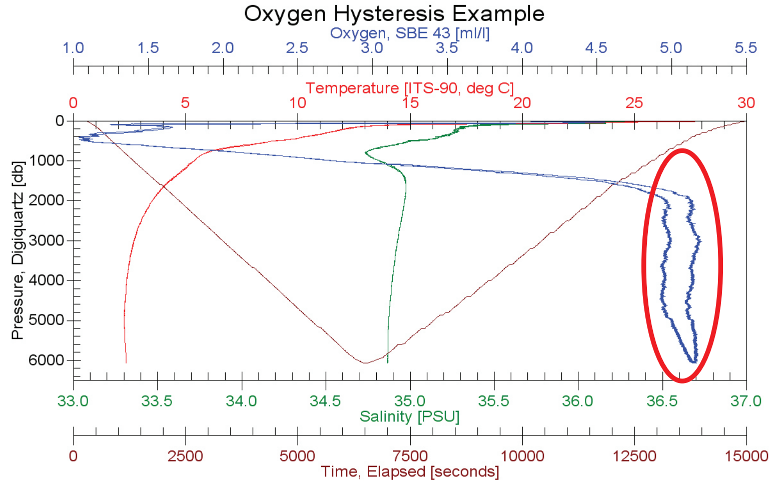


The figures below show temperature and pressure effect on nominal time constant.





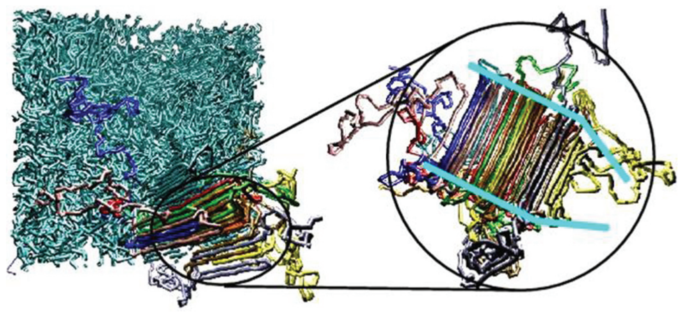
Correction of Hysteresis induced by High Pressure Effects on Teflon Membrane



Deep ocean profiles of dissolved oxygen often show a difference between up and down cast. This hysteresis results from physical changes of the Teflon membrane that occur with changes in pressure.

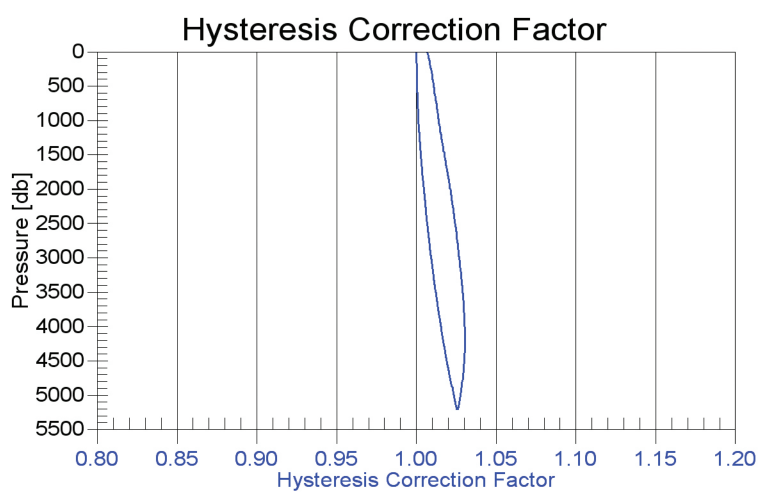
Phase Change and Plasticization in Teflon

Teflon has crystalline, amorphous and empty (voids) regions. Under pressure, amorphous regions of the Teflon polymer realign to become crystalline. Plasticization also occurs under high pressure, when gas molecules are incorporated into the long polymer chains. Both processes affect membrane permeability. State change processes are temperature and pressure dependent.



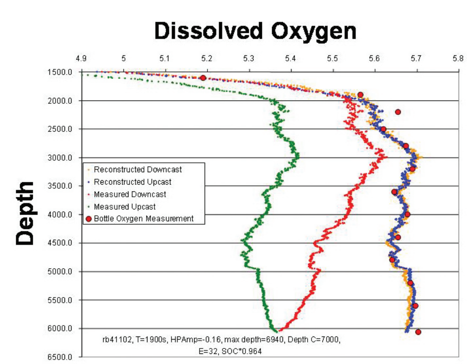
Effects of Pressure-Induced Hysteresis

- The effect has a long time constant.
- Effects depend on pressurization rate and the pressure and temperature history.
- Parameters of the model appear to be stable for a particular thickness of Teflon membrane material.
- The figure at right shows the correction that is applied to the sensor output voltage, for a 13 micron thickness film.



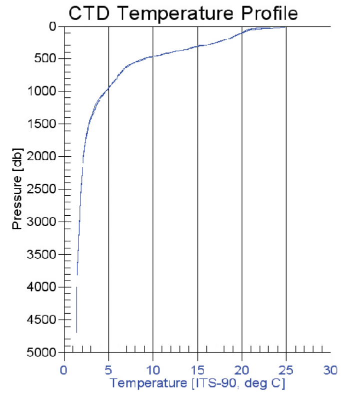
Comparison of Corrected Data to Winkler Oxygen Values

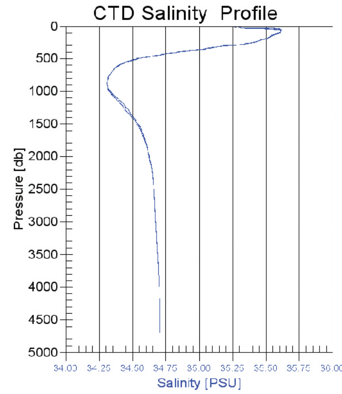
The figure at right shows the data set in the top plot hysteresis corrected and compared to oxygen concentration determined from Winkler titrations. Note the collapse of the oxygen trace to a common curve. Features in the down and up profile are well reproduced and corroborated by oxygen measurements from water samples.



Data Correction of a Profile from the Pacific Ocean

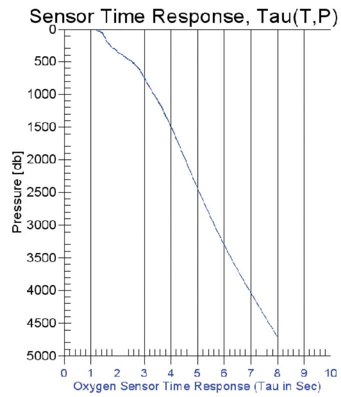
This profile was collected in Winter 2005. It was chosen because it exceeds 4500 decibars, has a wide temperature range, and shows little hydrographic variation between down and up casts.

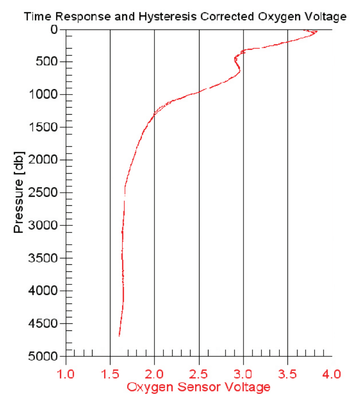




Correction for Sensor Time Response

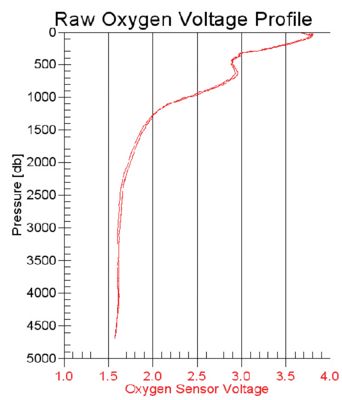
The change in sensor time constant or Tau during a profile is shown on the left. As discussed previously, the time constant of the SBE 43 is influenced by temperature and pressure. The plot on the far right is the data shown previously after sensor response sharpening.

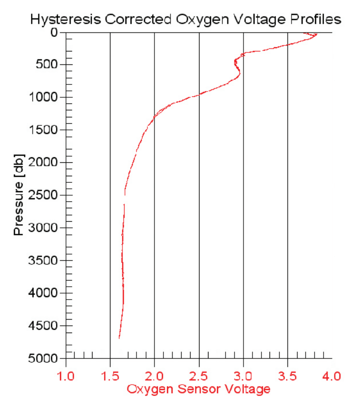




Correction of Hysteresis in Oxygen Voltage

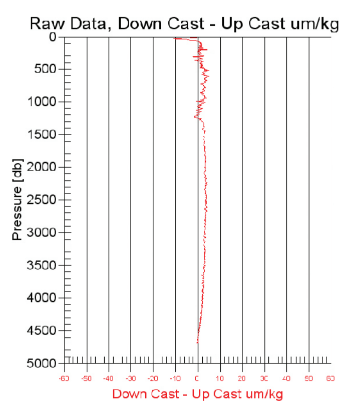
Hysteresis in the oxygen voltage profile is corrected before extracting data used for comparison with Winkler determined oxygen concentrations.

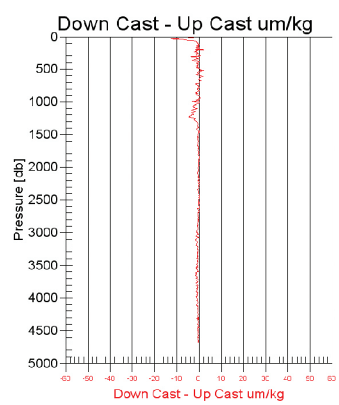




Comparison of Down and Up Cast

Oxygen concentration was calculated using coefficients derived from Winkler titrations of discrete samples collected with each cast. After oxygen concentration was calculated, data was binned on a 5-decibar interval and the difference was calculated for each pressure interval.





References and Acknowledgments

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Garcia and Gordon (1992) "Oxygen solubility in seawater: Better fitting equations", Limnology & Oceanography, vol 37(6), p1307-1312.
Atkinson, M.J., F.I.M. Thomas and N. Larson (1996) "Effects of Pressure on Oxygen Sensors", J. Atmospheric and Oceanic Technology, vol 13(6), p1267-1274.

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