Field Calibration of a Microhole Potentiostatic Oxygen Sensor for Oceanic CTDs

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(Manuscript received 26 January 1994, in final form 11 August 1994)

ABSTRACT

A new type of oxygen sensor for use on oceanic profiling CTDs has a response time that ranges from 0.4 to 0.7 s, depending on temperature. This oxygen (O_2) sensor was calibrated in the field against O_2 concentrations that were determined from Winkler titrations of Niskin-bottle water samples. Calibration coefficients were obtained from single casts and composite casts. When casts were calibrated separately, the mean error in predicting O_2 concentrations was 1.22 ± 0.72 μM O_2, n = 19 casts, and was not significantly different from the error between Niskin-bottle samples, which was 1.01 ± 2.33 μM O_2, n = 33 triplicate or duplicate bottles. When casts were combined into a composite cast for an entire cruise, however, the mean error in the calibrations increased to 5.03 ± 4.06 μM O_2, n = 19 casts. These results also indicate that only three Niskin bottles on a cast are required to obtain an error of 1.0 μM in predicted oxygen. For routine use, we recommend calibrating each cast separately using either three or four measured O_2 concentrations to obtain calibration coefficients.

1. Introduction

A new type of oxygen sensor for use on profiling CTDs, a microhole potentiostatic oxygen sensor, has been developed and field tested (Atkinson et al. 1995a). This sensor has no membrane, uses seawater as an electrolyte, and employs three electrodes: an anode, a cathode, and an Ag/AgCl reference. The cathode is an array of 1000 carbon fibers that are electroplated with platinum and recessed 50 μm within an epoxy matrix. The pressure effect on the output of the microhole sensor is small, near 0.7% per 1000 m (Atkinson et al. 1995b). In its present design, the microhole oxygen sensor has relatively fast response characteristics. The response term τ for this sensor ranges from 0.4 to 0.7 s over temperatures ranging from 1° to 21°C. In contrast, a Beckman membrane oxygen sensor commonly used on CTDs has a response term that ranges from 4 to 7 s over a similar temperature range (Thomas et al. 1995).

It is common for oceanographers to combine all casts taken on a cruise into a composite cast to obtain calibration coefficients for oxygen sensors. The use of a composite cast may create errors in predicting O_2 that depend on the drift and stability characteristics of individual oxygen sensors. The microhole sensor has a characteristic long-term drift. Therefore, creating composite casts for calibration of the sensor may produce significant calibration errors. In this paper, we quantify the error in predicting O_2 with the microhole sensor. We compare the error in predicting O_2 when casts are calibrated separately with the error obtained when all the casts on a cruise are combined into a composite cast for calibration. We also ascertain how many Niskin bottles are required on a cast to obtain good calibrations by using subsets of Niskin bottles for calibration. In addition, we compare the drift characteristics and stability of the microhole sensor for four cruises.

2. Methods

To calibrate the microhole sensor with measured O_2 concentrations, Niskin-bottle samples were taken on oceanic casts, and the O_2 concentration in them was determined by Winkler titration (Carpenter 1965). A Metrohm dosimat automatic titration system, in conjunction with a Sensorex redox probe, was used to determine the redox end point of the titration. Using this technique, the analytical error within a Niskin bottle is 0.1% of saturation, or about 0.2 μM O_2 (Winn et al. 1991). The number of Niskin-bottle samples taken per cast ranged from 13 to 23 bottles.

The casts were done at the World Ocean Circulation Experiment (WOCE)-GOFS Hawaii Ocean Times Series (HOTS) (Chiswell et al. 1990) station 100 km north of Oahu, Hawaii (Station Aloha, 22°45′N,

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158°W), and from a station near Kahe Point, Oahu (21°20.6′N, 158°16.4′W). The casts used were from HOTS cruises 31, 32, 34, and 35 (October 1991, December 1991, February 1992, and March 1992, respectively). Casts used for calibration were those casts in which O_2 concentrations were measured by both CTD sensors and Niskin-bottle samples. These included cruise 31, Kahe Point cast 1, Station Aloha casts 1, 2, and 3; cruise 32, Kahe Point cast 1, Station Aloha casts 1, 2, 4, and 16; cruise 34, Kahe Point cast 1, Station Aloha casts 4, 14, and 17; cruise 35, Kahe Point cast 1, Station Aloha casts 1, 6, 7, and 12, transect station 3, cast 1. These casts are either from the surface to 1000-m depth (shallow casts) or from the surface to near 4600 m (deep casts).

The microhole sensor was mounted downstream from a temperature, conductivity, and membrane oxygen sensor on a Sea-Bird SBE-09 CTD. Temperature, pressure, and oxygen sensor data for calibrations were recorded when each Niskin bottle closed. The Niskin bottles were closed during the upcast after stopping at depth for at least 15 seconds. This is at least 20 times longer than the response term τ of the microhole sensor (Thomas et al. 1995).

The output of the microhole sensor was calibrated to O_2 concentration in the Niskin-bottle samples using a calibration procedure developed by Atkinson et al. (1995a). The output of the sensor is corrected for temperature and pressure and then calibrated to measured O_2 concentrations as follows. The output of the microhole oxygen sensor responds to temperature according to $\exp(-E/RT)$, where E is the activation energy of diffusion to the electrode surface (cal mol^{-1}), R is the gas constant (1.987 cal K^{-1} mol^{-1}), and T is temperature (K). Pressure affects the solubility and diffusivity of oxygen in the 50-μm-deep diffusion channels. The effects of pressure can be approximated using a typical equation for the effect of pressure on equilibrium reactions, $\exp(VP/R'T)$ (Atkinson et al. 1995b), where V is the pressure term coefficient (cm^3 mol^{-1}), P is pressure (db), and R' is the gas constant (831.47 cm^3 mol^{-1} db K^{-1}).

To calibrate the microhole sensor in situ, output i of the sensor in amps was adjusted for the in situ temperature and pressure as follows:

$$i' = i\left[\exp\left(\frac{-E}{RT}\right)\exp\left(\frac{VP}{R'T}\right)\right]^{-1}. \quad (1)$$

A linear regression of i' versus the measured O_2 concentrations from the Niskin-bottle samples was performed:

$$O_2 = bi' + a, \quad (2)$$

where O_2 is the concentration of oxygen (μM) from Winkler titration, b is the slope (μM A^{-1}), and a is the intercept (μM).

To determine the best calibration coefficients, values of E in Eq. (1) were iterated between 1000 and 15 000 in steps of 100. The best E was chosen as the E that gave the maximum r^2 for a linear fit to Eq. (2). The slope b and intercept a obtained using the best E were then used to calculate predicted O_2 concentrations from the output recorded when each Niskin bottle was tripped. In addition, for deep casts, values for the pressure term coefficient were iterated in steps of 1 between −10 and +10. The best E and V were chosen as the pair of values that gave the maximum r^2 for the linear fit of Eq. (2). The mean value of V that was calculated for deep casts (−1.6 cal^3 mol^{-1}) was used as V for the shallow casts. This mean value was used because the effect of pressure at depths up to 1000 m is less than 0.7%. This pressure effect is small compared to that of temperature over this depth range, which is approximately 47%. For shallow casts a relatively large range of values of V yield nearly the same r^2 for a fit to Eq. (2).

The above calibration procedure was done using all of the Niskin bottles available on a cast (13–23 measured O_2 concentrations). After the coefficients were obtained for a cast, a predicted O_2 concentration was calculated for each measured O_2 concentration using the coefficients and Eqs. (1) and (2). The error in predicting O_2 concentration for the cast was then calculated as the standard deviation of the differences between the predicted and measured O_2 concentrations for all the Niskin bottles on a cast.

This error in predicting O_2 concentration was then compared to the sampling error between Niskin bottles. The sampling error was determined by tripping two or three Niskin bottles at selected depths on six deep casts (HOTS cruise 32, station Aloha cast 16; HOTS cruise 34, station Aloha casts 14 and 17; HOTS cruise 35, station Aloha, cast 12 and cast 1 from a transect point 40 km north of station Aloha). The sampling error was then calculated as the standard deviation of the mean of the measured O_2 concentrations for triplicate or duplicate bottles.

The effect that the number of Niskin bottles, or measured O_2 concentrations used for calibration, had on the error in predicting O_2 concentration was also assessed. This was done by using either 3, 4, 8, or 13 measured O_2 concentrations to obtain the calibration coefficients in Eqs. (1) and (2). Three measured O_2 concentrations were used on shallow casts and four were used on deep casts because three O_2 concentrations are the minimum required to determine the three unknown parameters for shallow casts. Four concentrations are the minimum for the four unknown parameters on deep casts. The coefficients obtained using the subsamples of measured O_2 concentrations were then used to calculate a predicted O_2 concentration for each Niskin bottle taken on a cast (13–23 Niskin bottles). The error in the prediction was calculated as the standard deviation of the mean difference between the predicted and measured O_2 concentrations for all Niskin bottles on a cast.

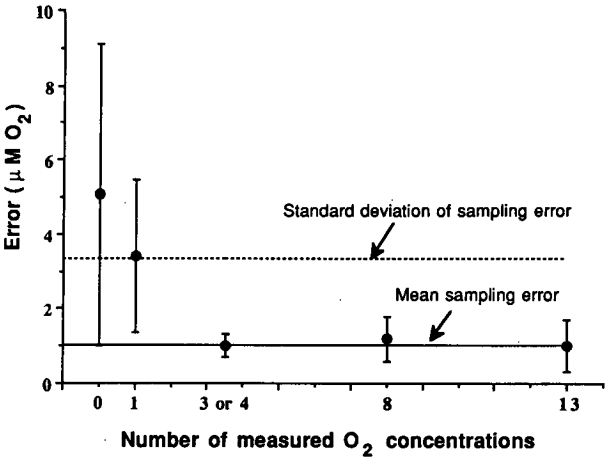

FIG. 1. Mean and standard deviation (error bars) of the errors in predicted O_2 concentration (standard deviation of predicted O_2 minus measured O_2 concentration) using a composite cast (0), 1, 3 (or 4), 8, or 13 Niskin-bottle O_2 concentrations for calibration of 19 HOTS casts. The point indicated at 3.5 bottles includes shallow casts calibrated with 3 bottles and deep casts calibrated with 4 bottles. The sampling error is the error between duplicate and triplicate Niskin bottles.

Calibration coefficients were also obtained by combining all of the casts in a cruise into a single composite cast. All of the measured O_2 concentrations on these casts were used with Eqs. (1) and (2) to obtain calibration coefficients. These coefficients were then used to calculate a predicted O_2 concentration for each measured O_2 concentration on a cast. The error of the prediction was calculated as described above.

To determine how handling of the sensor affected sensor drift and stability, the sensor was stored in seawater and power was applied to the sensor continuously throughout the cruise on HOTS cruise 31. On subsequent cruises (HOTS 32, 34, and 35), the sensor was stored in distilled water and power was applied to the sensor at different times prior to the beginning of each cast. The rate of drift throughout each cruise was determined by recording the output of the sensor in the surface water at the beginning of each cast (initial output). This gives an estimate of the drift through time because the oxygen concentration at the surface varies little throughout a cruise at this site.

Relationships between the ln slope b from Eq. (2) and the activation energy E from Eq. (1), obtained from the calibration of the 19 casts, were then determined to quantify the stability of the sensor on each cruise. If the activation energy of a sensor changes slightly, the calculated slope b must change. A stable sensor has a linear relationship between ln slope b and activation energy E over a number of casts. Changes in this linear relationship indicate that the diffusive barrier has changed, such as may occur with fouling of the diffusion channels. This stability was compared among the cruises.

3. Results

The mean error in the prediction of O_2 concentration for all 19 HOTS casts, which were calibrated separately, was not significantly different from the sampling error between Niskin bottles (mean error in predicted O_2: 1.22 ± 0.72 μM O_2, $n = 19$ casts; mean Niskin-bottle error: 1.01 ± 2.33 μM O_2, $n = 33$ triplicate or duplicate bottles; t test, $t = 0.39$, $df = 50$). The r^2 of the regressions for these calibrations ranged from 0.9981 to 1.0000 with a mean r^2 of 0.9995 (SD = 0.0005, $n = 19$). The mean activation energy E for the casts was 4665 ± 207 cal mol^{-1} (range is 4000–4900 cal mol^{-1}, $n = 19$). Slopes ranged from 0.78×10^5 to 2.88×10^5 μM O_2 A^{-1}, with a mean of $1.17 \times 10^5 \pm 0.47 \times 10^5$ μM O_2 A^{-1} ($n = 19$). Intercepts ranged from -3.6 to 5.6 μM O_2 (mean is -1.0 ± 2.1, $n = 19$). The mean of the calculated pressure term V for the "deep" casts was -1.6 ± 0.5 cm^3 mol^{-1} ($n = 8$).

Using just three or four measured O_2 concentrations for calibration resulted in mean errors in the prediction of O_2 concentration for the 19 casts that were within the standard deviation of the error between Niskin-bottle samples (Fig. 1). Using 8 or 13 bottles did not improve these errors (Table 1, Fig. 1). Combining casts into a composite cast for each cruise (termed zero bottle calibrations in Table 1 and Fig. 1) increased the mean error in predicting O_2 concentration. Examples of a shallow cast calibrated with three bottles and a deep cast calibrated with four bottles are shown in Fig. 2.

When the sensor was kept powered throughout a 6-day cruise, the output of the sensor at the water surface decayed at a rate of 0.37% per hour (Fig. 3, cruise 31).

TABLE 1. Mean plus/minus standard deviation of the error in predicting O_2 concentration (μMO_2) combining all the casts in a cruise into a composite cast (0) or using 3 (shallow casts), 4 (deep casts), 8, 13, or more than 13 Niskin-bottle oxygen concentrations for calibration.

	Number of Niskin bottles					
Cruise	0	3 or 4	8	13	13–23	n
31	4.6 ± 0.5	0.8 ± 0.4	1.4 ± 0.8	0.9 ± 0.8	0.8 ± 0.2	4
32	2.3 ± 1.7	1.0 ± 0.3	0.8 ± 0.3	1.1 ± 1.0	1.8 ± 1.1	5
34	10.8 ± 5.4	1.2 ± 0.3	1.7 ± 0.9	0.8 ± 0.4	1.0 ± 0.4	4
35	3.8 ± 1.7	1.1 ± 0.5	1.1 ± 0.7	1.2 ± 0.9	1.3 ± 0.5	6
All cruises	5.1 ± 4.1	1.0 ± 0.3	1.2 ± 0.6	1.0 ± 0.7	1.2 ± 0.7	19

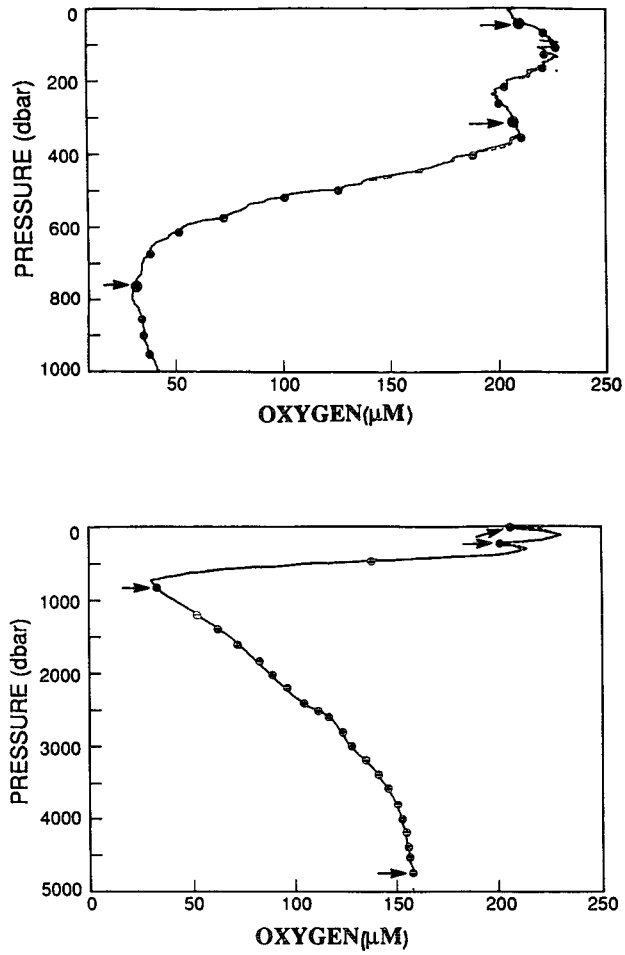

FIG. 2. Calibrated CTD output of upcasts (dashed line) and downcasts (solid line) on (a) a shallow cast using three measured O_2 concentrations and (b) a deep cast using four measured O_2 concentrations to obtain calibration coefficients. Both casts are from HOTS station Aloha (22°45'N, 158°W). The shallow cast is HOTS cruise 31 cast 2. The deep cast is HOTS cruise 31 cast 1. The oxygen sensor output was sampled at 24 Hz then averaged to 2 Hz. Dots indicate measured O_2 concentrations on the cast. Arrows indicate the measured O_2 concentrations used for calibration.

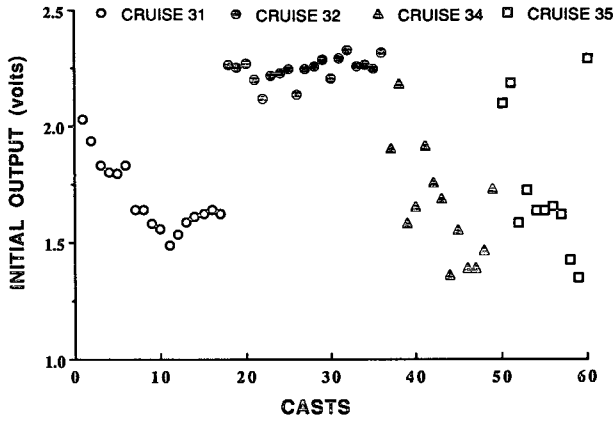

FIG. 3. The output of the microhole sensor at the surface (initial output) for each cast on cruise 31, 32, 34, and 35. On cruise 31 power was applied to the sensor for the entire cruise. On cruise 32 the power was interrupted before each cast. On cruise 34 and 35 the power was interrupted before some casts and not others.

When the sensor was turned off between each cast, the rate of decay dropped to 0.09% per hour (Fig. 3, cruise 32). When the sensor was turned off intermittently (power was off before some casts but left on between others) during the cruise, the sensor output decayed 0.52% and 0.53% per hour (Fig. 3 cruise 34 and 35). The relationship between $\ln(b)$ [the slope from Eq. (2)] and activation energy [E from Eq. (1)] for each cruise was linear except for cruise 34. However, the slope of this linear relationship between b and E changed between cruises (Fig. 4, Table 2).

4. Discussion

The best calibration results for the microhole potentiostatic sensor are obtained when casts are calibrated separately using at least three or four measured O_2 concentrations for calibration. It is probable that errors in predicted O_2 are greatest for composite casts because of sensor drift and instability. For example, the drift in the output was the smallest for cruise 32 (Fig. 3). This cruise had the lowest mean error in the prediction of O_2 concentration for the composite calibrations (Table 1). The relationship between $\ln(b)$ [the slope from Eq. (2)] and activation energy [E, from Eq. (1)] was not linear (Table 2, Fig. 4) for cruise 34. This cruise had the greatest mean calibration error of the four cruises when casts were combined into composite casts (Table 1).

Using one bottle on a cast to calculate an activation energy E for the cast alleviates some of the error in predicting O_2 (Fig. 1). However, when three or more measured O_2 concentrations are used to calibrate each cast separately, drift and instability have no detectable effect on the error in predicted O_2 concentration. For example, output of the sensor was drifting throughout cruise 31, 34, and 35 but was not drifting on cruise 32 (Fig. 3). However, when calibrations were performed on individual casts, the mean error in predicting O_2 on cruise 32 was not lower than the error on the other three cruises (Table 1). Similarly, the mean error for

TABLE 2. Linear regression results for the relationship between $\ln(b)$ versus E, where b is the slope in Eq. (2), and E is the activation energy E from Eq. (1). These are data from calibrations using all Niskin bottles on each cast. Slope is in units of 10^{-3} mol cal^{-1}.

Cruise	Intercept	Slope	r^2	n
31	17	−1.2	0.88	4
32	19	−1.7	1.00	5
34	13	−0.3	0.10	4
35	20	−1.9	0.97	6

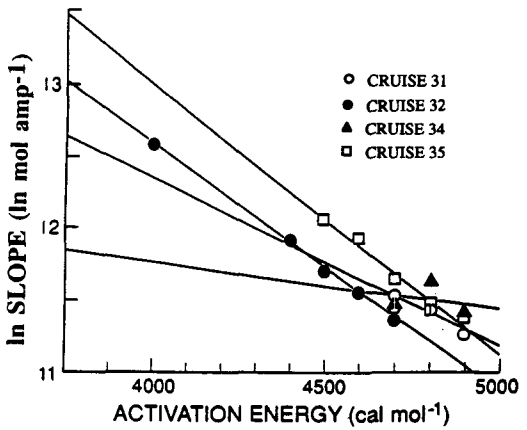

FIG. 4. The regression of activation energy E and $\ln(b)$ from Eqs. (1) and (2) for 19 casts calibrated on four HOTS cruises. The activation energies and slopes are from calibrations using all available Niskin-bottle O_2 concentrations for calibration. The y axis is unitless because it is divided by micromoles per amp.

individual casts for cruise 34 did not exceed the mean error of calibrations for the other cruises even though the relationship between $\ln(b)$ [from Eq. (2)] and activation energy E [from Eq. (1)] was not linear throughout cruise 34 (Table 2, Fig. 4). Therefore, if casts are calibrated separately, drift and stability characteristics of microhole sensors do not preclude the attainment of excellent O_2 calibrations.

5. Conclusions

Oceanic casts using a microhole potentiostatic sensor should be calibrated separately with three Niskin-bottle O_2 concentrations on each cast. These bottles should be placed in the water column so that the maximum spread in temperature and oxygen is obtained on a cast. If a cast is deeper than 1000 m, an additional bottle should be placed at the deepest part of the cast to obtain pressure term coefficients. If this sampling procedure and the calibration procedure outlined here and in Atkinson et al. (1995a) are followed, no special handling of the sensor is required to alleviate sensor drift.

Acknowledgments. This research was funded by NSF Oceanographic Technology, OCE 89-13258 and OCE 92-17590 to M. J. Atkinson. We wish to acknowledge the assistance provided by the HOTS program including Dr. Dave Karl, Dr. Roger Lukas, Richard Muller, and Dale Hebert. This is HIMB Contribution No. 957 and SOEST Contribution No. 3785.

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