A Gas Tension Device with Response Times of Minutes

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(Manuscript received 13 June 2005, in final form 18 April 2006)

ABSTRACT
The development and testing of a new, fast response, profiling gas tension device (GTD) that measures total dissolved air pressure is presented. The new GTD equilibrates a sample volume of air using a newly developed (patent pending) tubular silicone polydimethylsiloxane (PDMS) membrane interface. The membrane interface is long, flexible, tubular, and is contained within a seawater-flushed hose. The membrane interface communicates pressure to a precise pressure gauge using low dead-volume stainless steel tubing. The pressure sensor and associated electronics are located remotely from the membrane interface. The new GTD has an operating depth in seawater of 0–300 m. The sensor was integrated onto an upper-ocean mixed layer, neutrally buoyant float, and used in air–sea gas exchange studies. Results of laboratory and pressure tank tests are presented to show response characteristics of the device. A significant hydrostatic response of the instrument was observed over the depth range of 0–9 m, and explained in terms of expulsion (or absorption) of dissolved air from the membrane after it is compressed (or decompressed). This undesirable feature of the device is unavoidable since a large exposed surface area of membrane is required to provide a rapid response. The minimum isothermal response time varies from (2 ± 1) min near the sea surface to (8 ± 2) min at 60-m depth. Results of field tests, performed in Puget Sound, Washington, during the summer of 2004, are reported, and include preliminary comparisons with mass-spectrometric analysis of in situ water samples analyzed for dissolved N₂ and Ar. These tests served as preparations for deployment of two floats by aircraft into the advancing path of Hurricane Frances during September 2004 in the northwest Atlantic. The sensors performed remarkably well in the field. A model of the dynamical response of the GTD to changing hydrostatic pressure that accounts for membrane compressibility effects is presented. The model is used to correct the transient response of the GTD to enable a more precise measurement of gas tension when the float was profiling in the upper-ocean mixed layer beneath the hurricane.

1. Introduction

Dissolved gases in the ocean play important roles in the biogeochemical cycles of the elements carbon, oxygen, and nitrogen. Study of air–sea gas fluxes and dissolved gas transformations in the upper ocean, over a natural range of environmental conditions, requires reliable, accurate, and long-term stable dissolved gas sensors for use on moorings, drifters, and profilers. Several commercially available O₂ sensors have recently shown promise of providing reliable measurements in seawater over time scales of several months. This opens up the possibility of measuring dissolved O₂ on autonomous platforms in the open ocean (e.g., Joos et al. 2003; Körtzinger et al. 2004, 2005), as is presently done for...
water temperature and salinity. However, measurement of bioactive gases, such as Ar and N₂, rely on analysis using gas chromatographic or mass-spectrometric techniques. In the case of dissolved N₂, an additional analysis technique relies on simultaneous measurements of gas tension and dissolved O₂ (McNeil et al. 1995; McNeil et al. 2005).

Gas tension is a measure of the sum of the partial pressures, or more strictly fugacities, of all dissolved gases in seawater. Gas tension, therefore, is the total dissolved air pressure. It is measured using a gas tension device (GTD), an instrument that measures, in situ, the pressure of an equilibrated air sample (McNeil et al. 1995). Equilibration of the sample is achieved using a semipermeable membrane that allows the exchange of gases, including water vapor, but prevents the exchange of liquid water. Since the oceans are in approximate equilibrium with the atmosphere, the gas tension of seawater is typically about one standard atmosphere of pressure. The GTD uses a high-precision, long-term stable, barometric pressure sensor. Pressure sensors can have a repeatable accuracy of ±0.01%, a precision of 0.000 01%, and a calibration drift rate that is better than 0.01% yr⁻¹.

A major limitation to the interpretation of gas tension is that it does not provide discrimination of the dissolved gases. Noting that dissolved N₂, O₂, and water vapor typically compose more than 99% of the gas tension measurement, simultaneous measurements of water temperature, salinity, and dissolved O₂ can be used to calculate dissolved N₂. McNeil et al. (1995) described how the partial pressure of dissolved N₂ could be calculated from a measurement of gas tension pᵣ and dissolved O₂, using the following equation:

\[ p_{N₂} = pᵣ - \sum_{i \neq N₂} p_i = pᵣ - \sum_{i \neq N₂} (c_i/S_i), \]  

where \( p_i \) represents the partial pressure of any individual dissolved gas, denoted by \( i \) (i.e., \( i = O₂, H₂O, Ar, CO₂, Ne, etc. \)), \( c_i \) represents the dissolved gas concentration, and \( S_i \) is a gas specific solubility coefficient that depends on seawater temperature \( T \) and salinity \( s \). The relative humidity of the GTD air sample is assumed to be 100%, since the polydimethylsiloxane (PDMS) membrane used in the GTD is highly permeable to water vapor (Pauly 1999). A conservative error for \( c_{N₂} \) of ±0.7% was reported, based on the following: N₂ and O₂ solubility relationships of Weiss (1970); measurements of dissolved O₂ with accuracy of ±0.5%, typically by Winkler titration; \( p_{H₂O} \) determined from standard seawater temperature and salinity relationships, with an accuracy of ±0.01%, or better; and, the assumption that Ar was 100% saturated with respect to the atmosphere, an assumption that contributes an error of no more than ±0.05% for typical oceanic conditions. Gas saturation levels are expressed with respect to standard values of the molar fraction of the gas in dry tropospheric air (Glueckauf 1951).

Emerson et al. (2002) compared GTD measurements with discrete water samples, analyzed for dissolved N₂ and Ar by mass spectrometry, and O₂ by Winkler titration, over a 2-yr period at the Hawaii Ocean Time Series site. They found that it was possible to remotely measure the time history of \( p_{N₂} \) and \( p_{O₂} \), to better than ±0.5%; for this work, an improved N₂ solubility relationship of Emerson et al. (1999) was used, and O₂ solubility was determined using the relationships of Garcia and Gordon (1992), with a reported accuracy of ±0.12%. In recent work, Hamme and Emerson (2004) reported improved solubility relationships for N₂ and Ar with errors of ±0.14% and ±0.13%, respectively. With very careful calibrations against shipboard Winkler titrations, \( c_{O₂} \) can be determined to within ±0.2%. McNeil et al. (2005) reported a slight improvement to the N₂ calculation procedure that involved setting the Ar saturation level to the calculated N₂ saturation level; this assumption is justified when temperature changes dominate the gas saturation levels. Using these new relationships and assumptions, the minimum uncertainty in \( c_{N₂} \) is estimated, using Eq. (1), to be ±0.25%.

Estimates of dissolved N₂ by the gas tension technique have been used in laboratory studies (Anderson and Johnson 1992; Bowyer and Woolf 2004), lake studies (McNeil et al. 2006a), coastal ocean studies (Farmer et al. 1993; McNeil et al. 2006b), and open-ocean studies (Emerson et al. 2002; Karl et al. 2003). To date, high precision GTDs have been used on moorings and drifting arrays, and for shipboard sampling. Here, the development of a new, fast response GTD intended for use in profiling applications is described. Section 2 describes the new sensor, and explains the reasoning behind the choices made in the design processes. Section 3 describes results from laboratory tests designed to define the response of the new GTD. Section 4 describes results from a coastal and an open-ocean experiment. Conclusions of this work are presented in section 5, along with various suggestions aimed at further improving sensor design.

2. The profiling GTD

There are many factors that need to be considered in the design of a GTD suitable for profiling applications. These include size, response time, thermal response, power consumption, hydrostatic response, and any potential that may exist for membrane bulging in super-
saturated waters or upon decompression from depth. In addition, for air deployable systems, the instrument needs to be shock resistant. The instrument described here was designed to satisfy all these requirements, to various degrees, with as few compromises as possible.

The original, unpumped GTD was designed for moored applications. It has a rather large, cylindrical pressure housing with an outside diameter of 11 cm (McNeil et al. 1995). This size was required to allow a flat membrane interface to be mounted on the end cap of the pressure housing. The larger the surface area of the membrane, and the thinner the membrane thickness, the faster the GTD would equilibrate the internal sample volume of air measured by the pressure sensor. The surface area of membrane exposed to seawater in the original GTD was approximately 16 cm$^2$. The equilibration time of the instrument also depended on the water turbulence levels, since stronger turbulence decreases the diffusive boundary layer in the water adjacent to the membrane. Response times in surface water varied from 40 min in turbulent waters, to several hours in poorly mixed waters. The system was adapted for use in shipboard sampling by the addition of a flow-through plenum (McNeil et al. 2005). The plenum has a built-in, waterside, stainless steel screen that prevents the membrane from bulging in supersaturated waters, and also serves as protection for the membrane. The shipboard GTD is typically installed inside a 15-L container that is flushed with seawater from the bow intake at a rate of 3–15 L min$^{-1}$. A small 25-W bilge pump, installed in the sampling container, recirculates the seawater through the GTD plenum and jets it at the membrane surface using a baffle. This configuration enables underway sampling of gas tension with typical response times of (11 ± 2) min at 20°C. This is equivalent to a spatial sampling resolution of 3.5 km for a ship moving at a speed of 5 m s$^{-1}$ (approximately 10 kt).

a. A separate pressure housing and membrane interface

The profiling GTD, described here, uses a separate pressure housing and membrane interface. These separate components are connected using low dead-volume stainless steel tubing. Figure 1 shows a schematic of the new profiling GTD, and Fig. 2 shows how the new GTD was integrated onto D’Asaro’s [2003, see description of the mixed layer float (MLF-II)] neutrally buoyant float. The pressure housing, which contains the pressure sensor and electronics, has an outside diameter of 6.5 cm. The operating depth of the new instrument is 0–300 m in seawater. The membrane interface is tubular in shape and is contained within a hose that is pumped with seawater (patent pending; Johnson and McNeil 2006). Pumping reduces the waterside diffusive boundary layer adjacent to the membrane, thereby reducing the response time of the sensor, while keeping the response time of the instrument constant at any given depth. An Sea-Bird Electronics, Inc. (SBE) model 5T seawater pump was used. This pump can be adjusted for flushing rate and power drain over a range of approximately 1–7 W. For applications that do not require a rapid and constant response time, the hose and pump could be eliminated. If the GTD is to be integrated with a platform that has sufficient internal space, and a means to allow a bulkhead connector, then only the membrane interface need be waterside. This feature of the new design significantly reduces the overall size of the sensor and provides flexibility when integrating the GTD with different platforms.

The membrane interface was manufactured by Pro-Oceanus Systems, Inc. (Halifax, Novia Scotia, Canada).
The total dead volume of the GTD is distributed among four components: 1) the pressure sensor bellows, 2) the interconnecting tubes and fittings that connect the pressure sensor to the tubular membrane interface, 3) the inner core of the membrane interface, and 4) the free volume of the membrane available for dissolution of gases. These four components of the total dead volume are referred to generally by the subscript \( k \), or specifically by the subscripts \( b, t, c, \) and \( m \), which denote the bellows, tubes, core, and membrane, respectively. For any particular component \( k \) we can write

\[
p_k = \chi_k p_k,
\]

where \( p' \) is the partial pressure of a particular gas denoted by \( i \), \( P \) is the total air pressure, and \( \chi' \) is molar fraction of the gas. Using Dalton’s law this can be re-written as

\[
P_k = \sum_i p'_i \chi_k,
\]

where

\[
\sum_i \chi_k = 1.
\]

For an individual ideal gas within the system, it follows that:

\[
p'_i V_k = n'_i RT_k,
\]

where \( n \) is the number of moles of the gas, \( T \) is the temperature, \( V \) is the volume, and \( R \) is the gas constant. Hence, the total number of moles \( N \) of a particular gas in the system is

\[
N'_i = \sum_k V_k(\chi'_i p_k)/(RT_k).
\]

The total moles of all gases are given by

\[
N_T = \sum_i N'_i = \sum_i \sum_k V_k(\chi'_i p_k)/(RT_k),
\]

and the total dead volume of the GTD is

\[
V_T = \sum_k V_k = V_b + V_t + V_c + V_m.
\]

By assuming that no pressure gradients exist between the various components of the system, the total pressure of the GTD sample volume is

\[
P_T = \sum_i \frac{N'_T}{\sum_k (V_k \chi'_i)/(RT_k)}.
\]

and the pressure \( P_T \) is measured by the GTD pressure sensor. Note that the fractional composition and tem-
perature of the air in the pressure sensor bellows need not be the same as that of the air in the membrane interface. The long, thin, interconnecting tubes, allow pressure gradient–driven exchange of gases, but severely limit exchange by diffusion. The inside diameter of the tubes is of the order of 0.1 mm and the length is of the order of 10 cm, hence, diffusion can be considered to be one-dimensional with a time scale given by \( \bar{t} = (2D) \), where \( D \) is the tube length and \( D \) is the gas diffusivity. The diffusion time scale for \( N_2 \) is estimated to be 4.6 min using a typical value of \( D = 0.18 \text{ cm}^2 \text{s}^{-1} \) for \( N_2 \) in air. For the GTD to operate properly, the partial pressure of any particular gas in the seawater, membrane, and membrane interface core must be equal (i.e., these three components must be equilibrated by diffusion). Note that the change in dead volume of the pressure sensor bellows over a typical operating pressure (i.e., \( \partial V_m/\partial P_m \)) can be neglected.

The thermal response of the GTD, in the case of no-gas transfer across the membrane (i.e., constant \( N_T \)), can be assessed by assuming that any component of the total dead volume, subject to an initial step change in temperature \( \Delta T_{ko} \), will relax to thermal equilibrium with the seawater according to

\[
\Delta T_b(t) = \Delta T_{ko} \exp(-t/\Phi_k),
\]

where \( \Phi_k \) is the thermal response time of the component \( k \), and \( t \) is time. Temperature variability of an individual component will affect \( P_m \) according to Eqs. (8) and (9). When the GTD is used in profiling applications, changes in \( P_m \) can be expected. These are associated with loss or gain of gas across the membrane (variable \( N_T \)) and temperature fluctuations of individual components; the latter effect will be relatively small when the GTD is used in upper-ocean mixed layer studies, such as those used in the Hurricane Frances deployment, as described below.

The new GTD can be considered to be isothermal (i.e., \( T_b = T_s = T_c = T_m = T_o \)) if the water temperature fluctuations vary slowly over the time scale of the largest thermal response time constant of the system, which, as shown below, is \( \Phi_b \).

c. Membrane interface response characteristics

The response of the new tubular membrane interface to changes in hydrostatic pressure, heat transfer, and gas transfer are now discussed.

1) Compressibility

The membrane material, PDMS, is an elastic polymer that can be stretched to around 160% of its unstretched surface area before ripping. It is much more soluble to \( O_2 \) and \( N_2 \) than, for example, seawater. As the membrane is deformed and compressed, air dissolved in the membrane material is also compressed. Note that the dissolved air in the membrane is the only compressible component of the total sample volume of gases available to the pressure sensor in the GTD. When the instrument is subject to a rapid increase in hydrostatic pressure, air dissolved in the membrane escapes either to the water phase or to the core of the membrane interface. Because the membrane-to-water exchange rate is lower than the membrane-to-air exchange rate, due to differences in solubility and thickness of the diffusion boundary layers, the compressed air escapes preferentially to the core of the membrane interface. This then raises the GTD reading. Gases are exchanged among the various components of the total dead volume to eliminate pressure gradients. If the resulting sample volume pressure is higher (or lower) than gas tension, the GTD will equilibrate with the water by losing gas to (or gaining gas from) the water. Because the membrane’s permeability was initially reduced, due to the step increase in hydrostatic pressure, the membrane will be less permeable to gases after the membrane is compressed. The GTD will equilibrate more slowly, under the condition of increased hydrostatic pressure.

To model the dynamical response of the GTD to hydrostatic pressure changes, it is assumed that most of the air dissolved in the membrane occupies a compressible volume \( V_m \). It will be shown (section 4b) that this compressible volume is described adequately by a simple first-order Taylor series expansion as follows:

\[
V_m(p) = V_{m_0} + V_{m_2} + \rho \left[ \frac{\partial V_m}{\partial P_m} \right]_{P=0}. \tag{11}
\]

where \( \rho \) is the hydrostatic pressure acting on the membrane at depth \( z \) in the water column. We define \( V_{m_0} \) to be the volume of gas dissolved in the membrane that will be expelled from the membrane when it is fully compressed. In describing the operation of the new GTD, this volume can be considered to contribute to the total dead volume. Unlike all of the other contributions, however, this contribution is compressible. Note that the void volume of the membrane reduces to the solubility of the fully compressed membrane material, \( V_{m_2} \), as \( p \to \infty \). The membrane’s isothermal bulk modulus \( K_m \) at temperature \( T_o \) and isothermal compressibility \( \beta_m \) is then given by

\[
K_m = \frac{1}{\beta_m} = -V_{m_0} \left. \frac{\partial P}{\partial V_{m_2}} \right|_{P=0, T=T_o}. \tag{12}
\]
The compressibility of the membrane is the reciprocal of the bulk modulus. For the new GTD, \( V_{mc} \) is a significant fraction of the system’s total dead volume \( V_T \). It will be shown that for a typical membrane interface, \( V_{mc}/V_T \) is approximately 10%. This feature of the new GTD is undesirable, but it is also unavoidable since a large surface area of membrane is required to provide a small time response. Note, however, that if a shorter membrane interface is used, the time response can be compromised in favor of a less hydrostatically sensitive GTD.

Equations (11) and (12) can be combined to give

\[
V_m(p) = V_{mc} + V_{mo} \left( 1 - \frac{p}{p_{mc}} \right) \quad \text{for} \quad 0 \leq p \leq p_{mc},
\]

where \( p_{mc} = K_{mo} \) is the characteristic hydrostatic pressure at which the membrane is fully compressed and will not, upon further hydrostatic compression, expel more gas.

For rapid hydrostatic compression of the new GTD to a hydrostatic pressure \( p \), with no heat or gas transfer to or from the system, and all components of the GTD isothermal and at temperature \( T_o \), Eqs. (8) and (13) can be used to construct an expression for the GTD response in the following form:

\[
P_s(p) = \frac{(n_b + n_t + n_s + n_m)RT_o}{V_b + V_t + V_c + V_{mc} \left( 1 - \frac{p}{p_{mc}} \right) + V_{mc}} \quad \text{for} \quad 0 \leq p \leq p_{mc},
\]

where the total moles of gas in the GTD-sensing volume [see Eq. (7)] are constant. Note that as \( p \) increases, \( P_s \) also increases. Laboratory tests will be performed to determine \( p_{mc} \) experimentally using Eq. (14). More generally, however, one can expect \( K_{mo} \) to depend on \( p \).

In this case, the effective bulk modulus of the membrane will be determined from the GTD measurement using the following equation:

\[
K_{mo}(p) = \frac{1}{\beta_{mc}(p)} = \frac{P_{so}}{\partial p/\partial P_s},
\]

where \( P_s \) is the measured GTD pressure and \( P_{so} \) is the mean measured pressure. The effective compressibility of the membrane is \( \beta_{mc} \).

2) Thermal response of the membrane interface

The thermal equilibration time scale \( \Phi_m \) of the membrane material is estimated to be

\[
\Phi_m = (h^2 p_m c_m)/k_m,
\]

where \( h = r_2 - r_1 \) (see Fig. 1b) is the membrane thickness, \( p_m \) is the membrane density, \( c_m \) is the membrane specific heat capacity, and \( k_m \) is the membrane thermal conductivity. Using typical values for the membrane of \( h = 1.2 \times 10^{-4} \text{ m}, p_m = 1030 \text{ kg m}^{-3}, c_m = 1100 \text{ J kg}^{-1} \text{ K}^{-1}, \) and \( k_m = 0.18 \text{ W m}^{-1} \text{ K}^{-1} \), we estimate \( \Phi_m = 0.1 \text{ s} \). Thus, the dissolved air in the membrane material can be expected to be in thermal equilibrium with the water at all times. The air in the core of the membrane interface, however, will respond much more slowly to temperature fluctuations in the water. This is because the inner core of the membrane is more isolated from the water, and the rigid membrane support represents a significant thermal mass. The thermal equilibration time scale of the membrane support depends on the rate of heat transfer through the membrane, which depends on the flushing rate of the membrane. This thermal response time can be determined experimentally. Note that since the interconnecting tubes of the GTD are stainless steel, it is assumed that the air in the tubes is in thermal equilibrium with the water at all times.

If the water temperature changes faster than the response time of the membrane interface, the GTD will register a change in pressure according to the ideal gas law, in proportion to that fraction of the total dead volume that changes temperature [i.e., \( (V_m + V_c + V_s)/V_T \)]. The GTD pressure change \( \Delta P_s \) associated with a step change in water temperature \( \Delta T \) is

\[
\Delta P_s = P_{so} \left( \frac{V_m + V_c + V_s}{V_T} \right) \frac{\Delta T}{T_o},
\]

where \( P_{so} \) and \( T_o \) are the mean pressure and temperature, respectively. If a GTD is profiled through the thermocline, changes in temperature will create significant internal pressure transients that must fully equilibrate before the GTD can properly measure gas tension. For example, if \( (V_m + V_c + V_s)/V_T = 0.5 \), \( \Delta T = 1 \text{ K}, T_o = 300 \text{ K}, \) and \( P_{so} = 1000 \text{ mbar}, \) then using Eq. (17), it is found that \( \Delta P_s = 1.7 \text{ mbar}. \) The GTD must be held at this depth to allow the GTD to equilibrate gases with the water before a gas tension measurement can be made. It is important to note that when a GTD is used within the upper-ocean mixed layer, thermal effects on the GTD are usually insignificant, since maximum temperature changes are typically of the order of 1° day \(^{-1} \).

3) Gas transfer response of the membrane interface

The transfer of gases across the membrane occurs by permeation. Gases are absorbed into, and adsorbed onto, the membrane material. The gases diffuse across
the membrane, then desorb into the water. A key physical property of the membrane material is its permeability $P_m$ which is defined as the product of the membrane’s solubility $S_m$ and diffusivity $D_m$ to a particular gas $i$. (For ease of reading, the use of the superscript $i$ will be discontinued.) We can expect $D_m$ to be temperature dependent, and follow an Arrhenius-type equation:

$$D_m = D_{mo}e^{-E_a/RT},$$

where $D_{mo}$ is a material constant and $E_a$ is the activation enthalpy for diffusion. A similar equation for $S_m$ is appropriate.

The steady-state transport of an individual gas across the air–membrane–water interface, at constant pressure and constant membrane permeability, is now described. It is assumed that no pressure gradients exist between the bellows, the connecting tubes, and the entire length of the membrane interface core [see Eq. (9)]. The mass transfer across the air phase boundary layer $J_a$ is

$$J_a = 2\pi r_1 k_a(p_a - p_1)/(RT),$$

where $r_1$ is the inside radius of the membrane material, $L$ is the length of the membrane, $k_a$ is the airside gas transfer rate, $p_a$ is the partial pressure of the gas in the membrane interface core (i.e., $p_a = \chi P_a$), and $p_1$ is the partial pressure of the gas at the air–membrane interface. The mass transfer across the membrane $J_m$ is

$$J_m = 2\pi r_2 L k_m S_m(p_1 - p_2),$$

where $p_2$ is the partial pressure of the gas at the outer edge of the membrane material, at radius $r_2$, and

$$k_m = \frac{D_m}{\ln(r_2/r_1)(r_2 - r_1)},$$

where $k_m$ is the gas transfer rate across the membrane. The $\ln(r_2/r_1)$ term accounts for curvature of the membrane material. These formulations are standard in heat transfer literature for cylindrical coordinates.

The mass transport across the waterside diffusive boundary layer $J_w$ is

$$J_w = 2\pi r_2 L k_w S_w(p_2 - p_w),$$

where $k_w$ is the gas transfer rate across the diffusive boundary layer in the water adjacent to the membrane. Defining the total transfer across the outer surface of the membrane $J_T$ at $r = r_2$, to be

$$J_T = 2\pi r_2 L k_T [p_1/(RT) - S_w p_w],$$

and using Eqs. (19)–(23), it is found that the total effective gas transfer rate associated with transport across the three phases, $k_T$, is

$$\frac{1}{k_T} = \frac{r_2}{r_1 k_c} + \frac{1}{k_m} + \frac{1}{k_w}.$$

Using the analogy of electrical resistances, the inverse of the gas transfer rate can be considered a measure of the resistance of a layer to gas transfer. Equation (24) relates the total resistance to gas transfer between the air phase and the water phase as the sum of the individual resistances to gas transfer associated with the air phase boundary layer, the membrane, and the water phase boundary layer, respectively. For the GTD, which is controlled by the diffusive transport of $\text{N}_2$ and $\text{O}_2$, both of which are weakly soluble, nonreactive gases, the total resistance to transfer is dominated by the permeability of the membrane and the transport across the waterside diffusive boundary layer, hence $k_c \rightarrow \infty$ in Eq. (24).

For water flowing over a membrane surface, the gas transfer rate is enhanced above that of the stagnant boundary layer case by a factor known as the Sherwood number ($Sh$). For water flowing between two concentric tubes, where the inner tube loses gas to the water while the outer tube is gas impermeable, the relationship can be described as follows:

$$Sh \approx \text{Re}^{0.3}\text{Sc}^{0.7}(r_3/r_2)^3,$$

where Re is the mean Reynolds number of the flow, defined in this case as $Re = r_j U/\nu$, where $U$ is the flow rate down the tube, $r_j$ is the inside radius of the plastic hose that is used to flush the membrane interface (see Fig. 1), $r_2$ is the outside radius of the membrane, $\nu$ is the kinematic viscosity of water; and $Sc$ is the Schmidt number, defined as $Sc = \nu/D_m$, where $D_m$ is the molecular diffusivity of the gas in the water. Typical values are $a = 0.7–1.0$, $b = 0.3–0.4$, and $c = 0.4–0.6$ (see review by Petukhov 1970). Note that in this case, the gas transfer rate associated with a stagnant diffusion boundary layer around the membrane interface is $k_T = D/r_2$. Increased flushing of the hose reduces the thickness of this layer, thereby decreasing the response time of the instrument. Also, the equilibration time of the new GTD is much greater than the mean residence time of the water in the hose, the latter of which is $L/U$.

The isothermal response time of the profiling GTD to gas transfer $\tau$ is controlled by the rate at which the total dead volume of the GTD can equilibrate by gas exchange across the membrane. We can now describe the operation of the GTD by relating the change in dead-volume pressure to the flux of gas through the membrane:

$$\frac{dP_c}{dt} = -\frac{2\pi r_2 L k_m S_w RT(p_a - p_w)}{V_T},$$

where $V_T$ is the total dead volume of the GTD.
where $V_T$ is the total dead volume of the GTD and $k_T$ is given by Eq. (24) with $k_i = 0$. The solution of Eq. (26), with boundary conditions $p_c(t = 0) = p_w + \Delta P_c$ and $p_c(t \to \infty) = p_{w0}$, is

$$p_c(t) = p_w + \Delta P_c \exp(-t/\tau),$$  \hspace{1cm} (27)

where $\Delta P_c$ is the initial disequilibrium between the GTD reading and the true gas tension of the water, and

$$\tau = \frac{V_T}{2\pi k_T S_w RT}.$$  \hspace{1cm} (28)

The equations described thus far are applicable to a single gas. We now assume use of the superscript $i$ notation, where $i$ denotes a specific gas. To consider the equilibration time of the GTD to a step change in dissolved air pressure, all gases contributing to the gas tension signal must be considered. For an isothermal GTD, Eqs. (9) and (27) simplify to

$$P_s(t) = \sum_i p_s^i = \sum_i [p_{w0}^i + \Delta P_c^i \exp(-t/\tau^i)].$$  \hspace{1cm} (29)

The chief contributions to gas tension are from $N_2$ and $O_2$. Equation (29) can be rewritten in differential form as

$$\frac{dP_s}{dt} = -(P_s - P_T)/\tau_g.$$  \hspace{1cm} (30)

where $\tau_g$ is the mean response time of the GTD to a step change in dissolved air pressure, that is, $\tau_g \sim 1/[(0.79/\tau^{N_2^2}) + (0.21/\tau^{O_2^2})]$. In practice, because the membrane is compressible, hydrostatic pressure fluctuations $p(t)$ will change the thickness and permeability of the membrane. Also, the membrane’s permeability to air is slightly temperature dependent. Therefore, in profiling applications, we expect $\tau_g = f(T, p)$, where $f$ represents some functionality that can be determined empirically [see Eq. (18)].

4) EQUILIBRATION

As discussed above, the GTD must equilibrate its heat and gases with the seawater before the GTD will read precise in situ gas tension. Practically, when the GTD is used in profiling mode the instrument will rarely be in complete equilibrium, hence, a working definition of equilibration must be used. In this case, a threshold-based detection scheme is defined by specifying a tolerance (the difference between the measured and actual gas tension). For example, a tolerance of $\pm 0.1$ mbar (or 0.01%) would mean that the GTD reads to within $\pm 0.1$ mbar of actual gas tension. The required wait time will depend on the differences of temperature, salinity, and dissolved gases between the two sampling depths, and the value of $\tau_g$ at the new sampling depth. If the GTD at the new sampling depth has an initial disequilibrium of $\Delta P_s = 10$ mbar with respect to actual gas tension, a value of $\tau_g = 5$ min, and a specified tolerance of $\pm 0.1$ mbar, the GTD must be held at the new sampling depth for at least 23 min (i.e., $4.6 \times \tau_g$) based on gas equilibration alone. If, however, a tolerance of $\pm 1$ mbar (or 0.1%) was acceptable, then the wait time would be reduced to 12 min. Equivalently, the tolerance can be specified as a temporal rate of change in $P_s$. In this case, the tolerance of $\pm 0.1$ mbar can be expressed, using Eq. (30), as $|\tau_g \times (\partial P_s/\partial t)| < 0.1$ mbar, or $|\partial P_s/\partial t| < 0.02$ mbar min$^{-1}$. In other words, if the GTD reading changes by less than 0.02 mbar min$^{-1}$, the GTD can be read for gas tension then moved to the next sampling depth. In this way, the real-time reading from the GTD can be used to control an automated profiler’s buoyancy and energy-efficient vertical sampling can be performed. An accurate analysis of the GTD’s state of equilibration must also consider temperature and salinity variations, and effects associated with membrane compressibility. A full dynamical model of the GTD response, in terms of $P_s$, $\partial P_s/\partial t$, $p$, $\partial p/\partial t$, $T_p$, $\partial T_p/\partial t$, etc., is required to predict its “real-time” state of equilibration.

d. Modeling the dynamical response of the GTD

The isothermal, dynamical response of the new GTD to changing hydrostatic pressure is now considered. Changes in hydrostatic pressure will cause the membrane to compress or decompress. This signal will, as discussed previously, cause changes in $P_s$, the pressure reading of the GTD. By raising an initially equilibrated GTD from a particular depth, in a uniformly mixed water column of constant dissolved air pressure, the associated decrease in hydrostatic pressure will have two effects upon the GTD. First, the membrane will expand as it decompresses. This will cause some gas to be removed from the incompressible dead volume of the GTD to fill the expanding membrane. Since the sample volume is then distributed over a larger total volume, the pressure sensor reading will decrease. The reduced pressure of the total sample volume will cause gas to diffuse into the membrane interface from the water. Second, since the deflated membrane will have a greater void volume, the membrane will become more permeable to gases. This will increase the gas flux from the water to the membrane interface, facilitating equilibration of the GTD.

These effects can be incorporated into Eq. (30) to provide a dynamical model of the GTD as follows:
\[
\frac{dP_s}{dt} = -(P_s - P_g)/\tau_g + P_{sw}/K_{me},
\]  

(31)

where \(P_s\) is the pressure measured by the pressure sensor of the GTD, \(P_g\) is the actual gas tension of the water in the bulk fluid, \(\tau_g(p)\) is the gas transfer response time of the GTD where \(p\) is hydrostatic pressure, \(K_{me}(p)\) is the effective bulk modulus of the membrane [see Eq. (15)], and \(w = dp/dt\) is the vertical velocity of the platform, defined to be positive if descending and negative if ascending.

Note that Eq. (31) could be applied to individual gases \(i\) and components of the total dead volume \(k\) by treating each gas and component separately, and then combining their contributions according to Eqs. (8)–(10). In this case, the equilibration time of the GTD would be gas and temperature dependent. This more complete, nonisothermal, description of the GTD would benefit from temperature measurements at each of the various components within the system to fully evaluate the model against data collected in a profile through the thermocline. However, this additional level of complexity was not necessary to evaluate the present field data. The GTD was used in a “sample and hold” approach on an isopycnal float which, in many respects, is the ideal sampling platform. Note that if the operation of the GTD is restricted to the upper-ocean mixed layer, where typical thermal fluctuations are small, the GTD can be considered to operate isothermally.

3. Laboratory results

Various tests were conducted in the laboratory to determine the response of the new GTD to step changes in dissolved gases, water temperature, and pressure. The tests were performed using a precise temperature-controlled water bath, a small custom pressure test tank, and a large pressure test tank.

a. Partitioning of the total dead volume of the GTD

The various components of the dead volume were measured using different techniques. The dead volume of the bellows was measured by dismantling a broken sensor and filling it with water using a microsyringe. This provided a measure of \(V_b = (0.34 \pm 0.02)\) mL. The dead volume of the interconnecting tubes and fittings were calculated, using measurements of their dimensions, to be \(V_t = (0.06 \pm 0.01)\) mL. The dead volume of the core of the membrane interface was estimated, using measurements of its dimensions, to be \(V_c = (0.21 \pm 0.04)\) mL. The total incompressible volume of the GTD is \((0.61 \pm 0.07)\) mL.

The solubility of \(N_2\) and \(O_2\) in PDMS, \(S_m[N_2]\) and \(S_m[O_2]\), respectively, depends on the composition of the polymer. Fillers are sometimes added to strengthen the material, but this may decrease the permeability of the resulting membrane material to gases (Pauly 1999). In addition, the degree of cross linking of the polymer affects its solubility to gases. This can be controlled, to some extent, during the curing process. Results vary considerably in the literature. Hagg (2000) reported values, over the temperature range of \(25^\circ\text{C}–35^\circ\text{C}\), of \(S_m[N_2] = (0.221 \pm 0.018)\) cm\(^3\) (STP) cm\(^{-3}\) bar\(^{-1}\) and \(S_m[O_2] = (0.315 \pm 0.025)\) cm\(^3\) (STP) cm\(^{-3}\) bar\(^{-1}\). These values are consistent with Pauly (1999). However, Blume et al. (1991) reported corresponding values reduced by 44% and 59%, respectively. The total volume of air dissolved in the membrane material at STP is estimated to be \(V_{mo} = 0.93 \times 1.013 \times (0.79 \times S_m[N_2] + 0.21 \times S_m[O_2]) = 0.07-0.32\) mL of air at STP; note that this is the only compressible volume of air in the entire sample volume of the GTD. This estimate can be further refined for individual membrane interfaces using the additional laboratory measurements described below.

Full compression of the membrane, with no loss of gas to the water, and at constant temperature, would result in an increase in the GTD reading \(\Delta P_s\) of

\[
\Delta P_s = P_s\left(\frac{V_{mo}}{V_b + V_t + V_c}\right).
\]

(32)

Substituting the values above with \(P_s = 1013.25\) mbar, the expected range of \(\Delta P_s\) can be calculated to be 104–601 mbar. Uncertainty in membrane solubility and determination of the membrane thickness are the largest sources of error in this calculation. Fortunately, \(\Delta P_s\) can be determined in the laboratory or the field. It will be shown in section 3b that for a typical membrane interface, \(\Delta P_s\) is approximately \((135 \pm 20)\) mbar, with \(P_s = 1300\) mbar. Using the estimates of \(V_b\), \(V_t\), and \(V_c\) described above, Eq. (32) provides an estimate for \(V_{mo} = (0.06 \pm 0.01)\) mL. The total dead volume of the GTD is then estimated from Eq. (8) to be \(V_T = (0.67 \pm 0.07)\) mL.

b. Conductance of the membrane interface

To measure the time it takes for the membrane interface to pressure equilibrate along its entire length, the end cap at the end of the membrane interface was opened in the laboratory and the pressure was reduced using a syringe. The reduced pressure was held constant for several minutes. The interface was then quickly capped, and left for several more minutes to ensure no pressure gradients existed between the pressure sensor.
bellows and the farthest end of the tubular membrane interface. The pressure at all points in the GTD system were then ensured to be equal, and below that of atmospheric pressure. The cap at the far end of the membrane interface was then opened, and the pressure sensor reading was recorded. An exponential rise in pressure with time was observed as the laboratory air filled the entire dead volume of the GTD. Using this technique, the characteristic (\(e\)-folding) time scale for pressure equilibration within the GTD was measured.

This characteristic time scale was found to vary with the diameter to which the membrane interface was coiled. Generally, the tighter the coil was made, the longer the characteristic time scale. Results varied over the range 4–40 s. For the configuration shown in Fig. 2, where the inner diameter of the coil is (24 ± 1) cm, the time scale was measured to be (4.4 ± 0.3) s. This time scale is, by design, significantly less than \(\tau_g\).

c. Equilibration time versus water temperature (for dissolved air)

Various tests were performed to determine the response of the new GTD to step changes in dissolved gas pressure, over a wide range of water temperature and pump speeds. A temperature-controlled water bath (Hart-Scientific, Inc., model 7009), with a total volume of 157 L, was used. All tests were performed in freshwater. After the tank had reached its predetermined temperature, it was equilibrated with the atmosphere. The \(e\)-folding equilibration rate of the tank to a step change in dissolved air pressure varied from 1.7 h at 35°C to 3.1 h at 5°C. Tests were performed during periods of stable atmospheric pressure to ensure that the tank’s dissolved gas levels did not change appreciably due to changes in air pressure. Approximately 75 mL of bleach detergent were added to the tank every 2 weeks to limit biological growth; additions were more frequent when the tank was run at higher temperatures.

Step changes in dissolved air pressure were made by adding degassed water, typically 1–2 L, to the tank. The water was degassed by evacuating a 2-L sample of the tank water in a glass vacuum beaker that was stirred with a magnetic stirrer bar. Cavitation at the stir bar quickly stripped dissolved gases from the water, degassing a 2-L sample of water to approximately 80% of its original dissolved air content in 10 min. The degassed water was then poured into a plastic bottle, filled completely with no bubbles, capped, and returned to the temperature-controlled water bath to thermally equilibrate. Additions of degassed water to the tank provided a repeatable (10 ± 1) mbar drop in gas tension.

The results of these tests, for a pump power of 6 W, are shown in Fig. 3. The GTD equilibrates faster at higher water temperatures. The response time increases from 2.4 min at 35°C to 4.2 min at 5°C, or an average of 1.8% °C⁻¹. The temperature dependence of the gas equilibration time is chiefly the result of the temperature dependence of the membrane’s permeability to gases [see Eq. (18)].

d. Absolute accuracy check (for dissolved air)

The shipboard GTD, described at the beginning of section 2, was run alongside the new GTD in the tests described above (section 3c) for comparison purposes. McNeil et al. (2005) described the results for the shipboard GTD, and showed that it tracked atmospheric pressure to ±0.06% at 20°C, over a time scale of 1 week. The new GTD, described here, was found to agree with the shipboard GTD to ±0.03% over a temperature range of 5°C–35°C. Since the underway GTD has been shown to equilibrate with the atmosphere under controlled conditions, and the new GTD agrees with the shipboard GTD over a large temperature range, it is concluded from these results that the absolute accuracy of the new GTD has been demonstrated to ±0.09%. This is a conservative estimate. As described by McNeil et al. (2005), time lags associated with the time response of the shipboard GTD (typically...
11 min) and the water bath (typically 2 h), introduced an error of 0.06% in the comparisons. The fast-response GTD, with a time response of maximally 2 min, would be subject to similar errors.

e. Equilibration time versus pump speed (for dissolved air)

Tests were performed at 20°C covering the full range of power available to the SBE-5T pump. Disassembly of the pump to adjust the power setting was required for each test. Care was taken to ensure that the system was assembled in the same configuration for each test. Note that all tests were performed at atmospheric pressure using degassed water.

The results are shown in Fig. 4. The response time of the GTD decreases with increasing pump power and increasing flushing rate of the membrane interface tube. This response is expected since at increased flushing rates, the thickness of the diffusive boundary layer in the water adjacent to the membrane is reduced [see Eq. (25)].

f. Equilibration time for dissolved CO₂

Since the response time of the GTD is gas dependent [see Eqs. (25) and (28)], tests were performed using step changes in dissolved CO₂ levels by the addition of carbonated water to the tank. Note that the response time of the GTD to a step change in dissolved air, \(\tau_g\) [see Eq. (30)], is the time response that is relevant to the operation of the GTD in the field.

At a power setting of 6 W, the response time to a CO₂ addition at 20°C for a new and unused membrane was 0.6 min versus 2.5 min for a step change in dissolved air. The differences in response times reflect the fact that CO₂ is much more permeable in the PDMS membrane than either N₂ or O₂ (Pauly 1999).

g. Membrane stability tests

During development, the membrane interface was subject to rigorous pressure testing and pressure cycling. A custom benchtop pressure vessel was manufactured for this purpose. Tests were performed by cycling the hydrostatic pressure, more than 10 times, to 380 dbar. The production design is suitable for use over the range 0–300 dbar (equivalent to 0–300-m depth in freshwater).

The membrane interface appears to be reliable and stable over long periods of time, based on the fact that three shorter membrane interfaces were held at 300 dbar for approximately 3 months, and no failures were observed. A limitation of the membrane interface is that it should not be coiled to a radius less than approximately 10 cm.

h. Hydrostatic response tests

Pressure test tank measurements were performed at the Equipment Development Laboratory at the University of Rhode Island. The tank is approximately 0.75 m in diameter and 3 m tall. A bulkhead fitting provided power and data recording to the GTD and SBE-5T pump. Several complications were found in using the tank, and they are now described.

A light-grade grease was used on the o-ring seals of the tank, and it proved impossible to avoid contamination with the tank water. Under pressure, the oil emulsified and contaminated the membrane. This resulted in a significant, irreversible decrease in the permeability of the membrane. This problem was solved by placing the pumped GTD in a separate, carefully cleaned, sealed container filled with approximately 25 L of clean tap water. The container was then placed inside the pressure tank, bled of bubbles, and the tank was pressurized. Testing was performed during the summer months, and the tank would generally warm during the daytime and cool during the night. In addition, heating of the water in the container, by the GTD pump, resulted in supersaturation of the water.
Two GTDs were repeatedly subjected to a hydrostatic pressure of 300 dbar (equivalent to 300-m depth in freshwater). The first test was designed to show that all internal dead volume, external fittings, and interconnections were indeed incompressible. The connection to the membrane interface was removed and capped. The tank was then pressurized rapidly over a period of approximately 2 min to 300 dbar. A negligible increase in the pressure reading of the GTD was observed; this result confirmed that the internal dead volume of the GTD was incompressible.

Figure 5 displays results of a typical pressure test cycle with the GTD pump running at 6 W. After pressurization of the tank, a pressure increase of approximately 135 mbar was measured by the GTD. The increase in GTD reading was associated with near complete compression of the membrane. These results are comparable to the values of 104–601 mbar calculated in section 3a using Eq. (32). Results of unpumped tests, though not quantified, can be expected to be higher as some of the gas from the membrane was undoubtedly lost to the water phase during the pumped tests. As calculated in section 3a, this test implies that $V_{mo}$ is $(0.06 \pm 0.01)$ mL.

4. Field tests and discussions

We report results of two field experiments. The first was performed over the course of 10 days in Puget Sound, Washington, during July 2004, using two GTD-equipped, neutrally buoyant floats. In all field experiments, the GTDs were flushed using the SBE-5T pump running at 6 W. This experiment provided the first autonomous profiles of gas tension and N$_2$ using the new GTD. In addition, it served as preparation for the second experiment, air deployment of the same two floats into the advancing path of Hurricane Frances. The deployment occurred in the vicinity of 22°N, 70°W, in the northwest Atlantic, during early September 2004. This high-risk deployment was part of an (National Science Foundation) NSF-funded program to study air–sea gas exchange rates during hurricane-force winds. The two floats are identified by their serial number, floats 21 and 22.

4.1 Puget Sound deployments

Figure 6 displays results of an approximately 6-h deployment in Shilshole Bay of Puget Sound during 15 July 2004. Floats 21 and 22 were deployed at 1023 local time (LT) at 47°44.311’N and 122°23.824’W within 3 m of each other. Float 22 was equipped with an acoustic transponder to enable tracking of the float’s position. The buoyancy of each float was dynamically controlled during the entire 6-h period. The floats were programmed to sink to around 60 dbar then surface after approximately 45 min (Fig. 6a). This compressed the float and GTD, dissolving any air bubbles that may have been attached to the instruments. Figure 6b displays the corresponding GTD measurements. Corresponding water temperature is shown in Fig. 6c, and shows a strong thermal gradient of approximately 2.5°C over the hydrostatic pressure range of 0–60 dbar.

After performing their compression cycle, both floats surfaced at 1133 LT (Fig. 6a). Water samples were taken beside the floats from a small boat. All in situ seawater samples were taken using a Niskin-type sampler (General Oceanics, Inc, model 1010–2.5L) at the depth of the GTD’s seawater intake. Samples were taken for dissolved O$_2$ and subsequently returned to the laboratory for analysis by the Winkler titration method. Sampling was repeated at 1149 LT (Fig. 6a),
and additional samples were collected for mass-spectrometric determination of \( \text{N}_2 \) and \( \text{Ar} \) (sampling was performed by coauthor M. Horn, who was trained to take the samples at the University of Washington).

The sampling procedures were described by Emerson et al. (1999).

Shortly after noon, the float’s buoyancy was decreased so the floats sank rapidly to around 40 dbar (Fig. 6a). The floats then settled on their target isopycnal at approximately 1315 LT. During the period 1315–1400 LT, the buoyancy of each float was actively maintained to keep the density of the floats within ±0.01 kg m\(^{-3}\) (equivalent to ±0.5 m) of their target isopycnal. As shown in Fig. 6a, each float was subjected to internal waves with periods of 6–8 min and wave heights of approximately 4 m. Samples were collected for both Winkler and mass-spectrometric analysis from depths of 25, 40, and 50 m at 1350, 1416, and 1438 LT (Fig. 6a), respectively. Sampling depths were determined to within a few meters using a marked line and an estimate of the wire angle.

The floats then attempted to profile to 60 dbar again (Fig. 6a) before surfacing around 1530 LT (float 21 was unsuccessful in this attempt). When the floats surfaced, they were within 50 m of each other. Surface measurements were then made beside float 22 at 1548 LT (Fig. 6a) at 47°43.299′N and 122°23.351′W. The results of these gas measurements are summarized in Table 2.

Approximate equilibration times of the GTD can be inferred from these data (Fig. 6b). The equilibration time of the GTD was estimated to be approximately 5 min at the surface, in water of temperature (14 ± 0.5)°C, and approximately 12–18 min at 60 m, in water of temperature (11.5 ± 0.5)°C. Another deployment of float 21 on 9 July 2004 indicated that the GTD could take more than an hour to equilibrate at depths below 120 m and at a temperature of (11.2 ± 0.5)°C. The gas equilibration time of the GTD is known to depend on

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**Table 1. Calibration information for the dissolved gas sensors used in the Puget Sound and Hurricane Frances experiments.**

<table>
<thead>
<tr>
<th></th>
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<td>Float No.</td>
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<td>21 22</td>
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<tr>
<td>Pressure sensor</td>
<td>SN 89678 SN 90125</td>
<td>SN 89678 SN 90125</td>
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<tr>
<td>Range</td>
<td>0–6890 mbar 0–2070 mbar</td>
<td>0–6890 mbar 0–2070 mbar</td>
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<tr>
<td>Calibrations(^a)</td>
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<td>±0.1 mbar ±0.1 mbar</td>
</tr>
<tr>
<td>Max drift(^b)</td>
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<td>0.14 mbar week(^{-1}) None</td>
</tr>
<tr>
<td>Time between calibrations</td>
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<td>95 days 95 days</td>
</tr>
<tr>
<td>( \text{O}_2 ) sensor</td>
<td>SN 43F-0016 SN 43F-0015</td>
<td>SN 43F-0069 SN 43F-0038</td>
</tr>
<tr>
<td>Calibrations</td>
<td>(or ±0.34%) (^b) (or ±0.34%) (^b)</td>
<td>(or ±2%) (^c) (or ±2%) (^c)</td>
</tr>
</tbody>
</table>

\(^a\) For the Hurricane Frances experiment, predeployment GTD calibrations were performed at APL/UW on 17 Jul 2004, and postdeployment GTD calibrations were performed at WHOI on 18 Oct 2004.

\(^b\) Near-surface \( \text{O}_2 \) calibrations, performed using in situ samples that were analyzed by the Winkler titration method (see Table 2).

\(^c\) Derived using prepost deployment calibrations, performed at the manufacturer, and intercomparisons made in a seawater-filled container, performed at the recovery site aboard the recovery ship.

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**Fig. 6.** Results of field testing in Puget Sound, WA, during July 2004. Two neutrally buoyant floats, identified by serial numbers 21 and 22, were equipped with CTD/O\( \text{N}_2 \)/O\( \text{Ar} \) and the newly developed fast-response GTD. The float’s were deployed at the same time within 3 m of each other. The GTD pump ran at a continuous 6 W of power. The floats were deployed at 1023 LT, profiled to 60-m depth, and then surfaced. After resting at the surface to allow the GTD’s to equilibrate (*), water samples were taken (□) using a handheld Niskin sampler. Analysis of the samples was performed using the Winkler titration procedure, for dissolved \( \text{O}_2 \), and mass spectrometry, for \( \text{N}_2 \) and \( \text{Ar} \). The position of float 22 was tracked using an acoustic transponder. The floats surfaced at 1600 LT and were recovered within 50 m of each other. Shown are (a) hydrostatic pressure; (b) GTD reading, noting that only the data points marked by (*) are equilibrated, gas tension, readings; and (c) water temperature. Results of float 21 are shown in dark gray, and results of float 22 are shown in light gray.
water temperature [see Eq. (18) and Fig. 7]. From these field data, the most significant factor affecting the membrane’s isothermal permeability, and hence the GTD’s isothermal response time, is the effect of hydrostatic pressure. Increasing hydrostatic pressure crushes the membrane material, resulting in less interstitial void space to accommodate absorbed gases, increased tortuosity, and hence a lower gas permeability.

Hand-chosen points, marked by stars in Fig. 6b, indicate equilibrated gas tension values derived from both GTDs. The hand-chosen points correspond to a GTD reading when the instrument had been at the target isopycnal for the greatest period of time (rather than the trigger time of the Niskin samplers). These discrete data points correspond to the best available estimates of in situ gas tension [see section 2c(4)] because the GTDs were maximally equilibrated. It is assumed that the dissolved gas levels at the sampling depths did not change significantly during the 1-h period from 1345 to 1445 LT. This is reasonable because the floats were below the thermocline and presumably below the photic zone.

Figure 7 displays the measured signal of the GTD versus hydrostatic pressure for the same data presented in Figs. 6a,b. A clear hysteresis in the response of the GTD is seen, which is now explained. When the float sinks, the compressed membrane releases air to the dead volume of the GTD, resulting in an increased pressure reading. The GTD pressure readings are observed to peak at a hydrostatic pressure of approximately 9 dbar. As the float descends deeper than 9 dbar, the GTD reading decreases due to loss of gas from the membrane to the seawater. Left at a hydrostatic pressure of 40 dbar, the GTD will equilibrate with its surroundings, but the response time will be slower because, at greater depths, the compressed membrane is less permeable. The hand-chosen equilibrated data

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**Table 2. Water properties measured during Puget Sound experiments on 15 Jul 2004:**

<table>
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<th>Time (LT)</th>
<th>ID</th>
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<td>1410</td>
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<td>W/MS</td>
</tr>
<tr>
<td>1438</td>
<td>W</td>
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<tr>
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<td>1600</td>
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</table>

[Fig. 7. GTD readings from Fig. 6b, plotted as a function of hydrostatic pressure. Equilibrated data, which are the gas tension readings, are indicated by (*). The GTD showed a strong hydrostatic response associated with compression and decompression of the membrane. This response was significant over the hydrostatic pressure range 0–10 dbar. Near-surface gas tension values agreed to within ±0.1%, for both GTDs on two occasions that were separated by more than 4 h.]
points (Figs. 6b and 7) are, in fact, gas tension measurements. All other raw GTD data are transient, nonequilibrium measurements. As the float ascends, the membrane begins to decompress. Decompression of the membrane becomes significant at depths less than approximately 9 m. Air is drawn from the GTD’s dead volume to inflate the decompressing membrane, thereby resulting in a decrease of the GTD pressure reading. It is clear from Fig. 7 that the membrane’s effective compressibility was greater for float 22 than for float 21. After the float surfaced, the GTD equilibrated rapidly. Within a few minutes, both of the GTDs read within 1 mbar of each other.

Using the procedure described by McNeil et al. (2005), the dissolved N$_2$ concentrations were calculated from the equilibrium gas tension measurements and the dissolved O$_2$, T, and S. For these calculations, Ar levels were assumed to be saturated to the same level as N$_2$. This assumption is justified using the mass-spectrometric determinations, which show that both N$_2$ and Ar levels agree to within $\pm 0.15\%$ of saturation. Figure 8 displays the results expressed as dissolved gas concentrations; Fig. 9 displays the results expressed as percent saturations. Both are reported with respect to one standard atmosphere of moist air. The N$_2$ concentrations and saturation levels are greater for the GTD method than for the mass-spectrometric determinations. The cause of this discrepancy is not yet known, and the results are not in line with prior determinations by Emerson et al. (2002), who found that the methods could be reconciled to within better than 0.5%. However, both methods do show common variability, with lower concentrations found near the surface. This is consistent with the fact that the near-surface waters were supersaturated (Fig. 9), and therefore were degassing to the atmosphere. The overall supersaturation levels of N$_2$ indicate that seasonal warming has outpaced air–sea gas exchange.

Pressure sensor SN 89678 was subject to full-scale, and perhaps higher, pressure swings during pressure tank tests. This provides a likely explanation for calibration drift, rather than the air-deployment impact, although this cannot be confirmed from the information available.

b. Hurricane Frances deployment

Hurricane Frances was a category-4 hurricane on 1 September 2004. It was located just to the northeast of the Turks and Caicos Islands in the Caribbean, and was moving westward. Floats 21 and 22 were deployed into the path of the advancing hurricane in the vicinity of 21.5°N and 70°W, using a C130J aircraft. Float separation was initially approximately 5 km, but this increased to approximately 25 km during the storm. After shed-
during its parachute and air-deployment package, each float slowly profiled to 120 m in a sample-and-hold approach, stopping at various depths to equilibrate the GTD. The wait time was estimated from the sample response time versus pressure relationship estimated during Puget Sound experiments. The floats then moved into the upper-ocean mixed layer, continuously adjusting their buoyancy to be neutral. The hurricane’s eye passed approximately 50 km south of the floats’ positions, subjecting the floats to the strongest winds of the hurricane, roughly 55 m s\(^{-1}\). Hurricane-force winds in the vicinity of the floats were sustained for approximately 19 h. Strong vertical currents in the mixed layer cycled the floats through the upper part of the mixed layer, over a depth range of approximately 0–40 m, over 100 times. After the passage of the hurricane, the floats performed another series of vertical profiles to 120 m depth to record the posthurricane vertical water properties. D’Asaro and McNeil (2006, hereafter DM) interpreted the vertical budgets of gases to estimate air–sea gas exchange rates during the hurricane. Analysis here focuses on the performance of the new GTD.

Remarkably, the pressure sensor of the GTD on float 22 was unaffected by the impact of the air deployment and the sensor maintained its calibration (Table 1) to within 0.005% of the full-scale range. This cannot be said for float 21, since the pressure sensor was known to be drifting out of calibration during the Puget Sound experiments. However, it can be said that the pre/postcalibrations were within 1.8 mbar, or 0.026% of the full-scale range. It cannot be stated that the difference between pre/postdeployment calibrations, which was more than 3 months, was caused by continuous and slow sensor drift, or if the impact contributed to some of the calibration differences.

Figure 10 displays the equilibrated gas tension data obtained using the profiling method described above. Data are presented from before and after the passage of the hurricane. Before the hurricane, the gas tension profile reflected the profile of dissolved O\(_2\), which was observed (DM) to have a similar subsurface maximum due to net biological production. Both floats show very similar profiles. After the storm, gas tension increased due to bubble dissolution during the hurricane (DM). For the purpose of this paper, these tests demonstrate that the sensors are robust and capable of being air deployed.

During the passage of the hurricane, the floats were neutrally buoyant and cycled repetitively within the mixed layer. These data provide an excellent opportunity to calculate the membrane compressibility, according to Eq. (12), since the floats were in near–thermal equilibrium with the ocean. Also, because the membrane was pressure cycled many times, the membrane could, most likely, be described by a time-invariant bulk modulus. Figure 11 displays \((dP/dt)_{\text{avg}} = P_{so}/K_{me} = P_{so}\beta_{me}\) [see Eq. (15)], calculated from the data obtained by both floats during this period. Note that when a float ascended or descended rapidly (Fig. 11, dark blue dots and dark red dots, respectively), the GTD did not have sufficient time to equilibrate though the membrane; hence, the change in \((dP/dt)(w \times P_{so})\) can be attributed to the membranes’ effective compressibility. Over the depth range 0–10 dbar, \(P_{so}\beta_{me}\) was observed to decrease approximately linearly with increasing hydrostatic pressure (Fig. 11). Therefore, to first order, \(P_{me}\) is approximately constant. This justified the use of a first-order Taylor series expansion to describe the compressible volume of the membrane [see section 2c(1)]. Using Eq. (14), \(P_{me}\) was estimated to be (9 ± 2) dbar. This value of \(P_{me}\) is consistent with the Puget Sound and pressure test tank results.

c. Dynamical modeling of the field data

Equation (31) can be integrated forward in time to provide what will be referred to as the “forward” solution. This requires a best guess for \(P_T(t)\), for which a low-pass-filtered version of the data was used. The compressibility of the membrane was modeled using an empirical fit to the data of the form \(F(p) = ae^{-bp} + ce^{-dp}\), where \(F\) is the functionality with hydrostatic pressure \(p\); and \(a, b, c,\) and \(d\) are constants. The results...
The Hurricane Frances experiments were conducted during the pre-posthurricane period, with prior laboratory tests (see Fig. 3), at a temperature of \((27.7 \pm 1.2)^\circ C\). The results of the model are in good agreement with the observed GTD readings.

Equation (31) was then solved for the gas tension of the water \(P_g(t)\), which we refer to as the “inverse” solution. Since this solution involves the derivative of \(P_g(t)\), the solution was rather noisy. The noise was mostly associated with slight phase lags between the predictive model’s response and the data; this difference was greatest at depths less than a few meters. Different techniques were applied to try to reduce this noise, but it was concluded that it could best be removed by simply applying a low-pass filter to the result. This was justifiable because the gas tension did not change significantly, compared to the hydrostatic response of the GTD, over the time scale of the float’s circulations within the mixed layer. A low-pass filter with 12-min cutoff period was used to process these data. For this portion of the data, the difference between the low-pass-filtered raw data and the low-pass-filtered inverse solution was consistently less than 3 mbar (or \(0.3\%\)), and was no more than 11 mbar (or \(1.1\%\)) during the entire mixed layer deployment. The inverse solution was consistently lower than the low-pass-filtered version of the data, since the GTD equilibrated faster nearer the surface, and the low-pass-filtered version of the data represents a running average at the mean depth of the float. All of these results are consistent and reproducible with the model results for float 21.

d. Discussion

The Puget Sound experiments did not provide a sufficient number of profiles to infer a membrane compressibility relationship; however, those data that were collected are consistent with the Hurricane Frances results. Application of the dynamical model to the Puget Sound data, using the compressibility relationship derived from the Hurricane Frances data, provided reasonable agreement with the data. However, better agreement between the model and data were obtained for the Hurricane Frances dataset than for the Puget Sound dataset. This is not surprising, as the floats were cycled more than 50 times each during Hurricane Frances, but only a few times during the Puget Sound experiments. In addition, the “best-guess” gas tension profile for the Puget Sound dataset was more poorly constrained than that for the Hurricane Frances dataset. It is suspected that the membrane may require

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**Fig. 11.** Scaled membrane compressibility \([\beta_{mc} \times P_{mc}, \text{see Eq. (15)}]\) plotted against hydrostatic pressure, derived using all mixed layer data during the Hurricane Frances deployment. Results for floats 21 and 22 are superimposed, and comprise more than 100 cycles within the upper-ocean mixed layer. Float velocity is indicated by the color scale, where red indicates a descending float, and blue indicates an ascending float. Data are restricted to those measurements where the float speed was greater than 20% of the maximum observed speed. The compressibility was greatest near the surface, falling off rapidly with increasing depth. Using Eq. (14), \(P_{mc}\) was estimated to be \((9 \pm 2)\) dbar. An empirical fit to the data of the form \(F(p) = ae^{-bp} + ce^{-dp}\) is shown by the solid line. A slight asymmetry in the compressibility between the ascending and descending phase is apparent, as seen by the separation of the blue dots and the red dots. This observation is consistent with a membrane that inflates slowly during decompression on an ascending float, and deflates rapidly by compression on a descending float. The measured GTD pressure \(P_g(t)\) for float 22 with forward solutions during a representative 4-h period, just after the passing of the hurricane. Two forward solutions are presented. The first solution is derived assuming that the response time of the GTD to gas transfer is infinite at all depths. This predicts the response of the GTD for a nonpermeable membrane. The results show that, as the instrument ascends, the pressure sensor reading is predicted to decrease, and when the GTD descends, the pressure reading is predicted to increase. This response is specified by the compressibility of the membrane. Since the total number of moles of gas are constant (no loss or gain by the membrane), the GTD simply responds to changes in hydrostatic pressure. The second solution is for the case where gas exchange across the membrane is finite, increasing linearly with hydrostatic pressure over the range 0–60 dbar from 2.5 to 7.5 min. These response times are in general agreement with the observations made during the pre/posthurricane profiles, and prior laboratory tests (see Fig. 3), at a temperature of \((27.7 \pm 1.2)^\circ C\). The results of the model are in good agreement with the observed GTD readings.
several repeated cycles of compression and decompression to “work harden” the membrane. After repeated pressure cycling, it is suspected that the response becomes sufficiently well defined and reproducible, so as to allow precise dynamical modeling of the GTD.

One additional observation is that the membrane may not be perfectly elastic, and there may be a repeatable hysteresis cycle in the compressibility of the membrane. There is some evidence of this upon inspection of Fig. 11, which shows a slight difference between the shape of the compressibility curve for rising and sinking floats. It is suspected that this feature is associated with a slight hysteresis in the way the GTD responds to compression and decompression of the membrane. This can be explained by one of two possibilities. A compressing membrane can lose air to either the water- or airside of the GTD. Since the airside has less resistance to gas transfer, gases can be expected to diffuse preferentially into the incompressible dead volume of the GTD. When a compressed membrane decompresses, under decreasing hydrostatic pressure, it must do so by internal restoring forces, since the membrane material is elastic. Due to a lower permeability of a compressed and degassed membrane, relative to a fully decompressed and air-filled membrane, some delay can be expected after decompression of the membrane. In other words, the membrane will take longer to inflate than it will to deflate. An alternative explanation is that the membrane is, in some way, internally sticky. In this case, a deflated membrane must first overcome this stored internal energy before fully inflating under its own internal elastic-restoring forces.

5. Conclusions

We have developed and tested a new profiling gas tension device to measure total dissolved air pressure...
over an operating depth range of 0–300 m. The minimal
response time is (2 ± 1) min near the sea surface and (8 ± 2) min at 60-m depth. The response time decreases
with increasing water temperature, decreasing operat-
ing depth, and increasing pump power. The depen-
dence of response time on operating depth results from
compression of the membrane material under increased
hydrostatic pressure and an associated decrease in
membrane permeability to gases. The membrane is
found to compress significantly over a hydrostatic pres-
sure range of 0–9 dbar. The response time decreases
with increasing pump power as the diffusive boundary
layer around the tubular membrane interface is re-
duced. Though not yet demonstrated, it is suspected
that the membrane interface can be pumped in a duty-
cycle mode, to provide optimal gas equilibration and
power consumption rates.

The device has been tested against a mass-
spectrometer analysis of discrete water samples for N₂/
Ar concentrations, but a considerable offset was ob-
served. The offset varied over the range 1.26%–2.21%.
Clearly, this discrepancy needs to be investigated fur-
ther as the existing moored GTD has been shown in the
laboratory to track gas tension over a period of 1 week
in a temperature-controlled water bath to within
±0.06% (McNeil et al. 2005), and the new GTD was
found to equilibrate to the same level as the existing
GTD in the laboratory, over a temperature range of
5°–35°C, to within ±0.03%. Also, the existing GTD has
been shown to agree to better than ±0.5% using a simi-
lar mass-spectrometric procedure as was used here,
over a 2-yr period at the Hawaii Ocean Time-series
Station (HOTS; Emerson et al. 2002). It is suspected
that an explanation for this discrepancy will be avail-
able when further field comparisons can be made. In
the meantime, based on intercomparisons between two
independent systems in laboratory and in the first field
trials, it appears that the new GTD is a robust, useful,
and precise sensor.

It is recommended that laboratory experiments be
designed to investigate the slight, but evident, hys-
teresis in the compressibility of the membrane material. If
better understood, this feature could be included in the
equation describing the dynamical response of the
GTD [Eq. (31)]. This would provide an improved re-
sponse of the system when used in slow-profiling appli-
cations. This information, along with better numerical
procedures, should provide an improved dynamical
model result, thereby reducing the remaining minor lag
problems associated with the dynamical response
model in the near surface. This would reduce the
amount of smoothing needed to recover the gas tension
from the raw data. Finally, if the dynamical response of
the instrument is to be interpreted, it is recommended
that a sequence of hydrostatic pressure cycles be per-
formed prior to data collection.

Acknowledgments. We thank Bryan Schofield (Pro-
Oceanus Systems, Inc.) for all his efforts toward the
design, testing, and construction of the new profiling
GTD. We thank Mike Dempsey (Oceanetic Measure-
ments, Ltd.) for help with design, Cathy Cipolla and
Gary Savoe (EDL/URI) for expert assistance during
the pressure testing phase, and Mike Ohmart and Mike
Kenney (APL) for superb laboratory and field assist-
tance. We thank Steve Emerson and Chuck Stump
(UW) for providing very generous support to our Puget
Sound experiment, which included lending us special-
ized sampling equipment, and performing mass-
spectrometric analysis of samples; the interpretation of
the GTD data has benefited greatly from these mea-
surements. This work was supported by NSF Grants
OCE 0220692 and 0220687. Craig McNeil and Bruce
Johnson are co-owners of Pro-Oceanus Systems, Inc.,
Halifax, Nova Scotia, Canada. In addition, they are
president and vice president, respectively, of Pro-
Oceanus Systems, Inc.

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