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A gas tension device for the mesopelagic zone

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ABSTRACT

Gas Tension Devices (GTDs) are used to acquire accurate and stable measurements of gas tension, or total dissolved air pressure of the gases dissolved in water. GTDs operate by measuring the barometric pressure of a small sample volume of air separated from the water by a gas-permeable membrane resting on a rigid permeable support. Existing GTDs use a compressible polydimethylsiloxane (PDMS) membrane which exhibit several undesirable features: the membrane collapses with increasing hydrostatic pressure, which reduces the permeability; a collapsed membrane increases the response; collapse and expansion generate large transient signals [McNeil et al. 2006a]. Also, reverse osmosis becomes a problem at depths greater than approximately 330 m in seawater. We present a new GTD that solves the hydrostatic pressure-generated transients and changing response times, and alleviates reverse-osmosis. These improvements allow the new GTD to be used in the mesopelagic zone. The new GTD uses a custom designed small diameter (4 cm) thin (130 µm) incompressible composite Teflon-AF 2400 membrane. It can operate to a depth of at least 1000 m with a depth-independent response time of approximately 35 min. We estimated the hydrostatic pressure dependence of Henry's Law solubilities as we characterized the new Teflon-membrane GTD using data collected in the laboratory. Field testing occurred on two APL/UW Gas-Profiling Floats deployed in the Eastern Tropical North Pacific (ETNP) for 15 days during May 2014. The floats profiled between the surface and 400 m depth, sampling gas tension within the Oxygen Deficient Zone. The gas tension-profiles from the two GTDs were validated against gas tension derived from independent N_2:Ar and Ar concentrations measured by mass spectrometry, agreeing to within ± 0.6% and ± 0.4%.

1. Introduction

Measurements of dissolved gases are widely used in oceanography, limnology, and aquaculture, with dissolved O_2 being the third most frequently measured property of seawater after temperature and salinity. Dissolved gas measurements have been used to study: ocean carbon uptake and acidification (Takahashi et al., 1997); bubble mediated air-sea gas exchange (Emerson and Bushinsky, 2016); biological production and net community metabolism (McNeil et al., 2006b); water quality for juvenile hatchery fish downstream of dam spillways (Bragg and Johnston, 2016); denitrification/anammox in anoxic natural and waste waters (Löffler et al., 2011); and groundwater recharge and trapped gas phases (Manning et al., 2003). The four major atmospheric components, namely nitrogen (N_2), oxygen (O_2), argon (Ar), and carbon-dioxide (CO_2), are most easily measured using conventional techniques thanks to their large dissolved concentrations and partial pressures. Since they are important to numerous biological and chemical processes, and noting the widespread use of these measurements, there is a continued need to improve dissolved gas sensor measurement technology to overcome current limitations, such as depth dependence, response time, calibration stability, interferences, cost, cross-sensitivity, and power consumption, and improve basic performance characteristics, such as accuracy and resolution.

Of these four gases, dissolved CO_2 and O_2 are the most chemically reactive. Dissolved aqueous CO_2 is normally measured using a non-dispersive infrared sensor (NDIR) (Hales et al., 2004). Dissolved O_2 is measured most accurately using discrete water samples analyzed by the Winkler titration method (Langdon, 2010). Several commercially-

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available in-situ sensors based on polarographic or fluorescence quenching methods are also used for O_2. Less-reactive dissolved N_2:Ar are measured by mass spectrometry (MS) or gas chromatography (Groffman et al., 2006). All techniques that require collection, storage, transport, and subsequently analysis of discrete water samples are subject to numerous opportunities for contamination or alteration of the water samples. An in-situ sampling method for measuring dissolved N_2 will help address most of these issues.

A gas tension device (GTD) measures the gas tension which is subsequently used to derive in-situ dissolved N_2 if dissolved O_2 is also measured (McNeil et al., 1995). The first in-situ dissolved gas measurements made using the tensiometer from D’Aoust et al. (1975)) and the Weiss saturometer, had accuracies of 3% (Fickeisen et al., 1975). Gas tension is the total pressure of dissolved gases in a parcel of water. In a GTD, a semipermeable membrane is used to equilibrate a small volume of gas trapped behind the membrane with the gases dissolved in the surrounding water. When the GTD's gas volume is equilibrated with the seawater sample, a barometer in the GTD measures gas tension. Using concurrent measurements of gas tension, dissolved O_2, temperature and salinity, and measured or assumed saturation levels for Ar and pCO_2, dissolved N_2 can also be determined to a final accuracy of ± 0.7% (McNeil et al., 1995, 2005).

A custom GTD was designed and used on profiling floats (McNeil et al., 2006a) to measure the rapid changes in gas tension in the ocean mixed layer during the passage of a hurricane (D’Asaro and McNeil, 2007). That GTD used a tubular polydimethylsiloxane (PDMS) membrane with a large surface area and low-internal volume to achieve a response time of minutes. The compressibility of PDMS resulted in two major complications with this GTD. First, the membrane's permeability decreased with increased hydrostatic pressure which resulted in a significantly slower response at increased depths and a hysteresis in the gas tension profiles. Second, the release (uptake) of gases from the membrane during compression (decompression) resulted in large transient positive (negative) pressure fluctuations in the raw GTD measurements. Another more severe problem was sporadic clogging of the membrane, likely caused by reverse osmosis of liquid water through the membrane into the barometer. These limitations excluded GTD-equipped floats from deep (below 60 m) or extended deployment and increased measurement error.

This paper describes a new GTD designed to overcome these limitations. Our motivation is to measure dissolved N_2 on profiling floats deeper in the ocean and specifically in oxygen deficient zones (ODZs) to study the biological production of N_2 via the denitrification and anammox processes. We expect a N_2-excess signal of 10 – 20 mbar out of a background 850 mbar based on the N-excess from Chang et al. (2012). We begin by presenting the design of the new GTD and describing the new materials involved. Next, we lay out the background theory of gas tension measurements, which is used to construct a model which describes the temperature and hydrostatic pressure dependencies. The GTD is then characterized in the laboratory using the developed model, followed by testing in the Puget Sound, and finally deployment in the Eastern Tropical North Pacific (ETNP) ODZ. Then, we present the results of the lab experiments and field testing, with the Puget Sound and ETNP results validated against an independent gas tension estimate calculated with concurrent measurements of dissolved O_2 and N_2:Ar ratios determined by mass spectrometry. Lastly, we discuss how the new GTD-design is an improvement over the previous versions, what needs further development, and future field applications.

2. Instrument design

Autonomous profiling Gas-floats (Applied Physics Lab, University of Washington), which alter their buoyancy to settle at different isopycnals in the water column, offer a platform for frequent sampling of multiple seawater properties through time and space. An ideal float-mounted gas tension device would measure the gas tension with a rapid (seconds) equilibration (response) time, function independently of temperature and hydrostatic pressure, and function reliably for long-periods of time on autonomous platforms. The previous float-mounted GTD utilized a large (1 m length x 3 cm diameter) tubular PDMS membrane to achieve minute response times (McNeil et al., 2006a). However, the previously discussed issues of the PDMS-membrane meant the GTD required frequent maintenance and limited possible applications (McNeil et al., 2005, 2006a).

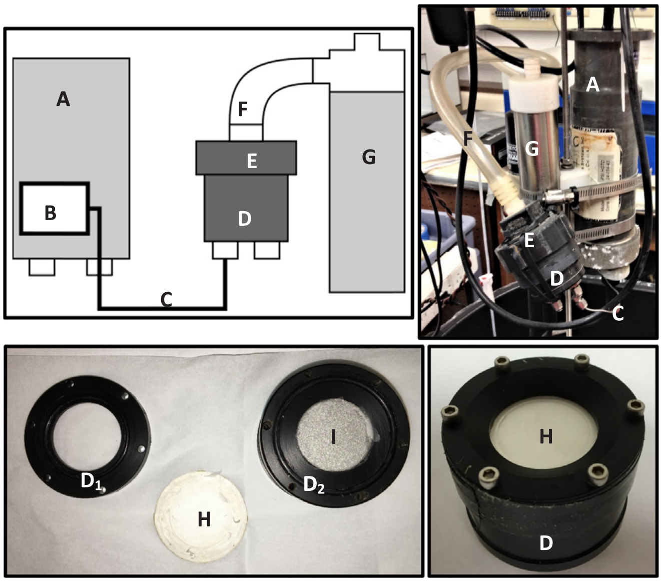

Fig. 1. Schematic and pictures of the new GTD, showing clockwise from the top left, the assembled GTD with pump, the disassembled membrane housing, and the membrane housing. A: Pressure housing and electronics, B: Paroscientific barometer, C: 1/16” stainless steel tubing, D: assembled membrane housing (D_1: membrane collar, D_2: main membrane housing), E: plenum, F: plastic tubing, G: Seabird 5T pump, H: Teflon membrane and support, I: Stainless steel mesh support.

The new GTD design is shown in Fig. 1. It has three main components: (1) a pressure housing, (2) a flushed membrane interface, and (3) a seawater pump. The new design is more compact than the previous version, making it easier to mount and protect. The compressible PDMS membrane is replaced with a nearly-incompressible Teflon-AF 2400 membrane (DuPont). This switch of material reduces response times with hydrostatic pressure and the hysteresis, improving performance and accuracy of the instrument.

However, Teflon-AF 2400 is a difficult material to make flat membranes from because it is brittle and thin sheets of it tend to curl. We settled on a 4 cm diameter by 130 μm thick membrane after some experimentation. The membrane is supported on the non-water side by a fine stainless-steel support mesh. The membrane and support mesh are anchored in a membrane-housing manufactured from Delrin. Stainless-steel 1/16” tubing connects the membrane housing to a Paroscientific Digiquartz Pressure transducer (0–30 psia), which has a manufacturer's stated precision of 0.0001%, accuracy of 0.01%, and drift of a few parts-*per*-million per year. The pressure transducer and associated electronics are protected in a separate pressure-housing. Barometric pressure and internal temperature of the GTD is recorded by the float.

The water-side face of the membrane is covered with a plenum that is connected to a SBE5T seawater pump. Flushing the membrane significantly reduces the equilibration time by shrinking the boundary-layer that forms along the membrane-seawater interface. The plenum is a plastic cap with the water inlet situated over the membrane and several small outlets, with their total area less than the inlet, spaced radially around the side of the plenum. This directs the water onto the membrane and shears radially, and maintains a slight positive pressure to ensure the membrane is held flat against its support. The pump is