N$_2$ measurements by the gas tension method

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Overview:

1. Measuring N$_2$ using gas tension method
2. Overview of the gas tension device (GTD)
3. Measurement errors
4. Some results from the field
5. Overview of pCO$_2$ sensor
1. Measuring $N_2$ using gas tension method

Gas tension (or total dissolved gas pressure) is:

$$P_T = p_{N_2} + p_{O_2} + p_{Ar} + p_{H_2O} + p_{CO_2} + \ldots$$

- $p_{N_2}$ ~ 78 %
- $p_{O_2}$ ~ 21 %
- $p_{Ar}$ ~ 1 %
- $p_{H_2O}$ 1 to 5 %
- Usually negligible

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Name</th>
<th>(O2)</th>
<th>(Ar)</th>
<th>(H2O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p_{N_2}$</td>
<td>Nitrogen</td>
<td>~78%</td>
<td>~1%</td>
<td>~21%</td>
</tr>
<tr>
<td>$p_{O_2}$</td>
<td>Oxygen</td>
<td>~21%</td>
<td>~1%</td>
<td>~78%</td>
</tr>
<tr>
<td>$p_{Ar}$</td>
<td>Argon</td>
<td>~1%</td>
<td>~21%</td>
<td>~78%</td>
</tr>
<tr>
<td>$p_{H_2O}$</td>
<td>Water Vapor</td>
<td>1 to 5%</td>
<td>~78%</td>
<td>~21%</td>
</tr>
</tbody>
</table>

Therefore:

$$p_{N_2} \approx P_T - p_{O_2} - p_{Ar} - p_{H_2O}$$

Use:

$$[\text{Gas}] = S_H(T,S) \times p_{\text{Gas}}$$

(Henry’s Law)
2. The gas tension device (GTD)

- Moored GTD

Response ~ hour

- Shipboard GTD

![Diagram of GTD components]

- Membrane
- V-notch
- O-ring seal
- A port, that leads to a pressure sensor with an internal void volume $V_p$
- Seawater flow
- Screen
- A baffle to jet seawater at the membrane
- Window

Response ~ 11 min
- Float GTD

\[ \tau \sim 2 \text{ min at surface} \]
\[ \tau \sim 10 \text{ min at 60 m} \]
More details on float GTD

$\tau \sim 2$ min at surface
$\tau \sim 10$ min at 60 m

Tank tests:

350 m (smaller HGTD)
1000m (larger CO$_2$)

Patented 2008
(Johnson & McNeil)
Equilibration time for float GTD

#1 pump speed

Pulse pumping is 2 times slower but 90% more efficient!

#2 water temperature

1.7 times faster at 35 °C than 5 °C

#3 hydrostatic pressure

Compressible
H < 10 m
Dynamical response of float GTD

Deconvolution NOT required for isopycnal sampling!!!
3. Measurement errors for N₂

1) Gas solubility coefficients, \( S_H(T,S) \) - big

\[
S_H(N_2) \sim 0.14\% \quad S_H(O_2) \sim 0.2\% \quad S_H(Ar) \sim 0.13\% \quad [\text{Hamme & Emerson, 2004; Garcia & Gordon, 1992}]
\]

2) Winklers - big

\([O_2]\) \sim \text{typical 0.5 \%, at best 0.2\%}

NB: error on pN₂ is 0.14\%, at best 0.06\%

3) Assume Argon levels - medium

a) best use Ar sat = N₂ sat (recursive approach); within 2\% at HOT/BATS

or b) Ar sat = 100\%, and conservatively within 10\% equilibrium

NB: error on pN₂ is 0.03\% for assumption (a), and 0.13\% for assumption (b).

4) Gas tension - small

accuracy: \( \pm 0.2 \text{ mbar or } \sim 0.02\% \)  
precision: \( \sim 0.00001\% \)

drift > 0.02\% per year!

Reported T controlled water bath tracks air pressure to within \( \pm 0.07\% \) over 8 days.
Minimum predicted error for $[N_2]$ is $\pm 0.25\%$
(requires careful Winklers and GTD equilibration)

Mass-spec (MS) intercomparisons

😊 Time series: *Emerson et al.* [2002] made comparisons over 2 yrs at HOTS, reported pN$_2$ better than $\pm 0.5\%$

😢 Vertical profiles: McNeil et al. [2006] using floats at $< 45$m depth in Puget Sound showed GTD-N$_2$ up to 2.8% higher than MS-N$_2$. Co-located sampling is hard to do, but this difference was large. Unresolved, needs more work!
Hurricane Frances 2004

4. Some results from the field

- mixed layer $N_2$ saturation
- 2 floats

Float 21 and Float 22

N2 Saturation (%)

245 245.2 245.4 245.6 245.8 246 246.2 246.4 246.6 246.8 247

Year Day, 2004

gas flux
mixing
Sea surface gas tension during DOGEE-II (NE Atlantic off Portugal)

Collaborators: Eric D’Asaro (APL/UW) Rob Upstill-Godard, (UK) Phil Nightingale (UK) Will Drenan (U Miami) Mike DeGrandpre (U. Montana) ....

![Graph showing sea surface gas tension during DOGEE-II](image-url)
1) Use isopycnal sampling for $N_2$ profiles.

2) Assuming $N_2$ is conservative in pycnocline (ie. linear $[N_2]$ versus density) can estimate precision of $[N_2]$ determinations to be ± 0.14% ($N=13$).
5. New CO$_2$ sensor uses same patented membrane interface

- Response: 3+ minutes
- Depth: 1000 m
- Size: 17x33 cm
- Power: 5+ Watts
- Accuracy: xCO$_2$ ± 1 ppm (approx)
- Precision xCO$_2$: ± 0.01 ppm
6. Summary

- Measurements of N$_2$ provide information on gas exchange and productivity; complements O$_2$ as proxy for ‘abiotic O$_2$’

- Gas tension is very precise and stable (± 0.02 % per year), has been measured on ships, moorings, and profiling floats

- Estimate N$_2$ to better than ± 0.5%; needs good TS and O$_2$ (Winklers)

- Expect new low power float sensor suit to measure O$_2$/N$_2$/CO$_2$/CH$_4$
Dynamical Response of Profiling GTD

\[ \frac{dP_M}{dt} = -\frac{(P_M - P_T)}{\tau_g} + w\beta_m(p) \]

\( \tau_g(p) \) = equilibration time of GTD
\( \beta_m(p) \) = isothermal compressibility of membrane (or 1/K_m)
\( w \) = vertical velocity of float
\( P_M \) = measured pressure of GTD
\( P_T \) = true gas tension of the water
\( P \) = hydrostatic pressure

**Forward Solution:** use ‘best guess’ for \( P_T(z) \), integrate then compare to \( P_M \)

**Inverse Solution:** solve directly for \( P_T \)