Nitrate and pH sensors for deployment in a global ocean observing array: simple sensors that operate for years without recalibration

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1. Why develop chemical sensors for multi-year deployments (with no chance for direct human intervention after deployment).
   a. Global problems demand global observing with seasonal resolution – only possible with large scale, sensor networks. Frequent service not possible

2. Examples – Nitrate/pH

3. Efforts in other labs focused on sensors for profiling floats
$106 \text{CO}_2 + 16 \text{HNO}_3 + \text{H}_3\text{PO}_4 + 122 \text{H}_2\text{O} \rightarrow (\text{CH}_2\text{O})_{106} (\text{NH}_3)_{16} \text{H}_3\text{PO}_4 + 138 \text{O}_2$
All sensor data I’ll show today is available online at FloatViz

www.mbari.org/chemsensor/floatviz.htm
Ship based science cannot address these problems at a global scale!
Annual nitrate observations at the surface.
20 min on sea surface
1000 m
1 to 10 days drifting
1000 m
Collect T/S profile on ascent
2000 m

Argo array – monitors ocean T
1,000,000 profiles to date

UW/MBARI Chem Sensor array

Five year life. Ascent driven by a volume change of ~250 ml
Nitrate has a moderate UV absorption band
$\pi \rightarrow \pi^*$

$\varepsilon \sim 4000\, \text{L mol}^{-1}\, \text{cm}^{-1}$ at 217 nm
In situ ultraviolet spectrophotometry for high resolution and long-term monitoring of nitrate, bromide and bisulfide in the ocean

MBARI ISUS nitrate sensor integrated into modified Apex profiling float.

- 60 NO$_3^-$ meas./profile to 1000 m
- Precision $<\pm 0.2$ µM (1 SD)
- Float endurance 320 profiles to 1000 m. ~4.5 year life at 5 day cycle time
- 44 joule/measurement = 20% of battery
- 800 grams (we were allowed 1 kg)
LETTERS

Nitrate supply from deep to near-surface waters of the North Pacific subtropical gyre

Kenneth S. Johnson¹, Stephen C. Riser² & David M. Karl³
North Pacific/Gulf of Alaska

Nitrate [µM]

Depth [m]

2009 2010 2011 2012 2013

Ocean Data View

MBARI Chemical Sensor Lab
Surface T and NO$_3^-$ for float 5143 at 50°N in the North Pacific. Station sampled 3x per year.
1000 m T and NO$_3^-$ for float 5143 at 50°N in the North Pacific. Station sampled 3x per year.
Acidification signal = -0.0017 pH/year

Production/Respiration signal = 0.03 pH/year
 Ion Sensitive Field Effect Transistor (ISFET)
- Nadine Le Bris
- Kiminori Shitashima

High-Frequency Dynamics of Ocean pH: A Multi-Ecosystem Comparison
Gretchen E. Hofmann¹, Jennifer E. Smith², Kenneth S. Johnson³, Uwe Send², Lisa A. Levin², Fiorenza Micheli⁵, Adina Paytan⁵, Nichole N. Price², Brittany Peterson², Yuichiro Takeshita², Paul G. Matson¹, Elizabeth Derse Crook⁵, Kristy J. Kroeker⁴, Maria Cristina Gambi⁶, Emily B. Rivest¹, Christina A. Frieder², Pauline C. Yu¹, Todd R. Martz²,
ISFET: Potentiometric pH Sensor

Amphoteric Metal Oxide insulator on FET gate
MeOOH⁻ MeO MeOH⁺
Low pressure DuraFET

Media seal (gasket)
ISFET die
Conductive Elastomer
PCB

Encapsulation of ISFET sensor chips

Deep-Sea DuraFET responds to the activity of HCl in seawater

\[ V_{RS} = [k_0 + k_2 \cdot t + f(P, T)] - \frac{RT}{F} \ln (a_{H^+} a_{Cl^-}) \]

\[ = [k_0 + k_2 \cdot t + f(P, T)] - \frac{RT}{F} \ln (\gamma_{\pm \text{HCl}}^2) - \frac{RT}{F} \ln (m_{H^+} m_{Cl^-}) \]

• Calibrate \( k_0, k_2 \) and \( f(P, T) \) in lab,
• Know \( \gamma_{\pm \text{HCl}} \) and \( m_{Cl^-} \) from literature (and salinity, T, P),
• Measure \( V_{RS} \) (Voltage between reference and source),

Calculate \( m_{H^+} \)

\( \pm 0.001 \) pH is equivalent to a 0.2% error in \( m_{H^+} \)
Alkalinity can be predicted using regional regressions of TAlk on Temp/Salinity/Depth and Dissolved Inorganic Carbon can be determined.
Other chemical sensors available
  - Fluorescence lifetime $O_2$ optode

Otto Wolfbeis

↓

Ingo Klimant

↓

Ocean community
Reagentless and Silicate interference free electrochemical method for Phosphate detection in seawater


Mo + 4 H₂O $\rightarrow$ MoO₄²⁻ + 8H⁺ + 6e⁻

PO₄³⁻ + 12 MoO₄²⁻ + 27 H⁺ $\rightarrow$ H₃PMo₁₂O₄₀ + 12 H₂O

pH = 1 ; H⁺/MoO₄²⁻ = 70

Amperometry at rotating gold electrode (0.29 V, 2000 rpm): Standard addition of phosphate 0.5 – 3.5 µM and silicate 8.5 – 154.5 µM in artificial sea water

Detection limit: 0.11 µM
Precision: 5.7 % (1.60 µM)
Measurement time: 15 min

J. Jonca, C. Barus, W. Giraud, M. Comtat, M. Armengaud, N. Striebig, V. Garçon
In Situ CO₂ and O₂ Measurements on a Profiling Float

Björn Fiedler, Peer Fietzek, Nuno Vieira, Péricles Silva, Henry C. Bittig, Arne Körtzinger

Abstract . Full Text . PDF (2902 KB)
Sensor for particulate inorganic carbon (PIC).

Polarizer Crossing efficiency 50,000 – 100,000:1
Particle Free Blank($V_{\text{cross Blk}}$): $\sim 10^{-5}$ of primary beam energy

birefringent particle: rotation of plane of polarization
& birefringent photons pass to detector.

Some light absorbed and/or scattered from beam by non-birefringent particles

Bishop, UC Berkeley  Funding: NSF-OTIC
The on-chip titration concept was invented in 1989 and developed in the Netherlands (Olthuis & Bergveld, 1995). NSF OTIC funded UCSD/SIO to modify the Honeywell Durafet chip to measure seawater total alkalinity (Award 1155122).

**Concept:** coulometrically generated protons diffuse across the pH sensitive gate at a rate determined by the total alkalinity. A titration curve is recorded in the time domain where longer endpoints correspond to higher alkalinity.

ISFET chips are currently being modified in the nano3 facility at UCSD. SIO will carry out tests using prototype chips in 2013.
Ocean chemistry will change from a ship board science to an autonomous sensor based science to address the global challenge.
In the future, “vessels will be support, not monitoring platforms” Mel Briscoe, 2010. Which means the next generation of global ships can be small to control costs. E.g., 28 meter R/V Kaharoa. Works globally supporting the Argo system.

Astronomers no longer go to the “observatory”. Data comes to them on the Internet - think Hubble Space Telescope.

Figure 3. The Argo voyages of RV Kaharoa are shown, with different colors indicating different years. Since 2004, this small RV has deployed 750 Argo floats, without which the Argo array would not have global coverage. Small RVs can perform many vital functions in global ocean observations.
The train is leaving the station!!