

Testing and Refinement of Long Pathlength Liquid Core Waveguide Sensors for Autonomous In-Situ Analysis of the Upper Ocean

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LONG -TERM GOALS

This research project is directed toward the development of *in-situ* optoelectronic instrumentation for measurement of key variables that influence oceanic biogeochemistry. The devices under development have extraordinary sensitivity and versatility, and will be used for rapid adaptive sampling of chemical gradients, and long-term ocean observations within large-scale monitoring networks.

OBJECTIVES

The broad objectives of this work are the testing, deployment and refinement of spectroscopic sensors for monitoring the distributions of reactive chemicals in seawater. The analytes of special interest in this work are iron, copper, nitrate, nitrite, ammonia, phosphate and CO₂-system variables (total inorganic carbon, total alkalinity, CO₂ partial pressure and pH). The desired accuracy of the in-situ instrumentation is 0.1%, and the anticipated limit of detection for micronutrients is approximately one nanomolar. The sensors will be capable of autonomous operations on a wide variety of platforms including AUVs, profiling floats, gliders and moorings.

APPROACH

Fluorimetry and absorbance spectroscopy are instrumental methods of choice for laboratory and shipboard measurements of key biogeochemical variables due to their specificity and sensitivity. However, because the concentrations of biologically essential nutrients in the upper ocean can be extremely low, conventional spectroscopic measurements are often incapable of resolving important relationships between ocean biology and ocean chemistry. Consequently, through the ONR funding on this project we have (a) pursued order of magnitude improvements in the sensitivity of conventional spectroscopic analysis for key oceanic nutrients and (b) undertaken the development of instrumentation which allows extremely sensitive and analyte-specific analyses to be performed in-situ. The salient benefits of this work include dramatic improvements in sensitivity, rates of sample analysis, and

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sample processing cleanliness. Furthermore, data acquisition is near real-time, whereupon data acquisition and sampling strategy can be closely and interactively linked.

The specific technological approach in this project involves the use of Teflon AF 2400 liquid core waveguides to achieve optical pathlengths as long as 10 meters in shipboard analyses (Lenes et al., 2001) and pathlengths between 30 cm and 5 meters for in-situ analyses. Through ONR support we pioneered the use of these waveguides for analysis of a wide variety of analytes in the laboratory: Fe, Cu, Cr, Mo, HS^- , NO_2^- , NO_3^- , NH_3 , total dissolved inorganic carbon and pH (Waterbury et al., 1997; Yao et al., 1998; Yao and Byrne, 1999; Byrne et al., 2000; Byrne et al., 2001). This work requires the refinement of conventional spectroscopic procedures, with detection limits only on the order of 100 nanomolar, to allow simple, robust measurements at nanomolar to subnanomolar concentration levels. Refined measurement protocols are subsequently adapted to in-situ spectroscopic instrumentation, developed at the USF Center for Ocean Technology, to provide robust in-situ chemical measurements (Steimle et al. 2002). As such this project entails chemical engineering, optoelectronic engineering, and scientific testing in both the laboratory and the field.

Current key personnel in this project include: R.H. Byrne (Lead Scientist), E.A. Kaltenbacher (Lead Engineer), Eric Steimle (Chemist), Xuwu Liu (Marine Physical Chemist), Michael Callahan (Marine Chemist), Lori Adornato and Kelly Quinn (students).

WORK COMPLETED

Spectrophotometric Elemental Analysis Systems (SEAS sensors) are currently being designed, improved and tested in the field. SEAS I (Figure 1) has a two-pump mixing system, and is suitable for analyses in which a single reagent, or mixed reagent, is combined with a seawater sample-stream.



Figure 1. The SEAS-I Sensor

[This picture of SEAS-I shows the system electronics and spectrophotometer housed in a transparent pressure housing (left) and the reagent/pumps/optical system (right) that is exposed to ambient seawater]

SEAS-I is suitable for measurements of Fe(II), Fe(III), NO_2^- , NO_3^- , pH and pCO_2 . We have assembled a total of eight SEAS-I sensors for at-sea testing. Calibrations of SEAS-I show absorbance vs. concentration responses that are highly linear over a wide range of concentrations (several hundred

micromolar to less than one nanomolar). SEAS-I has been used for vertical nitrite profiling in the Gulf of Mexico (Steimle et al., 2002), and in the Pacific Ocean on a month-long cruise between Honolulu and San Diego. A nitrite profile typical of those obtained in the Pacific is shown in Figure 2 along with comparative fluorescence measurements obtained at the same station. The SEAS-I instrument collected data every two seconds and provided unprecedented detail about the distribution of nitrite in the upper water column. This work shows that, using SEAS, the location of the nitracline can be studied with high precision. This capability will provide an improved understanding of upper-ocean biogeochemical processes, and improved models of the influence of ocean chemistry on the optical properties of the upper ocean. Figure 2 shows that the PNM has a strikingly sharp profile in the water column. NO_2^- concentrations vary by a factor of approximately 100 over distances of 15 to 25 meters. Conventional sampling and shipboard analyses are wholly incapable of resolving such distributions.

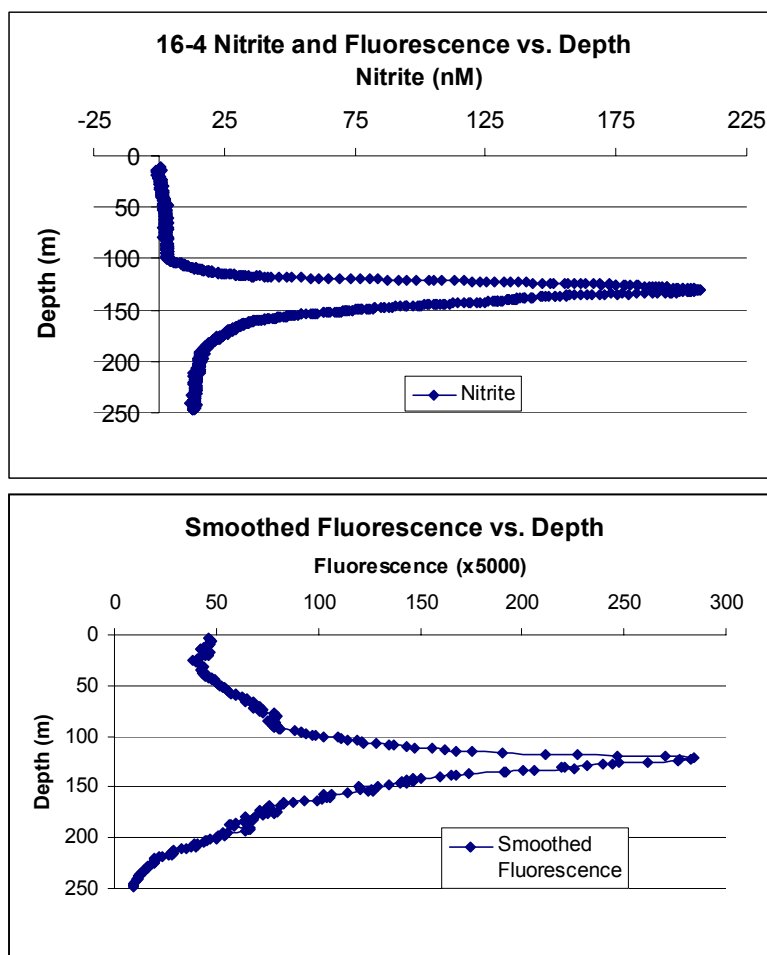


Figure 2. A Nitrite versus Depth Profile in Oligotrophic Seawater Obtained with SEAS
[This figure shows near zero nitrite concentrations between the surface and 110 meter depths, with concentrations sharply rising to a 210 nanomolar maximum at 130 meters. Concentrations at greater depth decline sharply and exhibit a shoulder at about 140 meters. The nitrite data, which were obtained every two seconds, exhibit a remarkably smooth profile that required no averaging. The fluorescence profile, shown for comparison with the NO_2^- profile, is remarkably similar in form and also with respect to the depth of its maximum. The fluorescence profile is far noisier than the NO_2^- profile and was processed using a moving average filter.]

Laboratory development of a SEAS-I system for pH analyses is now complete. Although we had thought that our pH measurement system was full satisfactory approximately one year ago, we subsequently discovered that further improvement was possible. A chemical, rather than instrumental, problem was identified and eliminated. Laboratory tests now show that our SEAS-pH system provides measurements with an accuracy and precision on the order of 0.001 pH units.

A second type of SEAS system (SEAS-II) has been designed to allow greater flexibility in chemical measurements. SEAS-II is based on the design of SEAS-I, but a third reagent pump and other features will allow new types of measurements and improvements in the quality of the analyses that are currently possible using SEAS-I. The improved design of SEAS-II will make this instrument exceptionally robust. Testing of the first SEAS-II sensor is expected to begin in early November. SEAS-II will allow measurements of total dissolved inorganic carbon (Byrne et al., 2002), ultra-trace levels of dissolved iron, and improved measurements of nitrate and copper.

A third type of SEAS system (SEAS-I-fluorescence) has been developed for fluorometric measurements of ammonia. Measurements show excellent linearity for concentrations up to 700 nanomolar with a current detection limit on the order of 2 nanomolar. The sample processing rate for ammonia at low concentrations is approximately 3 minutes per sample. Much higher rates are attainable at higher ambient ammonia concentrations.

RESULTS

Our work in 2002-2003 was particularly notable because our capabilities have progressed to a point that nearly all of our systems are being extensively tested in the field. Our field-testing program currently involves ammonia, nitrite, nitrate, copper, pH and pCO₂. Two manuscripts describing our ONR supported research are currently in review (Adornato et al. (2003) and Callahan et al. (2003)) The first of these works describes extensive *in-situ* observations of the primary nitrite maximum in the North Pacific Ocean. The second work describes extensive *in-situ* measurements of dissolved copper in an anthropogenically-impacted estuary. Our ONR funded project has, to date, resulted in eight peer reviewed publications, two technical reports and two manuscripts submitted.

IMPACT/APPLICATIONS

The SEAS sensors developed in this project can be used to markedly extend the limits of detection for a wide variety of influential chemicals in seawater, estuaries, rivers, lakes and subterranean waters. SEAS sensors provide real-time measurement capabilities, whereupon sampling strategies can be modified in response to prompt observations. SEAS sensors are robust and, although relatively inexpensive, are orders of magnitude more sensitive than conventional spectrophotometers.

TRANSITIONS

The Center for Ocean Technology is currently in discussions that may lead to commercial licensing of the SEAS-I sensor system. SEAS instruments are used as a teaching aid in the USF Oceanography Camp for middle-school-age girls each summer.

RELATED PROJECTS

The SEAS-I instrument forms the basis for a NOAA project funded through the University of New Hampshire, “In-Situ Monitoring of a Reactive Metal in Riverine and Estuarine Mixing Zones”. SEAS-I sensors form the basis for a USF proposal submitted to the National Science Foundation, “Testing and Development of a Buoy-Mounted Instrument of Iron Delivery to the Surface Ocean by Wet Deposition”. SEAS instruments constitute the principal chemical sensors that are being used in the ONR funded project, “Bottom Stationed Ocean Profiler”. SEAS sensors form the basis for a collaborative ONR project with the University of Maine (Mary Jane Perry), “The role of Nutrients in the Formation, Maintenance and Transformation of Phytoplankton Thin Layers”.

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PUBLICATIONS

Adornato, L., Kaltenbacher, E.A. and Byrne, R.H. 2003. "In-Situ Observations of the Primary Nitrite Maximum in a North Pacific Gyre". *Deep-Sea Research*. [submitted, refereed]

Callahan, M.R., Kaltenbacher, E.A. and Byrne, R.H. 2003. "In-Situ Measurement of Cu in an Estuarine Environment Using a Portable Spectrophotometric Analysis System". *Environmental Science and Technology*. [submitted, Refereed]

PATENTS

Variable Exposure Rotary Spectrometer
Fluorescence Based Liquid Core Waveguide