

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

Robert H. Byrne
Department of Marine Science
University of South Florida
140 Seventh Ave. South
St. Petersburg, FL 33701
phone (727) 553-1508 fax (727) 553-1189 email byrne@marine.usf.edu

Eric Kaltenbacher
Center for Ocean Technology
University of South Florida
140 Seventh Ave. South
St. Petersburg, FL 33701
phone (727) 553-3959 fax (727) 553-3967 email eak@marine.usf.edu

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LONG-TERM GOALS

Our research is directed toward the development of optoelectronic devices for measurement of key variables that influence oceanic biogeochemistry. The devices will have extraordinary sensitivity and versatility and, in time, their simplicity should lead to inexpensive deployments and utilization for comprehensive ocean-monitoring on long temporal scales and vast spatial scales.

OBJECTIVES

The broad objectives of this work are the deployment, testing and refinement of miniature, long-pathlength spectral analysis systems for monitoring elemental distributions in seawater. The analytes of special interest in this work are iron, copper, nitrate, ammonia, nitrite and CO₂-system variables (total inorganic carbon, total alkalinity, CO₂ partial pressure, and pH). The instrumentation under development is being designed to measure these variables with a resolution of approximately one part in a thousand. Thereby, we are developing systems capable of measurements over a wide dynamic range for each target analyte. Our in-situ devices are being developed to function autonomously in the upper ocean (0-2000m) for rapid short-term observations of chemical distributions (e.g. profiling platforms) and also observations of temporal changes on long time scales.

APPROACH

Our ONR funded research has been specifically directed to the field testing of our current Spectral Elemental Analysis System (SEAS-I) and development of a refined sensor (SEAS-III) with improved sensitivity and expanded capabilities. Observations of SEAS-I performance at sea and in the laboratory have been used to improve sensor performance with respect to (a) system optics (lamp and detector stability), (b) system fluidics (reagent mixing and storage), (c) catalysts of chemical reactions and (d) development of multiple-analyte analysis capabilities.

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WORK COMPLETED

During the past year SEAS-I (Figure 1) has been extensively tested in the laboratory and at sea. Tests in the laboratory demonstrated the existence of corrosion problems that interfered with iron analyses. These problems, which originated in the SEAS fluidics system, have been corrected and SEAS-I has now been shown to be capable of Fe^{II} and Fe^{III} analysis at the nanomolar concentration level. Laboratory tests of SEAS-I configured for pH analyses demonstrated excellent agreement with analyses obtained on conventional spectrometers (i.e. agreement within approximately ± 0.006 pH units). However, long-term drift in the spectral content of our source lamp necessitated frequent reference measurements whereby the sample acquisition rate was compromised. The substantial efforts dedicated to solving this problem led to the identification of a lamp with suitable intensity, stability and power requirements. As such, SEAS-I is now capable of providing continuous pH measurements of very high quality. At-sea pH and NO_2^- measurements with SEAS-I identified occasional problems with the integrity of the pressure housing. The source of these problems has been identified and a protocol for eliminating future problems has been effected.



*Figure 1: SEAS-I
[The SEAS-I sensor.]*

Work with SEAS-I has indicated that this instrument is highly effective for a variety of types of measurements. However, the inability of SEAS-I to mix a combination of reagents in sequence is analytically limiting, and the performance of commercially available miniature spectrometers does not meet our requirements. For these reasons an advanced system (SEAS-III) has been designed and is under construction. This system will be capable of multiple types of measurements with superior performance (stability and sensitivity).

In addition to our improvements in SEAS(I+III) hardware and software, ongoing methods-development in the laboratory has led to (1) a novel spectrofluorometric system for very sensitive

ammonia analyses and (2) a novel system for CO₂-system measurements wherein all primary CO₂-system variables can be measured in-situ.

RESULTS

The results of our SEAS-I investigations of NO₂⁻ profiles in the Gulf of Mexico have been submitted for publication in *Marine Chemistry* (Steimle et al, 2001). The results of our methods developed for CO₂-system parameter measurements has been accepted for publication in *Analytica Chimica Acta* (Byrne et al, 2001). A manuscript describing our novel spectrofluorometric system for ammonia analysis is in preparation.

The design of SEAS-III (Figure 2) is nearly complete and construction is in progress. SEAS-III incorporates a novel, multi-spectral spectrometer design (patent application submitted to USF) that should provide spectral measurements of extraordinary sensitivity and reproducibility.

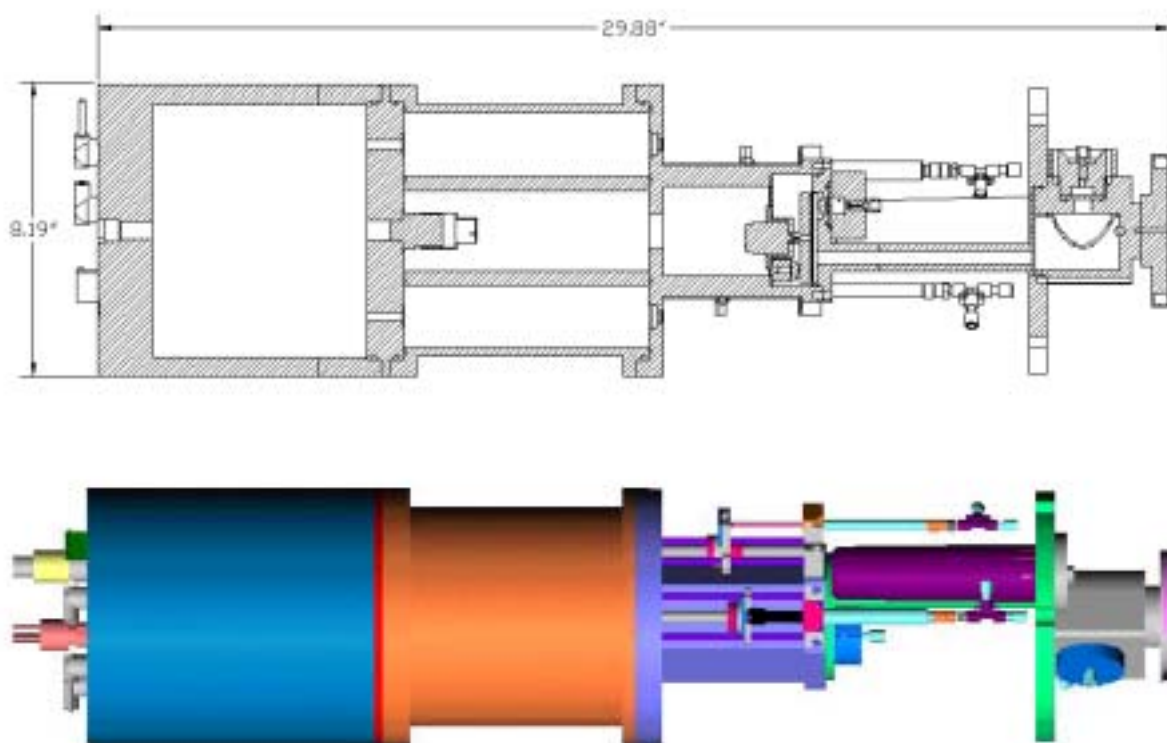


Figure 2: SEAS-III
[Top view shows a cross-sectional view of SEAS-III and a solid-model of SEAS-III is shown on the bottom.]

IMPACT/APPLICATIONS

The SEAS instruments described in this work can be used to markedly extend the detection capabilities of many existing solution-based measurements obtained via absorbance spectroscopy. Applications of these sensors will include both seawater, freshwater (rivers, lakes, subterranean waters), drinking water (Yao and Byrne, 1999) and rainwater. Our instruments are simple, portable, far less expensive than conventional spectrophotometers and yet are orders of magnitude more sensitive.

TRANSITIONS

The SEAS instrument tested in this project was used as a teaching aid during the USF Oceanography Camp Especially for Girls. The goal of this camp is to introduce middle-school-age girls to the world of science. Interest has also been expressed in commercial licensing of the technology developed under ONR support.

RELATED PROJECTS

Our SEAS-I instrument will be the principal sensor used on a moored platform for long-term, autonomous measurements of dissolved iron (Fe^{III} and Fe^{II}) in rainwater. The compact size, low-power requirements, small sample volume, and high sensitivity of SEAS-I make it particularly well suited for this application. This Fe measurement project is funded by the National Science Foundation (award number 9906614). The SEAS-Fe system used in this project is essentially identical to the system developed under ONR support. The principal engineering task in this work involved interfacing SEAS with a WHOI rain collector. The SEAS-I instrument will also form the basis for a project approved for funding by the Cooperative Institute for Coastal and Estuarine Environmental Technology (NOAA). This proposal will involve the use of SEAS-I to monitor Cu distributions in riverine and estuarine mixing zones.

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