

Autonomous In-Situ Analysis Of The Upper Ocean: Construction Of A Compact, Long Pathlength Absorbance Spectrometer.

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
Award #: N000149715011

LONG-TERM GOALS

Our research is directed toward utilization of modern optoelectronic technology for real-time monitoring of the ocean's chemical environment with a subtlety and sophistication equivalent to senses of taste and smell. We strive to construct a compact instrument capable of measuring many chemical species concurrently via fluorescence and absorption spectroscopy.

OBJECTIVES

The broad objective of this work is the development of a miniature, long pathlength spectrophotometer/fluorometer for *in-situ* elemental analysis. The long pathlength of this spectrometer (5 meters) extends the limits of detection of conventional spectrophotometric analyses by close to two orders of magnitude. In addition, spectrophotometric and fluorescence measurements are being combined in a single instrument. Realization of our objectives is being pursued through system miniaturization to an extent that will allow construction of a system capable of rapid, simultaneous analysis of a wide variety of solutes.

APPROACH

This proposal is specifically directed to the design and construction of a Spectrophotometric Elemental Analysis System (SEAS-1) which will provide an integrated view of the ocean's chemical environment. The underlying design approach behind SEAS-1 is the development of a miniature, inexpensive and easily reconfigurable instrument to measure a wide variety of solutes. Liquid Core Waveguides (LCW) provide a simple and powerful means of implementing long pathlength absorbance spectroscopy (LPAS) and very sensitive fluorescence measurements. The methods outlined in this work can be used to extend the spectrophotometric detection limits of many chemical species.

Key personnel: EA Kaltenbacher (Lead Engineer), RH Byrne (Lead Scientist), W Yao (Post Doctoral Research Associate) and Center for Ocean Technology Engineers.

Report Documentation Page

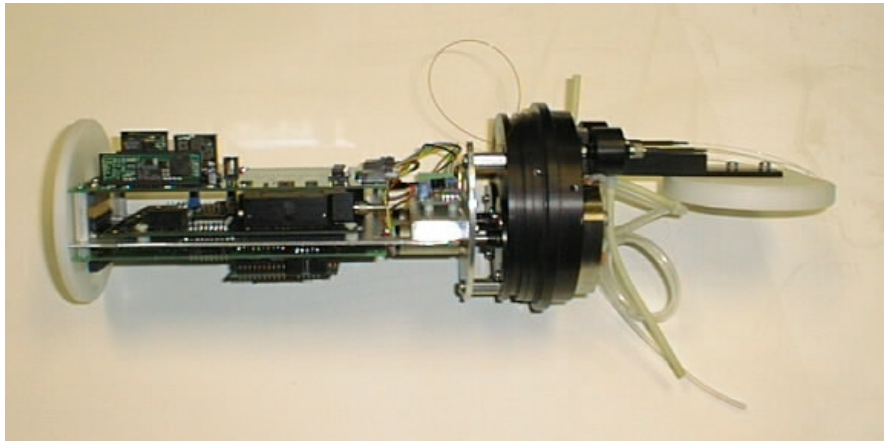
*Form Approved
OMB No. 0704-0188*

Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

1. REPORT DATE 30 SEP 1999		2. REPORT TYPE		3. DATES COVERED 00-00-1999 to 00-00-1999	
4. TITLE AND SUBTITLE Autonomous In-Situ Analysis Of The Upper Ocean: Construction Of A Compact, Long Pathlength Absorbance Spectrometer				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of South Florida, Department of Marine Science, 140 Seventh Ave. South, St. Petersburg, FL, 33701				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a REPORT unclassified	b ABSTRACT unclassified	c THIS PAGE unclassified			

WORK COMPLETED

We have constructed three SEAS instruments and have successfully deployed these instruments on autonomous underwater vehicles (AUVs) and on a buoy. Figure 1 shows photographs of the SEAS instrument with and without its pressure case. Each instrument is 4.5 inches in diameter, 20.0 inches long and weighs roughly 10 pounds. These devices have been pressure tested to a depth of 500 meters. Our sensor is designed to operate autonomously given a set of user preferences which are programmed at the start of each mission.



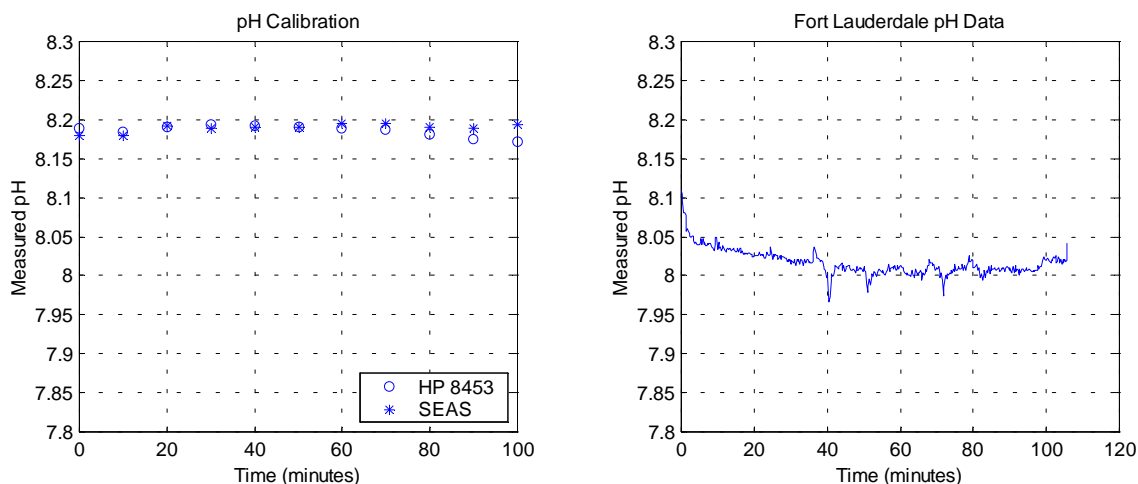
1. Photographs of the SEAS instrument. The top picture shows the complete sensor sealed in its pressure case. The lower photograph shows the interior design of SEAS. The electronics, visible on the left, are maintained in a dry environment, while the reagent delivery system and LCW are immersed in ambient seawater (right side of instrument).

A significant portion of our SEAS development efforts involved research and testing of individual components within the instrument to yield optimal performance. The instrument's optical design (light source, light coupling and layout of the liquid core waveguide) is the most crucial aspect of this work. Several configurations were tried before achieving the current design. Custom circuitry has been designed for control of all instrument functions. At the heart of this circuitry is a microcontroller. Substantial efforts were devoted to writing the control software for this microcontroller.

Testing of the instrument included laboratory setups and field deployments. Laboratory testing included experiments to determine optimal reagent concentrations, fluid flow rates, and optical configuration. This experimentation was conducted for pH, nitrite and nitrate. Current experimentation is directed towards nitrate, ammonia, and iron. The instrument's first field test was at the Coastal Benthic Optical Properties site near Lee Stocking island in June 1999. However, this deployment was unsuccessful due to errors in software. Another AUV deployment occurred in August 1999 off the coast of Ft. Lauderdale. We successfully measured pH and nitrite during this mission. We have also deployed SEAS on a buoy in the North Pacific in October 1999 under a project funded by The National Oceanographic Partnership Program (NOPP).

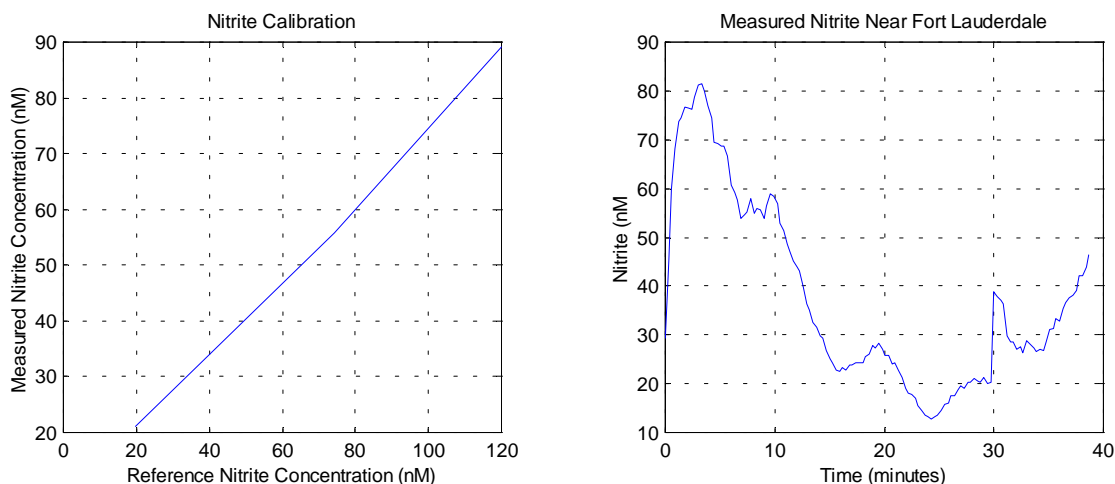
RESULTS

Deployments of the SEAS instrument to date have yielded pH and nitrite measurements of surface seawater. Laboratory measurements of standard solutions were used to verify the accuracy of our sensor before the field missions.



2. Laboratory calibration data for pH measurements are shown on the left and pH measurements in waters near Fort Lauderdale are shown on the right.

Figure 2 illustrates our laboratory and field pH data obtained using SEAS. These laboratory results were obtained over a period of 100 minutes with discrete readings every 10 minutes. A Hewlett Packard 8453 spectrophotometer was used to assess the accuracy of the SEAS measurements. These data indicate good agreement between SEAS pH measurements and those obtained using conventional instruments. The right side of Figure 2 shows the pH of surface seawater about 1 mile off the Fort Lauderdale coast. During the acquisition of this data, the AUV which carried SEAS traveled within an area on the order of $4 \times 10^4 \text{ m}^2$. Measurements of pH were taken once every twenty seconds.



3. Nitrite data obtained with SEAS. The curve on the left shows measured nitrite versus reference nitrite levels. Nitrite data from Fort Lauderdale in August 1999 are plotted on the right.

Our nitrite data are graphed in Figure 3. The left plot shows a nitrite(NO_2^-) calibration curve using SEAS. Due to the abbreviated time allowed for color development in these tests, our nitrite measurements are reproducibly 70% of the actual values and are linear as the nitrite concentration increases. The graph on the right shows measured nitrite at the test location near Fort Lauderdale. These data were obtained in surface seawater and represent samples from the 200 meter box described above.

We are currently receiving pH data from our SEAS instrument mounted to a buoy in the North Pacific. Data are received every two days via a GOES satellite. This deployment is scheduled to last for one year and should provide useful sensor endurance information.

IMPACT/APPLICATIONS

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

TRANSITIONS

The SEAS instrument developed in this project is being used as a basis for research funded by the National Oceanic Partnership Program (NOPP BAA/ONR32) supported by the Office of Naval Research under Award No. N00014-98-1-0803 with the University of South Florida as a subcontractor to the Regents of the University of Southern California. In this project oceanographic systems (including SEAS instruments) are being configured for long-term autonomous operations on deep-sea moorings.

RELATED PROJECTS

Our SEAS instrument will be the principal sensor used on a moored platform for long-term measurements of dissolved iron (Fe^{III} and Fe^{II}) in rainwater. SEAS's compact size, low-power requirements, small sample volume and high sensitivity make it particularly well suited for this application. This Fe measurement project is funded by the National Science Foundation (award number 9906614).

REFERENCES

J. Stone, "Optical Transmission Loss in Liquid-core Hollow Fibers", IEEE Journal Quantum Electronics, QE-8, 1972, pp. 386-8.

J. Stone, "Optical Transmission Loss in Liquid-core Quartz Fibers", App. Phys. Lett., 20, 1972, pp. 239-40.

Yao, W. and Byrne, R.H., "Determination of trace Chromium (VI) and molybdenum (VI) in natural and bottled mineral waters using long pathlength absorbance spectroscopy (LPAS). Talanta 48:277-282, 1999.

PUBLICATIONS

Byrne, R.H., Kaltenbacher, E. and Waterbury, R., "Autonomous *In-Situ* Analysis of the Upper Ocean: Construction of a Compact, Long Pathlength Absorbance Spectrometer Aimed at Order-of-Magnitude Improvements in the Sensitivity of Spectrophotometric Analysis," *Sea Technology*, pages 71-75, February 1999.

Byrne, R.H., Yao, W., Kaltenbacher, E. and Waterbury, R.D., "Construction of a compact spectrofluorometer/spectrophotometer system using a flexible liquid core waveguide," Talanta, in press.

Waterbury, R., Yao, W., and Byrne, R., "Long Pathlength Absorbance Spectroscopy: Trace Analysis of Fe(II) using a 4.5 meter Liquid Core Waveguide", *Anal. Chim. Acta.*, 357:99-102, 1997.

Yao, W. and Byrne, R.H., "Determination of trace Chromium (VI) and molybdenum (VI) in natural and bottled mineral waters using long pathlength absorbance spectroscopy (LPAS). Talanta 48:277-282, 1999.

Yao, W., Byrne, R., Waterbury, R., "Determination of Nanomolar Concentrations of Nitrite and Nitrate in Natural Waters using Long Pathlength Absorbance Spectroscopy", *Environ. Sci. Technol.* 32:2646-2649, 1998.