Development of an Autonomous Ammonium Fluorescence Sensor (AAFS) with a View Towards *In-situ* Application

Peter B. Ortner
UM/RSMAS/CIMAS
4600 Rickenbacker Causeway
Miami, FL
phone: (305) 421-4619 fax: (305-421-4999 email: portner@rsmas.miami.edu

Award Number: N000141010210

LONG-TERM GOALS

Our goal is to develop a portable autonomous ammonium sensor. Such a sensor could be deployed for periods of up to a month aboard ships, upon moorings or drifting buoys or used as a component in lowered or towed oceanographic instrument packages for vertical profiling.

OBJECTIVES

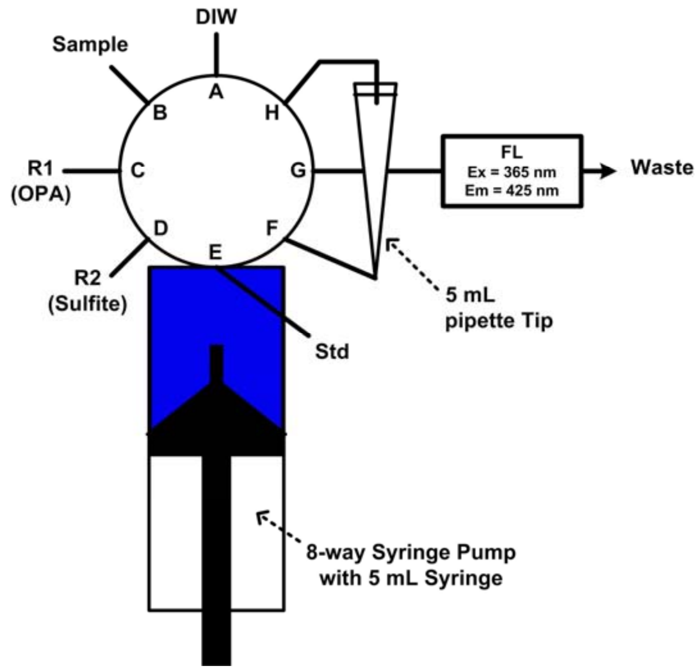
Our technical objective is to develop a robust, relatively simple, inexpensive, low power compact instrument with a detection limit in the nM range and a sampling frequency of at least 6 samples per hour is our goal. Robustness, simplicity, low cost, lower power and small size are the practical desiderata for commercial application. Commercialization and the economies of scale that can result will permit wider application in the oceanographic community.

APPROACH

Our approach has been to design, assemble and demonstrate engineering models suitable for benchtop laboratory use, take these aboard ship and once we have achieved key design objectives to test them first in an ongoing sampling program at coastal sewage outfalls along the east coast of Florida and then underwater taking advantage of a "permanent" large mooring associated with the NOAA underwater habitat in the Florida Keys. Once we have achieved all our basic design objectives to then concentrate upon further miniaturizing, reducing power consumption as much as possible and re-packaging for alternative applications. These efforts at optimization will be facilitated by the large and diverse South Florida user community earlier identified and the related instrument development activities occurring both at UM/CIMAS and AOML. Key personnel in the initial steps are Drs. Amornthammarong and Dr. Zhang. Dr. Ortner, his graduate student and Mr. Shailer Cummings, while assisting in these initial steps, will take a much larger role with regard to underwater deployment and field testing.

WORK COMPLETED

Work has progressed rapidly over the seven months that have passed since the project was intiated. First an effective mixing chamber was designed that could be used in conjunction with syringe pump for flow analysis. It was tested in the laboratory. We then combined this mixing chamber, the syringe pump, multiposition valve technology and a previously described continuous flow FIA shipboard analyzer for underway measurement of ammonium in seawater (Amornthammarong and Zhang, 2008) to create an autonomous batch analyzer (ABA) which was then tested in the field. It is diagrammatically depicted below:



RESULTS

A simple, effective mixing chamber used in conjunction with a syringe pump for flow analysis was developed and thoroughly evaluated in the laboratory. It was constructed using a conventional 5 ml pipette tip and its performance compared with a widely-used mixing coil. The results obtained demonstrated that the mixing coil does not rapidly and completely mix solutions. Utilizing a configuration that reversed solution positions in the chamber with each mixing cycle, the proposed mixing chamber was able to achieve complete mixing in a significantly shorter time than the mixing coil. The influence of injected sample volume on absorbance signals was then evaluated by calculating an $S_{1/2}$ value for the system. As tested with a minimal rinse, the system has no discernable carryover. Testing this new approach in our previously described silicate measurement system resulted in a more than two fold improvement in sensitivity. Results were published in (Amornthammarong et al, 2010).

An autonomous batch analyzer (ABA) was then developed for the measurement of ammonium in natural waters. The system combines previously described batch analysis and continuous flow analysis methods and our new mixing chamber. With its simpler design, the ABA system is robust, flexible, inexpensive, and requires minimal maintenance. The sampling frequency is ca. 8/hr and the potential limit of detection ca 1 nM which is comparable to the most sensitive flow through or batch analysis methods previously described and within the design specifications we had set for our project. In addition, the system produces a calibration curve by autodilution from a single stock standard solution with the same accuracy as traditional manual calibration methods. This aspect will greatly facilitate in situ application. A manuscript describing the ABA has been submitted to >>>>>>>>>>>>>>>>>>>

IMPACT/APPLICATIONS

The sensor being developed will have broad applicability/impact with respect to Economic Development and with respect to Quality of Life. With respect to Economic Development it has considerable market potential for mandated environmental monitoring of ammonium by the waste water/recycling water industries. In that same context, using this monitoring tool to keep ammonium releases within allowable limits will have positive effects upon the coastal ecosystem in that ammonium is rapidly taken up by plants and can induce local eutrophication.

TRANSITIONS

Since development is in an early stage, although we have filed for a patent, the sensor system is not being manufactured and distributed. That said, it is already being incorporated into planning activities with respect to ecosystem health in that we are in close communication with prospective users in the wastewater industry through project FACE (see below).

RELATED PROJECTS

See http://www.aoml.noaa.gov/themes/CoastalRegional/projects/FACE/faceweb.htm for information regarding FACE. The study area of FACE covers 467 km of coastline in Miami-Dade to Brevard counties. The area includes six treated wastewater plants [TWWP]: Miami Central, Miami North, Hollywood, Broward, Boca Raton, and South Central, which together contribute ~1 million cubic meters (284 millions of gallons) per day to the region. In addition, this coastal area receives fresh water discharged through six inlets, from the Miami Harbor inlet in the south to the Boynton inlet in the north. This area is the home of nearly 5.5 million people (U S Census Bureau, 2006) and an economy heavily dependent on a healthy offshore environment. We will be testing the sensor system in the FACE context and are in close communication with wastewater industry partners. We have also submitted an NSF proposal to monitor coral reef habitats throughout the Florida Keys and if that is funded we will be using the sensor system in that context to measure natural non-anthropogenic biological excretory ammonium inputs to those habitats.

REFERENCES

Amornthammarong, N. and Zhang, J.-Z. (2008). Shipboard Fluorometric Flow Analyzer for High-Resolution Underway Measurement of Ammonium in Seawater*Anal. Chem*. 80, 1019-1026

PUBLICATIONS

Amornthammarong, N.; Ortner, P.B. and J.-Z. Zhang (2010). A Simple, Effective Mixing Chamber Used in Conjunction with a Syringe Pump for Flow Analysis *Talanta*: 81, 1472-1476.

Amornthammarong, N.; Zhang, J.-Z and P.B. Ortner. An Autonomous Batch Analyzer for the Measurement of Ammonium in Natural Waters. Submitted to Analytical Chemistry September 20, 2010.

PATENTS
The University of Miami Patent and Copyright Committee has accepted the AAFS (Case Number UMJ-178) and is proceeding with test marketing to determine commercial interest. This process will take about six months. At the end of this time (assuming such an interest is confirmed) they will proceed to file a U.S. Provisional Patent Application.