

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

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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 initiated. 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:

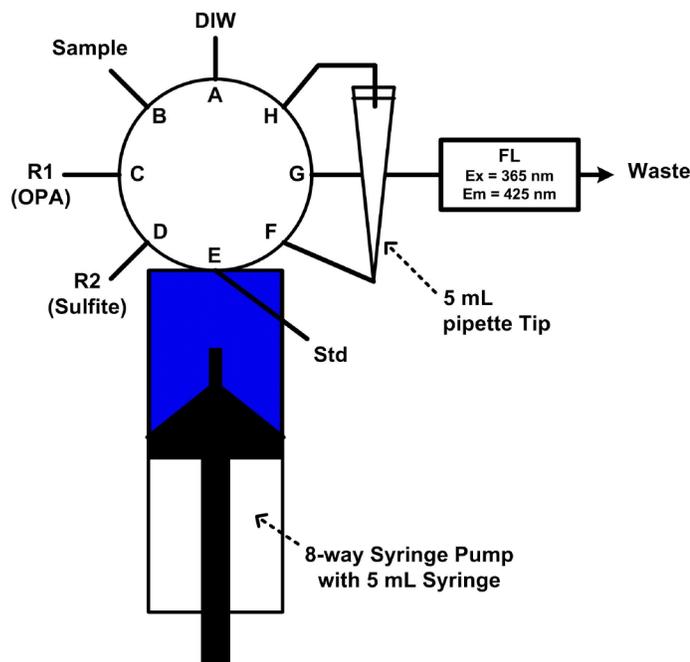


Figure 1. Autonomous Batch Analyzer (ABA) for ammonium determination: Std, Standard; R1, Phthaldialdehyde (OPA) solution; R2, Sulfite in formaldehyde solution; FL, Fluorescence detector; and DIW, Deionized water.

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 Analytical Chemistry.

IMPACT/APPLICATIONS

The sensor being developed will have broad applicability as a research tool in oceanography as well as market potential for mandated environmental monitoring of ammonium. Our primary application is the former. When the development and testing is complete we will be able to deploy such an instrument to monitor in situ ammonium in the coastal and ocean water column to study the variable influx of this rapidly assimilated nutrient that is associated with demersal zooplankton populations in benthic communities (including coral reefs), zooplankton and mesopelagic fish vertical migration, grazing by schooling herbivorous fishes and intermittent physical processes such as breaking internal waves, wind-mixing etc.

RELATED PROJECTS

None.

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.

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.