# Autonomous Measurements of Oceanic Dissolved Nitrate from Commercially Available Profiling Floats Equipped with ISUS

Stephen C. Riser

School of Oceanography, Box 355350, University of Washington, Seattle, WA 98195 Phone: (206) 543-1187 FAX: (206) 685-3354 E-mail: riser@ocean.washington.edu

Ken Johnson

Monterey Bay Aquarium Research Institute, 7700 Sandholdt Road, Moss Landing, CA 95039 Phone: (831) 731-1081 FAX: (831) 775-1620 E-mail: johnson@mbari.org

Ernest Petzrik

Teledyne/Webb Research Corp., 82 Technology Park Drive, E. Falmouth, MA 02536 Phone: (508) 548-2077 FAX: (508) 540-1686 E-mail: Ernest.Petzrick@Teledyne.com

Marlon R. Lewis Satlantic, Inc., Richmond Terminal Pier 9, Halifax, Nova Scotia, Canada B3K 5X8 Phone: (902) 492-4789 FAX: (902) 492-4781 E-mail: Marlon.Lewis@dal.ca

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#### LONG-TERM GOALS

The goal of this work has been to design, build, and produce a commercially available version of the In Situ Ultraviolet Spectrometer (ISUS) suitable for use on commercially-built profiling floats. Moored versions of ISUS already exist, and a profiling float version has been built and deployed, with excellent and exciting results. However, fabrication of the sensor and integration with the float have been to date difficult from an engineering perspective, and as a result possible by only a very few technical groups. The goal of this work is to simplify the design so that a commercial version of the float/ISUS can be produced and ultimately be widely used in the physical and biogeochemical oceanographic communites. As this project ends, we can say that we have met and exceeded our long-term goals.

#### **OBJECTIVES**

The 3000 profiling floats deployed and maintained by the Argo project have provided a global-scale ocean observing system that samples the ocean at 10 day and 300 km scales to depths of 2000 m. Argo floats make observations of temperature and salinity as functions of pressure. In the past 5 years dissolved oxygen and optical sensors capable of measuring chlorophyll and particulates have been added to some floats in the array. These measurements have shown that, in addition to Argo's utility in observing basic physical parameters, profiling floats are likely to become an important tool in observing biogeochemical parameters. Such work is in its infancy, as sensors for use on floats must be small and lightweight and consume minimal power. Several types of such sensors are now under development, and the use of profiling floats in biogeochemical studies in the ocean is likely to increase greatly in the coming years as this sensor technology matures. One parameter that is crucial to many

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Standard Form 298 (Rev. 8-98) Prescribed by ANSI Std Z39-18 biogeochemical studies is nitrate; measurements of dissolved nitrate in the ocean have long been made from shipboard platforms, and in recent years the MBARI group developed the ISUS technology as an optical measurement of nitrate. ISUS has been used in moored applications for several years, and in 2007 the MBARI and UW groups teamed up to deploy the first ISUS on a profiling float, which wdeployed at the Hawaii Ocean Time Series (HOT) site. This float continued to work well for nearly 4 years, and provided an outstanding record of the evolution of nutrients, dissolved oxygen, and temperature and salinity at the HOT site during this time. Results from this deployment, including a scientific analysis of the results, were published in *Nature* in 2010 (Johnson et al., 2010). While the float provided a wonderful dataset, the construction of such floats was at the time quite difficult and pushed the technical capabilities of the MBARI and UW groups to near their limits. Based on this preliminary success, we modified our design so that it could be made simple enough to be produced commercially, and that such instruments can be widely used in the oceanographic community. This task has been completed, and there are now several commercially-produced versions of this float/sensor pair operating in the ocean due to a fruitful collaboration between the industrial partners Satlantic (sensors) and Webb (floats) and the research groups (UW and MBARI).

#### APPROACH

Our approach has been to modify the ISUS electronics used successfully on moorings to fit inside a float pressure case, to modify the ISUS fiber optics to fit the float, and to design a new mounting for the ISUS external sensor. The results of this work is shown in Figure 1, included at the end of this report. In this case the ISUS sensor is mounted on the bottom of the float. This is due to the fact that upper endcap of the float is mounted, removed, and remounted many times during construction, in order to carry out the required CTD checks and calibration. If the ISUS were on the upper cap, the position of the fiber optics, and the resulting ISUS calibration, might change each time the endcap was removed. To get around this problem, in the initial float the sensor was bottom mounted. Due to the extra weight of ISUS, a carbon fiber hull was substituted for the usual aluminum hull used on most Argo floats. Since all the ISUS floats use Iridium communications, a CTD sample is collected at 2 meter intervals. Since the float is less than 2 m in length, it means that the pressure (depth) of the nitrate values inferred from ISUS are within one pressure bin (ie, within 2 meters) of the nearest CTD saple; this does not seem to be a serious limitation. On later floats the ISUS unit has been completely redesigned and is now on the upper endcap (see Figure 2). After refining this upper endcap design on several more floats, it appears that commercial production can begin on a trial basis.

#### WORK COMPLETED

Eighteen ISUS units similar to the one shown in Figure 1 were fabricated by UW and MBARI and deployed at various locations in the Pacific and Indian Oceans. Several years ago we designed and built a second generation version of the float/ISUS unit, with the ISUS sensor placed on the upper endcap of the float in the data stream of the SeaBird CTD unit (Figure 2); most of the eighteen floats deployed were of this design. In this case the same seawater flowing through the CTD unit and being measured for temperature and salinity is subsequently flowing through the ISUS unit just a few centimeters away. This design assures that all the relevant parameters here are measured nearly concurrently, and it also means that the ISUS is protected by the same biocide that is used to inhibit biological fouling on the CTD unit. In addition to this, we also built a few floats using Satlantic's SUNA (Submersible Ultraviolet Nitrate Analyzer) technology. This sensor is similar to ISUS but contains no fiber optics, which is a possible advantage for float-based use. The unit is considerably

larger than ISUS and requires a totally different mount than has been used previously. The SUNA unit has to be mechanically stapped to the side of the profiling float as it is too large to fit on either endcap (Figure 3). This is a distinct disadvantage to SUNA, although SUNA has been found to be somewhat simpler to manufacture than ISUS. Overall 6 floats were built (both SUNA and ISUS) by Satlantic and Teledyne/Webb, with good success. The transition to a commercial version is essentially complete. A paper describing some of the major results of this commercialization project has recently appeared (Johnson et al., 2013).

## RESULTS

An example of the data from one of the UW/MBARI instruments (UW float 6391, near Bermuda in the western North Atlantic) is shown in Figure 4. The plot shows data from 266 profiles to a depth of 1000 m, collected at 5 day intervals between October of 2009 and May of 2013. The ISUS sensor is generally stable over this time with the exception of jump in calibration of ~1  $\mu$ mol/kg after the first 3 profiles. The cause of this jump is under investigation and is likely due to a thin bacterical film growing on the sensor window, although other causes are possible. This is within our goal of having precision and accuracy of the instrument to be 1  $\mu$ mol/kg or less. Included here in Table 1 is a list of all the commercially-produced versions of float with ISUS or SUNA deployed by UW and MBARI.

## IMPACT AND APPLICATIONS

It is clear that such instruments will likely have wide use in the biogeochemical oceanography community in the coming years. In April of 2009 a workshop was held at MBARI (with PIs Johnson and Riser on the organizing committee, which was chaired by Johnson) with 60 scientists and agency representative in attendance to assess the use of floats and gliders for making useful geochemical measurements. There was a great deal of excitement in the group concerning the future of such work. It seems highly possible that in a few years the deployment of a float-based global biogeochemical observing network will begin, in parallel with the Argo array already in place. A paper discussing the future of geochemical measurements from floats and gliders summarizing many of the discussions held at the meeting has recently appeared (Johnson et al., 2009a). Teledyne/Webb and Satlantic are now fielding orders for commercial versions of floats with ISUS or SUNA, and in a few years it is likely that the global Argo array will be augmented with many floats of this type; the use of such instruments is clearly not limited to Argo, and there are a large number of potential uses of these new instruments.

#### REFERENCES

Johnson, K., W. Berelson, E. Boss, Z. Chase, H. Claustre, S. Emerson, N. Gruber, A. Kortzinger, M.J. Perry, and S. Riser (2009a) Observing biogeochemical cycles with profiling floats and gliders: prospects for a global array. *Oceanography*, **22**, 217-225.

Johnson, K., S. Riser, and D. Karl (2010) The nitrate supply from deep to near-surface waters of the North Pacific subtropical gyre. *Nature*, **465**, 1062-1065.

Johnson, K., L. Coletti, H. Jannasch, C. Sakamoto, D. Swift, and S. Riser (2013) Long-term nitrate measurements in the ocean using the In Situ Ultraviolet Spectrophotometer: sensor integration into the Apex profiling float. *Journal of Atmospheric and Oceanic Technology*, **30**, 1854-1866.

## PUBLICATIONS

Johnson, K., W. Berelson, E. Boss, Z. Chase, H. Claustre, S. Emerson, N. Gruber, A. Kortzinger, M.J. Perry, and S. Riser (2009a) Observing biogeochemical cycles with profiling floats and gliders: prospects for a global array. *Oceanography*, **22**, 217-225.

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Johnson, K., L. Coletti, H. Jannasch, C. Sakamoto, D. Swift, and S. Riser (2013) Long-term nitrate measurements in the ocean using the In Situ Ultraviolet Spectrophotometer: sensor integration into the Apex profiling float. *Journal of Atmospheric and Oceanic Technology*, **30**, 1854-1866.



FIGURE 1. The initial design of ISUS for a profiling float. In this version the sensor is located on the lower endcap of the float. The float is also equipped with an Aanderaa Optode dissolved oxygen sensor and uses Iridium communications.



FIGURE 2. The upper endcap of a profling float with the inline ISUS unit. A number of floats of this design have been deployed, both the research version produced by UW and MBARI and the commercial version produced by Teledyne/Webb and Satlantic.



FIGURE 3. A profiling float with a Satlantic SUNA nitrate sensor unit attached. Several commercially-built floats of this design were deployed as part of this project.



Float 6391 (All profiles as of 07 May 2013)



FIGURE 4. Top panel: Temperature, salinity, dissolved oxygen, and nitrate data from 266 profiles from UW profiling float number 6391 in the North Atlantic near Bermuda. The profiles were collected at 5-day intervals between October 2009 and May 2013. Bottom panel: Salinity, dissolved oxygen, and nitrate plotted as functions of temperature from float 6391.



Figure 5. 4 years of temperature, oxygen, and nitrate data from the upper 300 m for float 6391 near Bermuda. The seasonal cycle can clearly be seen.

**Table 1**. A list of commercially-produced ISUS/SUNA floats deployed during the course of this project. Floats were designed by UW and MBARI and the design was tested over a number of years. The commercial versions were produced by Teledyne/Webb and Satlantic.

Float Number	Date	Coordinates (Lat,	Туре	Comments
(UW ID)	Deployed	Lon)		
7593	6/12/2012	22.9° N, 158.2° W	ISUS	Died after 24 profiles; cause undetermined.
7597	5/23/2012	22.7° N, 158.1° W	ISUS	Died after 7 profiles from a leak.
7622	12/14/2011	23.2° N, 159.2° W	SUNA	Functioning normally after 135 profiles.
7641	7/31/2013	50.4° N, 145.2° W	SUNA	Functioning normally after 20 profiles.
7663	8/23/2012	31.7° N, 64.2° W	SUNA	Functioning normally after 80 profiles; some nitrate drift.
8497	2/17/2013	22.9°N, 157.9° W	SUNA	Functioning normally after 59 profiles.