Development of an In Situ Ultraviolet Spectrophotometer (ISUS) for Nitrate Determination

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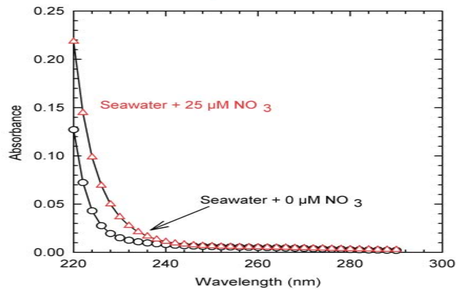
Abstract

Many dissolved inorganic compounds absorb light in the ultraviolet region at wavelengths less than 280 nm. Among these are several compounds of interest to oceanographers, including nitrate, nitrite, bisulfide (HS-), bromide and dissolved organic carbon. High resolution spectra (1 nm resolution from 200 to 300 nm) are required to separate the overlapping signals from these compounds in complex mixtures such as seawater. Technology has evolved to the state where it is now feasible to develop In Situ Ultraviolet Spectrophotometers (ISUS) that have sufficient stability, sensitivity and resolution to detect the light absorption signals of these compounds in seawater and which have sufficient endurance to operate for long periods of time. The fundamental simplicity of a system that can measure chemical concentrations directly with no chemical manipulation is overwhelming. We describe an ISUS system that has the potential to detect nitrate in seawater with a precision of 0.5% in deep water. The detection limit is <1 M and substantial improvement appears possible. Response time is <1 s and the instrument is capable of operating > 1 year at 1 sample per hour with a 30 amp-hr Li battery pack. We will show results obtained with the instrument deployed on a CTD/rosette system and on a SeaSciences Acrobat towed, undulating vehicle. The potential of the instrument for measuring sulfide at concentrations from 0.1 M to 10 mM in hydrothermal environments will also be demonstrated.

Design Goals



Nitrate appears as a shoulder on the bromide peak in seawater. Detection requires an instrument with performance characteristics of a high quality laboratory instrument. We also want to deploy on deep sea moorings for long time periods. These requirements lead to the following design goals:

- Photometric stability better than 0.001 A from 215 to 400 nm for 1 day - NO_3 detection limit = 0.001/ 4000 L/mol/cm / 1 cm = 0.25 µM.
- Wavelength resolution better than 1 nm.
- Operation to 4000 m = 5600 psi.
- Operation for 1 year.
- Temporal resolution of approximately 1 second.

The prototype ISUS appears to have the capability to meet all of these characteristics except depth (current limit is 3000 psi). A modification to allow the full depth is in the works.

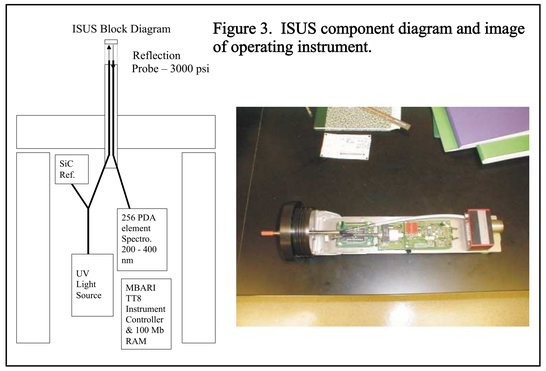
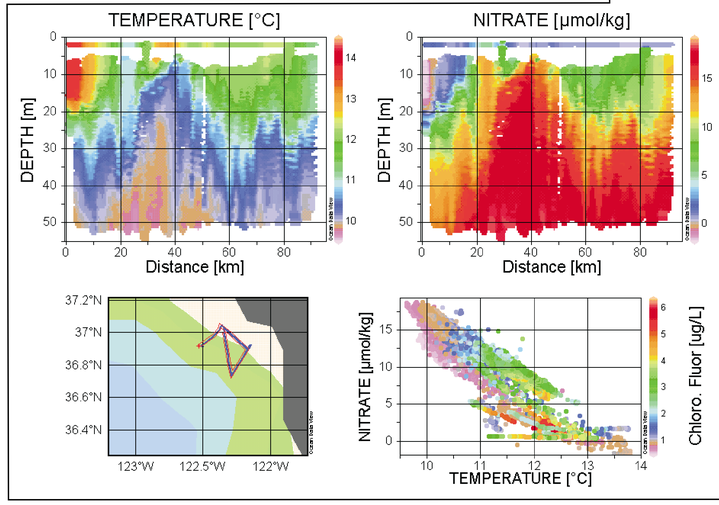
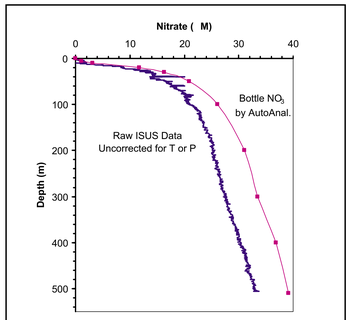


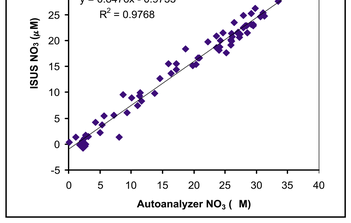
Figure 3. ISUS component diagram and image of operating instrument.

ISUS has been deployed on a SeaSciences ACROBAT undulating vehicle. The graphic at left shows data from a 10 hour tow over 90 km. Temperature and nitrate concentrations from 8000 points are contoured along the rectangular tow grid in the upper panels. The data at 2 m are from shipboard measurements. The lower panels show the tow location, which passes through the upwelling center N of Monterey Bay and a plot of NO_3 versus temperature with each data point colored by the amount of chlorophyll fluorescence.



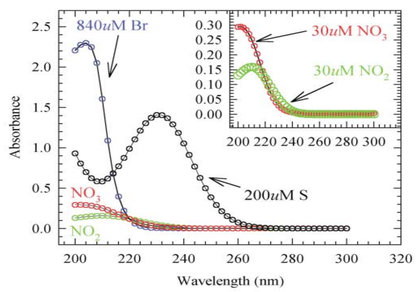


Vertical profile of nitrate determined with ISUS mounted on a CTD/Rosette compared with autoanalyzer measurements from bottle samples (top panel). ISUS data collected over a two week cruise are plotted versus bottle samples (lower panel). Many discrepancies arise due to internal wave offsets between downcast and sample collection on upcast. All ISUS values were determined from a single calibration at laboratory temp. and press. before the cruise. The discrepancy at 500 m illustrates the magnitude of pressure and temperature effects on system response; ~15% error.

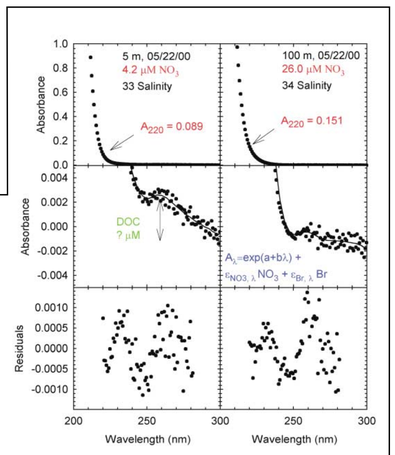


Background

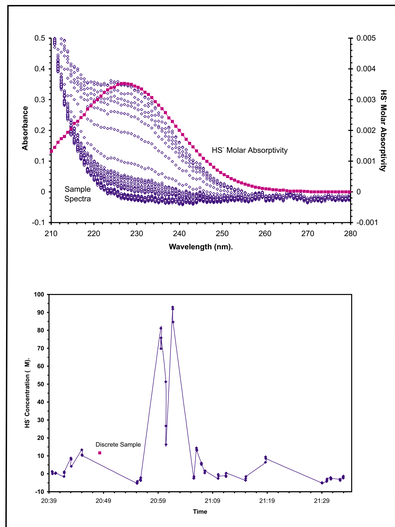
UV absorbance spectra for compounds of interest to oceanographers, including nitrate, nitrite, bisulfide (HS^-) and bromide are shown at right. In the past 40 years, there have been several analytical methods developed for the direct determination of these compounds based on their UV absorption , including an APHA standard method for nitrate analysis. These methods have not become widely used, in part because the analytical methods were usually based on measurements at a single wavelength. A measurement at a single wavelength does not allow chemicals with overlapping spectra to be differentiated. However, advances in the development of diode array spectrophotometers now make it simple to rapidly collect full spectra in the UV region. Spectral deconvolution techniques make it feasible to determine these compounds directly in seawater, without any interferences, and with no chemical manipulations. Robust, multispectral methods for nitrate determination in such difficult solutions as unfiltered waste water or ground waters have recently been developed (Thomas et al., 1990; Karlsson et al., 1995; Holm et al., 1997).



Absorption spectra of nitrate, nitrite, bromide and bisulfide ions at typical concentrations in the marine environment.



Spectra collected in situ at 5 m and 100 m depth with ISUS deployed in Monterey Bay. The top panel shows the full spectrum of the two samples, which have 4 and 26 µM nitrate, respectively. Note the small difference in absorbance at 220 nm. The middle panels show the baseline, on an expanded scale, where dissolved organic matter absorbs. The difference in baseline slope between shallow and deep samples, indicative of DOC concentration, is very reproducible. The bottom panels show the residuals from the regression analysis. The largest residuals are on the order of 0.001 Absorbance unit, indicating the instrument is meeting design specifications for photometric stability and accuracy.



ISUS can be used for the determination of the bisulfide ion (HS^-) in marine environments. UV spectra measured in situ at 960 m depth at a height of several cm above a cold seep in Monterey Bay are shown below along with the molar absorptivity of bisulfide (top left). The spectra clearly show the presence of bisulfide. Calculated concentrations are shown in the lower left panel along with one measurement by the methylene blue method in a sample collected at the same time. Very good agreement is obtained.

Conclusions

Optical measurements of nitrate and sulfide concentrations can be made in seawater with a submersible, low power spectrophotometer. This approach has the potential to measure nitrate and sulfide at concentrations near 0.1 µM. High resolution measurements (~1 s) are possible from vertically profiling platforms. The instrument appears to be stable and we believe that long term measurements from deep sea moorings and high resolution vertical profiles will be achievable.

M B A R I
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