

# APPLICATION OF LIQUID WAVEGUIDE TO SHIPBOARD UNDERWAY AND IN SITU LOW-LEVEL NUTRIENT MEASUREMENTS IN SEAWATER

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Colorimetry is the conventional method for measuring a suite of nutrient species in seawater. In colorimetry, utilization of absorbance signals for quantitative analysis relies upon the Lambert-Beer's law, according to which the magnitude of absorbance signals is proportional to the optical pathlength, the molar absorptivity, and the concentration of substance under investigation. The molar absorptivity is an inherent characteristic of specific chromophoric compounds utilized in the colorimetric measurements and therefore intrinsic to a given method. It is always a challenge to find a new chromophoric compound that surpasses the existing one in both molar absorptivity and selectivity to an analyte of interest. Moreover, the molar absorptivities of the most chromophoric organic compounds utilized in the modern colorimetry lie in a narrow range of  $10^3$  to  $5 \times 10^4$   $\text{l mol}^{-1} \text{cm}^{-1}$ . Therefore, increasing the optical pathlength of the measurement cells becomes the most feasible approach by which a significant enhancement in the sensitivity of colorimetry-based analytical systems can be achieved.

A conventional cuvette longer than 10 cm requires a large sample volume and is not practical in many analytical applications. In 1980's, long capillary cells have been developed to accommodate the requirements for both long optical path and small sample volume. A compact design was achieved by constructing the long capillary cells in a helical rather than a linear shape. However, the surface reflectiveness of these long capillary cells was relied upon the metal coatings. Such metal-coated long cells suffered severe source light loss and non-linearity response, which limit their applications to measurements of gaseous samples. To effectively utilize the long capillary cells for liquid samples, the light propagation must be constrained within a liquid medium; in other words, the cells must function as a liquid core waveguide. This requires the refractive index of cell material being smaller than that of the liquid contained in the cells. Due to its mechanical property suitable for microfabrication and high resistance to most chemicals, glass from fused silicon is often used as a building material for the long capillary cells. The hydrophilic property of glass also makes it a suitable material for constructing flow cells used for aqueous solution. However, the refractive index of glass (1.474) is greater than that of water (1.33), and therefore the glass cells cannot confine the light

transmission in aqueous phase. Such glass cells can only be used in measuring absorbance in organic solvents with high refractive index, such as benzene (1.50) and carbon disulfide (1.63).

Recently Dupont (DuPont Fluoroproducts, DE, USA) manufactured amorphous fluoropolymers (Teflon AF family) that have refractive index (1.29-1.31) lower than that of water. Total internal reflection of light can be achieved with a liquid waveguide capillary flow cell made by Teflon AF. The liquid waveguide capillary flow cells have been used to enhance the sensitivity of spectrophotometric analysis of trace constituents, such as ferrous, nitrite, molybdate and chromate ions, as well as colored dissolved organic matter in natural waters. The porous structure of amorphous fluoropolymers also provides a high gas permeability, which has been utilized to construct gas sensors. However, its porous structure is prone to adsorb surface-reactive species from aqueous samples and hence cause a decline in its waveguide performance. Furthermore, amorphous fluoropolymers have a water contact angle of  $106^\circ$ , hence its hydrophobic internal surface is resistant to the flowing stream and prone to adhere air bubbles. Air bubbles attached on the cell walls can scatter the incident light and cause a cell loss its liquid waveguide characteristics. A new design of capillary cell with cladding Teflon AF on the outer surface of capillary quartz tubing has been found to minimize the potential contamination and possibility of trapping air bubbles while maintaining its liquid waveguide function.

The enhancement of colorimetric sensitivity by long path flow cells was tested in a flow injection analysis of nitrite using a short flow cell (1 cm) and 500cm, 2m and 4m liquid waveguide capillary flow cells. As shown in Fig. 1, the sensitivity of flow injection analysis increased proportionally with increasing the length of the flow cells as predicted by the Lambert-Beer's law. Using a conventional 1 cm flow cell, the detection limit of flow injection analysis is 100 nM for nitrite. By using a 500cm long liquid waveguide flow cell the detection limits of nitrite analysis were reduced to 6 nM. The detection limits of 2 and 4 nM have been achieved by using 4 m and 2 m liquid waveguide flow cells, respectively. The slopes of linear calibration curves obtained from the analytical systems are directly proportional to the lengths of the flow cells used in the analyses with a correlation coefficient of 0.999999. This

indicates that the flow injection analytical system coupled with long-path flow cells obeys the Beer-Lambert's law within the linear dynamic range of

method, which in turn depends upon the length of a capillary flow cell used for the system (1).

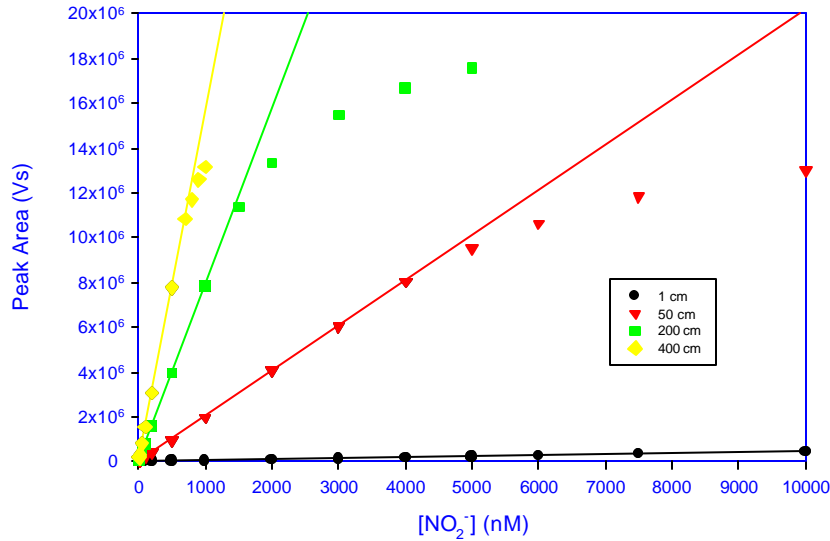


Figure 1. Comparison of sensitivity and linear dynamic range of nitrite analysis using a conventional short flow cell (1 cm) and the liquid waveguide flow cells of different pathlengths in flow injection analysis.

Since the gas-segmented continuous flow auto-analyzer was developed in 1950's, its high precision has made it oceanographers' favorite instrument for routine analysis of nutrient samples at sea. However, the sensitivity of auto-analyzer is insufficient to accurately measure surface nutrients in oligotrophic waters. Recently, we have successfully incorporated a liquid waveguide capillary flow cell to a gas-segmented continuous flow auto-analyzer to significantly enhance the sensitivity for measuring iron, nitrate, nitrite, ammonium, and phosphate in natural waters (2-5).

The auto-analyzer equipped with a liquid waveguide flow cell was first successfully used in

studying nitrate dynamics in oligotrophic waters in North Atlantic on board the NOAA Ship Ronald Brown in 1998. A detailed diurnal cycling of nitrate at nM levels in the euphotic zone of open ocean waters was observed for the first time. Measured nitrate change due to photosynthesis is consistent with the observed trends in solar radiation and oxygen concentration changes (Fig. 2). The observed nitrate increase during nighttime is due to upward eddy diffusive flux of nitrate across the base of the mixed layer. The daytime nitrate inventory change in the mixed layer together with eddy diffusion derived from the SF<sub>6</sub> tracer was used to estimate the new production in these waters (6).

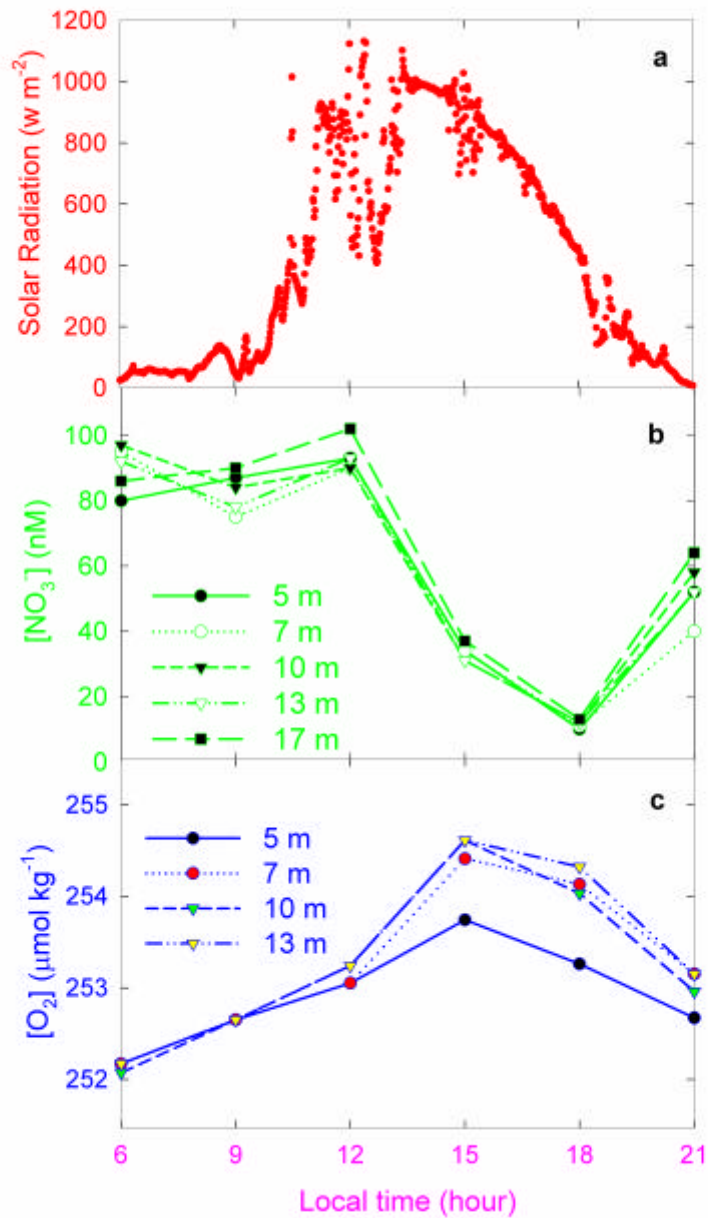


Figure 2. Observed changes in (a) solar radiation, (b) nitrate concentrations, and (c) dissolved oxygen concentrations at different depths in the mixed layer during the diurnal study of nutrient biogeochemistry in the photic zone in North Atlantic in 1998.

Recently, we have also applied liquid waveguide technology to study the spatial distribution of low-level phosphate in a tropical carbonate lagoon, Florida Bay (5). The large spatial gradients in surface water dissolved phosphate are mainly due to numerous mud

banks that divide the bay into several sub-basins and limit water exchange between sub-basins. The strong similarity between the spatial distributions of dissolved phosphate concentrations in the water column and the exchangeable phosphate in sediments suggests that

concentrations of dissolved phosphate in shallow Florida Bay water are mainly regulated by the phosphate buffering mechanism of carbonate sediments (7). Higher concentrations of phosphorus in the western bay are mainly due to the supply of phosphorus from the west Florida shelf current. This current carries phosphate-laden water and particles originated from run-off in phosphorus mining areas in the central Florida, along the west Florida coast. Low phosphate was found in the eastern basin where sediments are poor in phosphorus. Although the eastern bay receives most freshwater input from the Everglades, it contains relatively low phosphate concentration as a result of rapid retention of phosphate by carbonate soil and uptake by vegetations while water flows through the Everglades wetland.

In summary, an enhancement of sensitivity of nutrient detection by an order of magnitude in shipboard auto-analyzers have been achieved by incorporating the liquid waveguide flow cells to colorimetric analysis. A wider application of this technique requires investments by commercial manufactures to adapt the long flow cells to the auto-analyzers and make them available to the market. The liquid waveguide technology also has potential application in shipboard underway and in situ low-level nutrient measurements in seawater (8, 9). At present, we are developing an automated resorcinol method for measuring low-level nitrate in seawater using automated analytical system equipped with a liquid waveguide flow cell. In this method, toxic cadmium is no longer used as a reagent, eliminating its hazardous effect (10).

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