Laser Sensor Development for Fluorescence Detection of Plastics and other Anthropogenic Compounds Dissolved in Seawater

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LONG TERM GOALS

The long-term goal is to build and deploy a highly sensitive, *in situ* AUV-mounted instrument optimized for distinguishing natural colored dissolved organic matter (CDOM) in seawater as well as locating and identifying plastic and rubber-coated objects, such as mines, in the water column and buried within the seafloor. Oceanographic applications include UV-vis spectral characterization of dissolved and particulate (phytoplankton) fluorescence for remote sensing, plume tracking, and pollution applications. The multi-channel UV laser-induced fluorescence sensor (MUVLIFS) will ultimately be integrated and deployed on an autonomous underwater vehicle (AUV) to enhance strategic and oceanographic applications.

OBJECTIVES

The short-term goal is to improve the design for a compact UV laser multi-channel fluorometer system for shipboard use in enhanced measurement of UV-stimulated fluorescent compounds in seawater. During the past year, we have developed a compact, multi-laser LIF (laser induced fluorescence) system with optical filtered PMT detector that provides increased sensitivity by several orders of magnitude over existing *in situ* instrumentation.

APPROACH

During this funding year the LIF system was modified to enhance the detection of CDOM in natural waters, including doubling the number of fluorescence emission channels at selected CDOM wavelengths, adding another laser excitation wavelength, and adding laser (optical path) absorption measurements. The control electronics were enhanced, reduced in size for portability, and extensive automated software was developed to permit automated data collection and real-time display. The new multi-laser induced fluorescence (LIF) system was tested successfully on a five day extended cruise

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14. ABSTRACT
The long-term goal is to build and deploy a highly sensitive, in situ AUV-mounted instrument optimized for distinguishing natural colored dissolved organic matter (CDOM) in seawater as well as locating and identifying plastic and rubber-coated objects, such as mines, in the water column and buried within the seafloor. Oceanographic applications include UV-vis spectral characterization of dissolved and particulate (phytoplankton) fluorescence for remote sensing, plume tracking, and pollution applications. The multi-channel UV laser-induced fluorescence sensor (MUVLIFS) will ultimately be integrated and deployed on an autonomous underwater vehicle (AUV) to enhance strategic and oceanographic applications.

15. SUBJECT TERMS

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into the Gulf of Mexico in which a variety of water masses were sampled to determine instrument sensitivity under environmental conditions. In addition, a cruise off the coast of Australia was also made, but this was not as successful due to equipment damage going through customs/shipment. This system serves as the prototype for the *in situ* MUVLIFS sensor.

WORK COMPLETED

Previous work (1996-2001) reported the laboratory tests of three different LIF prototype configurations. The most sensitive and portable of the prototypes consisted of a microchip laser (5 mW) at 266 nm, a PMT detector and 5 optical filter channels, and improved upon the sensitivity of current *in situ* fluorometers by a factor of 100 to 0.01 ppb of quinine sulfate.

During the previous year (FY02), this configuration was further modified to include more spectral band filters allowing for greater fluorescence characterization of environmental samples. The current portable system uses a (4x) Nd:YAG microchip laser source operating at 266 nm and thirteen (spectral-band filter) detection channels monitoring scatter and fluorescence: 239 nm, 266 nm (Rayleigh), 289 nm (Raman), 301 nm, 314 nm, 334 nm, 370nm, 400 nm, 420 nm, 436 nm, 451 nm, 470 nm and 685 nm. Absorption filters were installed with cutoff at 285 nm and 295 nm, with a PMT detector and a boxcar integrator averaging system. A laptop computer is used via GPIB interface for data acquisition and controlling the filter wheel. The collection system has been improved by using multi-pass geometry of the laser beam through the cell, and adding a spherical mirror at the back of the flow cell along the collection axis. The multi-pass and spherical mirror configuration of the optical system show 67% increase in signal at the 450 nm optical channel over single-pass configurations. The detection limit of the modified portable system is 0.001 ppb of quinine sulfate. This is 10 times more sensitive than originally predicted, and 1000 times more sensitive than current multichannel *in situ* fluorometers. It should be noted that the increased sensitivity of this LIF configuration is due to the use of a high PRF (Pulse Repetition Frequency) laser that operates at a 8 KHz pulse rate, the use of a high speed box car integrator that can detect and average the individual fluorescence pulses at 8 KHz, and the use of a PMT for increased light sensitivity.

During the past year (FY03), 11 additional filter wavelength channels (and an additional filter wheel) have been added to permit greater spectral resolution. New software programs were written in Labview to acquire, store and monitor the optical channels in real-time. The emission channels can be switched every few seconds, resulting in a complete scan in about one minute. In addition, another excitation laser at a different wavelength (355 nm) has been added so that different fluorescence signatures can be measured. Also, the optical layout of the system was changed to permit direct absorption (transmission) measurements of the water samples for both the 266 nm and the 355 nm wavelengths. Figure 1 shows a schematic of the two wavelength portable LIF system. Figure 2a shows the portable system in two sealed cases: case 1 contained the boxcar, filter wheel electronics and case 2 contained the laser source, filter wheel, PMT, and the optical collection system (Figure 2b).

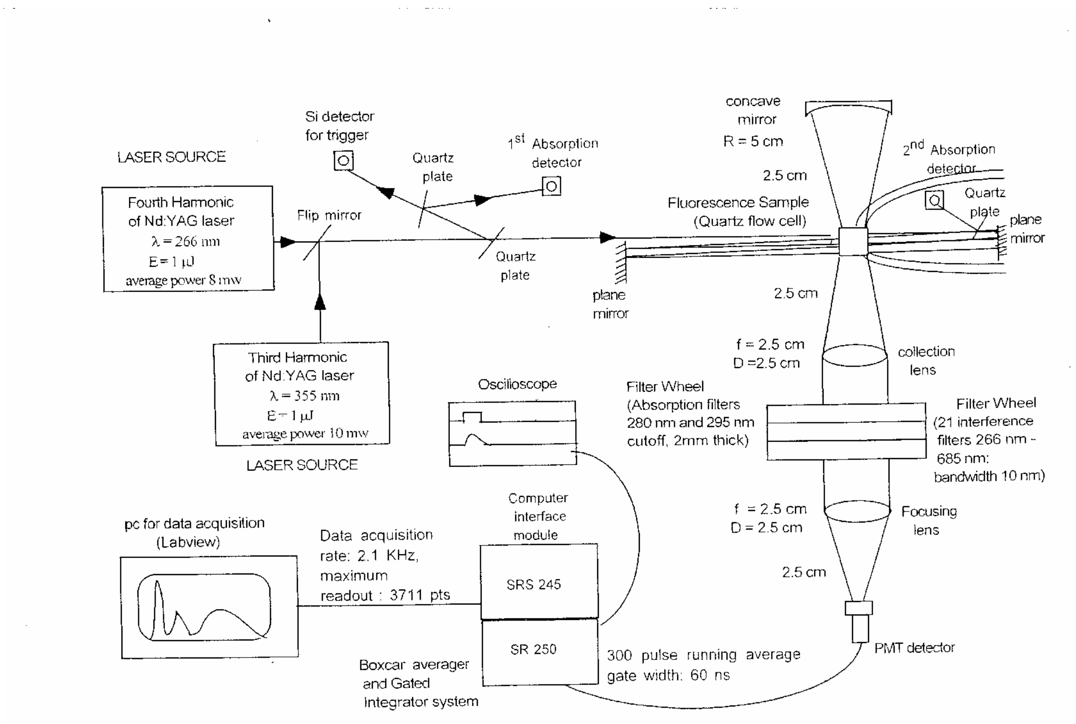
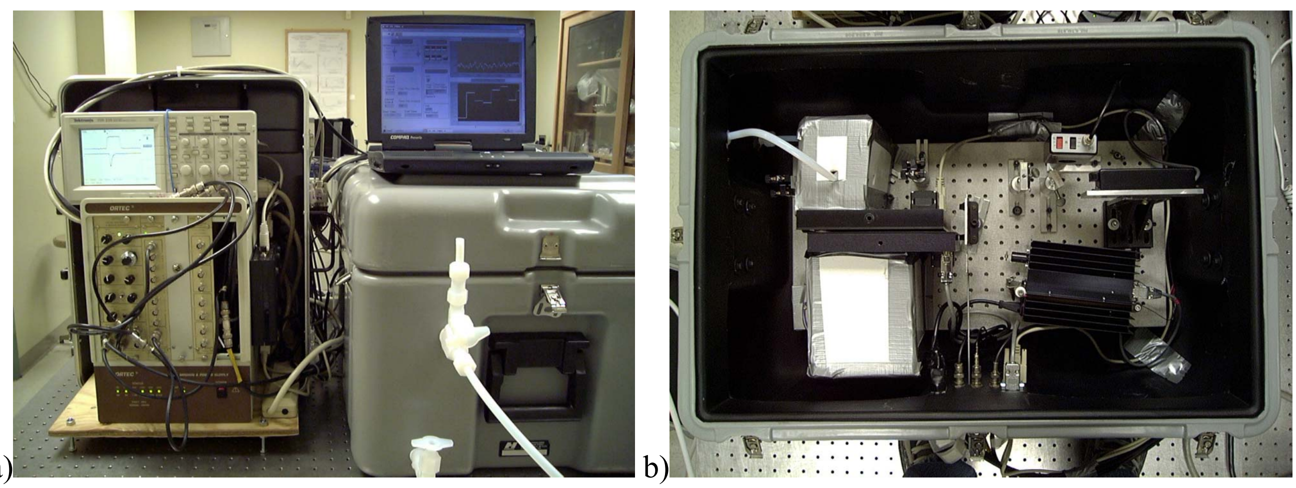


Figure 1. Schematic of the equipment setup of the portable Laser Induced Fluorescence (LIF) system



a) b)

Figure 2a. Picture of the portable laser induced fluorescence system; b. Picture of the optical system for the portable LIF showing laser souce, filter wheel and PMT detector

RESULTS

The modified LIF prototype was tested on a 5 day cruise (RV Suncoaster; May 16-21, 2003) to determine instrument sensitivity in a variety of water masses using the ships underway water supply. The cruise track was in the Gulf of Mexico from Kew West to Tampa Bay which also included clean water masses, up-river samples, and DOC plume detection. In addition to the portable LIF system, a commercially available multi-channel *in situ* fluorometer was also used to monitor real-time CDOM fluorescence from the underway water system. The SAFire (Wetlabs; Philomath, OR, USA) represents the state of the art for *in situ* fluorometers. Its estimated sensitivity is 1 ppb of quinine sulfate, and its multiple excitation and emission channels make it unique in the market.

Discrete water samples taken from the underway system for comparison were analyzed by excitation emission matrix (EEM) spectroscopy on a FluoroMax-2 (JY-SPEX; Princeton, NJ, USA). EEM spectroscopy samples were filtered (0.7 micron GFF), corrected for instrument variability, blank subtracted and normalized to quinine sulfate equivalents (Coble, 1996).

We are now analyzing the data and expect to be able to report on the sensitive LIF measurements shortly. Of importance is the fact that the system also provided real-time fluorescence and absorption data so that an estimate of the DOC signal and water composition could be made as the cruise progressed. Figure 3 shows an example of the real-time data during the 5-day Gulf of Mexico cruise.

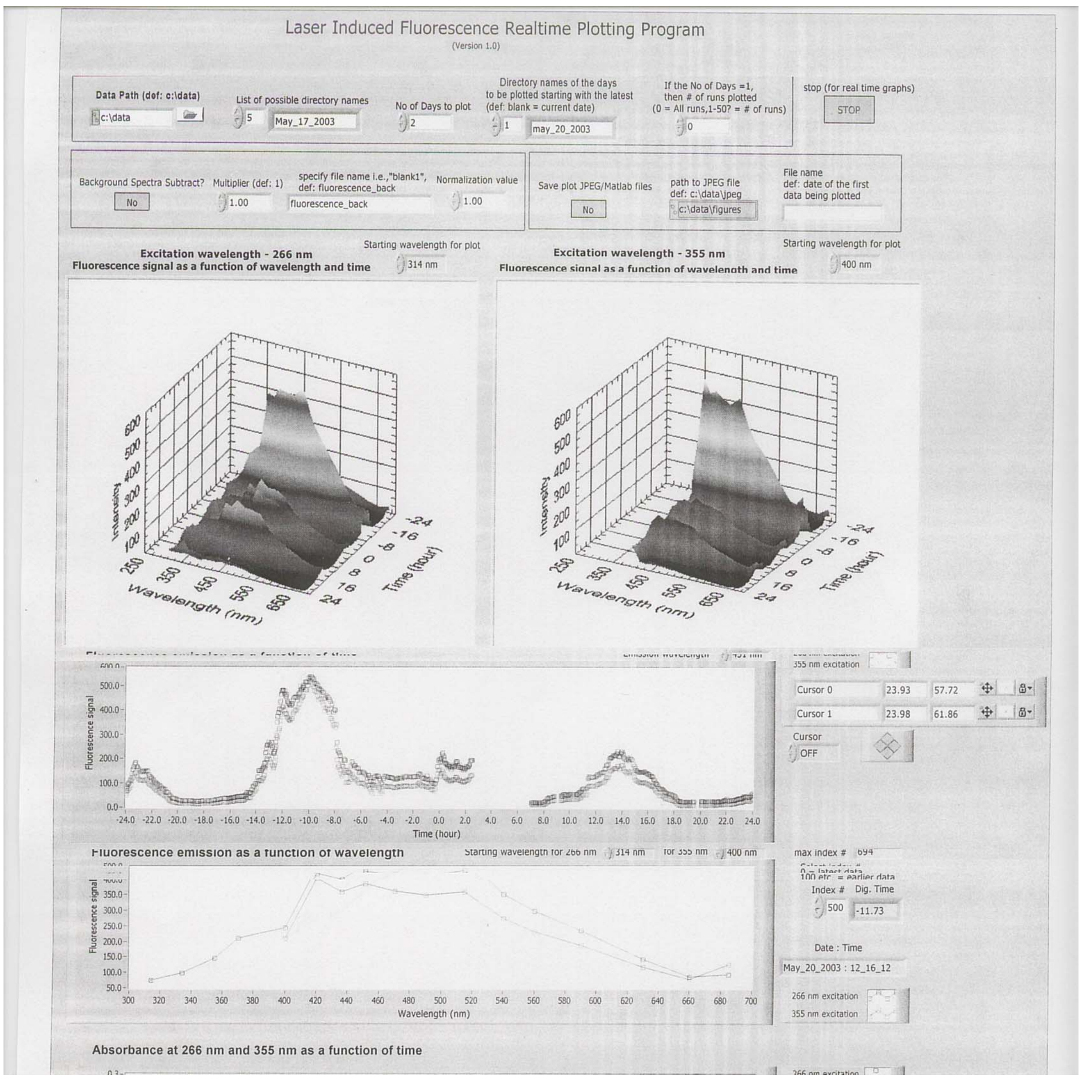


Figure 3: Image of computer screen showing real-time and time-history plot of fluorescence signal, absorption signal, and individual fluorescence channel

IMPACT/APPLICATIONS

Development of a compact, *in situ*, UV multi-channel LIF sensor is at the cutting edge of scientific and technological development. Applications range from study of trace constituents in the atmosphere to tracking pollutants in natural waters. Miniaturization, multi-channel spectral capability, low detection limits and extension of detection into the UV are features now being rapidly advanced. As with most past examples of instrument development, the full range of applications and their value to science, defense, industry and society have yet to be fully explored.

RELATED PROJECTS

The MUVLIFS unit is targeted for multisensor applications to increase the level of certainty that a mine does or does not exist. We will test the performance of both shipboard and AUV systems in local waters in conjunction with an ongoing study. We will assess sensor performance for oceanographic applications.

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