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 of this project is to develop a compact fluorescence sensor capable of the detection and fingerprinting of trace-level chemical substances present in seawater. The resulting multichannel UV laser-induced fluorescence sensor (MUVLIFS) will be applicable in several areas of research. Oceanographic applications include UV-vis spectral characterization of dissolved and particulate (phytoplankton) fluorescence. Compounds of interest relating to mine countermeasures and other Navy interests include: diesel fuel marine, oils, plastic and rubber material, industrial chemicals, river-borne soil materials and marine organisms.

OBJECTIVES

The short-term goal is to examine the usefulness and ultimate sensitivity of fluorometry as a method for locating and identifying plastic or rubber coated objects such as mines in the water column and/or buried in sediment. Consideration must be given to the seawater fluorescence caused by natural organic matter, which will comprise most of the background signal. We also propose to develop and construct a UV laser multichannel fluorometer that can be used in situ to detect and monitor artificial and natural organic substances in seawater.

APPROACH

During this funding year the analyses of chemicals responsible for fluorescence from mine substances was concluded, which provided a list of pure chemical substances that were examined individually. Experiments with miniaturized laser components proceeded with the aim of beginning fluorometer construction in late 1998.

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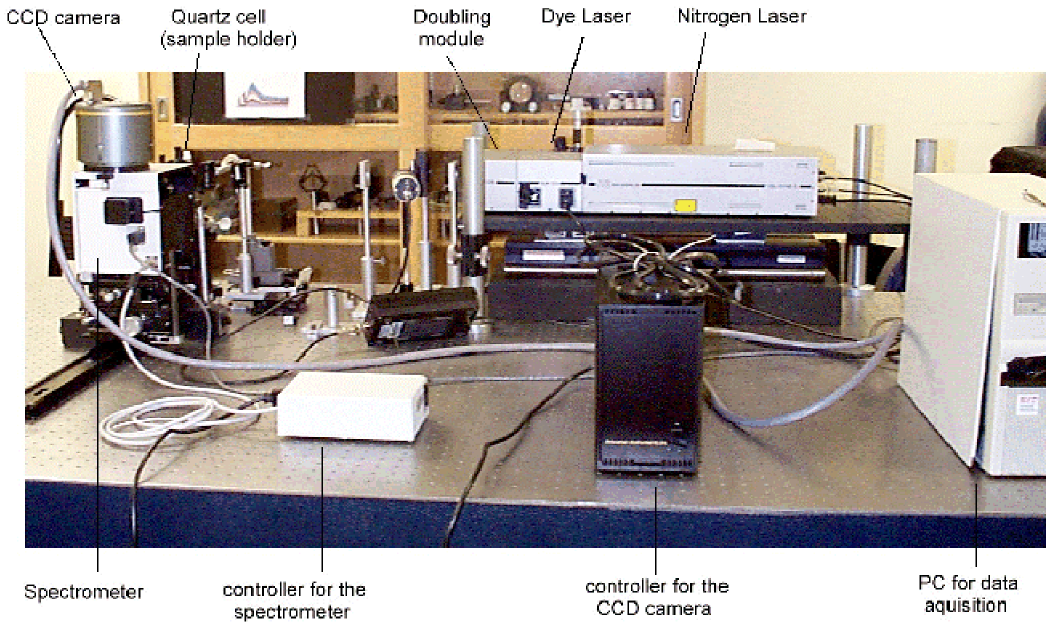
WORK COMPLETED

Previously, solid plastic objects (including the outer plastic shells of the authentic mines obtained from the NUWC Lab in Rhode Island) were placed in distilled water and analyzed for fluorescence fingerprints and chemical content. Mass spectrometry (MS) analyses of leachates indicated that commercially available epoxy resins were important components. We have analyzed three types of commercial marine resins and found that they have fluorescence characteristics similar to those of the mine sample leachates. In order to identify specific chemical components in the leachates, samples of three types of two-part epoxies was sent to Chemir/Polytech, Inc., a company which specializes in deformulation and chemical analysis of epoxy systems. From the results of these analyses, we were able generate fluorescence fingerprints of the individual chemical components that make up the epoxy.

We have continued to optimize the Compact LIF Sensor System shown in Figure 1. Figure 2 shows the measured fluorescence intensity as a function of the magnification of the collection optics. An optimal setting of the magnification associated with the spectrometer's f-number and the sample cell dimension and detector array size was shown to improve the sensitivity of the system. We are currently working to automate the LIF system by putting the variation of the laser wavelength under computer control.

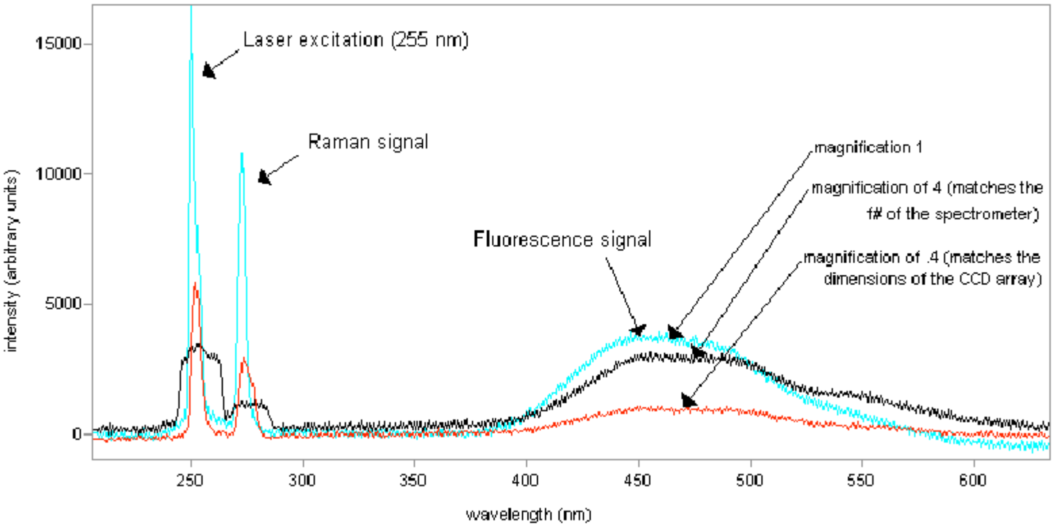
Fig. 1 LIF experiment setup using a CCD detector



RESULTS

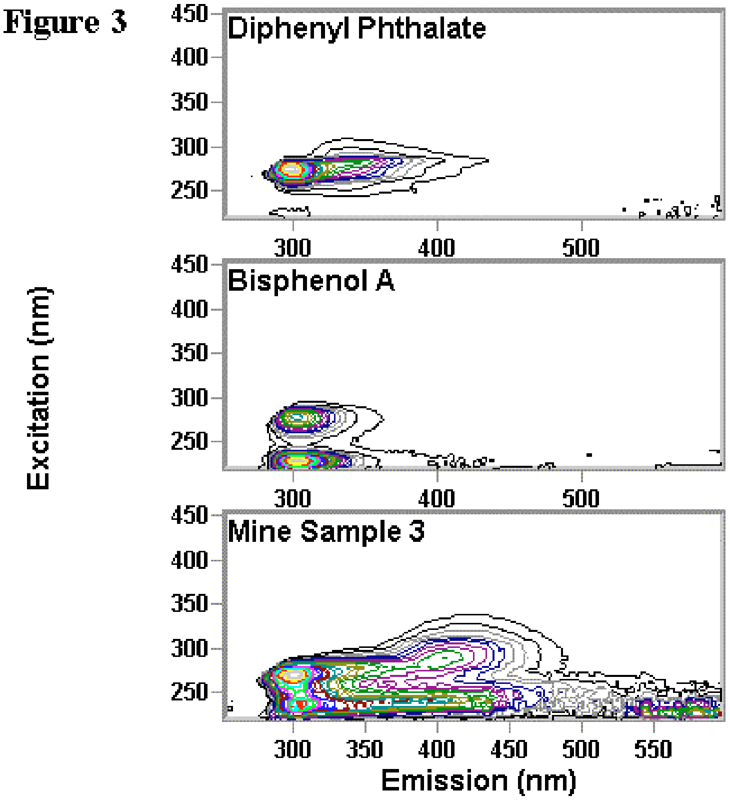
Results of the chemical analyses indicate that the water leachates contain components derived from epoxy systems based on bisphenol A, and also contain a variety of plasticizing agents, oxidants and stabilizers. Bisphenol A is the basis of many polycarbonate plastics and has wide application for food and drink packaging. Bisphenol A is also under scrutiny by health researchers due to its ability to mimic estrogen (1).

Fig. 2 Variation of fluorescence intensity for various combinations of the collection optics



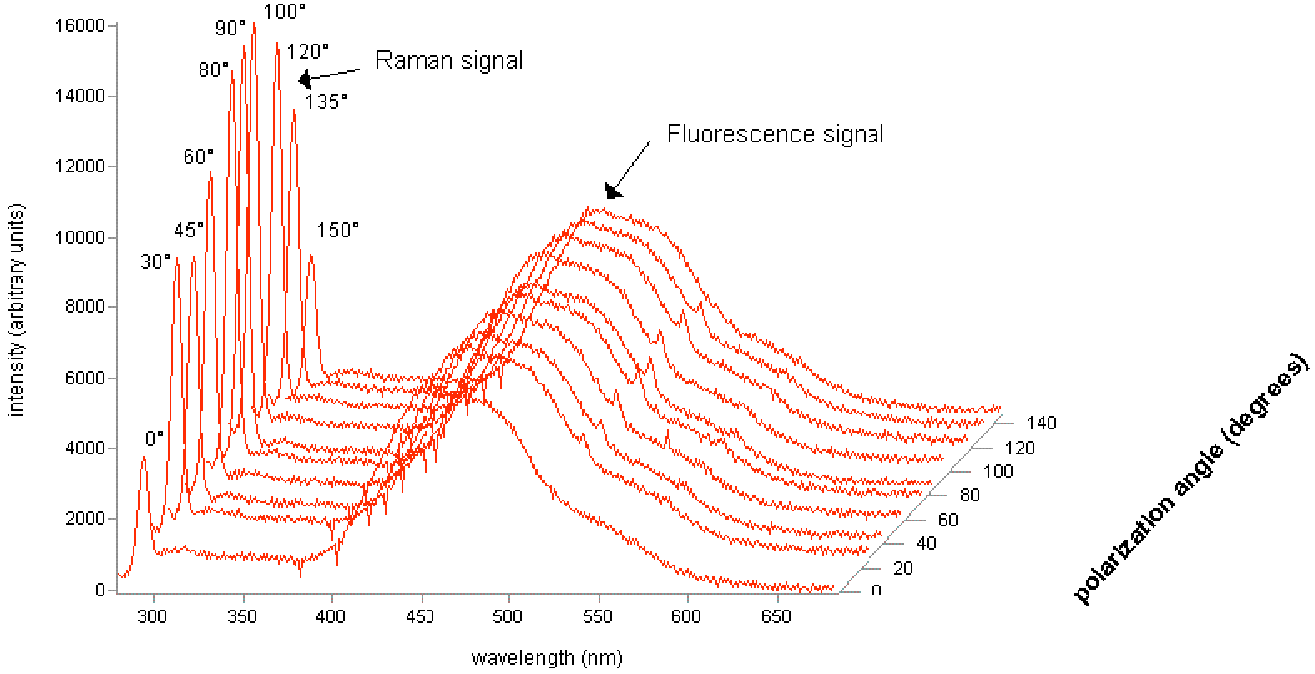
Several chemicals identified by the Chemir/Polytech analysis were ordered from Fisher Scientific in the purest form available. These components were analyzed for their fluorescence signature. By comparing the fluorescence fingerprints of mine leachates with those of the pure components we were able to match bisphenol A itself with the characteristic UV peaks found in the mine leachates. Figure 3 shows the fluorescence fingerprints of the leachate of mine sample #3 when compared with bisphenol A and diphenyl phthalate, a plasticizing agent.

Figure 3



The ratio of the intensity of the Raman to the fluorescence peaks from quinine sulphate is often used as a standard for comparisons from one experimental setup to another. However, when polarized laser light is used, the polarization angle has a strong effect on this ratio. Figure 4 shows the measured Raman and fluorescence spectra as a function of the polarization angle. As is seen, there is only a slight increase in intensity of the fluorescence peak with polarization, but there is a systematic decrease in the intensity of the Raman peak as the polarization angle moves away from 90^{o}. We are studying this further to better improve and quantify this effect.

Fig. 4 Raman and fluorescence spectra of Quinine Sulphate (10 ppb) as a function of polarization angle for a collimated excitation beam of 3 μJ at 266 nm



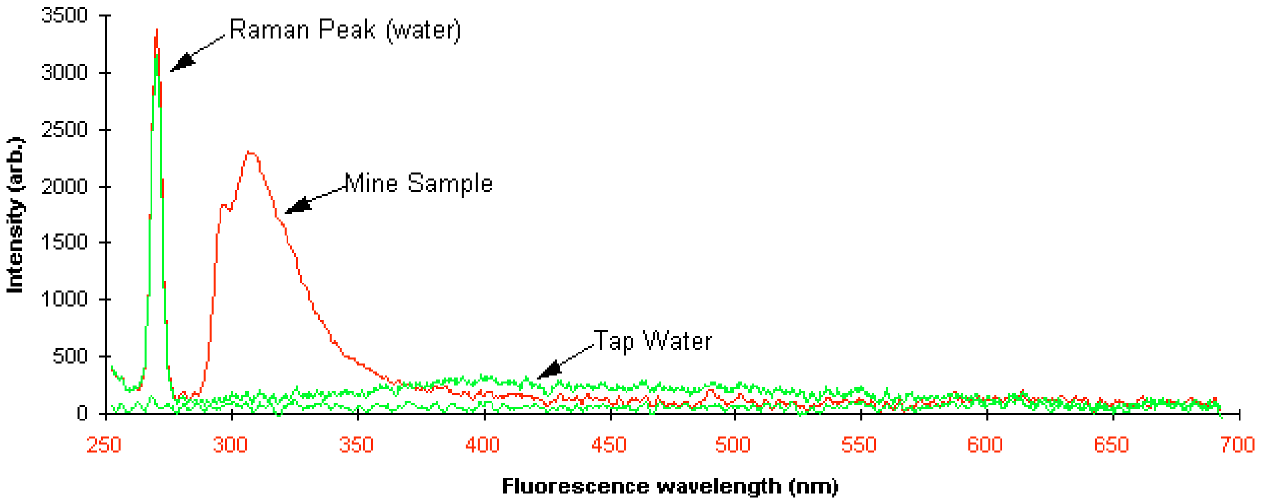
For reference the fluorescence from a mine sample is shown in figure 5 and shows the fluorescence signal from the mine sample (320nm) to be distinct from that of tap water (450nm). This difference can be seen better in figure 6 which shows data on water collected from Bayboro harbor (St. Petersburg) as well as several sources of drinking water for comparison. As expected the Bayboro sample fluorescence is much stronger than that of drinking water, but does not appear to interfere with that from mine samples (as in Figure 5).

Finally, a paper was presented at the CLEO ’98 conference on our results and a Masters degree thesis is being published based upon these experiments.

IMPACT/APPLICATIONS

Development of a compact multichannel UV LIF sensor for use in situ is at the cutting edge of scientific and technological progress. The instrument is potentially useful to many areas of environmental investigation, from tracking pollutants in natural waters to the study of trace components in the atmosphere. Currently, rapid advances are being made on instrument features including miniaturization, multichannel spectral capability, low detection limits, and extension of detection into the UV spectral range. As with many past examples of instrument development, its full value to science, defense, industry, and society is yet unexplored.

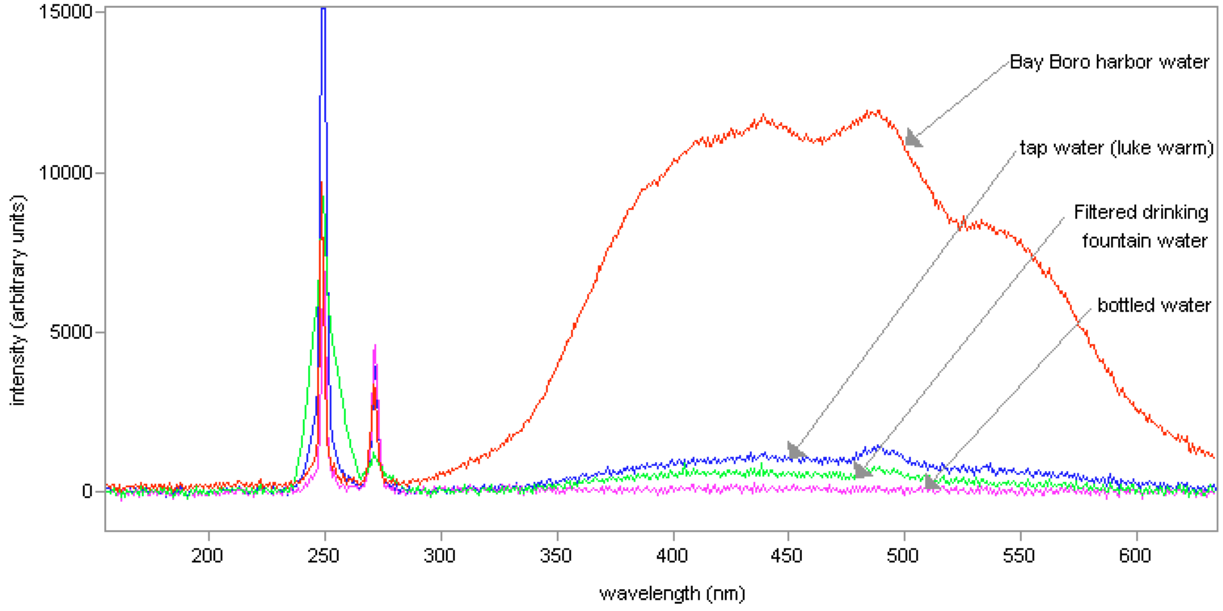
Fig. 5 Laser-induced fluorescence for a mine sample and tap water at excitation wavelength 245 nm



RELATED PROJECTS

The MUVLIFS unit is targeted for multisensor applications in order to increase the level of certainty that a mine does or does not exist. The sensor will be integrated with other sensors under development at USF into an autonomous underwater vehicle (AUV) platform that can be deployed to enhance strategic and oceanographic applications.

Fig. 6 Laser Induced Fluorescence of water



REFERENCES

1. Krishnan, A. V., Starhis, P., Permuth, S. F., Tokes, L. and Feldman, D. 1993. Bisphenol-A: an estrogenic substance is released from polycarbonate flasks during autoclaving. Endocrin. 132: 2279-2286.

PUBLICATIONS

Bengtsson, M., and L.-G. Nilsson. 1996. Development and evaluation of a laser-induced fluorescence experiment for the detection of trace compounds in water using a tunable UV-OPO system. Master Thesis, Lund University, Lund, Sweden.

Boehme, J.R., and P.G. Coble. UV Fluorescence Contouring of Dissolved Organic Matter in the Tampa Bay Estuary. ASLO Santa Fe, NM. Feb. 10-14, 1997.

Boehme, J.R., and P.G. Coble. Laser-induced Photodegradation of Dissolved Organic Matter in the Tampa Bay Estuary System. Ocean Optics XIV Kailua-Kona, HI. Nov. 10-13, 1998 (accepted).

Boehme, J.R., and P.G. Coble. High-energy Laser Fragmentation of Dissolved Organic Matter: a New Approach for Studying Chemical Characteristics of Dissolved Organic Matter. ASLO Santa Fe, NM. Feb. 1-5, 1999.

Nase, V. 1998. Dependence of CCD Signal-To-Noise Values on Optical Excitation and Collection Geometry in Laser Induced Fluorescence, Master Thesis, Dept. of Physics, University of South Florida, Tampa, Florida.

Timperman, A.T., and Paula G. Coble. Analysis of proteins and peptides in seawater using capillary electrophoresis. (in press).