Multispectral fluorometric sensor for real time in-situ detection of marine petroleum spills

John M. Andrews & Stephen H. Lieberman
Space and Naval Warfare Systems Center San Diego
Environmental Chemistry/Biotechnology Branch D361
53475 Strothe Road, San Diego, CA 92152-6325
e-mail: jandrews@spawar.navy.mil

Abstract

This paper describes the development of a fluorescence based in-situ sensor system for real time monitoring and detection of petroleum hydrocarbon contaminants in the marine environment. The system consists of an array of underwater sensors deployed just below the water surface. The sensors can detect floating product (surface sheen) from below the surface as well as detect emulsified or dissolved phase petroleum in the water column. Data from each of the sensors is transmitted to a central base station computer for display, logging, and analysis. The primary intended use of the system is to protect marine facilities from accidental petroleum discharges by providing responding authorities with immediate notification of the occurrence of a leak or spill. The detection of petroleum is based upon the fluorescence of polycyclic aromatic hydrocarbons found within petroleum derived products. The sensors utilize broadband ultraviolet excitation from a pulsed xenon lamp to generate fluorescence in contaminated sea water. The intensity of the resulting fluorescence emission is proportional to both the oil concentration in water, and/or the oil film thickness on the water surface. Multispectral fluorescence emission information is used to distinguish between several possible petroleum classes and eliminate false positive interference from non-petroleum based fluorophores such as chlorophyll. Real time qualitative identification yields an important advantage in terms of rapidly resolving questions of spill origin or in determining an appropriate response. To enable long term underwater deployment, the optical energy of the ultraviolet excitation source also serves to prevent the occurrence of biofouling on the surface of the optical window. The results of initial testing in San Diego Harbor and at the Ohmsett wave tank facility in New Jersey demonstrate the system’s ability to detect petroleum products under a variety of conditions, including the presence of strong harbor chop.
1 Introduction

Rapid reliable spill detection is an essential yet often overlooked part of oil spill prevention and response strategies. Early detection of a petroleum leak or spill enables responders to take immediate corrective action to stop and contain the released material. By enhancing the responders’ ability to exercise timely countermeasures, early detection offers an effective means of minimizing the environmental and financial impact of a spill event. On the other hand, failure or delay in recognizing the existence of a spill will lead to a delayed response. Depending upon the specific spill scenario, a delayed response may result in a larger spill volume, is likely to impact a larger total area, and will almost certainly result in a costlier cleanup effort.

The oil spill detection methods currently being practiced at most marine facilities rely solely upon the use of human observation to visually identify the presence of the surface sheen indicative of a petroleum spill. Plans may call for the use of active observers during high spill risk activities or may simply rely upon passive casual observation. Response teams are mobilized only after someone has observed the spill and taken the time to notify the appropriate authorities.

The practice of relying upon human observers to detect spills, even when conscientiously applied, has severe shortcomings. Spills often occur at unanticipated times or places in which no one is present to see and report the event. It is not uncommon for pipeline and container leaks to go undetected for many hours and sometimes days, allowing small leaks to accumulate into large volume spills before corrective action is applied. Visual observation is especially unreliable at night or during foul weather when it can be virtually impossible to detect sheen on water. At many facilities, weekends and holidays are also considered periods of increased risk as reduced manning and a possibly undependable watch increases the likelihood that a spill will go undetected for extended periods of time.

To address this issue, the U.S. Navy has developed an automated oil spill sensing technology to assist responders by providing early notification of the presence of a petroleum spill on water. The fluorescence based sensor operates from just below the water surface, continuously testing for an increased hydrocarbon concentration or surface sheen indicative of a spill. It can be deployed as a single unit but is more likely to be installed as an array of multiple sensors to provide
area coverage. When a spill is detected, a signal is immediately transmitted to base station computer for analysis, display, and telephonic alarming.

Ultraviolet (UV) fluorescence provides a very sensitive and convenient means of detecting petroleum hydrocarbons in aqueous media. When petroleum is excited by UV light, the aromatic constituents such as benzene, napthalene, anthracene, etc. fluoresce, that is they emit light at longer wavelengths. The intensity of the fluorescence emission can be measured and quantified to determine concentration. UV fluorescence has served as the basis of numerous hydrocarbon detection systems. It has been used from airborne platforms for remote sensing of large open ocean oil spills. UV fluorescence has also been used over optical fibers to acquire point measurements of petroleum hydrocarbons in situ. At least one fluorescence based oil spill detection/alarm system has been offered commercially.

2 Sensor design

The sensor can be described as an upward-looking multispectral underwater fluorometer. It detects petroleum hydrocarbons by fluorescence. The overall hardware design, utilizing discrete optical filters and photodetectors, is intended to be rugged and inexpensive to manufacture while providing high optical throughput for enhanced sensitivity. When deployed, the sensor housing is suspended in the water from a low profile buoy. This allows the sensor to move freely with tides and waves while maintaining a constant fixed distance between the sensor window and the water surface. Four ports in the buoy let water and any potential oil slick flow unimpeded past the sensor window.

A schematic diagram of the sensor appears in Figure 1. The excitation source is a pulsed xenon flash lamp operating at 10 watts average electrical power. The lamp’s broadband optical output is collimated by an f/1 lens, then turned and spectrally separated by a pair of dichroic beam splitters into visible and UV (< 315nm) components. The spectral separation is further enhanced by the use of an optical high pass (frequency) filter to achieve an extinction ratio in excess of $10^6$. The second dichroic beam splitter reflects the excitation light through an optical window out into the water column. Fluorescence resulting from the presence of petroleum hydrocarbons is collected back through the optical window (180°) and passed through a series of dichroic filters for separation into three spectral bands. The light in each pass band is quantified by a single photodiode. An additional photodiode is used to
monitor the intensity of the first split beam for the purpose of normalizing the fluorescence emission signal for pulse-to-pulse variations in the lamp intensity. The output of this photodiode also serves to trigger the detection electronics which are gated to prevent interference from DC light sources such as sunlight. The lamp triggering, analog-to-digital conversion of the photodetector output, and signal processing is managed by an embedded microprocessor located within the underwater housing. Data and power are transferred via a hard-wired umbilical.

As different classes of petroleum products fluoresce at different characteristic wavelengths, multispectral analysis provides a means to discriminate between various classes of oils and fuels. It also allows for discrimination between petroleum and non-petroleum (e.g. chlorophyll) fluorescence. Figure 2 shows the fluorescence emission spectra of three common petroleum products, marine diesel fuel, lube oil, and jet fuel.
Figure 2. Fluorescence emission spectra of three different petroleum products: marine diesel fuel, lube oil, and JP5 jet fuel.

Each emits a uniquely shaped spectral curve. The differences in spectral shape may be used to help identify the fluorescing material. The advantages of using this spectral information include helping responders determine the source of a spill and to determine the best method of treating a spill, i.e. resolving whether it is a light or heavy product. The sensor performs simple classification and interference rejection by measuring the fluorescence intensity at three different wavelength bands. These pass bands correspond approximately to 320-380nm, 380-450nm, and >450nm.

2.1 Advantages and features

Remote automated detection of petroleum hydrocarbons from below the water surface achieves several important advantages. Since the optical window is placed in direct contact with the subsurface environment, dissolved phase and emulsified hydrocarbons within the water column can be measured directly. Placing the sensor near the water surface provides a means of simultaneously detecting the presence of floating petroleum from below the oil-water interface.
Underwater deployment also provides an inherently safe means of delivering excitation energy to the sample. With an above water sensor, there exists the potential to be in direct contact with explosive fuel vapors during a spill. The high voltage electronics that trigger the flashlamp excitation source would have to be isolated in an explosion proof housing for safety. The problem is avoided entirely through underwater placement.

Because the sensor is intended to remain underwater for indefinitely long periods of time, the question of biofouling on the external surface of the optical window was an initial concern. Hence, the optical geometry of the sensor system has been designed to prevent biological fouling from occurring on the window. By using a single window to transmit both the UV excitation light and the fluorescence emission, the only exposed optical surface is continually being treated with UV light, an effective biocide. Biological growth is thereby inhibited from forming.

3 Performance Evaluation

The prototype sensor has undergone initial testing in the laboratory, wave tank testing to evaluate performance during various simulated sea states, and field testing in San Diego Harbor to assess the effectiveness of using UV light to prevent biofouling.

3.1 Laboratory Measurements

Initial testing of the sensor was conducted under controlled conditions in the laboratory to verify that the sensor could in fact detect petroleum. Several experiments were conducted in which a one liter polycarbonate tube was sealed against the top surface of the sensor housing. Sea water was added until the sensor window was covered by five centimeters of water. The five centimeter height corresponds to the sensor’s approximate fixed distance below the surface when deployed from a buoy in the field. A 25ul aliquot of oil or fuel was added to create a sheen on the water surface. If one may assume a uniform distribution, this corresponds to a 3.6 micron thick oil film floating on top of the sea water. Figure 3 shows the multichannel response to four different petroleum products and a sea water blank. The tested products include two types of lube oil, marine diesel fuel, and JP5. It can be seen in both the 350nm and 425nm pass bands, that the relative signal intensity from each of the petroleum products is 20-50 times
Figure 3. Three-channel response to sea water, lube oil 2190, JP5 jet fuel, lube oil 9250, and marine diesel fuel. The fourth channel measures lamp intensity.

higher than the blank signal. Even when uncorrected for the small variations in lamp intensity, the relative standard deviation of the blank measurements is only 0.53%. The relative standard deviation of the petroleum products varies between 0.7 and 10 %. The bigger variance for petroleum is due mostly to uneven spreading of the oils on water. As expected the >450nm pass band did not respond to petroleum fluorescence. It primarily serves as a means of detecting non-petroleum fluorescence.

3.2 Ohmsett Wave Tank Study

To take advantage of more realistic test conditions, the sensor system was tested at the Ohmsett National Oil Spill Response Test Facility operated by the U.S. Department of the Interior’s Minerals Management Service in Atlantic Highlands, New Jersey. The facility is specifically designed for testing oil spill response equipment and spill detection instrumentation. Ohmsett’s main feature is an above ground concrete tank measuring 203 meters long by 20 meters wide filled with nearly 10 million gallons of sea water. Wave height and frequency may be directly controlled within the test tank. Testing at Ohmsett offers a key advantage over other types of field testing in that oil may be freely “spilled” in the vicinity of the tested
Several experiments were conducted over a period of one week at Ohmsett. In each, a prototype sensor was deployed within the confines of test ring defined by an eight foot diameter boom. An individual experiment involved the series addition of a specific petroleum product to the water surface. The oils were added to the test ring less than one meter distance from the sensor. The sensor response would then be recorded under wave conditions ranging from dead calm to a simulated harbor chop with waves heights up to 38cm. The results for two tests which typify the study are shown in figure 4.

The upper chart of the figure 4 shows the response recorded for a series of additions of a diesel/hydrocal oil mixture. The tank conditions were calm for the first 25 minutes after which the wave generator was started. The sensor exhibited a strong but varying response to the initial additions of oil. Only after the wave generator was started did the signal begin to stabilize. The initial fluctuations in response were due to an uneven distribution of the petroleum slick on the water surface. The sensor only detects oil within a 2cm spot directly above the window. The variations in signal intensity actually correspond to the changing oil film thickness moving across the window’s field of view. The agitation provided by the wave motion tended to distribute the oil more evenly throughout the test ring, resulting in a somewhat more stable signal. It is important to note that the sensor continued to detect surface oil even in the presence of a strong harbor chop. A similar result can be seen in the lower chart of Figure 4. In this study, diesel fuel was added to the test ring. There was a strong response to the first addition but subsequent additions appear to have had little increased effect. Once again this was due to an uneven distribution of the diesel slick within the test ring.

### 3.3 Biofouling field study

A thirty day test was performed in San Diego Harbor to evaluate the effectiveness of using UV light to prevent biofouling on the surface of the optical window. The test was conducted during the months June and July, a period of peak biological growth for many of the organisms living in the bay. During the study, the UV lamp was set to flash every three minutes for two seconds at 100 Hz. This is within the range of typical duty cycles planned for use in monitoring spills. Figure 5 is a photograph
Figure 4. (Top) Sensor response to a 50/50 mixture of diesel and hydrocal oil. Notice that response stabilizes after start of waves. (Bottom) Sensor response to diesel fuel. Response is poorly correlated with additions due to inhomogeneous fuel distribution.
Figure 5. Sensor after 30 days under water in San Diego Bay

of the top of the sensor after 30 days underwater. Despite heavy growth on the sensor housing, the window remained completely free of fouling for the duration of the study. A control window that was not treated with UV light was entirely covered by growth during this same period. Further work is currently underway to determine the minimum optical power densities required prevent window fouling.

4 Conclusions

We have developed a novel under water fluorescence sensor for real time automated monitoring and detection of petroleum spills. Initial laboratory and wave tank testing confirms the sensor is very effective at detecting the presence of petroleum on water. Diesel fuels, lube oils, and jet fuel have all been tested. The latter is significant because jet fuels fluoresce at relatively short wavelengths where many fluorescence based systems have little or no sensitivity. Simulated heavy chop does not hinder the sensor’s ability to accurately detect oil. In fact the agitation provided by wave motion can lead to better signal averaging. On the
other hand, calm water may make precise quantification over an area more difficult due to inhomogeneous, slow moving and discontinuous slicks. It is likely however that an array of sensors would allow one to achieve better averaging over an area. Finally, the use of UV light has proven very effective at preventing the formation of biological growth on the optical window.

References


