

Low Cost Optic Sensor for Hydrocarbon Detection in Open Oceans

Lorena Parra, Sandra Sendra, Jaime Lloret, Jonatan Mendoza

*Instituto de Investigación para la Gestión Integrada de zonas Costeras, Universidad Politécnica de Valencia, C/ Paranimf, 1. 46730 (Grao de Gandia), Spain

loparbo@upvnet.upv.es, sansenco@posgrado.upv.es, jlloret@dcom.upv.es, jomenal@epsgr.upv.es

Abstract— Hydrocarbons are one of the most important toxics in the oceans. Their presence may cause the death of organisms. They even can affect to the human beings, when they consume products that have been in contact with the hydrocarbons. After a hydrocarbon spillage, the fishing activity, the tourism, the safety and the wildlife are endangered. The fast detection is very important in order to start as soon as possible the cleaning tasks. It can be done using sensor networks. The first step in order to create a water quality monitoring system is to obtain a good hydrocarbon sensor. The sensor must be robust and cheap. There is no needed of high accuracy, the objective is just to detect the presence of the hydrocarbon in the water surface. In this paper, we present a low cost optic sensor capable of distinguishing the presence or absence of hydrocarbon in the water surface. The sensor is formed by light-emitting diode (LED) as a light source and photoreceptor as a receiver. In order to create the sensor, several tests have been done using different light sources. The light sources have different wavelength (violet, blue, green, orange, red and white). In order to test our samples, six samples are prepared. The samples are made of sea water and fuel (as they are one of the typical hydrocarbons). After the first tests, the best wavelength is selected and it is studied in detail. The lights selected were violet, orange and white. After the detailed tests, the light source that offers best results was the white light.

Keywords—hydrocarbon pollution; optic sensor; photodiode; hydrocarbon detection; LED light

I. INTRODUCTION

One of the causes of hydrocarbon pollution in oceans is the ship accidents. They generally become an international affair. Hydrocarbon pollution affects several organisms from terrestrial to marine ones. The plants and animals, even the human society are affected. According to [1] between 2002 and 2006 there were up to 7500 spills in US waters. The number of spills caused by vessels has been reduced in the last decades; nevertheless the number of spills related to pipelines has quadrupled from 1990 to 2010 [2]. One of the worst problems to remove the hydrocarbon spillages is that hydrocarbons tend to disperse and mix with the water. This dispersion complicates the possibility of removing the pollution. The sooner the decontamination task begins, the more efficient the fuel removal is.. While some pollutants

affect only one specific animal the hydrocarbon effects can be seen in all the species of the polluted area [3]:

- Hydrocarbon creates an impermeable layer over the water that avoids the gas exchange between water and atmosphere.
- Oil layers reduce the incident light, affecting the photosynthetic capacity of the phytoplankton
- Birds have several problems such as intestinal problems and skin irritation, among others.
- Fishes death by asphyxia because of their skin and gills are covered by the hydrocarbon.
- Marine mammals are covered by hydrocarbon which causes the loss of their floating capacity.

The use of satellite images is the most common way to detect the spills and determine their dimensions. However, the temporal resolution of some satellite and the time that the images take to arrive to the interested person are not optimal enough. To avoid higher damages and increase the effectiveness of decontamination tasks, the detection must be as faster as possible. Because of this the use of other technology to detect the presence of spillages is needed. The use of sensors has demonstrated to be a feasible option for water quality monitoring.

The aim of this work is to present the design and development of a low cost hydrocarbon sensor. The sensor is based on the photoluminescence effect linked to the hydrocarbons. As a source light, we use different light wavelength generated by a LEDs (light-emitting diode). The light detection is performed using a photoreceptor. The sensor is able to detect the presence of a layer of hydrocarbon on the water. However, our sensor cannot determine the thickness of hydrocarbon layer. The developed sensor will be a feasible option to be included in a sensor network for water quality monitoring. In addition, the use of this sensor networks can be applied in some exposed areas as ports where the presence of hydrocarbons is quite common [4], or even in fish farms [5] and very vulnerable areas where the exposition of the organism to the spills can cause huge economic loses.

The rest of paper is structured as follows. Section 2 presents some related work about different ways to detect hydrocarbons. Section 3 presents the design of our sensor and the test bench performed to check the correct operation. The results are presented and discussed in Section 4. Finally, Section 5 presents the conclusion and future works.

II. RELATED WORK

This section shows a summary of some previous works on systems and sensors based on different operational principles for hydrocarbon detection. Moreover, we discuss the feasibility of applying these sensors to real environments in order to implement a sensor network for water quality monitoring.

O. Péron et al. [6] presented a sensor able to detect the presence of polycyclic aromatic hydrocarbons in artificial sea water. They used the technique of surface-enhanced Raman scattering. A gold colloidal monolayer was used as an active substrate. Authors used naphthalene and pyrene as polycyclic aromatic hydrocarbons. They used naphthalene concentrations, from 0.01ppm to 10 ppm and concentrations from 0.01 ppm to 0.1 ppm for pyrene. This sensor is suitable for detecting low concentrations of hydrocarbons when they are mixed with water.

An optical sensor was presented by A. MacLean et al. in [7]. The sensor was able to detect the presence of hydrocarbons related to spills. The system is based on the standard optical time domain reflectometry. The sensor consisted on a wire which is in contact with the water. The signal intensity changes when it is in contact with the spills. Tests were performed in real environments. In the first test a wire of 375m was deployed in the sea. At a specific length, 1m of this wire was saturated with petrol. The signal of the sensor informed about the presence of hydrocarbon at the correct length. The maximum time that the wire was placed in the sea was 2 weeks. This test confirmed that the wire can resist at least this time in adverse conditions. The sensor seems to be a good option to monitor lineal areas, like the places where tubes for hydrocarbons transport are placed. However, its application for natural environment monitoring is no good. If a squared area were necessary to monitor, the amount of wire needed to cover this area increases because of the linearity of the sensor.

R.P. McCue et al. presented their sensor for hydrocarbon detection in water [8]. They used a mid-infrared wavelength as a source. As a detector, authors used a silver halide fibre optic cable coated with a polymer. In the laboratory test, authors used benzene as hydrocarbon at four different concentrations, from 500ppm to 2000ppm. Authors tested the optic fibre coated with the polymer and uncoated. The optic fibre coated with the polymer presented better response. The sensor was able to work in dynamic pattern. However, the sensor was not tested in a real environment. The design of the sensor is optimum for laboratory conditions but its application for monitoring real environments is not clear.

Other sensor based on infrared light was presented by J. S. Albuquerque in [9]. Authors created a probe to measure the presence of hydrocarbon in seawater. The light source used in their test was a tungsten lamp. As a detector, authors used a GaAs detector with a range of detection from 850 nm to 1800 nm. Authors used different compounds as hydrocarbons such as benzene, toluene, ethylbenzene and m-Xylene. Different

concentrations of each compound were used. For toluene, the minimum concentration was 27 mg/l and the maximum 237 mg/l. Benzene presented concentrations up to 375 mg/l. This sensor was presented as a laboratory sensor to analyze processed samples. However, its application for analyzing real samples is not demonstrated.

The most used way to detect the presence of spills in the water is the use of remote sensing. However, if we want to perform a real-time detection of spills with low delay, the use of sensors in the water is the most appropriate technology. The current sensors have some deficiencies. Most of them are specific for laboratory conditions and they have to be in contact with the water. The contact with such harsh environment can cause drifts in the sensor calibration due to the effect of corrosion, sediment depositions and other problems that are going to reduce the time that the sensor can be in the environment before the need of cleaning or replacing. Our proposal has the advantage that it does not need to be in contact with the water.

III. TEST BENCH

In this section, we present the materials used for the design and calibration of our low cost optic sensor for hydrocarbon detection. We also explain the tests performed to evaluate the effectiveness of sensors when different light sources are used to detect the presence of hydrocarbon in the water surface.

The operation principle of this sensor is the photoluminescence. According to this principle, if the correct wavelength is used, the molecules can absorb a photon from light and this photon pass to an excited state. To come back to their natural state, the molecules emit a photon of other wavelength. This phenomenon allows distinguishing between different molecules, in this case, water of hydrocarbons. We emit light at different wavelength from LEDs to generate the photoluminescence effect. We tested six different colour lights. We changed the light wavelength to violet, blue, green, orange, red and white. The emitted light is registered by a photodetector, S186P. It is able to detect light above 900nm. Both, light source and photodetector are placed in an opaque material that separates them. In this way, the light detected is the result of reflected light and photoluminescence. The light source is placed at 1cm from the sample. The disposition of the source, detector and water is shown in Fig. 1.

To make the samples, it is used real sea water. As hydrocarbon pollutant, it is used 97 octane gasoline. The sea water was filtered and maintained at low temperatures to avoid the proliferation of organisms. Several samples with different concentration of gasoline are prepared at laboratory. The samples have a total volume of 30ml (seawater and gasoline), and different amounts of gasoline are added at each one. The volume of gasoline added at each sample and the final concentration of each sample can be seen in Table 1.

The light intensity recorded by the photodetector is related to the presence or absence of hydrocarbon. The lights with better results are selected for deeper analyses.

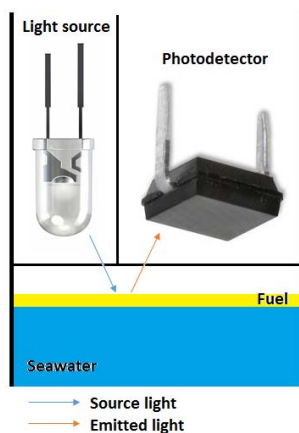


Fig. 1. Disposition of the light source, detector and water sample

Table 1. Concentration of gasoline in the samples

Sample n°	Added gasoline 97 octanes (ml)	Gasoline 97 octanes concentration (g/l)
1	0	0
2	2	50
3	4	100
4	6	150
5	8	200
6	10	250

IV. RESULTS

In this section, we show the results of the performed tests. First, the tests with different concentrations of gasoline and different light sources are shown. The tests with the lights that offer the best results are explained. Finally, we perform a second test where a statistical analyze of the data is shown in order to evaluate if the observed differences are statistically significant. Fig. 2 shows the position of the sample and the light source used during the tests where the sample, with a concentration of 0g/l of gasoline, is illuminated with white light.

The first test uses six color lights with different gasoline concentrations. The colours of lights are violet, blue, green, orange, red and white. With this, we will be able to select the light that offers best results. The results of this test can be seen in the Fig. 3. We can see that each light offers different results. Blue and green light are not useful. They offer the same values when the gasoline is present on the water and when the water is clean. The output voltage registered at a gasoline concentration of 200g/l when red light is used is similar to the output value when there is no gasoline. So, red light must be rejected. The white, orange and violet light offers good results. The output voltage value in presence of gasoline is quite different than the output voltage in absence of gasoline. The white and violet are the lights that offer more promising results according to the difference of output voltages in presence and absence of gasoline.

The three light sources, i.e., violet, orange and white are selected to make a deeper analysis. In this new analysis, we used the sample with lower concentration (50g/l). The measurements were repeated 10 times with gasoline and without gasoline. In this way, it is possible to evaluate the signal variations and be sure that the proposed system is able to detect the presence of hydrocarbons in the water.

The results of this test are presented in Fig. 4. We can see that in all cases, the average value of output voltage is different in absence or presence of gasoline. The white light is the one that presents the highest standard deviation in absence of gasoline, i.e., 0.003 mV. The orange light is the one that presents lowest standard deviation in both cases, less than 0.0006 mV. The difference between the average values of output voltage is 0.008 mV for white light, 0.0037 mV for orange light and 0.0072 mV for violet light.

Statistic test were performed using Statgraphic Centurion software to validate the observed differences between the average values. First of all, the normality of the samples is tested. The values of asymmetry and kurtosis reveal that the data does not follow a normal distribution. In order to evaluate if the observed difference between the results when gasoline is present on water and there is no gasoline on the water is statistically significant a non-parametric test is used. In this case, we have selected the Kolmogorov-Smirnov test. The value that indicates if the observed difference is statistically significant or not is the p-value. Assuming a 95% of confidence level, it is possible to assume that the differences observed between lectures in samples with and without gasoline are statistically significant in the three cases. The p-value in all cases are lower than 0.05.

According to these values, the three light offers good results where the values in absence or presence of gasoline which are statistically significant. This fact is important to select which light will be used in the prototype. To make this decision, it is important to pay attention to the output values. The light that offers higher output voltages values is the best one to implement our sensor because it is easier to detect higher voltages. The light with higher voltage is the white light.

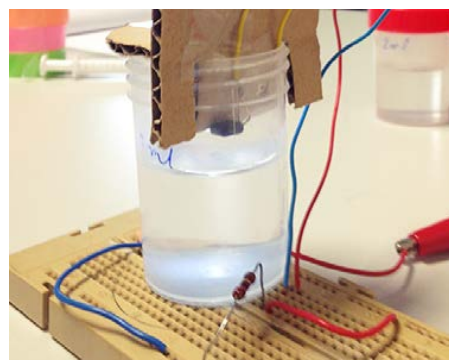


Fig. 2. Circuit and sample used in our test bench.

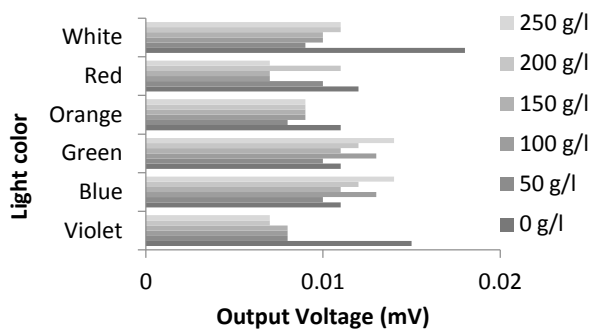


Fig. 3. Output voltage registered with the photoreceptor using different light colors.

The cost of all the electronic components needed to assembly the prototype is only 3€. Its application in real environments lies in the possibility to avoid the direct contact between the sensor and the water. The prototypes were tested at 1cm of the water sample.

V. CONCLUSION AND FUTURE WORKS

In this paper we present a prototype of sensor able to detect the presence of hydrocarbon on sea water. The sensor is based on the photoluminescence effect linked to the hydrocarbons.

To define the best setups our sensor, we have tested different light colors to excite the molecules of a hydrocarbon, gasoline. As light source and receptor, we have used a LED and a photodetector, respectively. We have used different amounts of gasoline over sea water. The lights that offer best results (white, orange and violet) are used to perform a deeper test. This test has demonstrated that white light provides the best results. It presents higher voltage difference between the values obtained with and without hydrocarbon. The results of the second test were statistically analyzed to validate that the observed results are statistically significant.

The sensor presents good performance in order to be used as system to detect the presence of spills as a part of sensor network to be installed in a real environment object of monitoring. The best characteristic of our sensor is mainly the low price of the electronic components needed, less than 3 €. Moreover, it is easy to use and the operation principles avoid the direct contact between sensor and water.

As future work, we would like to use this sensor in a real environment as a part of a wireless sensor network for water quality monitoring. Concretely, in port areas, it is common the presence of hydrocarbons in the upper layer of the water. A smart protocol for detect and track pollution in aquatic environments is already defined in [10]. The device where the sensor will be implemented is described in [11].

ACKNOWLEDGMENT

This work has been partially supported by the “Ministerio de Ciencia e Innovación”, through the “Plan Nacional de I+D+i 2008–2011” in the “Subprograma de Proyectos de

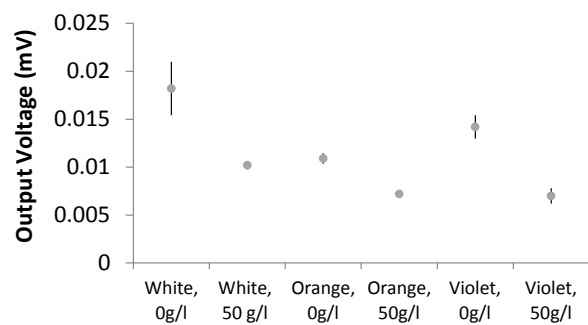


Fig. 4. Average value and the standart deviation of the output voltage using the selected light of test 1 after 10 repetitons.

Investigación Fundamental”(Project TEC2011-27516), by the postdoctoral grant “Contratos Postdoctorales UPV 2014 (PAID-10-14)” by the “Universitat Politècnica de València”, by the student grant “Ayudas para la contratación de personal investigador en formación de carácter predoctoral, programa VALi+d 2015 (ACIF 2015)” by the “Consellería de Educación, Cultura y Deporte”.

REFERENCES

- [1] T. Dalton and D. Jin, “Extent and frequency of vessel oil spills in US marine protected areas”, *Marine pollution bulletin*, vol. 60, no 11, pp. 1939-1945, 2010.
- [2] A. Jernelöv, “The threats from oil spills: Now, then, and in the future”, *Ambio*, vol. 39, no 5-6, pp. 353-366, 2010.
- [3] H. J. Celis, “Efectos de los derrames de petroleo sobre los habitats marinos”, *Ciencia Ahora*, vol. 24, no 12, p. 22-30, 2009. Available at: http://sgpwe.izt.uam.mx/files/users/uami/patt/4_Contaminacion_Quimica/10_derrames_petroleo.pdf [Last access: April 29, 2015].
- [4] M. Garcia, D. Bri, S. Sendra, J. Lloret, “Practical deployments of wireless sensor networks: a survey”, *International Journal on Advances in Networks and Services*, Vol. 3, No. 1&2, pp. 163-178. 2010.
- [5] M. Garcia, S. Sendra, G. Lloret, J. Lloret, “Monitoring and control sensor system for fish feeding in marine fish farms”. *IET communications*, 2011, vol. 5, no 12, p. 1682-1690.
- [6] O. Péron, E. Rinnert, M. Lehaitre, P. Crassous, and C. Compère. “Detection of polycyclic aromatic hydrocarbon (PAH) compounds in artificial sea-water using surface-enhanced Raman scattering (SERS)”. *Talanta*, 2009, vol. 79, no 2, p. 199-204
- [7] A. MacLean, C. Moran, W. Johnstone, B. Culshaw, D. Marsh, P. Parker. “Detection of hydrocarbon fuel spills using a distributed fibre optic sensor”. *Sensors and Actuators A: Physical*, 2003, vol. 109, no 1, p. 60-67.
- [8] R. P. McCue, J. E. Walsh, F. Walsh, and F. Regan. “Modular fibre optic sensor for the detection of hydrocarbons in water”. *Sensors and Actuators B: Chemical*, 2006, vol. 114, no 1, p. 438-444.
- [9] J. S. Albuquerque, M. F. Pimentel, V. L. Silva, I. M. Raimundo, J. J. Rohwedder and C. Pasquini, “Silicone sensing phase for detection of aromatic hydrocarbons in water employing near-infrared spectroscopy”. *Analytical chemistry*, 2005, vol. 77, no 1, p. 72-77.
- [10] S. Sendra, L. Parra, J. M. Jiménez, J. Lloret, “Smart System to Detect and Track Pollution in Marine Environments”. In *Proceedings of Workshop on Smart Communication Protocols and Algorithms (SCPA 2015)*, 2015, London, U. K., June 8-12, 2015.
- [11] Diana Bri, Hugo Coll, Miguel García, Jaime Lloret, “A wireless IP multisensor deployment”, *International Journal on Advances in Networks and Services* Vol. 3, No. 1 & 2, pp. 125-139, 2010.