Oil Fluorescence Spectrum Analysis for the Design of Fluorimeter

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Abstract – To evaluate the degree of contamination caused by oil spill accident in the sea, the in-situ sensors which are based on the scientific method are needed in the real site. The sensors which are based on the fluorescence detection theory can provide the useful data, such as the concentration of oil. However these kinds of sensors commonly are composed of the ultraviolet (UV) light source such as UV mercury lamp, the multiple excitation/emission filters and the optical sensor which is mainly photomultiplier tube (PMT) type. Therefore, the size of the total sensing platform is large not suitable to be handled in the oil spill field and also the total price of it is extremely expensive. To overcome these drawbacks, we designed the fluorimeter for the oil spill detection which has compact size and cost effectiveness. Before the detail design process, we conducted the experiments to measure the excitation and emission spectrum of oils using five different kinds of crude oils and three different kinds of processed oils. And the fluorescence spectrometer were used to analyze the excitation

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and emission spectrum of oil samples. We have compared the spectrum results and drawn the each common spectrum regions of excitation and emission. In the experiments, we can see that the average gap between maximum excitation and emission peak wavelengths is near 50 nm for every case. In the experiment which were fixed by the excitation wavelength of 365 nm and 405 nm, we can find out that the intensity of emission was weaker than that of 280 nm and 325 nm. So, if the light sources having the wavelength of 365 nm or 405 nm are used in the design process of fluorimeter, the optical sensor needs to have the sensitivity which can cover the weak light intensity. Through the results which were derived by the experiment, we can define the important factors which can be useful to select the effective wavelengths of light source, photo detector and filters.

Keywords: Oil Spill Detection(유출유 탐지), In-situ Sensor(현장탐지 센서), Fluorimeter(형광 광도계), Fluorescence Spectrum(형광 스펙트럼), Fluorescence Spectroscopy(형광 분석법)

1. Introduction

To evaluate the degree of contamination caused by oil spill accident in the sea, the in-situ sensors which are based on the scientific method are needed in the real site. Various kinds of in-situ sensors have been developed to detect the oil in the seawater (Denkilkian et al.[2009]; MacLean et al.[2003]; Oh et al.[2011]; Oh and Lee[2012]; Oh and Lee[2013]). Among the several developed in-situ sensors for the monitoring of oil spill in the sea, the sensors which are based on the fluorescence detection theory can provide the quantitative analysis result such as the concentration of oil (Chase et al.[2005]; Jociš and Vuorenskoski[2014]; Malkov and Sievert[2010]). These kinds of sensors commonly are composed of the ultraviolet (UV) light source such as UV mercury lamp, the multiple excitation/emission filters and the optical sensor which is mainly photomultiplier tube (PMT) type. Therefore, the size of the total sensing platform is large not suitable to be handled in the oil spill field and also the total price of it is extremely expensive. These limitations prevent the wide use of in-situ oil spill sensor when the oil spill accident occurs.

Whereas, in the biomedical application, various research groups have developed the eletro-optical sensors having compact size and low cost, to analyze the biomedical elements for the point of care (POC) (Jin et al.[2012]; Ozcan and Demirci[2008]; Roy et al.[2014]; Roy et al.[2015]; Seo et al. [2009]). To realize this aspect, they used the light-emitting diode (LED) as the light source and a lensless complementary metal-oxide semiconductor (CMOS) image sensor as the optical sensor for the analysis of biomedical elements such as blood cells. However, so far, the fluorescence detector for the purpose of in-situ oil spill sensing based on the UV light-emitting diode (LED) as the light source and a complementary metal-oxide semiconductor (CMOS) image sensor has not been demonstrated yet.

In this paper, we describe the design process of fluorescence detector, specially focused on the selection of effective wavelength of light source, photo detector and excitation/emission filters. The planned platform of fluorimeter for the oil spill sensing is composed of the UV light-emitting diode (LED) as the light source and a complementary metal-oxide semiconductor (CMOS) image sensor as the photo sensor for the evaluation of light intensity from the fluorescence phenomenon. A schematic of the proposed system in this paper is shown in Fig. 1.

The experiments in this research were conducted by using five different kinds of crude oils and three different kinds of processed oils. The fluorescence spectrometer were used to analyze the excitation and emission spectrum of oil samples. We have compared the spectrum results and drawn the each common spectrum regions of excitation and emission. Through this analysis process, we have defined the effective wavelengths of light source, photo detector and optical filters.

2. Material and Methods

2.1 Oil sample preparation

To draw the results of the excitation and emission spectrum,
we have used five different kinds of crude oils and three different kinds of processed oils. Five crude oil samples have the origins from Iraq, UAE, Qatar, Russia and Papua New Guinea. The kinds of processed oils are bunker A, B and C. The oil samples have processed by using water accommodated fraction (WAF) for the reproduction of oil-spilled condition in the sea (An et al. [2014]; Singer et al. [2000]). WAFs were prepared for the every oil sample using the standard WAF method (An et al. [2014]; Singer et al. [2000]). The oil and filtered seawater were mixed with the ratio of 1:40 and stirred with the mixing speed of 130 rpm for 24 h. Seawater used in these experiments have been sampled in the coast of Incheon, Korea. The WAF processed oil samples have also extracted using Hexane. Extracted samples and non-extracted samples both have been analyzed using the fluorescence spectrometer.

2.2 Fluorescence spectroscopy

The excitation and emission spectrum of processed oil samples have been measured by the fluorescence spectrometer (Fluoro-Mate FS-2, Scinco, Korea). We have carried out the measurement experiments three times for the single oil sample and used the average value. Ten different crude oil samples (Hexane-extracted five samples and non-extracted five samples) and six processed oil samples (Hexane-extracted three samples and non-extracted three samples) with the same condition were measured using fluorescence spectrometer. To obtain the excitation and emission spectrum of oil samples, two different condition were taken in the fluorescence spectrometer. First condition was to find out the maximum value of excitation wavelength which causes the maximum fluorescence. So, in this condition, we can figure out the single value of excitation wavelength at which the emission of fluorescence occurs the maximum intensity of emission light. Otherwise, in the second condition, we can select and fix the excitation wavelength, and then the emission spectrum can be deducted at that excitation wavelength. In the first several sets of experiments, we have measured the excitation spectrum which can occur the maximum fluorescence phenomenon. In the second step of experiments, we selected and fixed the excitation wavelength which were reflected from the value of actual ultraviolet (UV) light source which can be considered at the design process of the fluorimeter. Through these two experiments, we compared the results and derived the correlation between the excitation and the emission wavelength.

3. Results and Discussion

The excitation and emission spectrums of the processed oils are shown in Fig. 2. In this experiment, the excitation spectrum

![Excitation and emission spectrum graphs of processed oils in this experiment.](image-url)
was selected for the condition of maximum fluorescence.

Fig. 2(a) and Fig. 2(d) show the excitation and emission spectrums of WAF processed bunker A oil and extracted WAF processed bunker A oil by Hexane, respectively. In the non-extracted oil sample, maximum wavelength of excitation for the fluorescence was 277.9 nm. And in the same sample, the maximum wavelength of emission was 300.6 nm. The gap between maximum wavelengths of excitation and emission is 22.7 nm. Fig. 2(b) and Fig. 2(e) show the excitation and emission spectrums of WAF processed bunker B oil and extracted WAF processed bunker B oil by Hexane, respectively. In the non-extracted oil sample, maximum wavelength of excitation for the fluorescence was 333.2 nm. And in the same sample, the maximum wavelength of emission was 390.3 nm. The gap between maximum wavelengths of excitation and emission is 57.1 nm. And in the Fig. 2(c) and Fig. 2(f), we can see the excitation and emission spectrums of WAF processed bunker C oil and extracted WAF processed bunker C oil by Hexane, respectively. In the non-extracted oil sample, maximum wavelength of excitation for the fluorescence was 288.3 nm. And in the same sample, the maximum wavelength of emission was 342.5 nm. The gap between maximum wavelengths of excitation and emission is 54.2 nm.

The difference between the experiment of non-extracted and Hexane-extracted oil samples is that the excitation and emission spectrum peak of Hexane-extracted oil sample is sharper than that of non-extracted one. This aspect can be seen under the same condition in other experiments.

The excitation and emission spectrums of the crude oils is shown in Fig. 3. In the Fig. 3(a) and Fig. 3(d), we can see the excitation and emission spectrums of WAF processed crude oil from Iraq and extracted WAF processed crude oil from Iraq by Hexane, respectively. The gaps between maximum wavelengths of excitation and emission are 25 nm and 32.1 nm. Fig. 3(b) and Fig. 3(e) show the excitation and emission spectrums of WAF processed crude oil from UAE and extracted WAF processed crude oil from UAE by Hexane, individually. In the non-extracted oil sample, maximum wavelength of excitation for the fluorescence was 293.9 nm. And in the same sample, the maximum wavelength of emission was 351.5 nm. The gap between maximum wavelengths of excitation and emission is 57.6 nm.

And in the Fig. 3(c) and Fig. 3(f), we can see the excitation and emission spectrums of WAF processed Russian crude oil and extracted WAF processed Russian crude oil by Hexane, respectively. In the Hexane-extracted oil sample, maximum wavelength of excitation for the fluorescence was 288.6 nm. And in the same sample, the maximum wavelength of emission was 337.4 nm. The gap between maximum wavelengths of excitation and emission is 48.8 nm.

Fig. 3. Excitation and emission spectrum graphs of crude oils in this experiment. The excitation spectrum was selected for the condition of maximum fluorescence. (a) Excitation and emission spectrum of WAF processed crude oil from Iraq. (b) Excitation and emission spectrum of WAF processed crude oil from UAE. (c) Excitation and emission spectrum of WAF processed Russian crude oil. (d) Excitation and emission spectrum of WAF processed crude oil from Iraq extracted by Hexane. (e) Excitation and emission spectrum of WAF processed crude oil from UAE extracted by Hexane. (f) Excitation and emission spectrum of WAF processed Russian crude oil extracted by Hexane.
In the experiments of processed oil and crude oil, we can see the average gap between maximum excitation and emission peak wavelength is near 50 nm for the every case. And the excitation and emission spectrums’ shapes of Hexane-extracted oils are shaper than those of non-extracted oils. Hexane can extract polycyclic aromatic hydrocarbon (PAH) from the WAF processed oil sample. In this condition, PAH is the single component which can cause the fluorescence phenomenon and this component influences the shape of fluorescence spectrum.

In the Fig. 4, the emission spectrums of crude oils which are the origins from Papua New Guinea and Qatar. In each experiments, the excitation wavelengths were fixed at 280 nm, 325 nm, 365 nm and 405 nm. So, we can see the four different emission spectrums at each fixed excitation wavelength. In the case of experiment which were used by non-extracted Papua New Guinea crude oil, the excitation wavelength which occurs the maximum intensity of emission light was 288.5 nm. However, it is quite difficult to use the UV light-emitting diode (LED) having the wavelength of 288.5 nm. So we selected and fixed the excitation wavelength for the use of light source. In the experiment which were fixed by the excitation wavelengths of 365 nm and 405 nm, the intensity of emission was weaker than those of 280 nm and 325 nm. So, if the light sources having the wavelength 365 nm or 405 nm are used in the design process of fluorimeter, the optical sensor needs to have the sensitivity which can cover the weak light intensity.

4. Conclusions

In summary, we conducted the experiments to measure the excitation and emission spectrum of oils using five different kinds of crude oils and three different kinds of processed oils. The water accommodated fraction (WAF) method was applied in this experiment for the reproduction of oil-spilled condition in the sea. And the fluorescence spectrometer were used to analyze the excitation and emission spectrum of oil samples. We have compared the spectrum results and drawn the each common spectrum regions of excitation and emission. In the experiments, we can see that the average gap between maximum excitation and emission peak wavelengths is near 50 nm for the every case.
In the experiment which were fixed by the excitation wavelengths of 365 nm and 405 nm, we can find out that the intensity of emission was weaker than those of 280 nm and 325 nm. So, if the light sources having the wavelength of 365 nm or 405 nm are used in the design process of fluorimeter, the optical sensor needs to have the sensitivity which can detect the weak light intensity. Through the results which were derived by the experiments, we can define the important factors which can be useful to select the effective wavelengths of light source, photo detector and filters.

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