Experimental Analysis on the Optimal Excitation Wavelength for Fine-Grained Identification of Refined Oil Pollutants on Water Surface Based on Laser-Induced Fluorescence

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Abstract
Laser-induced fluorescence (LIF) is an effective and all-weather oil spill identification method that has been widely applied for oil spill monitoring. However, the distinguishability on oil types was seldom considered while selecting the excitation wavelengths. This study is intended to find the optimal excitation wavelength for fine-grained classification of refined oil pollutants using LIF by comparing the distinguishability of fluorometric spectra under various excitation wavelengths on some typical types of refined oil samples. The results show that the fluorometric spectra of oil samples significantly vary under different excitation wavelengths, and the four types of oil applied in this study are most likely to be distinguished under the excitation wavelengths of 395 nm and 420 nm. This study is expected to improve the ability of oil types identification using LIF method without increasing time or other cost, and also provide theoretical basis for the development of portable LIF devices for oil spill types identification.

Keywords Laser-induced fluorescence · Fluorometric spectra analysis · Oil spill · Oil types classification · Fine-grained classification

Introduction
As the fast development of offshore oil exploitation and maritime transportation, oil spill events that were caused by leakages from platforms and collisions of ships frequently occurred, and negatively affected maritime transportation and oceanic environment [1, 2]. With the awareness of the destructive impacts of oil spills, the detection and prevention of oil spill events have become an important and interdisciplinary topic. Thanks to the international cooperation on the oil spill prevention and response, such as the International Convention on Oil Pollution Preparedness, Response, and Co-operation (OPRC), the number of large oil spill events has significantly decreased in the past few decades. However, medium and small oil spill events (from 7 to 700 ton) still occurred frequently and endangered the oceanic environment [3]. Besides the collisions of ships, medium and small oil spill events could be caused by loading, unloading, fuel charging, tank cleaning, and various maritime activities. Refined oil, such as diesel, gasoline, and lubricant, were commonly witnessed in medium and small oil spill events [4].

For the purpose of the oil spill detection, a coarse-grained classification that distinguishes the presence of oil slick from clean water is adequate. While for the purpose of oil pollutants tracing, a fine-grained classification that distinguishes between different types of oil pollutants is necessary. Despite the importance of determining the source of leakage and the plan for responses, rapid oil pollutants classification methods were somewhat lacking. Gas chromatography combined with mass spectroscopic (GC–MS) or flame ionization detector (GC-FID) analysis have been commonly used for oil pollutants tracing. These methods can provide accurate inferences on the compositions of oil samples, which further indicate the types of oil pollutants [5]. Researchers have documented the GC-FID chromatograms and GC–MS traces of various types oil and formed the archives for oil spill fingerprinting [6–10]. Some other methods that follow the hyphenated mass spectroscopic approach were also developed in the previous studies, such as two-dimensional gas
Almost all types of petroleum hydrocarbons (PHCs) have unique fluorometric characteristics, which can be used for PHC identification on soil, seawater, ice, and other complicated background [13, 14]. Therefore, laser-induced fluorescence (LIF) is an effective and all-weather oil spill identification method that has been widely applied for oil spill monitoring. Brown et al. [15] conducted an airborne LIF test by mounting an excimer laser and an intensified diode array spectrometer on airplane. The flight results confirmed the fluorosensors' ability on detecting the presence of oil slick on water surface. But the fine-grained classification on oil types was not investigated. Hou et al. [16–18] conducted a series of studies on the fluorometric characteristics of polycyclic aromatic hydrocarbons in different types of oil. They designed a port-based device for oil spill monitoring based on LIF. Although LIF could effectively identify the presence of oil pollutants, it was difficult to distinguish between various types of oil that have the similar fluorometric spectra. In order to solve this problem, Chekalyuk and Hafez [19] proposed the “Advanced Laser Fluorometry” (ALF) method by using lasers with multiple excitation wavelengths. However, both LIF and ALF methods overlooked the selection of excitation wavelengths: they usually determined the excitation wavelength based on the laser frequency doubling of the equipment, or the excitation efficiency of the material [20]. Distinguishability was seldom considered while selecting the excitation wavelengths. In order to have a comprehensive understanding on the characteristics of LIF, researchers combined the fluorometric spectra under different excitation wavelengths and formed excitation-emission matrix (EEM). EEM introduced additional information in the dimension of excitation wavelength, and thus had the potential to provide more accurate classification on oil pollutants [21, 22]. Researchers have attempted to identify oil spill pollutants [23], and develop oil spill fingerprinting methods based on EEM [24]. Nevertheless, the measurements of EEM are also too costly and time-consuming to be applied to the medium and small oil spill events [16].

Considering the limitations in the previous works on LIF and EEM researches, this study is intended to compare the distinguishability of fluorometric spectra on some typical refined oil samples under various excitation wavelengths, and find the optimal excitation wavelength for fine-grained oil pollutants identification using LIF. By examining and analysing the classification results using the fluorometric spectra that were collected under different wavelengths, this study is expected to improve the ability of fine-grained oil pollutants classification using LIF method without increasing time or other cost. Furthermore, this study is expected to provide theoretical basis for the development of portable LIF devices for rapid oil pollutants identification.

Methodology

Equipment and Material

The fluorescence of oil slick on water surface was excited using a xenon arc lamp and collected using a hyperspectral sensor in the experiments. A xenon lamp that is adjustable in wavelength was used as the light source in order to collect the fluorometric spectra under different excitation wavelengths. The model of the xenon arc lamp that was used in the experiments is TLS-300XR (Fig. 1a), which is produced by Oriel Instruments, Newport Corporation, America. The xenon arc lamp is composed of a high-stability broadband light source, of which the power is 300 W, and a high-precision monochromator. With an automatic wheel of optical filters, the xenon arc lamp can generate stable monochromatic light with adjustable wavelength. The adjustable range of wavelength is 250–1800 nm, and the step length is 5 nm. Only the wavelengths ranging from 355–455 nm that are strong enough to excite fluorescence were used for the purpose of the experiments.

Intensity of the fluorescence was then measured using a portable hyperspectral sensor: Analytical Spectral Devices (ASD) FieldSpec3 (Fig. 1b). ASD FieldSpec3 is a commonly-used portable instrument for spectral measurement. Its measurement range is 350–2500 nm, which covers ultraviolet, visible, and near infrared bands. Different detectors are used for different detection bands. In this study, LIF within the visible band (400–700 nm) were recorded using silicon photodiode arrays in ASD FieldSpec3. For the visible spectral range, the spectral sampling interval is 1.4 nm, and the spectral resolution is 1 nm.

Seawater and various types of oil samples were prepared for the purpose of the experiments. The seawater was collected in the port of Lingshui, China, in the northern Yellow Sea. Diesel, gasoline, and two types of lubricant were selected as the objects of identification in this study: (1) 0# diesel solidifies at 0 °C, and has the density of 830 kg/m³. It is commonly used as ship fuel; (2) 92# gasoline contains 92% isooctane and 8% heptane, and has the density of 730 kg/m³. It is commonly used as the fuel for small ships; (3) Mobile 0W40 has the density is 850 kg/m³, and it is commonly used as the lubricant for gasoline engine; (4) DAZIRAN CF-4 has the density is 880 kg/m³, and it is commonly used as the lubricant for diesel engine. A photograph of these four types of oil samples used in the experiments are shown in Fig. 2.
Experiment Design

Fluorometric spectra under different excitation wavelengths were collected in the lab experiments as the training and testing dataset of the classifier. The experiments were conducted under darkroom condition in order to prevent the inferences of ambient light on LIF measurements. The range of excitation wavelengths ($\lambda_{ex}$) from the xenon arc lamp was set at 355–455 nm, and the step length was set at 5 nm. Thus, the fluorometric spectra were collected under 21 different excitation wavelengths. The classifier made predictions using the fluorometric spectra collected under each of the 21 bands, and the optimal excitation wavelength can be determined by examining the accuracies of classification results under these 21 bands.

The range of emission wavelengths ($\lambda_{em}$) was set at 370–700 nm at the spectral resolution of 1 nm. Thus, there are 351 bands in each fluorometric spectrum. A schematic diagram of the experiments is shown in Fig. 3a, and a photograph of the experimental setting is shown in Fig. 3b. The fluorometric spectra collected by ASD FieldSpec3 was affected by the instrumental noise, the direct reflection of the laser, Rayleigh scattering, and the fluorescent substance in the seawater. Therefore, the data needed to be pre-processed before they could be used for classification. Specifically: (1) the instrumental noise was suppressed by taking the arithmetic mean of 5 raw spectra; (2) for each excitation wavelength, the measurements from 350 to 15 nm more than the excitation wavelength were filled with blank, so that the effects of the direct reflection and Rayleigh scattering were eliminated; (3) the collected fluorometric spectra of oil samples were corrected with those of the seawater samples based on background subtraction in order to eliminate the background fluorescence.

In order to form the training dataset and test the robustness of the classifier, multiple measurements on the fluorometric spectra of each type of oil samples were conducted not only under different excitation wavelengths, but also at various oil thicknesses. 1 ml, 2 ml, and 4 ml of oil samples were collected using pipette and dropped into glass bottles with seawater. The bottles with oil samples were placed statically until the stable oil films were formed. Since the
oil samples used in the experiments were refined oil and relatively easy to spread on water surface, they did not need to be warmed before use. It usually took less than 1 min to form the stable oil films. It should be noted that the bottles needed to be covered with frosted caps because the refined oil samples could easily volatilize. Additionally, a bottle with only seawater was prepared to measure the background fluorescence.

Oil thickness can be estimated using the diameter of the glass bottle and the volume of the oil sample. The glass bottles used in the experiments are 40 mm in diameter and 25 mm in height. Thus, the oil thicknesses of 1 ml, 2 ml, and 4 ml oil samples are about 0.8 mm, 1.6 mm, 3.2 mm, respectively. It should be noted that although the oil thicknesses were recorded in the experiment, they were not fed to the classifier in order to test whether the model was able to recognize the types of oil pollutants without the pre-knowledge about the oil thickness. 1000 fluorometric spectra were collected for each type of oil under each set of oil thickness and excitation wavelength. Thus, there were totally 12,000 fluorometric spectra collected to form the training and testing data under each set of excitation wavelengths. 80% of the collected fluorometric spectra were used as training dataset and 20% of those were used as testing data.

**Implementations of the Classifier**

After the fluorometric spectra had been collected for the four types of refined oil pollutants at different thicknesses and under different excitation wavelengths. 21 identification experiments were conducted using the fluorometric spectra collected under each excitation wavelength. The accuracies of the experiments were evaluated and compared in order to find the optimal excitation wavelength for oil types classification. Because the types of oil pollutants were labelled when taking fluorescence measurements, supervised learning methods that provide more accurate classification results with smaller number of calculations are preferable for the oil types identification task. Specifically, bagged random forest (RF) is selected as the classifier in this study. RF is a classical method of supervised machine learning that consists of a number of tree-like classification units and a majority vote [25]. Each classification unit makes the prediction based on its own decision tree. The votes from all classification units are collected and the prediction with the largest number of votes is considered as the final output [26]. RF is able to handle high-dimensional data effectively, and has been applied to spectral analysis and classification [27].

In this study, the whole fluorometric spectrum that consists of 351 bands was considered as the input data. The size of output was 4, which represented for the 4 categories of oil pollutants used in the experiments. The bagged RF model consisted of 200 tree-like classification units. The working flow of RF applied in this study is shown as Fig. 4.
The model was constructed using Statistical and Machine Learning Toolbox in MATLAB R2019a, and trained on a computer of 2.5 GHz Intel i5-7300HQ CPU and 8.0 GB of RAM.

**Results**

**Laser-induced Fluorometric Spectra**

As mentioned above in the subsection of experimental design, the collected fluorometric spectra were preprocessed in order to eliminate the influences induced by the instrumental noise, the direct reflection of the laser, Rayleigh scattering, and the fluorescent substance in seawater. Two examples of the processed fluorometric spectra collected under the excitation wavelengths of 385 nm and 420 nm are shown as Fig. 5.

The fluorometric spectra at all 21 different excitation wavelengths were combined and form EEM in order to provide better visualization, and conduct more comprehensive analysis on the fluorometric spectra. EEMs generated using the fluorometric spectra of the four types of oil pollutants are shown as Fig. 6. As shown in the EEMs, obviously, there are significant differences in the fluorometric spectra collected under different excitation wavelengths. Therefore, it is certainly necessary to examine the distinguishability on oil pollutants classification under different wavelengths.

**Oil Types Identification Under Different Excitation Wavelengths**

As mentioned above in the methodology part, 21 classification experiments were conducted using the fluorometric spectra under each excitation wavelength, and the accuracies of all experiments were compared in order to determine the optimal wavelength. The accuracies of identification results were quantitatively evaluated through producers’ accuracies (PA), users’ accuracies (UA), and overall accuracies (OA). PA, UA, OA for the four types of oil pollutants under all excitation wavelengths are plotted in Fig. 7. Additionally, the general accuracy of the model, which is defined as the ratio between the number of all the correct predictions on all the four types of oil pollutants and that of the testing dataset, are plotted as Fig. 8.

**Discussion**

**Interpretation of the Fluorometric Spectra**

According to the fluorometric spectra collected in the experiments (Fig. 5), the measured fluorescence intensities of diesel and diesel engine oil were relatively low, and had the similar pattern under the excitation wavelengths of 385 and 420 nm. The fluorescence intensities of 92# gasoline were about three time higher than those of the diesel and diesel engine oil. And the fluorescence intensities of gasoline engine oil were about one time higher than those of the diesel and diesel engine oil. 92# gasoline had similar peak of fluorescence at about 450 nm under these two excitation wavelengths; while that for 0W40 shifted from 450 to 520 nm under these two excitation wavelengths. The shapes of fluorometric spectra for diesel and diesel engine oil were visually identical under these two excitation wavelengths. The peaks of fluorescence for these two types of oil shifted from 440 nm to about 500 nm under the two excitation wavelengths, while the peaks were not as significant as those of gasoline and gasoline lubricant.
According to the EEMs in Fig. 6, these four different types of oil had similar peak of fluorescence at about 450 nm under the excitation wavelength of 380 nm. 0W40 had an additional peak of fluorescence at about 550 nm under the excitation wavelength of 445 nm. These results generally conformed with the observations of LIF in previous studies [4, 20–22].

Fig. 6 EEMs of four different types of oil pollutants used in the experiment: (a) 0# diesel; (b) 92# gasoline; (c) 0W40; (d) CF-4

Optimal Excitation Wavelength for Oil Pollutants Identification

According to the OA of the classification results for the four types of oil under all excitation wavelengths (Fig. 7c), the classifier had low identification accuracies under the
excitation wavelengths from 365 to 385 nm. Diesel and diesel engine oil were also difficult to be identified over 440 nm, while gasoline and gasoline engine oil also had low identification accuracies from 400 to 410 nm.

Referring to the general accuracy graph (Fig. 8), the model was not able to provide very accurate classification results in the same spectral range as described above. Combining the OA for the identification results of all four types of oil, the model was able to achieve identification results with the highest accuracy under the excitation wavelengths of 395 nm and 420 nm. This result indicates that the four types of oil applied in this study are most distinguishable under these two excitation wavelengths.

Fig. 7 Accuracies of the identification results on four types of oil under different excitation wavelengths: (a) users’ accuracy; (b) producers’ accuracy; (c) overall accuracy.
Conclusion

The selection of the optimal excitation wavelength for the fine-grained classification of refined oil pollutants using LIF is studied through experimental analysis in this study. Comparing the accuracies of the identification results using the fluorometric spectra collected under different excitation wavelengths, the four types of oil are most likely to be distinguished under the excitation wavelengths of 395 nm and 420 nm. This study provides a guidance to the choices of excitation laser for fine-grained oil pollutants identification using LIF method. In the future study, the authors’ team will consider including more types of oil pollutants and their mixtures in the experiments in order to establish an optimal excitation wavelength for distinguishing between broader types of oil pollutants.

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Authors’ Contribution MX designed the methodology, constructed the identification model, prepared the original draft, and completed the reviewing and editing of the paper. YJ conducted the experiment, processed the data, and participated in the preparation of original draft. YL proposed the concept, provided supervision and completed the reviewing and editing of the paper. XC participated in the experiment and data processing, as well as results investigation. KC coded the software, investigates and validated the classification results. All authors read and approved the final manuscript.

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Data Availability Statement The data and codes that support the findings of this study are publicly available online at https://github.com/349898680/Dr-Xie-code/tree/main/CNN%20model%20for%20EEM%20oil.

Declarations

Ethics Approval Not applicable.

Consent to Participate Not applicable.

Consent for Publication Not applicable.

Competing Interests The authors declare no conflicts of interest.

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