

Detection of thin oil films on water surface from a remote distance when fluorescence is excited by 447nm laser light

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This paper describes the research results on the detection of thin oil film formed on the surface of water from a remote distance. Peculiarities of fluorescence, of the oil film (thickness of ~ 90 μm), when fluorescence is excited by 447nm laser light, were investigated using digital methods of registration. Image processing of the fluorescence signals was accomplished remotely.

(Received June 15; 2016; accepted April 6, 2017)

Keywords: Crude oil fluorescence; Remote sensing

1. Introduction

Extraction and transportation of liquid hydrocarbons in the maritime areas are inevitably accompanied by oil spills that cause unwanted contamination of the surface of the water. Identification of oil spills on the water surface from a remote distance can help identify defective oil equipment and prevent environmental pollution of the environment. In the paper [1] experimental results of the laboratory investigation of the fluorescence of the crude oil products and colored dissolved organic matter (CDOM) were presented. The fluorescent investigations were carried out using a fluorometer, and fluorescence was excited by a Xenon lamp with excitation in the spectral range 222 nm – 532 nm. Based on the experimental results, the authors propose the light detection and ranging (LIDAR) system for oil diagnostic with two excitation wavelengths. The first excitation wavelength must be chosen from the spectral range 220 nm - 308 nm and the second wavelength from the spectral range 350 nm - 499 nm. This method can be used for discrimination between oil and dissolved organic matter of natural origin. In the paper [2] was presented the analysis of the induced fluorescence of eight oil brands using a 355-nm LIF LIDAR and a spectral fluorescence signature sensor based on recording and analyzing of fluorescent response obtained by a set of various excitation wavelengths 308 nm and 355 nm. The presented results confirm that LIF LIDAR may be successfully used not only for detection of oil spills, but also for categorization of oil composing the spill. In the paper [3] are presented some results of research on the fluorescence properties of petroleum oil-in-water emulsions using a Fluorat-02 Panorama spectrofluorimeter. The fluorescence was excited by radiation of wavelengths 220 nm, 240 nm, 260 nm, 300

nm and 340 nm. The test was carried out on seven different types of petroleum emulsified in seawater and was shown that fluorescence was proportional to the oil concentration in an emulsion. In [4] was analyzed crude petroleum at different dilution in Nujol, a transparent mineral oil. The emission spectra were obtained by exciting the samples with a 400 W Xenon lamp at 350 nm, 450 nm and 532 nm. It was studied the fluorescence characteristics of solutions containing fixed amount of Nujol pure oil and different concentrations of crude oil. The research results of investigations from remote distance of spatial distribution of the natural CDOM components and fluorescence spectra of oil pollution on seawater were presented in [5]. Three systems KLS-10, FLS-12 and FLS-UV were used for experiments on the sea water. For excitation of the oil film and CDOM were used UV-laser wavelengths (299 nm and 308 nm) and visible spectral components. Obtained fluorescent spectra of crude oil and CDOM allowed the detection of oil pollution and separating it from the CDOM with estimation of concentration in the sea water. The FLUORES system for detecting the fluorescence of water ingredients: oil spills; natural and anthropogenic organic matter; and pigments, was presented in paper [6]. Proposed technique is based on laser induced fluorescence and analysis of fluorescence spectra, induced in the target object by illumination with a laser beam. The LIDAR system consists of three units: the laser - the detection system - and the acquisition unit. The laser radiation at 308 nm is emitted by an excimer laser, while 367 nm and 460 nm are emitted by a tunable dye laser. The detection system includes a telescope, a polychromator with two concave diffraction gratings, and an optical detector, which combines an image intensifier and a linear CCD camera. In [6] an analytical model for the luminescence data picked-up by the CCD camera was

suggested. In the papers [7 - 8], laser-excited fluorescence was used for remote detection of oil. In the paper [7] LIDAR was used with 308 nm laser and spectrometer. Results of investigations on the sea water can be used to separate fluorescence signals of crude oil films from the signals from organic compounds. Paper [8] describes experiments with LIDAR consisting of UV laser 355 nm, scanner, telescope, spectrograph, and registration electronics, controlled by computer. The oil spill detection is possible at distances of up to approximately 50 m during both day and night. The methods described above allow non-contact detection of oil spills with high sensitivity, but need bulky instrumentation (polychromators, monochromators, spectrophotometers). In the paper [7] LIDAR system weight was 52 kg with dimensions (70 cm x 50 cm x 40 cm), that requires to the use of ships or aircraft. However, a technical failure of the subsea pipes used for the production and transportation of oil can begin with just minor leaks of the petroleum products: for example, a volume of ~ 1 ml. For fast detection of such minor leaks, a compact unmanned aerial vehicle (UAV) equipped with lightweight small size equipment can be used. In our paper we describe the method for the appropriate identification of a small quantity of oil on the water surface from a remote distance that can help identify defective oil equipment and prevent environmental pollution.

2. Experimental setup

The experimental setup for the investigation of the fluorescence spectra is based on the telescopic system with a set of narrowband interference filters, CCD camera, and excimer laser at 447 nm. For excitation wavelength 447 nm the fluorescence emission maximum (~530 nm) of the investigated oil is located in the middle of the range of spectral sensitivity of the digital camera (400-700 nm). The experimental setup to study the spectra of fluorescence of crude oil is presented in Fig. 1.

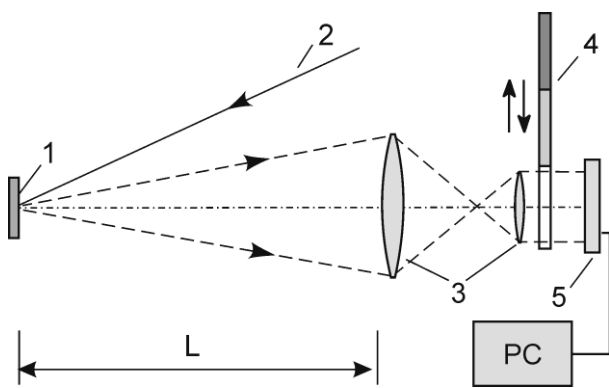


Fig. 1. Experimental setup: 1 - Oil sample, 2 - Laser $\lambda = 447$ nm, 3 - Telescopic system, 4 - Set of interference filters, 5 - Digital camera matrix

The analyzed sample (1) is located at a distance of $L = 15$ m from the source of laser radiation (2) with a wavelength of $\lambda = 447$ nm for inducing the fluorescence of crude oil. Using a telescopic system (3) laser-excited fluorescence passes through a set of narrowband interference filters (4) and is projected onto the digital camera matrix (5). Each filter transmits a narrow spectral range of visible light, which is located in the spectral sensitivity of the digital camera in the range of 400-700 nm. Spectral dependencies of narrowband bandwidth interference filters are presented in Fig. 2.

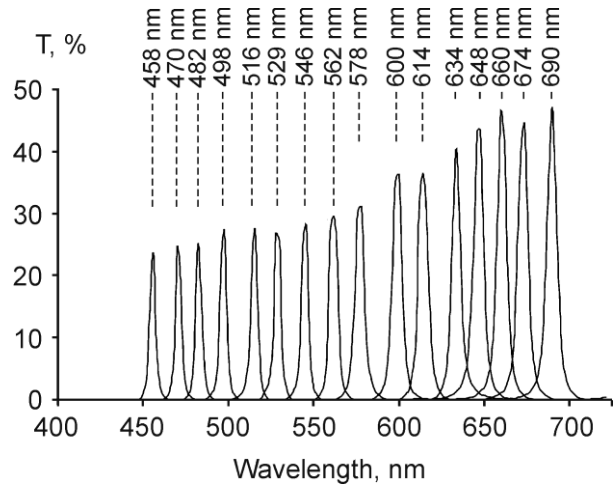


Fig. 2. Spectral dependencies of narrowband interference filters

Fluorescence investigation of oil on the water surface from a remote distance is done by registration of the digital images using the consecutive changes of the interference filters. To plot the spectral fluorescence of oil it is necessary to calibrate the system: telescope - interference filters - digital camera for each filter. This procedure is critical due to the various transmission ranges of interference filters (Fig. 2) and nonlinear characteristics of the spectral sensitivity of digital cameras [9]. The spectral dependence of the photosensitivity of the Nikon D3100 digital camera is presented Fig. 3.

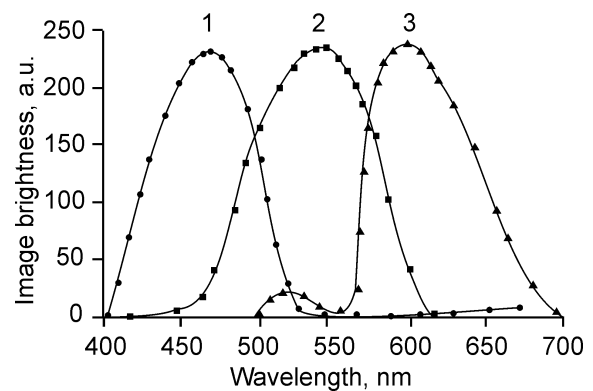


Fig. 3. Spectral dependence of digital camera photosensitivity for Nikon D3100: 1 - Blue channel, 2 - Green channel, 3 - Red channel

The calibration of telescope - interference filters - matrix digital camera for each filter was carried out using the same values for digital camera sensitivity (ISO 3200) and image recording time $t = 1/5$ s, and intensity of the incident light signal. The radiation source was located at a distance of $L = 15$ m from the telescopic system. Images were recorded by digital camera and saved as RAW files. By digital processing of the RAW files in a graphical editor (for example, Adobe Photoshop), it is possible to define the image brightness in conventional units (from 0 to 255) separately for each RGB channel of the system. Thus, filters that registered 458-498 nm brightness were determined according to the blue channel; filters that registered 516-562 nm - the green channel; and filters that registered 578-690 nm - the red channel. As an example, Fig. 4 shows the brightness dependence of images (in conventional units of the RGB system, from 0 to 255) on irradiance for some of the interference filters.

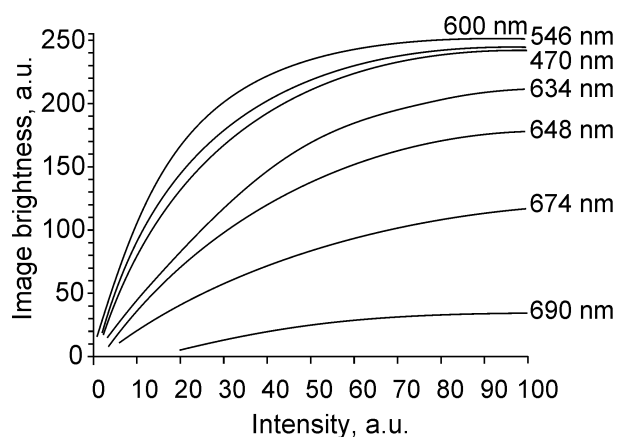


Fig. 4. Dependence image brightness vs. intensity for different wavelengths

For filters in the blue (458 nm, 482 nm, and 498 nm) and green (516 nm, 529 nm, and 562 nm) regions of the spectrum calibrated curves are located close to the dependencies of 470 nm and 546 nm, respectively, because these wavelengths are close to the maximum spectral sensitivity of the digital camera (curves 1 and 2, Fig. 3). For the red spectrum the sensitivity of telescope - interference filters - digital camera is reduced due to the lower sensitivity of the digital camera in the spectral range 600-690 nm (curve 3, Fig. 3).

3. Results and discussion

Crude oil (1 ml) was placed on the water surface (Fig. 5(a)). After 25 minutes the oil slick had spread on the water surface up to a diameter of ~ 12 cm (Fig. 5(b)). The estimated thickness of the oil film was approximately 90 μm .

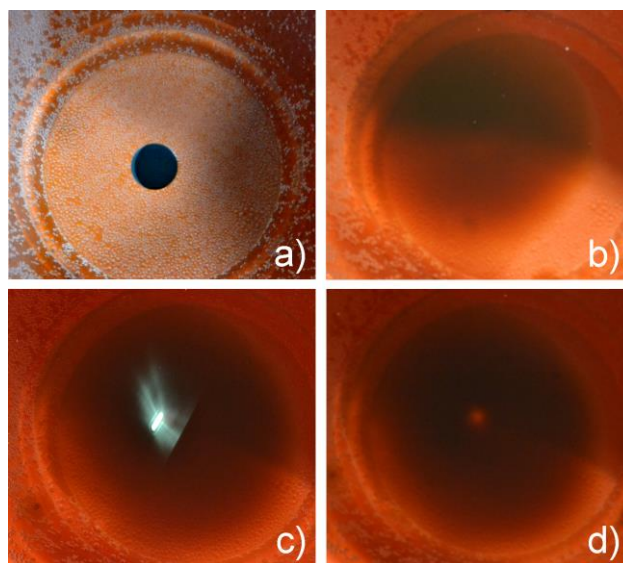


Fig. 5. Images of crude oil on water: (a) Oil slick volume of 1 ml on the water surface, (b) Image of oil spots after 25 min, (c) Fluorescence of oil during laser ($\lambda = 447$ nm) illumination, (d) Degradation of oil slick

During the laser ($\lambda = 447$ nm) illumination fluorescence of the oil slick was observed (Fig. 5(c)). However, for the study of fluorescence spectra of oil films on the water surface three factors that influence the measurement process should be taken into account: formation of thermal lenses on the surface when illuminated by a laser beam [10], degradation of the oil film under the influence of laser radiation [11], and presence of solar illumination during the daytime. Formations of thermal lenses on the oil surface were due to Gaussian distribution of the laser beam intensity [10]. To prevent thermal lenses, the oil slick was illuminated by the collimated laser beam ($\lambda = 447$ nm) in the form of a 2×8 mm strip (Fig. 5(c)). An important parameter in this experiment was the power of the laser radiation, since the intensity of fluorescence, and the rate of degradation of the oil film, depends on it. Experimentally, it was recognized that the registration of the spectral distribution of fluorescence of thin oil film can be accomplished by laser power $P = 60$ mW (at a constant value of the laser beam cross-section 2×8 mm). During the laser illumination the surface oil slick degraded in 5 minutes (Fig. 5(d)). Mechanisms of degradation may include evaporation (as shown in [11]) and photo-chemical degradation. Identification of these mechanisms is beyond the scope of this paper. Fig. 6 shows the dependence of the fluorescence image brightness on the time of irradiation with the laser ($\lambda = 447$ nm, $P = 60$ mW) obtained using the optical system (Fig. 1) for interference filters at 529 nm and 600 nm.

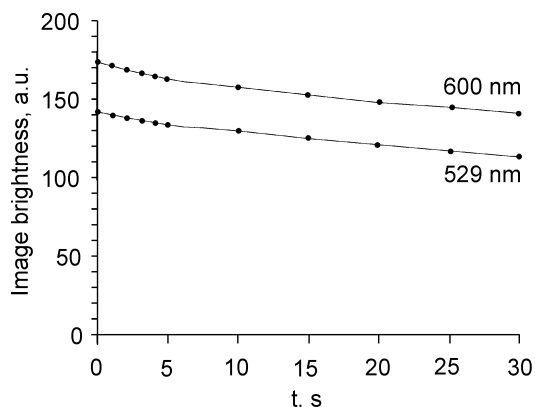


Fig. 6. Degradation of thin oil film on water surface

As seen from Fig. 6, the degradation process of thin oil film can have a significant impact on the study of fluorescence spectra. Therefore, the laser beam (2, Fig. 1) was shifted approximately 5 mm for each of the interference filters. It is also necessary to take into account that during the oil film identification on an open water surface in real conditions of illumination, the luminosity can be from 1000 lx at sunrise to 100,000 lx at noon when the atmosphere has the highest possible transparency [12]. The reflected integral light from the oil surface can affect the accuracy of the measurement of the fluorescence spectrum.

Based on the above characteristics of fluorescence studies of thin films of oil on the water surface, the experiment was conducted at a distance of 15 m from the sample. The first frame (top left) of Fig. 7 represents an image of the surface of the oil film (thickness $\sim 90 \mu\text{m}$) illuminated by integral radiation of 75000 lx and the laser beam $\lambda = 447 \text{ nm}$ ($P = 60 \text{ mW}$). The images of fluorescence were registered in a consistent change of the interference filters (Fig. 7).

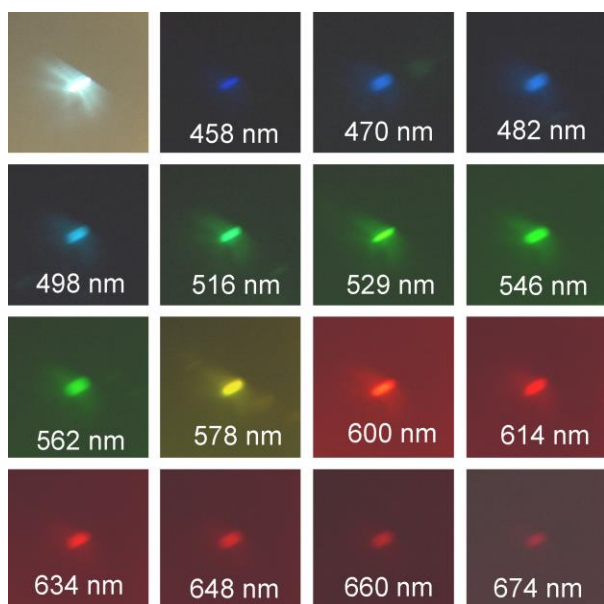


Fig. 7. Fluorescence of thin oil film on water surface

The images were recorded on a digital camera matrix as RAW files with the same exposure values for each filter (sensitivity per ISO 3200 and registration time $t = 1/5 \text{ s}$). For images obtained using filters 458-498 nm, brightness is determined according to the blue channel, for filters 516-562 nm according to the green channel, and for filters 578-690 nm according to the red channel. Then, the brightness fields of fluorescence and background signal were measured in standard units of the RGB system for each of the images (Fig. 7). The brightness of a luminescence signal was measured at the center of the area illuminated by laser radiation. The brightness of the background signal was measured away from the area of fluorescence. The brightness values are converted into fluorescence signal intensity using calibrated curves (Fig. 4). The difference between the background signal and the signal from the area illuminated by laser radiation allows one to define the fluorescence signal intensity. Based on this data, the spectral distribution of fluorescence (normalized to the maximum value) from a distance of 15 m was plotted (dotted line, Fig. 8).

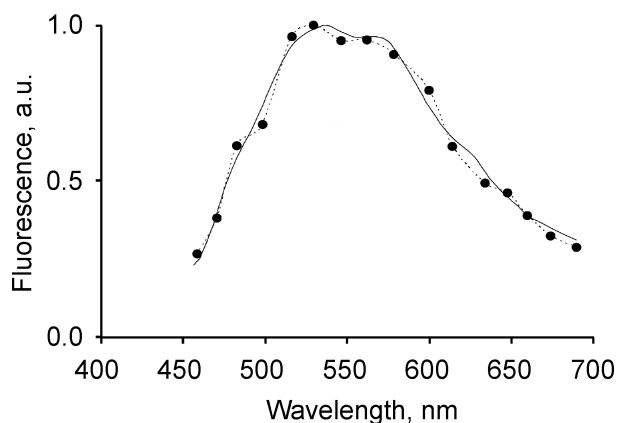


Fig. 8. Fluorescence of crude oil: thin film on the water surface (dotted line, received using the set of filters from a distance of 15 m) and received using a monochromator in stationary conditions (solid line)

Fig. 8 also shows the fluorescence of crude oil under laboratory conditions using a monochromator (solid line). Variations in spectral characteristics were dependent on several factors: a discrete set of interference filters and a lower precision digital camera compared to the photomultiplier of the monochromator. However, the characteristic curve of the fluorescence of the crude oil obtained from a distance of 15 m is comparable to the fixed terms that will identify thin oil film on the water surface from a remote distance.

4. Conclusions

Simultaneous registration of the remote oil slick image and fluorescence spectra on the digital camera allow detecting crude oil thin films on the water surface at daytime illumination without using of bulky monochromators

or spectrophotometers. Using modern compact UAV for the visual monitoring requires using compact telescopic system and CCD camera. Suggested in our paper placement of a set of compact narrowband interference filters between the optical system and the CCD camera allows not only visual monitoring but also registering fluorescence spectra of the oil spills. Excitation of the fluorescence can be done using compact laser diode. Further investigation of the mechanisms in photo induced degradation of oil spills may help identify oil spills and the source of pollution and optimize the active remediation of pollution.

Acknowledgments

This research was supported by the STCU Project nr. 5808 and institutional project ASM 15.817.02.34A.

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