Experimental studies of efficient sensing fluorescence radiation bands to detect oil and petroleum product spills

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Abstract. We have experimentally studied the laser-induced spectra of petroleum products at the excitation fluorescence wavelength of 266 nm. The paper depicts a schematic diagram of the laboratory setup, gives data resulted from processing of laser-induced fluorescence spectra, and shows that, in comparison with spectra of petroleum products, the laser-induced fluorescence spectra of oil have a shift toward the longer wavelength spectral region and a far wider spectral bandwidth. For oil, an efficient band of sensing fluorescence radiation, is of ~ 390 – 600 nm in average. For gasoline, an efficient band of sensing fluorescence radiation has a significant shift toward the shorter wavelength region (~ 320 – 360 nm) as compared to the efficient sensing fluorescence radiation band for diesel and engine oils (~ 330- 395 nm).

1. Introduction

Oil and petroleum products take one of the leading places among the environmental pollutants [1-5]. Therefore, to develop methods and equipment to detect oil pollution on the soil and water surface is a challenge.

Laser fluorescence methods are, currently, the most efficient to detect oil pollution on the soil and water surface [1], [6] – [14].

The use of lidar sensing allows us to detect oil pollution at any time of day or night in the fairly wide interval of weathering conditions. A laser fluorescence lidar provides high spatial resolution thereby enabling to detect small-sized oil pollution (that is important, for instance, when detecting the pipeline leaks at the early stage).

A good many publications consider a laser fluorescence sensing task of oil pollution on the soil or water surface at the fluorescence excitation wavelengths of 266 nm (the forth harmonic of a YAG:Nd laser) and of 355 nm (the third harmonic of a YAG:Nd laser) which are the most appropriate for remote detecting of pollution (for instance, from an aircraft).

However, some points of practical importance for development of fluorescence lidars remain unstudied. A possibility for a lidar to use one spectral band of sensing fluorescence radiation at the excitation wavelength of 266 nm to detect oil and petroleum products spilled on the soil and water surface is still obscure.

The paper deals with the experimental study of efficient bands of sensing fluorescence radiation to detect the spilling oil and petroleum products at the fluorescence excitation laser wavelength of 266 nm.
2. Experimental setup
To measure laser-induced fluorescence (LIF) spectra of oil and petroleum products at the fluorescence excitation wavelength of 266 nm, a laboratory setup was used (figure 1). The Q-switching diode-pumped solid-state pulse YAG:Nd laser provided fluorescence excitation. A system to sense fluorescence radiation is based on the polychromator and highly sensitive ICCD.

The setup calibration involved a wavelength calibration of the polychromator (employing a calibration line spectrum optical source based on the mercury-argon lamp and a standard calibration procedure using three wavelengths, namely 253.65 nm, 435.85 nm, and 696.54 nm) and a detection limit calibration of the fluorescence detection system from 250 to 750 nm (a calibration DH2000-CAL optical source was used).

For laboratory setup control, the LabVIEW software in visual development environment was used.

Table 1 presents basic parameters of the laboratory setup.

| Parameter                      | Value                  |
|--------------------------------|------------------------|
| Fluorescence excitation wavelength, nm | 266                   |
| Laser pulse energy, mJ         | 0.27                   |
| Laser pulse length, ns         | <8                     |
| Repetition frequency, Hz       | Up to 500              |
| Spectral detection band, nm    | 290 – 750              |
| Spectral resolution, nm        | 5                      |
| Receiving lens diameter, mm    | 15                     |
| Distance to the sample under study, m | ~ 1.4                |

In the course of measurements a laser output power value was under control. The measured laser output power value was used in measurement data processing. A correction factor was introduced to lead the intensity level of detected fluorescence radiation to the single laser output power value of 100%.
To control the experimental laboratory setup calibration, was used a Raman-scattering spectrum of distilled water.

3. Experiment description
As a result of the experimental measurements at the fluorescence excitation wavelength of 266 nm, LIF spectra for various oil and petroleum products were obtained. For experimental measurements, were employed the following oil and petroleum products: stock-tank oil of the Moscow and Ryazan refineries; crude oil (Almetyevsk); diesel fuel (diesel fuel of the Samara refinery, marine diesel fuel, NORSI diesel fuel, gasoline (AI-92, AI-95); motor oil (Lukoil mineral motor oil - 10W30 standard; vacuum motor oil; Lukoil synthetic blend motor oil, used motor oil).

4. Results
Figures 2 – 6 show the examples of typical LIF spectra measured using the laboratory setup. The peak at the wavelength of 532 nm in spectra corresponds to the second harmonic of the YAG: Nd laser, which could not be completely suppressed in the laboratory setup.

The LIF spectrum of the AI-92 gasoline is shown in figure 2.

![Figure 2. Fluorescence spectra of AI-92 gasoline (a) and Samara refinery diesel fuel (b).](image)

Figures 2b, 3a и 3b show LIF spectra of various diesel fuels: Samara refinery (2b), marine diesel fuel (3a) and NORSI diesel fuel (3b).

![Figure 3. Fluorescence spectra of marine diesel fuel (a) and NORSI diesel fuel (b).](image)

Figure 4 depicts LIF spectra of motor oils: vacuum motor oil (4a) and Lukoil synthetic blend motor oil (4b).
The spectra comparison (figures 2 – 4) reveals the following. The LIF spectra maximum for gasoline has a shift toward the shorter wavelength spectral region (~ 333 nm) as compared to the LIF spectra maximum of diesel fuels and motor oils (~ 345…355 nm). Correspondingly, for gasoline, the efficient band of sensing fluorescence radiation has a significant shift toward the shorter wavelength region (~ 320 - 360 nm) in comparison with the efficient band for diesel fuels and motor oils (~ 345…355 nm).

Figure 4. Fluorescence spectra of vacuum motor oil (a) and Lukoil synthetic blend motor oil (b).

For oil spill control, a situation with the efficient band of sensing fluorescence radiation is different. Figures 5 and 6 depict the LIF spectra of various types of oil: stock-tank oil of the Moscow refinery (figure 5a), stock-tank oil of the Ryazan refinery (figure 5b), crude oil of Almetyevsk (figure 6).

Figure 5. Fluorescence spectra of stock-tank oil of the Moscow (a) and Ryazan (b) refineries.

Figures 5 and 6 show that LIF spectra of oil have a shift toward the longer wavelength spectral region as compared to the spectra of petroleum products and their spectral bandwidth is far wider. The maximum position of the fluorescence spectrum is not particularly informative for them. The efficient band to sense oil fluorescence emission is of 390 - 600 nm in average.

Analysis of experimentally studied LIF spectra of various types of oil and petroleum products shows that there is a substantial difference between the spectra of oil and petroleum products. Efficient detection of oil pollution requires, at least, two spectral bands to sense fluorescence emission: one for oil and another for petroleum products.
5. Conclusion

The conducted experimental studies of the LIF spectra of oil and petroleum products at the excitation fluorescence wavelength of 266 nm has shown that the oil fluorescence spectra have a shift toward the longer wavelength spectral region as compared to the spectra of petroleum products and a far wider spectral bandwidth: ~ 390 – 600 nm, in average. For gasoline, the efficient band of sensing fluorescence radiation is significantly shifted toward the shorter region (~ 320 – 360 nm) as compared to the efficient band of sensing fluorescence radiation for diesel fuels and motor oils (~ 330 - 395 nm in average). Thus, for efficient detection of oil pollution, it is necessary to use, at least, two spectral bands to sense fluorescence radiation: one for oil and another for petroleum products.

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