Oil product fluorescence spectra analysed under excitation at a wavelength of 266 nm

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Abstract. Experimental studies of the laser-induced fluorescence spectra of oil products for the fluorescence excitation wavelength of 266 nm were performed. A schematic diagram of the experimental setup and results of processing the laser-induced fluorescence spectra are presented. It is shown that the laser-induced fluorescence spectra of various oil products are in different spectral bands and have different spectral widths. The light-end oil products (gasoline, kerosene) have the narrowest spectra (a spectral width of ~30 nm) with a spectrum maximum at the wavelength of ~ 330 nm. Oil has the widest spectral width (~ 200 nm and more) with a spectrum maximum at the wavelength of ~ 440-450 nm. The heavy-oil products (diesel fuel, engine oil) and gas condensate fall in between. The heavy-oil products have a spectral width of ~ 60-100 nm with a spectrum maximum at the wavelength of ~ 360 nm. The gas condensate has a spectral width of ~ 150 nm with a spectrum maximum at the wavelength of ~ 430 nm.

1. Introduction
Currently, oil and oil product pollution control of water and terrestrial surfaces is one of the vital tasks of environmental monitoring [1,2].

Laser fluorescence methods [2-17] really work a treat for monitoring the oil and oil product spills over water and terrestrial surfaces.

Laser sensing allows monitoring of oil and oil product spills regardless of light conditions. A laser fluorescence sensor ensures high spatial resolution thereby providing detection of small-sized pollution (which is important when detecting oil and oil product spills early on). In most cases, the use of laser fluorescence methods is based on the fact that the fluorescence signal from the oil pollution (in the spectral band chosen as a result of the preliminary analysed fluorescence spectrum) significantly exceeds the fluorescence signal from the clean (with no pollution) surface [2].

Different authors studied laser-induced fluorescence (LIF) spectra of oil, oil products, and oil spills over various surfaces mainly at the excitation wavelengths of 266, 308, 337, 355 nm [2-17].

A solid-state YAG: Nd laser (the fourth and third harmonics being of 266 and 355 nm, respectively) is a promising one for on-board remote sensing systems. Furthermore, most papers consider laser fluorescence sensing of oil pollution on the water or terrestrial surfaces at the fluorescence excitation wavelength of 355 nm [4-11]. This is due to considerably higher laser pulse energy at the wavelength of 355 nm and much less absorption by ozone in the atmosphere at this wavelength [18].
Although most publications are concerned with the wavelength of 355 nm to excite fluorescence of oil products, the wavelength of 266 nm also provokes interest in development of oil pollution monitoring devices. This is because a fluorescence excitation efficiency of some oil bases at the wavelength of 266 nm is significantly higher than at the wavelength of 355 nm [19]. Besides, the fluorescence excitation efficiency of vegetation (which is the interfering factor) at the wavelength of 266 nm is considerably less than that of at 355 nm wavelength [20].

However, up to date there are only a small number of publications, which can present few data about LIF spectra of oil products at the fluorescence excitation wavelength of 266 nm ([11-13] and other papers of authors).

The paper deals with the experimental study and conducts a comparative analysis of the LIF spectra of various light-end and heavy-oil products, gas condensates, and a diversity of oil grades at the fluorescence excitation wavelength of 266 nm.

2. Experimental Setup
A laboratory setup (figure 1) was used to measure the LIF spectra of oil products at the fluorescence excitation wavelength of 266 nm.

![Figure 1. Schematic diagram of the laboratory setup for measuring LIF spectra.](image)

The laboratory setup employed a Q-switching diode-pumped solid-state pulse Nd:YAG laser (Ekspla NL204). A subsystem to detect emission was based on the polychromator and highly sensitive ICCD. It enabled fluorescence spectra detection within 290 – 750 nm band with a spectral resolution of 5 nm. A distance from the laser source to the sample under study was ~ 20 mm.

The setup calibration (before the LIF spectra measurements) involved a wavelength calibration of the polychromator (employing a standard calibration technique and a calibration line spectrum optical source based on the mercury-argon lamp) and a detection limit calibration of the detection system (using, when calibrating, the deuterium arc and halogen lamps with continuous emission). When measuring, a laser output power of fluorescence excitation was under control. In measurement data processing, a correction factor was introduced to lead the intensity level of detected fluorescence to the single laser output power value of 100%.
To control the experimental setup calibration, was used a Raman-scattering spectrum of distilled water.

For laboratory setup control, the LabVIEW software in visual development environment was used. Table 1 presents laser basic parameters of the laser source used in the laboratory setup.

**Table 1. Basic parameters of the laser source.**

| Parameter                        | Value  |
|----------------------------------|--------|
| Fluorescence excitation wavelength, nm | 266    |
| Laser pulse energy, mJ           | 0.3    |
| Laser pulse length, ns           | <8     |
| Repetition frequency, Hz         | Up to 500 |

A laboratory setup measurement error of the LIF spectra allows us to estimate data (figure 2), which exemplify the setup-detected LIF spectra of river sand a fluorescence level of which is low.

Comparing the data in figure 2 with the measurement data given in figures 3 – 8 shows that the detection system noise is small and has little effect on the measured LIF spectra of oil products.

### 3. Experimental studies of oil product LIF spectra

The experimental laboratory setup measurements at the fluorescence excitation wavelength of 266 nm enabled us to measure the LIF spectra of various oil products among which the following ones were employed: crude oil (Almetyevsk); stock-tank oil of the Moscow and Ryazan refineries; 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), kerosene, gas condensate.

Figures 3 – 8 exemplify the typical LIF spectra measured using the laboratory setup.

The peak at the wavelength of 532 nm in the spectra corresponds to the elastically scattered emission at the second harmonic of the YAG: Nd laser, which could not be completely suppressed in the laboratory setup.

Figures 3 and 4 show the LIF spectra of light-end oil products (gasoline and kerosene).
Figure 4. LIF spectra of AI-92 gasoline (a) and pollution due to AI-92 spill over the soil (b).

Figures 5 and 6 represent the LIF spectra of heavy-oil products (diesel fuel and engine oil) and gas condensate.

Figure 5. LIF spectra of diesel fuel of the Samara refinery (a) and Lukoil mineral motor oil (b).

Figure 6. Laser induced fluorescence spectra of gas condensate at 266 nm laser excitation wavelength.

Figures 7 and 8 show the LIF spectra of various oil bases. Figure 7 depicts the LIF spectra of the stock-tank oil of the Moscow refinery (a) and Almetyevsk oil (b). Figure 8 shows the LIF spectra of the stock-tank oil of the Ryazan refinery.

Figure 7. LIF spectra of the stock-tank oil of the Moscow refinery (a) and Almetyevsk oil (b).
4. Oil product LIF spectra analysis

The analysis of the LIF spectra measured has shown that at the fluorescence excitation wavelength of 266 nm, LIF spectra of various oil products are in different spectral bands and their spectral width is different.

The light-end oil products (gasoline, kerosene) have the narrowest spectra (a spectral width of \(~30\) nm) with a spectrum maximum at \(~330\) nm wavelength. Oil has the widest spectral width \((\sim 200\) nm and more) with a spectrum maximum at \(~440-450\) nm wavelength. The heavy-oil products (diesel fuel, engine oil) and gas condensate fall in between. The heavy-oil products have a spectral width of \(\sim 60-100\) nm with a spectrum maximum at the wavelengths of \(~360\) nm. The gas condensate has a spectral width of \(\sim 150\) nm with a spectrum maximum at the wavelength of \(~430\) nm.

Localising the LIF spectra of oil products of various bases in a variety of spectral bands opens up a possibility for creating an efficient method to classify oil pollution (light-end oil products, heavy-oil products, gas condensate, oil). However, on the other side, this presents a problem for creating a method of pollution detection that is equally efficient in case of spilling both oil and light-end products.

5. Conclusion

The experimental study and analysis of the LIF spectra of oil products at the fluorescence excitation wavelength of 266 nm have been carried out. It has been shown that the LIF spectra of various oil products are in different spectral bands and have different spectral width. The light-end oil products (gasoline, kerosene) have the narrowest spectra (a spectral width is \(~30\) nm) with a spectrum maximum at \(~330\) nm wavelength. Oil has the widest spectral width \((\sim 200\) nm and more) with a spectrum maximum at \(~440-450\) nm wavelengths. The heavy-oil products (diesel fuel, engine oil) and gas condensate fall in between. The heavy-oil products have a spectral width of \(\sim 60-100\) nm with a spectrum maximum at the wavelength of \(~360\) nm. The gas condensate has a spectral width of \(\sim 150\) nm with a spectrum maximum at the wavelength of \(~430\) nm.

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