COMPARATIVE LASER-INDUCED FLUORESCENCE EVOLUTION ANALYSIS OF DIFFERENT OIL POLLUTION ON THE TERRESTRIAL SURFACE

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Abstract. We have studied the time evolution of the laser-induced fluorescence spectra of oil pollution on the terrestrial surface at a fluorescence excitation wavelength of 355 nm. The paper presents a block-diagram of the experimental setup and data processing results of the laser-induced fluorescence spectra for the oil-polluted soil and sand and conducts a comparative analysis of the fluorescence spectra evolution of pollution due to spilling crude oil and heavy and light petroleum products.

Introduction

Oil and petroleum products are high on the list of pollutants in the environment. Therefore, development of methods and means to control the oil and petroleum product pollution of water and terrestrial surfaces is a challenge.

Currently, the problem of oil pollution on the terrestrial surface is especially relevant due to leaks of oil during its transfer through pipelines because of their wear-out or mechanical damages. Now available current oil pipeline control systems have a detection limit ranging from units to one-tenths of a percent of the pipeline capacity. Existing control systems do not detect the lower rate leakages.

The most efficient techniques to control oil pollution are laser-induced fluorescence (LIF) methods. However, presently, a great majority of papers on the experimental study of the oil pollution LIF deal with measuring the fluorescence spectra of oil pollution on the water surface.

One of the promising laser wavelengths (in terms of laser pulse power and eye-safety) to excite the fluorescence of petroleum products is the wavelength of 355 nm (third harmonic of Nd: YAG laser).

The paper deals with the time evolution of the LIF spectra of different oil pollution on the terrestrial surface at the fluorescence excitation wavelength of 355 nm.
Experimental Setup

To measure LIF spectra of oil and oil pollution on various terrestrial surfaces, was used an experimental laboratory setup a schematic diagram of which is shown in Fig.1.

As the excitation source of the fluorescence emission, the third harmonic of the Q-switching diode-pumped solid-state pulse Nd: YAG laser (Ekspla NL204) was used. On the sample under investigation, the optical system forms a laser spot of about 20 mm in diameter.

A system to detect laser-induced emission is created on the basis of the polychromator and the high sensitivity array detector with a brightness amplifier. After the brightness amplifier the optical system transmits an image to the CCD (charge-coupled device) detector. The detector converts the image into a digital dataset and transmits this dataset to the computer data processing unit. Calibration of equipment involved a wavelength calibration of the polychromator (employing a calibration line spectrum optical source based on the mercury-argon lamp and a standard calibration technique using three wavelengths, namely 253.65 nm, 435.85 nm, and 696.54 nm) and a detection limit calibration of the fluorescence detection system within 250 - 750 nm (a calibration DH2000-CAL optical source was used).

Fig.1. Schematic diagram of the experimental setup

Table 1. Basic parameters of the laboratory setup
Parameter & Value
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Laser energy pulse, mJ & 0.8
Excitation wavelength, nm & 355
Laser pulse width, ns & <8
Repetition rate, Hz & Up to 500
Band of spectral registration, nm & 290 –750
Spectral resolution, nm & 5
Receiving lens diameter, mm & 15
Distance to the sample under study, m & ~ 1.4
Laser beam diameter in the sample plane, mm & ~ 20
Detector viewing field diameter in the sample plane, mm & ~ 20

**Experiment description**

The experimental laboratory setup measurements for a fluorescence excitation wavelength of 355 nm enabled us to obtain LIF spectra of various oil pollution at different times after spilling petroleum products on a diversity of terrestrial surfaces (black soil, river sand, sandy soil, garden soil, forest soil, clay, a mixture of black soil and clay, a mixture of soil and sand, etc.).

As soil pollutants, the following petroleum products were used: crude oil (Almetyevsk); stock-tank oil of the Moscow and Ryazan refineries; diesel fuel (some types); gasoline (some types); engine oil (some types); used engine oil.

**Results**

Figures 2 – 7 below illustrate examples of the typical LIF spectra measured at different times after spillage of various petroleum products on the sand (Figures 2 - 4) and on the garden soil (Figures 5-7).

Figures 2 - 4 show the fluorescence spectra of pollution on the sand, when spilling AI-92 gasoline, semisynthetic engine oil of Lukoil, and crude oil (Almetyevsk), respectively, a pollution spectrum detected immediately (curve 1), after 5 days (curve 2) and 12 days (curve 3) upon spilling petroleum product on the sand.
Fig. 2. Fluorescence spectra when spilling gasoline on the sand.

Fig. 3. Fluorescence spectra when spilling engine oil on the sand.

Fig. 4. Fluorescence spectra when spilling oil on the sand.
Furthermore, the LIF spectra of pollution are given when spilling gasoline AI-95 (Fig.5), used engine oil (Fig.6), and marine diesel oil (Fig.7) on the garden soil.

Figures 5-7 show the spectrum of pollution detected upon the spillage of petroleum products as follows: immediately (curve 1); in two hours (curve 2); after 3 days (curve 3 in Fig. 5) and after 9 days (Fig. 6, 7); after 16 days (curve 4 in Fig. 6, 7).

Fig. 5. Fluorescence spectra when spilling gasoline on the soil

Fig. 6. Fluorescence spectra when spilling used engine oil on the soil
The time evolution analysis of the LIF spectra shows that for light petroleum products (gasoline), a fluorescent signal value is reduced with time considerably faster than for oil and heavy petroleum products and in a few days becomes insignificant.

For oil and heavy petroleum products, a nature of decreasing fluorescent signal value with time is approximately of the same order (though there is, certainly, a dependency on the type of a petroleum product and a soil) - after 12-16 days upon spilling petroleum product on the terrestrial surface the fluorescent signal value is about 2-6 times less.

Conclusion

The LIF evolution of oil pollution on the terrestrial surface with time (after contamination) depends heavily on the type of a petroleum product. For petroleum product pollution on the terrestrial surface, the fluorescent signal value is decreased with time considerably faster than for oil and heavy petroleum products and in a few days becomes negligible. For oil and heavy petroleum product pollution, the nature of decreasing fluorescent signal value with time is the same: after 12-16 days the value becomes approximately 2-6 times less. Comparison of the experiment results with other authors’ data shows that with oil pollution of the terrestrial surface, the fluorescent signal value is decreased with time considerably slower than after contamination of water surface.