Experimental studies of laser-induced fluorescence spectra of natural objects on the ground surface

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Abstract. The paper depicts the experimental studies of laser-induced fluorescence spectra of natural objects on the ground surface using an eye-safe fluorescence-exciting wavelength of 355 nm. Shows that a value of the laser-induced fluorescence signal from natural objects can be comparable with the laser-induced fluorescence signal value from pollution on the ground surface. A development of laser-induced fluorescence methods to detect pollution at the eye-safe fluorescence-exciting wavelength of 355 nm holds promise. These methods rely on the analysis of the fluorescence spectra shape of pollution and natural objects on the ground surface.

1. Introduction

Nowadays, methods of fluorescence analysis have a wide application in various fields of science and technology. Environmental monitoring (atmosphere, water and ground surfaces) holds promise for using the fluorescence methods [1-3]. Here, one of the most relevant tasks is pollution monitoring of ground surface.

Ground pollution is due to many human-made reasons such as pipeline damage, leakage from the storages of oil or other pollutants, discharge of dirty water, accidents in points of fuel transfer and storage, etc.

The fluorescence method capabilities allow on-board ground surface monitoring (at the aircraft flight altitude up to 100 – 150 m) thereby ensuring detection of pipeline leakages and oil product spills [4]. Fluorescence monitoring of ground pollution is a complicated task, since, along with the fluorescence signal from pollution on the ground surface, a receiving detector of the fluorescence sensor also will detect the fluorescence signals from the landscape elements.

Therefore, the most important stage in development of laser fluorescence methods for pollution monitoring of the ground surface is to study laser-induced fluorescence (LIF) spectra of natural objects on the ground surface.

The paper concentrates on the study of LIF spectra of natural objects to solve the task of laser fluorescence detection of pollution on the ground surface.

2. Problem description

The paper [5] and other ones issued by these authors have already considered the problem of laser fluorescence monitoring of ground oil pollution on the ground surface at 266 nm fluorescence excitation wavelength.
Along with the 266 nm wavelength to excite the oil product fluorescence the wavelength of 355 nm holds promise as well (in terms of both laser pulse energy and laser system eye-safety [6]). Here, a choice of the fluorescence excitation wavelength to solve a particular problem, of course, depends on the oil product [7,8].

The experimental studies described below represent the LIF spectra of the natural objects on the ground surface at the fluorescence excitation wavelength of 355 nm.

3. Experimental studies of LIF spectra of nature-made objects at 355 nm excitation wavelengths

Up to date, for the fluorescence excitation wavelength of 355 nm, a reasonably large amount of experimental LIF spectra of merchantable oil products, and various types of water and vegetation has been gained [7-19].

However, firstly, different authors, who used various measuring devices, provided this amount of experimental spectra and therefore, their quantitative comparison and merging into single database is impossible. Secondly, actually measurement results of LIF spectra of the landscape elements are very few [15].

A laboratory setup was created to experimentally study the laser-induced fluorescence spectra of natural objects.

A schematic diagram of the laboratory setup is shown below (figure 1). To excite fluorescence the third harmonic of a Q-switching diode-pumped solid-state pulse YAG: Nd laser (Ekspla NL204) was used. A LIF detection system is based on the polychromator and highly sensitive ICCD. An optical system transfers the image to the CCD of detector. The detector converts the image into digital array and transfers it into computer measurement data processing unit.

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

| Parameter                        | Value  |
|----------------------------------|--------|
| Laser pulse energy, mJ           | 0.8    |
| Excitation wavelength, nm        | 355    |
| 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, m        | ~ 1.4  |
| Laser beam diameter in the sample plane, mm | ~20    |

Figure 1. A schematic diagram of the laboratory setup to study the laser-induced fluorescence spectra.
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 technique with three wavelengths used, namely 253.65 nm, 435.85 nm and 696.54 nm) and a calibration of the receiving recording system by sensitivity within 250 - 750 nm band (using a DH2000-CAL calibration optical source).

While measuring, a laser output power value was under control. The laser output power value measured was used when processing measurement data that is 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. Figure 2 shows the detected Raman-scattering spectrum of water (with a peak at the wavelength of ~ 403 nm), which agrees well with data known for the excitation wavelength of 355 nm [14].

In the context of realization, the curves 1 – 4 (figure 2) represent the Raman-scattering spectra of distilled water measured during the two-week experimentation. It is seen from the figure 2 that a setup measurement signal error of the Raman-scattering spectra of distilled water is ~ 10 % (of the signal value measured). Thus, although the laboratory setup does not provide absolute measurements of the fluorescence intensity, it, however, enables quantitative measurements and making a judgement about a relative value of the fluorescence signals obtained from various samples being under study at different times.

**Figure 2.** Raman-scattering spectra of distilled water measured during two weeks. 1 – before starting measurement run; 2, 3, 4 – 4, 7 and 12 days after starting measurements.

The LIF spectra measurement error of samples under study caused by noise of detection system allows us to estimate figure 3, which exemplifies the background noise measurements (noise of detection system when a laser source is off). 1 - 30 minutes later; 2 – an hour after setup calibration.

**Figure 3.** Background noise measurements of detection system (noise of detection system when a laser source is off). 1 - 30 minutes later; 2 – an hour after setup calibration.

Comparing the curves in figure 3 with the measurement data such as below (figures 4 – 9) shows that detection system noise is low, and therefore it has little effect on most measured fluorescence spectra of nature-made objects.

4. Analysing LIF spectra of natural objects

Figures 4 - 8 depict the LIF spectra of typical natural objects.

Figure 4 presents typical examples of vegetation LIF spectra measured. It is well seen from figure 4 that even in one species of vegetation, both the fluorescence signal value in a certain spectral band and the fluorescence spectrum shape can vary greatly. The most important here is the possibility to have a strong fluorescence of vegetation in the spectral band of 400 – 500 nm (wherein there is a fluorescence maximum of most oil products).
A fluorescence spectra peak at the wavelength of 532 nm corresponds to the second harmonic of the YAG: Nd laser.

The fluorescence spectra of water objects are shown in figure 5.

Figure 4. Fluorescence spectra of vegetation. 4a: 1 – green grass, 2,3 – cut grass after 7 and 11 days, 4 – dried grass; 4b: 1,2 – various samples of moss, 3 – moss in water.

Figure 5. Fluorescence spectra of water objects. 1 – fluorescence spectrum of turning green pond water, 2 – Moscow Canal water, 3 – Lebedyansky pond water (relatively clear) in Moscow, 4 – test sample spectrum of distilled water.

Figure 5 shows that water objects (as well as vegetation) are characterised by the greatly changeable fluorescence signal (depending on the type of object) and the possibility for strong fluorescence in 400 – 500 nm spectral band. The natural objects (figures 4,5) are the most important factors that are a hindrance to the fluorescence sensors for pollution monitoring on the ground surface. The other factors show far slighter impact.

Figure 6 shows the fluorescence spectra of soil diversity. And if in figure 6a the fluorescence signal significantly exceeds the background noise of the detection system, in figure 6b the fluorescence signal is of the same order with the background noise of the detection system.

Figure 6. Fluorescence spectra of soil diversity. 6a: 1 – sandy soil, 2 – sandy soil with water, 3 – soil from piny wood; 6b: 1 – clay, 2 - clay with water.
Figure 7 shows the fluorescence spectra of different nature-made objects, which are possible on the ground surface. Here (like in figure 6) the fluorescence signal significantly exceeds the background noise for certain natural objects, and it is of the same order with the background noise for the other ones.

![Fluorescence Spectra of Natural Objects](image1)

**Figure 7.** Fluorescence spectra of natural different objects. 1 - limestone, 2 - cobblestone, 3 - the bark of a birch, 4 - dry wood (apple tree).

Since human-made objects are also available on ground surface, the fluorescence spectra of such objects are shown in figure 8. The spectra of human-made objects with relatively high fluorescence intensity (soft roof, slat, and asphalt) are shown in figure 8a while the spectra of human-made objects with low fluorescence intensity (of the same order with the background noise of the detection system) are depicted in figure 8b.

![Spectra of Human-Made Objects](image2)

**Figure 8.** Spectra of human-made objects. 8a. 1 – soft roof, 2 – slat, 3 – asphalt, 4 – bitumen-coated surface; 8b: 1 – brick, 2 – wooden surface coated by heat-resistant silicon enamel.

The above-mentioned LIF spectra of typical objects on the ground surface (figures 4 – 8) exhibit their great changeability in both the spectral shape and the fluorescence radiation value.

This is one of the factors greatly complicating the task of detecting pollution on the ground surface. Another factor is time dependence of fluorescence spectra of pollution on the ground surface (in due time a ground pollution fluorescence signal becomes smaller).

Figure 9 shows the time-varying fluorescence spectra of pollution on the ground surface.

![Time-Varying Spectra](image3)
Figure 9. Time-varying fluorescence spectra of pollution on the ground surface. 9a - pollution due to gas condensate spilled over the garden soil: 1 – right after spilling, 2 – 9 days after spilling, 3 – 24 days after spilling, 4 – 42 days after spilling; 9b - pollution due to used motor oil spilled over the sand: 1 – right after spilling, 2 – 2 hours after spilling, 3 – 7 days after spilling, 4 – 12 days after spilling.

It is well seen from figure 9 that even if, right after spilling, the fluorescence signal from pollution is considerably greater than that of from nature-made formations on the ground surface, in the course of time the pollution fluorescence signal becomes several times smaller and can be comparable in value with the fluorescence signal from nature-made formations.

Thus, to detect pollution on the ground surface, using LIF, a development of methods based on the analysis of fluorescence spectra shape (rather than on the comparison between the values of an oil pollution fluorescence signal and that of a nature-made objects) holds promise.

Such detection methods can use the features of the LIF spectra of pollution and nature-made objects on the ground surface. To develop these methods it is, above all, necessary to provide experimental data acquisition about the fluorescence spectra of pollution and nature-made objects.

5. Conclusion
Thus, the LIF spectra of nature-made objects on the ground surface have been experimentally studied at the eye-safe fluorescence excitation wavelength of 355 nm. The value of the LIF signal from nature-made objects is shown to be comparable with that of the LIF signal from pollution on the ground surface. The development of LIF methods for detecting pollution at the eye-safe fluorescence-excitation wavelength of 355 nm, which rely on the analysis of the fluorescence spectra shape of pollution and nature-made objects on the ground surface, appears to have promise.

The paper was fulfilled under support of the Ministry of Education and Science of the Russian Federation, Project No 13.7377.2017/BCh.

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