INVESTIGATION OF THE UPPER VOLGA WATER SURFACE POLLUTED BY OIL SPILLS

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In this paper we present the results of field tests of a remote spectrofluorimeter designed for detection and analysis of oil spills on water surface. They have been obtained during the summer expedition along Upper Volga onboard "Il'ya Repin" ship. The construction of the device and its operational algorithm are described. Making field measurements we took into account large extent of the measurement path. The recorded signals of the fluorescence intensity and decay time are presented in the paper for two cases of oil spills detected. A fragment of the data summary for a 200 km *path near Yaroslavl city is also presented. It is shown in the paper that waters investigated have high background level of fluorescence what makes it necessary to improve essentially the fluorimeter construction.*

The water reservoirs of Upper Volga forming the part of the Moscow–Volga channel and feeding with water the populous industrial regions of Russia are at the same time the intense navigation ways and run the danger of being polluted by oil. The oil ingress into water is followed by immediate formation of surface films of different sizes and thickness, which can be detected both by means of water sampling and remote contactless methods. A spectrofluorimeter for remote contactless detection and analysis of oil films on water surface was designed in the Institute of Atmospheric Optics of Siberian Branch of the Russian Academy of Sciences. In summer of 1993, the apparatus was set onboard "Il'ya Repin" ship for testing under freshwater conditions as well as for investigating the water surface polluted by oil films over Moscow––Nizhny Novgorod path.

The principle of the spectrofluorimeter operation is water surface exposure to pulses of UV–laser radiation and the subsequent record of the fluorescence optical signal from the water surface arised under the exposure. Clean natural water always contains some quantity of soluted organic matter along with suspended minerals, which produce background fluorescence under exposure to sounding radiation.

Oil products, crude oil among them, are characterized by relatively high magnitude of fluorescence quantum efficiency (up to 90%), therefore signals from thin enough oil films are observable against background fluorescence of clean water. Numerous investigations had shown the degree of detectability of thin oil films to depend on the oil product type, wavelength of radiation exciting the fluorescence, constructive peculiarities of the apparatus, and the purity of water in surface layers.

The principle of our fluorimeter operation is based on computerized spectral–temporal analysis of the fluorescence response. Special–purposed laboratory investigations had shown the capability of the principle to identify oil products by the fluorescence decay time[1] when exposuring the water surface to short (2 nc) pulse of UV–laser radiation. During investigation the fluorescence spectrum is divided into a series of spectral intervals, in which the intensities I_{fl} and the fluorescence decay times τ are measured. The built–in computer analyzes the obtained data in order to identify the type and quality of the oil product by comparing them with those from the computer databank. The computer databank was compiled of data obtained during regular laboratory investigations and it could be complemented by the experimental ones at any moment. The laboratory data from the databank contain as well the coefficients of radiation absorption of different oil products for the separated spectral intervals of interest, which allow computation of their film thicknesses.

The fluorimeter block diagram is shown in Fig. 1. Its peculiarity is module structure with monofibre connection lines for transferring the signals between modules. Such construction allowed us to locate main opto–electronic modules inside the ship. Only transceiving lens was situated outdoors (on bulwark). There are four spectral channels in our fluorimeter to record the received fluorescence signal from water surface. Intensity and fluorescence decay time are determined in each channel.

The results of the fluorimeter laboratory tests are presented in the table.

The oil films form spots on water surface. If they are more than from units to dozens meters in diameter, they are an environmental hazard. Some methodological problems arise when measuring such pollution while the ship running. First, the spots should be detected and their dimensions and frequency of appearance estimated. Second, despite large extent of the path, the obtained information should be limited in volume and suitable to processing. Therefore a cyclical operation mode of the apparatus was chosen. One cycle consisted of an active period, during which 25 sounding events of 1 pulse/sec frequency were performed and a passive period from 10 to 30 min duration free of sounding events. At the ship speed of 18 km/h it had passed from 3 to 10 km per cycle and the distance of sounding thereat was about 125 m.

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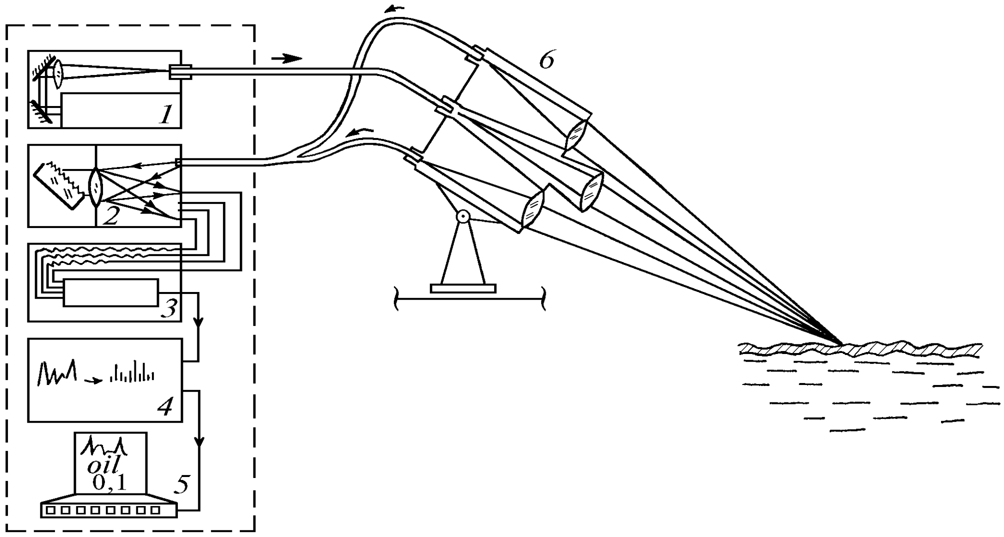

FIG. 1. A block diagram of spectrofluorimeter analyzing oil films on water surface: 1 – pulsed laser source of UV–radiation, 2 – polychromator, 3 – 4–channel system of optical signals recording, 4 – fast 4–channel ADC, 5 – personal computer, and 6 – transceiving lens.

TABLE. Fragment of the list with results of laboratory tests of fluorimeter.

Oil product type	Computed thickness of film, μm	Measurement results	
		identification	thickness
Oil	2	yes*	2.1 ± 0.5
Oil	4	yes	4.3 ± 0.5
Disel fuel	60	yes	57 ± 10
Disel fuel	120	yes	110 ± 10

* "Yes" denotes that identification is reliable.

Figures 2 and 3 present the results of one measurement cycle made near Novookatovo village. Each of four curves corresponds to measurement results in one spectral channel. Three legs of 20 m length are seen there in Fig. 2 characterized both by higher intensities (4–fold increase against the background fluorescence) and by longer decay times. We interpret these cases as legs with oil spills. Judging on short decay times, these may be films of light oil products, i.e., gasoline or Diesel fuel.

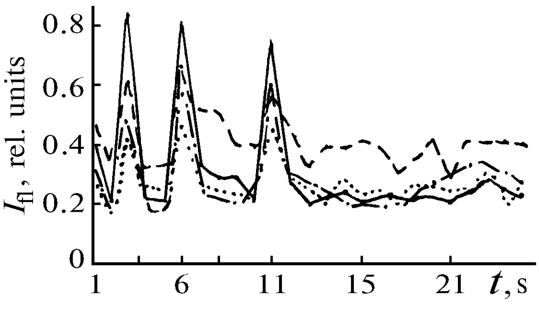

FIG. 2. Measurement results on intensities of fluorescent signals from water surface at 25 sequential sounding events in 4 spectral channels of the fluorimeter.

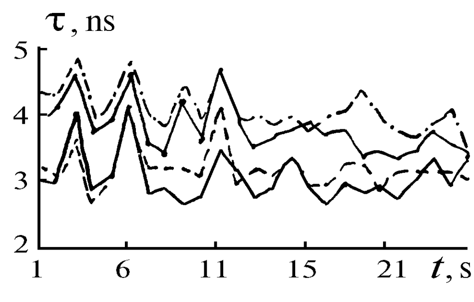

FIG. 3. Results of measuring the fluorescence decay times corresponding to intensities measurement presented in Fig. 2.

Figure 4 demonstrates one more typical record of a signal, which we interpret as a spill with periodic structure of spots. Such structure may be formed both due to natural waviness of water and waviness in the ship wake.

Figure 5 presents the fragment of generalized data including parameters of signals together with their quantity and space distribution interpreted by the fluorimeter as the signals from surface oil films along the ship path of about 200 km near Yaroslavl city. As seen from the figure, such cases are rare enough, though the fragment corresponds to the most "dirty" leg among the studied ones.

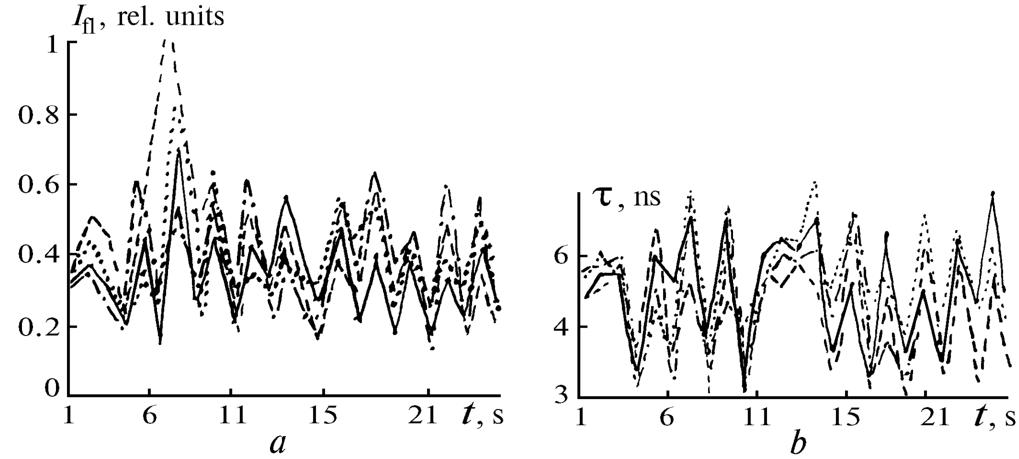

FIG. 4. Variations of intensity (a) and fluorescence decay times (b) in the fluorimeter spectral channels at the ship passing a spill with periodical structure of film.

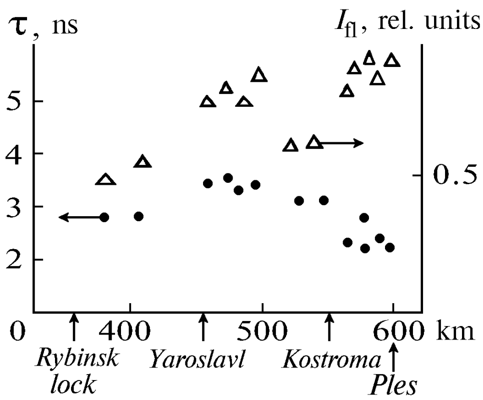

FIG. 5.

In order to calibrate the fluorimeter and compare the experimental data with the laboratory ones, a few spills of oil products were made by us along the ship path. The consequent experiments had shown the fluorimeter to detect only relatively thick films ($h \geq 10$ μm) of dark oil products (oil, Diesel fuel) because of high intensity of the background fluorescence. Consequently, the results on Figs. 2–5 correspond to detection of such films only. In real situations in warm water the spectrum of thicknesses primarily consists of thin films ($h \leq 1$ μm) rather than thick "fresh" ones. Therefore, the obtained results are sooner the qualitative ones. Nevertheless, an adaptation of the fluorimeter to such kind of water improving its physical and technical parameters and aiming to suppress the background fluorescence signals may increase the detecting and analytical abilities of the apparatus for use it in operative monitoring of water state.

REFERENCES

1. V.M. Klimkin, V.G. Sokovikov, and V.N. Fedorishchev, Atmos. Oceanic Opt. **6**, No. 2, 115–123 (1993).