

NEW POSSIBILITIES FOR REMOTE ANALYSIS OF OIL PRODUCTS ON WATER SURFACE

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Optical methods of detection, analysis, and measurements of amounts of oil products on water surface are considered. It is shown that modern means of laser sounding make it possible to detect oil spills, to identify them, and to measure the thickness of the oil film from onboard a ship or helicopter without taking the samples.

The methods for detection of oil spill are based on monitoring of a certain water parameter and recording of anomalous change in this parameter when going from clear water to polluted water surfaces. Multispectral survey by cameras and videos, radars, infrared scanning devices, and microwave radiometers is used for remote detection of water surface polluted by oil products (OP's). However, none of the above-mentioned devices is capable of determining the character of the anomaly or especially of identifying it. These problems may be solved by airborne or shipboard laser fluorimeter operating in pair with a simpler continuously tracking device. The fluorimeter is switched on when any anomaly is detected on the water surface. In the case of oil pollution it allows one to identify the OP and thereby to determine the pollution source, to measure the thickness of the oil film, and to calculate the amount of pollution. These capabilities are based on the OP spectroscopic characteristics presented below.

1. PHYSICAL PRINCIPLES OF THE OP IDENTIFICATION BY FLUORESCENCE SPECTRA

Petroleum from various fields differs by percent content of methanoic, naphthenic, and aromatic hydrocarbon constituents as well as by oil sublimation fractions: gasoline, kerosene, diesel and boiler fuel, different kinds of oil, and asphalt. Since every hydrocarbon constituent has individual fluorescence characteristics, one can hope to determine the OP kind by its fluorescence spectrum. Though in reality the OP fluorescence spectra have not a clearly expressed structure, the comprehensive approach allows one to determine successfully not only the type of the OP (petroleum and its light crude or heavy crude) but also its kind (for example, kerosene, diesel fuel, and some other types of oil have approximately equal density and belong to one type) and the brand and sort of the product, if any.

Among the main parameters of laser-induced fluorescence are the quantum yield ϕ_λ at the fluorescence wavelength λ_f , the total quantum yield $\phi = \int \phi_\lambda d\lambda$, the fluorescence decay time τ_λ , the quenching coefficient κ_1 at the laser wavelength λ_1 , the quenching coefficient κ_λ at λ_f , the total quenching coefficient $\kappa = \kappa_1 + \kappa_\lambda$, and the normalized quenching coefficient $K_\lambda = \kappa_1 / (\kappa_1 + \kappa_\lambda)$.

The fluorescence signal from the thin oil film with the thickness h at the wavelength λ_f can be represented in the form

$$S_\lambda^h = AK_\lambda \phi_\lambda E_\lambda^h, \quad (1)$$

where A is the instrumental factor which includes the laser pulse power and $E_\lambda^h = 1 - \exp(-\kappa h)$.

This expression shows that the fluorescence spectrum depends on the nature of the fluorophor, the film thickness, and the exciting radiation wavelength. For optically thick films (when $\kappa h \gg 1$) the dependence on the film thickness disappears. For many of the OP's the quenching coefficient falls off rapidly with λ increase. Therefore, for particular laser source the spectral range of the fluorescence may be chosen for which $K_\lambda = 1$. In this case the interpretation of the fluorescence signal is simplified because it may be considered as fluorescence quantum yield being individual for every OP. To calibrate the signal, i.e., to determine the instrumental factor A from Eq. (1), the water Raman scattering signal is commonly used. It is also proportional to A .

In the ideal case in which $K_\lambda \approx E_\lambda^h \approx 1$, by integrating expression (1) over λ we obtain the integral fluorescence signal which depends on the total quantum yield

$$S = A \phi. \quad (2)$$

Thus even a simple detection system with narrow-band Raman spectral channel and wide-band fluorescence channel can be used for preliminary identification of the OP by the total quantum yield. Multichannel spectral system, which records S_λ , extends the capabilities of identification through the use of both ϕ and ϕ_λ .

The method of determining the absolute fluorescence conversion efficiency from real lidar signals was developed by Kung and Itzkan.¹ In the course of oil film detection on the water surface by an airborne lidar, the water Raman signal shifted by 3300–3400 cm^{-1} relative to the laser frequency and background water fluorescence due to dissolved, suspended, and floating impurities² were observed along with the OP fluorescence. The background fluorescence has low intensity in clear ocean water and may compete with the signals of the OP fluorescence in coastal and river water.

Let us consider a lidar system with a set of spectral channels. Let i be the serial number of the arbitrary channel, r be the number of the Raman channel, and f be the number of the fluorescent channel at the wavelength λ_f . Then the signal from the water surface free of the oil film can be written as

$$J_i = (\xi_i + \delta_{ir} \psi) P_1, \quad (3)$$

where P_1 is the laser power, ξ_i is the conversion efficiency of the background water fluorescence, Ψ is the water Raman conversion efficiency, and δ_{ir} is the delta function, which indicates the fact that the Raman signal is observed only in the r th channel.

The signal from the film with the thickness h is

$$K_i = \eta_i P_1 [1 - e^{-c_i h}] + J_i e^{-c_i h}, \tag{4}$$

where η_i is the OP fluorescence conversion efficiency (here $\eta_i = \phi_\lambda K_\lambda T_1 T_\lambda$, where T_1 and T_λ are the transmissions of the air—water interface), $c_i = \kappa_1 + \kappa_\lambda$. It should be noted that instrumental factor was neglected in Eqs. (3) and (4). This had no effect on the final result.

Let us introduce the normalized quantities

$$\Theta_i = K_i/R \text{ and } \Xi_f = K_f/J_f, \tag{5}$$

where $R = \Psi P_1$ is the Raman signal, which can be obtained by subtraction of the background fluorescence from the received signal J_r . The value of the background signal is obtained by the interpolation of signals from adjacent spectral channels J_{r-1} and J_{r+1} .

By introducing the ratio

$$\Delta_r = R'/R, \tag{6}$$

where R' is the water Raman signal depressed by oil film, we may derive the expression for the OP fluorescence conversion efficiency from Eqs. (3)–(5)

$$\eta_f = \Psi \left(\frac{\Theta_f}{1 - \Delta_f^\varepsilon} \right) \left(1 - \frac{\Delta_f^\varepsilon}{\Xi_f} \right), \tag{7}$$

where $\varepsilon = (\kappa_1 + \kappa_f)/(\kappa_1 + \kappa_r)$. Thus, the absolute conversion efficiency of the OP fluorescence can be determined without any *a priori* information about the film thickness by measuring the return signals in channels $r, r + 1, r - 1$ (or $r + 2$), and f above the surface free of oil film and covered with oil film with the thickness h given that the Raman conversion efficiency Ψ is known.

The Raman conversion efficiency Ψ is given by the formula

$$\Psi = \frac{\sigma n_w T_1 T_r}{\alpha_1 + \alpha_r}, \tag{8}$$

where σ is the water Raman scattering cross section; n_w is the water density, T_1 and T_r are the transmissions of the air—sea interface at λ_1 and λ_r , respectively; and, α_1 and α_r are the radiation extinction coefficients in the sea water at λ_1 and λ_r , respectively. It can be seen from Eq. (8) that Ψ depends on water transparency and, therefore, a method is required for obtaining the extinction coefficients for every concrete water type. In Ref. 1 it was proposed to determine the total extinction coefficient by measuring the Raman signal decay as a function of time

$$R(t) \sim \exp(-t/\tau), \tag{9}$$

where

$$\tau = \frac{n}{c(\alpha_1 + \alpha_r)}. \tag{10}$$

Here n is the refractive index of water and c is the speed of light. It should be noted that Eq. (9) holds only when $t \gg \Gamma$ (where Γ is the laser pulse duration) because the real signal $R(t)$ is the convolution of the exponent with laser pulse and instrumental response function. In general the same methods as for determining the fluorescence decay time (they are presented below) may be used for obtaining τ .

Hoge and Swift³ used an empirical formula for the radiation attenuation coefficient in water as a function of the depth of vision of the Secchi disk.

Possible uncertainties in the OP parameters estimated in Ref. 1 showed that the above—described method of determining the absolute conversion efficiency of the OP fluorescence ensures an accuracy of about 50%. This accuracy is quite sufficient for primary identification of the OP because for the real OP's the fluorescence conversion efficiency may differ by one or two orders of magnitude.

The fluorescence decay time τ_λ , which is related to the fluorescence lifetime of a molecule $\tau_{0\lambda}$ by the equation $\tau_\lambda = \phi_\lambda \tau_{0\lambda}$, is another important characteristic of the OP. In general, the time dependence of the observed fluorescent signal is expressed as

$$P_\lambda(t) = I_1(t) * \xi_\lambda(t) * F_\lambda(t), \tag{11}$$

where $I_1(t)$ is the excitation pulse, $\xi_\lambda(t)$ is the impulse transfer function of the recording system, $F_\lambda(t)$ is the fluorescence excitation function, and $*$ denotes the convolution. For a simple molecule

$$F_\lambda(t) = \frac{\phi_\lambda}{\tau_\lambda} \exp(-t/\tau_\lambda), \tag{12}$$

while for a complicated molecular system, such as most of the OP's

$$F_\lambda(t) = \sum_i \alpha_i \exp(-t_i/\tau_\lambda). \tag{13}$$

Thus the problem of signal shape interpretation is reduced to reconstruction of the fluorescence excitation function $F(t)$ from the convolution and to determination of the parameters α_i and τ_i . This problem is ill—posed and the existing methods of its solution are cumbersome and probably unsuitable for signal processing in real time.

In Ref. 4 an attempt was made to determine the parameters describing the fluorescence decay profiles for light and heavy crude and petroleum under laboratory conditions while it was irradiated by light from a nanosecond flash lamp with $\lambda_{exc} = 337$ nm. For the reconstruction of the fluorescence excitation function, the model function of the form

$$F(t) = ae^{(-t/\tau_a)} + be^{(-t/\tau_b)} \tag{14}$$

was used. The reconstruction procedure consists in adjustment of the parameters $a/b, \tau_a,$ and $\tau_b,$ which provide the best agreement between experimental curves and resulting convolution of the model function with excitation pulse. It appears that Eq. (14) adequately describes light crude and petroleum while for the heavy crude a single—exponential dependence is more suitable. The typical values of the decay time τ_b of the long—lived constituent near 436 nm vary from 3 to 10 ns for petroleum, are about 20 ns for light crude, and are smaller than 1 ns for the heavy

crude. The decay time of the short-lived constituent τ_a is smaller than or equal to 1 ns for petroleum and is about 4 ns for light crude. The measured values of τ are three-four times greater in green spectral region. The experimental results as a whole indicate that the decay time of the long-lived constituent is more informative.

If the decay time of the substance is described by the average value τ_λ , i.e., the fluorescence excitation function is represented in the form $F_\lambda(t) = \frac{\phi_\lambda}{\tau_\lambda} \exp\left(-\frac{t}{\tau_\lambda}\right)$, τ_λ will be obtained from the fluorescence signals integrated over time

$$S_\lambda \sim \int_0^\infty F_\lambda(t) dt \quad (15)$$

or

$$S_\lambda^0 \sim \int_{t_0}^\infty F_\lambda(t) dt, \quad (16)$$

where t_0 is the time at which the intensity of fluorescence reaches its peak value. It can be shown that the integral quantities S_λ and S_λ^0 are invariant to the shape of the excitation laser pulse

$$S_\lambda = \xi K_\lambda E_\lambda^h \phi_\lambda E_1, \quad (17)$$

$$S_\lambda^0 = P_\lambda^0 (\Gamma + \tau_\lambda), \quad (18)$$

where ξ is the instrumental factor ($\xi E_1 \equiv A$), E_1 is the energy of the laser pulse, P_λ^0 is the signal amplitude given by Eq. (11) at the instant t_0 , Γ is the effective laser pulse duration.

Thus the measurement of the two integral quantities S_λ and S_λ^0 allows us to determine the spectrum and shape of the fluorescence signal given that the laser pulse duration Γ is known (it can be measured using the signal of Rayleigh or Raman scattering by water or fluorescence signal of the substance with an *a priori* known value of τ_λ).

The proposed method of the τ determination based on the integral signals can be used also in the above-described lidar method of determining the absolute fluorescence conversion efficiency for calculation of the Raman conversion efficiency Ψ .

2. DETECTION OF OIL SPILLS

In general the lidar equation for laser fluorimeter depends on many unknown parameters including geometric, instrumental, and atmospheric factors as well as on water surface and fluorescence sample properties.⁵ It should be noted that various authors use different physical quantities as the fluorescence conversion efficiency. For example, the fluorescent properties of a molecule are determined by the quantum yield ϕ_λ used in Eq. (1) and defined as a ratio of the emitted quanta to the absorbed ones. However, the detected fluorescence signal is proportional to the quantity $\eta_\lambda = \phi_\lambda K_\lambda$, which describes the interaction of radiation with the medium as a whole. Though the quantity η_λ is not a pure fluorescent characteristic, it is well suited for the detection and identification of the OP's. The fluorescence conversion efficiency is more nearly approximated by another quantity

$$\Psi_\lambda = \phi_\lambda \kappa_1 = \eta_\lambda (\kappa_1 + \kappa_\lambda), \quad (19)$$

because it is proportional to ϕ_λ for any fluorescence wavelength. Many scientists use Ψ_λ though there are no reasons to favour Ψ_λ over ϕ_λ .

Taking the above-mentioned reasons into account, the detected fluorescence signal P_f can be written in the simplified form

$$P_f = \left(\frac{P_1 A}{H^2}\right) \frac{\Psi_f}{C_f}, \quad (20)$$

where P_1 is the laser pulse power, H is the sounding altitude, A is the instrumental factor including the radiation losses due to propagation through the atmosphere, Ψ_f is the fluorescence conversion efficiency, and C_f is the total extinction coefficient of the fluorofor at the excitation and fluorescence wavelengths. Analogous expression can be written for water Raman signal

$$P_R = \left(\frac{P_1 A}{H^2}\right) \frac{\Psi_w}{C_w}, \quad (21)$$

where $\Psi_w = n_w \sigma_w$ is the Raman conversion efficiency (here σ_w is the water Raman scattering cross section and n_w is the water density) and C_w is the total water extinction coefficients at laser and Raman wavelengths.

We can see from Eqs. (20) and (21) that the ratio of the fluorescence signal to the Raman signal allows us to eliminate the unknown instrumental-geometric factor A and thereby to simplify the interpretation of the detected signals.

The Raman signal from the water surface covered by an optically thin oil film would be observed against the broadband background fluorescence. In this case the relation for the total signal takes the form

$$P_f = \left(\frac{P_1 A}{H^2}\right) \left[\frac{\Psi_0}{C_0} + \left(\frac{\Psi_w}{C_w} - \frac{\Psi_0}{C_0} \right) \exp(-C_0 h) \right], \quad (22)$$

where Ψ_0 and C_0 have the same meaning as Ψ_f and C_f in Eq. (20). It follows from this equation that the Raman signal weakens with increase of the thickness of the oil film. Thus the detection of the water Raman signal allows us to identify the presence of the oil spill on the water surface and to measure its dimensions.

3. MEASUREMENT OF THE THICKNESS OF AN OIL FILM

The method of measuring the oil film thickness h proposed in Ref. 6 is based on Eq. (22). In this method the signal from clear water P_w [see Eq. (21)] is measured along with the signal from the oil film P_f and the difference

$$\begin{aligned} \Delta P &= P_f - P_w = \left(\frac{P_1 A}{H^2}\right) \left(\frac{\Psi_w}{C_w} - \frac{\Psi_0}{C_0} \right) [1 - \exp(-C_0 h)] = \\ &= (P_w - P_0) [1 - \exp(-C_0 h)] \end{aligned} \quad (23)$$

is determined, where $P_0 \approx \Psi_0/C_0$ is the signal from optically thick oil film (typical of the central part of the oil spill). Here the OP extinction coefficient C_0 must be known *a priori*; for example, it can be measured under laboratory

conditions. In Ref. 7 the thicknesses of the film of the bunker fuel spill in the spectral region from 0.5 to 5.0 μm were measured from the decay of the Raman signal at 344 nm ($\lambda_1 = 308$ nm) using $C_0 = 0.7 \mu\text{m}^{-1}$. There the feasibility of measuring the films with thicknesses up to 50 μm was demonstrated in principle.

Kung and Itzkan⁴ developed theoretically the analogous method of determining h based on measurement of the ratio of the Raman signals from clear water and from the water surface covered with oil film

$$h = -\frac{1}{\kappa_1 + \kappa_R} \ln\left(\frac{R'}{R}\right), \quad (24)$$

where κ_1 and κ_R are the petroleum extinction coefficients at λ_1 and λ_R . The Raman signals R' and R with and without oil film are obtained from the total signal by interpolation of the background fluorescence of the OP and dissolved organic matter. This method is also based on preliminary identification of the OP and laboratory measurement of the extinction coefficients. It was used by Hoge and Swift⁸ for measurement of the oil film thicknesses varying from 0.05 to 5 μm . A nitrogen laser was used as a source of exciting radiation at 337 nm. To measure thicker films, it is necessary to shift the laser wavelength toward the red spectral region. Though in this case the water Raman scattering cross section and photomultiplier efficiency decrease, numerical estimates indicate the feasibility of measuring the films with thicknesses up to 0.5 mm. Less stringent physical limitations are imposed for shorter laser wavelengths, and films with thicknesses $\ll 0.01 \mu\text{m}$ can be measured.

4. IDENTIFICATION OF THE OP'S

Let us consider several known identification methods. Burlamacchi et al.⁹ investigated the fluorescence excitation efficiency of the OP irradiated by various lasers with $\lambda_1 = 249, 308, 337,$ and 420 nm. The fluorescence spectra of five types of petroleum were obtained and the conclusion was made that the samples cannot be identified by spectrum

$$\rho = \frac{N \sum_i (X_i Y_i) - \sum_i X_i \sum_i Y_i}{\left[N \sum_i X_i^2 - \left(\sum_i X_i \right)^2 \right]^{1/2} \left[N \sum_i Y_i^2 - \left(\sum_i Y_i \right)^2 \right]^{1/2}}, \quad (25)$$

where X_i and Y_i are the fluorescence intensities in the i th channel measured by lidar and obtained under laboratory conditions, N is the number of channels. The correlation coefficients $\rho = 1$ when two spectra are identical, $\rho = 0$ for uncorrelated spectra, and $\rho = -1$ for two specularly symmetric spectra. Sensitivity only to the spectrum shape rather than to the absolute values of the signals is the salient feature of the correlation coefficient ρ .

This method was tested in the course of airborne sounding of petroleum from the Merban field. The correlation coefficient between the lidar signals and spectra of Merban or La Rose petroleum or rhodamine WT dye was calculated. When the aircraft flew over the oil spill, the value of ρ increased and was close to unity for both types of petroleum while it varied from 0 to 0.5 for the dye.

Thus the correlation method allows us (a) to separate the valid signal against the water background fluorescence, (b) to identify the OP type, and (c) to improve the signal-to-noise ratio and to detect the weak signals.

shape or spectral position of the maximum intensity. The fluorescence quantum yield increases with λ_1 , but the extinction coefficient decreases. For this reason an excimer XeCl laser with $\lambda_1 = 308$ nm was chosen to be optimal. The water background fluorescence was observed for oil film thicknesses $h < 10 \mu\text{m}$, and its intensity was comparable with the oil fluorescence at $h \sim 0.01 \mu\text{m}$.

Numerous studies relating to the problem of fluorescence spectrum identification allow us to make a conclusion that fluorescence of any OP may be characterized by three main parameters: spectral distribution of the fluorescence intensity (i.e., spectrum shape or position of its maximum), fluorescence conversion efficiency, and fluorescence decay time. Because any OP consists of several hydrocarbon constituents, the fluorescence parameters will be functions of not only fluorescence but also laser wavelengths. A weakly pronounced structure, which depends on excitation wavelength stronger than on the OP type, is the characteristic feature of the fluorescence spectra. Only three types of the OP's, such as refined light OP's (for example diesel fuel), petroleum, and heavy residual oil, may be identified by the spectrum shape or position of its maximum.¹⁰ Naturally, this identification seems to be ineffective.

The differential fluorescence method, which is based on determination of the ratio of the received signals at two different fluorescence wavelengths, was proposed by Cecchi et al.¹¹ Spectra of more than 60 oil samples were analyzed to adjust the optimal values of λ_1 and λ_2 . The results showed that the laser fluorimeter with two spectral channels allows petroleum and light and heavy crude to be identified. Cecchi et al.¹¹ suggested that finer classification may be obtained using additional spectral channels.

In Ref. 10 the correlation method was used for detection and identification of two different types of petroleum. In this case the lidar signals recorded in 16 spectral channels in the spectral region from 380 to 660 nm were compared with the predetermined OP spectra. For every laser shot the pairwise correlation coefficient ρ was calculated from the formula

Identification capabilities of the laser fluorimeter may be improved by simultaneous measurement of the OP fluorescence spectrum and decay time. Unlike the simple substance characterized by a single value of τ_{dec} , the concept of fluorescence decay time spectrum (FDTS) may be introduced for the OP, because different hydrocarbon constituents with their individual τ_{dec} correspond to different sections of the fluorescence spectrum. In this case the OP may be identified both by fluorescence spectrum and the FDTS.¹²

The advantage of the FDTS method consists in the determination of absolute values of decay time, whereas it is very difficult to obtain remotely the absolute fluorescence spectrum (i.e., to measure the fluorescence conversion efficiency) of the unknown OP. At the same time, all OP's are characterized by small decay times (from several nanoseconds for petroleum to several tens of nanoseconds for various types of mineral oil). This makes the measurement difficult.

Advantages of integrated approach to the problem of the OP identification are obvious. For example, petroleum and gasoline have the decay times close in values but different spectra, while gasoline and mineral oil spectra are quite similar but their decay times τ_{dec} differ by an order of magnitude. Thus the use of the FDTS in combination with the fluorescence spectra allows us to identify the OP of one type.

Nonstandard approach to the identification problem was used by Camagni.¹³ The regression parameters a and b were determined from the experimental data

$$Y_{\lambda}(t) = a[X_{\lambda}(t)]^b,$$

where $Y_{\lambda}(t)$ is the measured response of the given type of the OP in the spectral region centered at λ and $X_{\lambda}(t)$ is the reference response of the OP with known decay time. Experiments with various oil samples and reference petroleum show that a generalized expression can be obtained for $Y(t)$. When time responses $Y(t)$ and $X(t)$ are the convolution of the instrumental response with the fluorescence decay function, then average decay time τ and relative fluorescence conversion efficiency ρ of the oil sample may be obtained from the regression parameters a and b . In this case every oil sample will have an individual surface in the space (ρ, τ, λ) which can be used for unambiguous identification of this sample.

The following conclusions can be made from the foregoing analysis.

1. The water polluted by the OP is one of the most important factors of anthropogenic impact on the environment. Appropriate detection and analysis of the oil spills allow us to identify rapidly the OP source thereby decreasing the scale and consequence of the spill.

2. Remote analysis of oil films is a difficult scientific and technical problem. At present there are no reliable methods and devices for remote routine determination of the type and amount of the spilled oil products.

3. It is very important to study optical properties of the oil films and to seek for the informative parameters. The problem may be solved only by integrated use of various physical factors accompanying irradiation of oil films by lasers and including kinetic, absorption, fluorescence, wave, etc. factors.

5. CONCEPT OF DESIGN OF AIRBORNE AND SHIPBOARD FLUORIMETER

An airborne or shipboard laser fluorimeter must solve the following problems: (a) detection of oil spill, (b) identification of its type, and (c) measurement of the OP amount (i.e., film thickness and spill area). These problems must be solved by day and night with the use of the airborne or shipboard fluorimeter which ensures the sensing range of 30–50 m. The measuring period must be less than 10 sec to obtain an acceptable spatial resolution less than 100 m limited by the moving carrier. The recorded physical parameters must be independent of range, so the absolute values of backscattered radiation are undesirable for informative parameters because they vary as the square of the distance. The recording system must have a wide dynamic range or automated adjustment of sensitivity because the return signals vary from shot to shot due to surface roughness and unstable altitude of the carrier. Since the background fluorescence of dissolved organic matter and bioplankton and phytoplankton as well as Raman scattering limit the fluorimeter sensitivity, a special optical system is required to receive signals only from the upper water layers.

At least two of the informative fluorescence parameters are independent of altitude. They are the decay time and the shape of the OP fluorescence spectrum. As follows from the foregoing literature review and our experimental data presented below, the absolute values and wavelength dependence of the FDTS are individual characteristics of the oil product. We used the FDTS for identification of the OP type.

Knowing the OP type, we can use earlier obtained data on extinction coefficients and fluorescence spectra of thin oil films to measure the film thickness by relative fluorescence intensities in different spectral regions. This method is described in detail below. Different approach to the problem is based on the high power of modern computers. All possible spectra corresponding to various types and thicknesses of the oil films are stored in a computer and then the type and film thickness of the OP are determined by means of comparison of measured and stored spectra with the use of the computer. Using stored background fluorescence spectrum of clear water, we can detect an oil spill.

6. FLUORIMETER DESCRIPTION

The shipboard laser fluorimeter intended for recording the floating OP's was designed on the basis of critical analysis of the existing lidar systems. A compact modular structure and low power consumption allow us to use it both onboard the sea and small river ships, including launches.

The fluorimeter consists of a laser, a matrix head of a telescope, a polychromator, a PMT unit, a transient ADC, and a computer. All the units are stand-alone and may be placed at distances ranging from 3 to 5 m. The units are connected by quartz light guides and electric cables.

The third harmonic (355 nm) of a Q-switched Nd:YAG laser is used as an excitation wavelength.¹⁴ An unstable resonator and passive mode-locking based on a LiF crystal with F_2^- -centers allow us to decrease the laser beam divergence and to shorten the pulse duration to 2.5–3 nsec. Nonlinear crystals used for the radiation conversion do not require thermostabilization. The laser output at a wavelength of 355 nm is 3–5 mJ/pulse at a pulse repetition rate up to 10 Hz.

The compact matrix telescope consists of six I-37 receiver objectives with $f = 300$ nm centered around the quartz transmitting objective. The matrix telescope is connected with the excitation laser and polychromator by light guides. This design on the one hand, allows us to simplify and to reduce the price of the receiving-transmitting system and on the other, makes the system mobile and allows us to put it in a convenient place at a distance up to 10 m from another system unit. It is particularly important when the fluorimeter is located onboard a ship.

The compact polychromator with diffraction grating having 300 lines/mm serves to select four spectral channels in the spectral region from 350 to 700 nm with bandwidths varying from 5 to 10 nm depending on the diameter of the used light guide. Through the light guides the spectral signals are fed into the unit of four transient photomultipliers. Small-size high-frequency power supply units built in this unit are used to energize the PMT. After amplification the signals are fed into a 4-channel 6-bit ADC. Every ADC channel has 128 5-nsec strobes.

Other configuration of the fluorimeter has a PMT and a single-channel ADC with 256 5-nsec strobes. In this case the signals from different spectral channels are delayed in time in light guides inserted between the polychromator and the PMT. The ADC is triggered by a photodiode.

7. EXPERIMENTAL MEASUREMENT OF THE OP FLUORESCENCE CHARACTERISTICS

Five kinds of the OP's including petroleum from two fields in Western Siberia were investigated to estimate experimentally the feasibilities of identification by fluorescence spectra. Main characteristics of the OP are given in Table I.

TABLE I.

Oil sample	Density g/cm ³	κ (mm ⁻¹), $\lambda=308\text{nm}$	Critical film thickness (μm)	Quantum yield ϕ , %
Petroleum (Samotlor)	0.90	1860±40	2	16
Petroleum (Sovetskoe)	0.90	1170±50	3	17
AI-76 gasoline	0.67	2.2±0.1	1800	15
VM-6 vacuum mineral oil	0.81	227±7	17	95
Diesel fuel	0.78	99±4	40	90
Rhodamine 6G dye (10 ⁻³ mole/liter)*		1.1	3500	92**

Note: * used as reference and ** reported in the literature

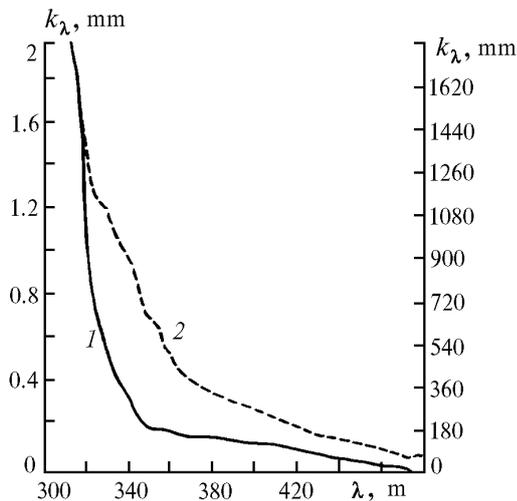


FIG. 1. Quenching coefficients in the spectral range 310–460 nm. 1) AI-76 gasoline and 2) petroleum (Samotlor).

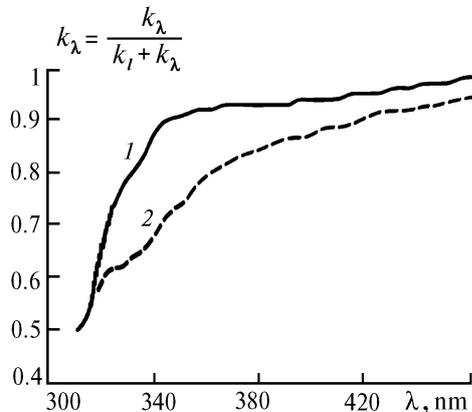


FIG. 3. Relative quenching coefficient K_λ for $\lambda_1 = 308$ nm. 1) AI-76 gasoline and 2) petroleum (Samotlor).

The absorption coefficient at the laser wavelength $\lambda_1 = 308$ nm was measured by attenuation of the laser radiation in solutions of the oil products in toluene with different concentrations. The critical thickness of the oil film h_c at which $E_\lambda^h \approx 1$ is given in Table I. The quenching coefficients κ_λ measured by a spectrometer are shown in Figs. 1 and 2. Figures 3 and 4 show the values of $K_\lambda = \frac{\kappa_1}{\kappa_1 + \kappa_\lambda}$ calculated from the measured values of κ_λ .

A laser fluorimeter being used for fluorescence spectra measurements consisted of a XeCl laser with $\lambda_1 = 308$ nm, monochromator with a focal length of 600 mm and a reciprocal linear dispersion of 1.3 nm/mm, a transient PMT FÉU-157 with a high-frequency amplifier and a 6-bit ADC with 256 5-nsec strobes. The sample was irradiated at an angle of 45° with respect to the axis of fluorescence observation.

The OP layers were taken with thicknesses varying from 3 to 5 mm ($h \gg h_c$) to simplify the spectrum interpretation. For measuring the instrumental factor A , the fluorescence spectrum of water solution of the rhodamine 6 G with a concentration of 10⁻³ mole/liter, for which the quantum yield was assumed to be equal to 92%, was recorded.

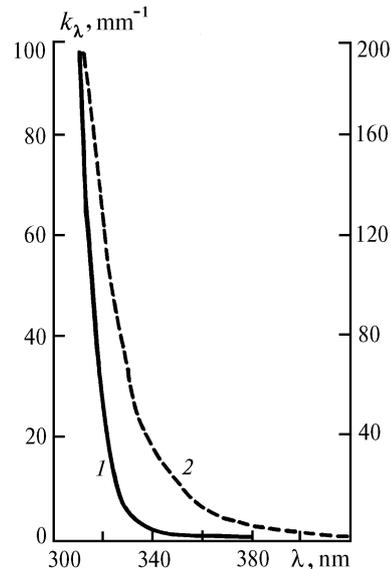


FIG. 2. Quenching coefficients. 1) Diesel fuel and 2) VM-6 vacuum mineral oil.

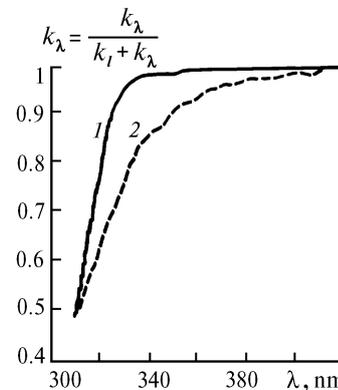


FIG. 4. Relative quenching coefficient K_λ for $\lambda_1 = 308$ nm. 1) Diesel fuel and 2) VM-6 vacuum mineral oil.

Since the ADC has only 6 bits, we recorded the fluorescence signals with different widths of the monochromator input slit and subsequently corrected the signal in order to extend the dynamic range of the ADC. The signals were integrated over 10 laser shots and then three parameters were calculated: the signal amplitude P_λ^0 , the integral quantity S_λ , and the integral S_λ^0 taken over time from the instant at which the signal reaches its peak value to the instant of complete decay of the signal. Relation (18) was used to calculate the fluorescence decay time τ_λ . The laser pulse duration $\Gamma = 35$ nsec was determined by Rayleigh scattering from a screen.

Figures 5–7 show the fluorescence spectra S_λ . As can be seen from Figs. 3 and 4, the relative quenching coefficient K_λ makes significant contribution to the determination of the quantum yield $\phi_\lambda = S_\lambda / AK_\lambda$ only for petroleum and gasoline and in general the shapes of the S_λ and ϕ_λ curves differ slightly. Therefore, the quantity S_λ shown in Figs. 5–7 may be assumed to be proportional to ϕ_λ . In the same figures and in Table I the values of the integral quantum yield ϕ are given. It can be seen from the figures that the OP spectra differ primarily by the spectral fluorescence conversion efficiency ϕ_λ . A shift of the position of fluorescence maximum toward the red region of the spectrum is pronounced with increase of the OP density. The examined samples may be divided into two groups by their total quantum yield: mineral oil and diesel fuel ($\phi \approx 90\%$) and gasoline and petroleum ($\phi \approx 15\%$).

Figures 8 and 9 show the fluorescence decay time spectra (FDTS). One can see that they differ markedly for various OP's especially in the violet spectral region. Agreement of the values of τ obtained by us with the data obtained by other authors with the use of the short laser pulses testifies the feasibility of the employed method of determining τ even in case of a long pulse of irregular shape.

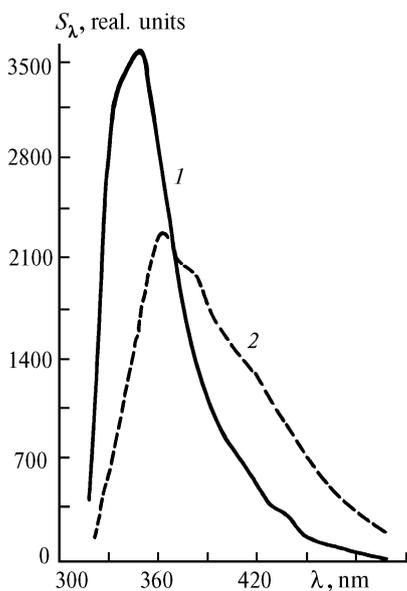


FIG. 5. Fluorescence spectra S_λ induced by laser radiation at $\lambda_1 = 308$ nm. 1) Diesel fuel and 2) VM-6 vacuum mineral oil.

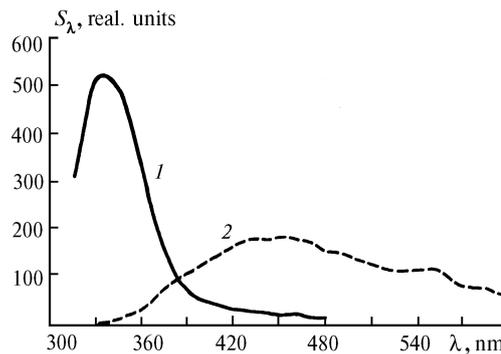


FIG. 6. Fluorescence spectra S_λ induced by laser radiation at $\lambda_1 = 308$ nm. 1) AI-76 gasoline and 2) petroleum (Samotlor).

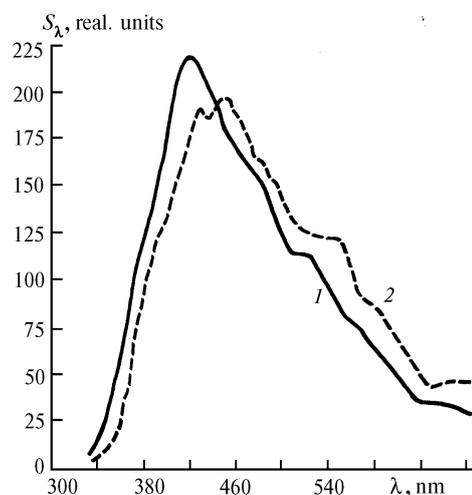


FIG. 7. Fluorescence spectra S_λ of petroleum. 1) Samotlor and 2) Sovetskoe.

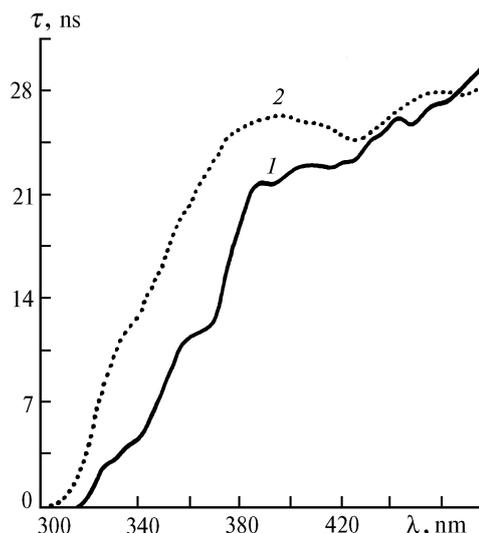


FIG. 8. Fluorescence decay time spectra. 1) VM-6 vacuum mineral oil and 2) diesel fuel.

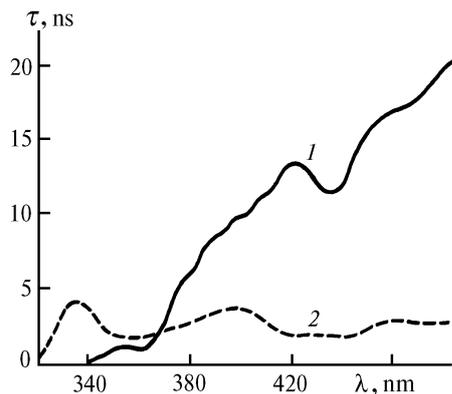


FIG. 9. Fluorescence decay time spectra. 1) AI-76 gasoline and 2) petroleum (Samotlor).

8. SYSTEM FOR IDENTIFICATION OF THE OP

Available laser fluorimeter is intended for the detection and identification of floating OP's. Further development of the instrument will be tailored toward broadening its capabilities such as measurement of oil film thickness and applications to sea biology, mineralogy, forestry, and agriculture.

The oil identification system is based on the modified correlation method. The correlation coefficient is determined simultaneously from fluorescence and decay time spectra. The fluorescence spectrum normalized on its maximum is jointed with the FDTS represented in absolute units. As a result, we have a joint spectrum individual for any oil sample. The identification procedure consists in the determination of the correlation coefficients for the measured spectrum of the oil sample and spectra of reference oil products catalogued in the lidar database.

Thus, in the available fluorimeter the samples are identified by three parameters: fluorescence spectrum shape, shape of the FDTS, and absolute values of the FDTS. In this case it is possible to identify such oil products as petroleum, gasoline, diesel fuel, kerosene, and mineral oil using only four spectral-temporal channels, that is, to identify different kinds of oil of one type. Further development of the method may be in the use of the fourth parameter — the fluorescence conversion efficiency. In this case we hope to identify brands of gasoline or kinds of mineral oil.

The fluorimeter may operate in two modes, i.e., identification and training. In the latter mode the fluorescence time spectrum of measured sample is introduced in lidar database. This mode of the fluorimeter operation may be useful in three cases:

1) When information about new substance is lacking in the database.

2) When it is necessary to choose one sample from their collection (e.g., to define a pollution source).

3) When the device is detuned (e.g., when the characteristics of the polychromator spectral channels such as their spectral boundaries and/or sensitivities are unknown).

The lidar database is formed by the set of the existing spectral channels from the fluorescence spectra database. It may be created when the fluorimeter starts to operate or may be stored in the computer memory. In the latter case the lidar database may be extended by new records obtained when the device operates in the training mode. Such an approach makes the system adaptable and allows one to tune the fluorimeter on new spectral channels, broaden or narrowing the spectral range thereby changing the specialization of the device.

Effective algorithms of data processing allow the fluorimeter to operate in real time. It takes from 1 to 10 sec depending on the computer type for sample identification using the database comprising 50 spectra.

The fluorimeter software includes program package intended for recording of the fluorescence spectra and FDTS, for creation and editing of the spectrum database, for modeling of the device functions and its operation. All the programs were written in PASCAL for PDP and IBM PC.

TABLE II. Specifications of the fluorimeter.

The range of the thicknesses of the measured oil films:	
Petroleum	0.8–3.7 μm
Mineral oil	1.2–140 μm
Diesel fuel	40–5000 μm
Gasoline	> 1400 μm
Accuracy of identification of the OP's	up to 100%
Measurement time	2–10 sec
Sounding range	up to 30 m
Power consumption	1–2 kW
Weight	< 100 kg
Service	one operator

CONCLUSION

The following conclusions can be made based on the foregoing study.

1. The remote laser fluorimeter located onboard a ship or helicopter can be used for detection of the OP water pollution, the OP identification, and measurement of oil spill dimensions and oil film thickness.

2. Integrated application of both spectral fluorescent characteristics and signal shape allow one to identify not only the OP type (petroleum or light crude or heavy crude), but also the OP kind (mineral oil, diesel fuel, etc) and possibly the brand of the individual OP.

3. A laser with short pulse duration and a recording system with nanosecond time resolution must be used in the fluorimeter because of small duration of the OP fluorescence. The third or fourth harmonic of a Q-switched Nd:YAG laser can be employed for the fluorescence excitation due to its high peak power, short duration and absence of aggressive medium in comparison with commonly used N_2 and XeCl lasers.

4. Modular structure and widespread use of light guides make the fluorimeter design more adaptable and convenient for placement onboard a small-size carriers. Further development of the design will be tailored toward the decrease of the overall dimensions and weights of a laser and telescope and toward the use of the unified modules.

5. We performed experiments on the measurement of oil film thickness by the absolute intensity method. This method needs preliminary calibration of the fluorimeter against the thin oil films with known absorption coefficients. We succeeded in measuring the film thicknesses varying from 0.8 to 3.5 μm for petroleum, from 2 to 80 μm for vacuum mineral oil, and from 60 to 600 μm for diesel fuel. Average measurement accuracies were 20–30% for light crude and 30–50% for petroleum.

6. The problem of ecological application of the laser fluorimeter is closely related with its certification. It is necessary to develop some concepts and methods for certification of the identification potentials of the device and of the feasibility of determination of the thicknesses of the oil films.

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