

Laser sensing of surface water in the Atlantic Ocean and European seas

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Results of sensing seawaters with a shipborne UV laser are presented. Measurement techniques and instrumentation were developed at the Institute of Oceanology and the Electrotechnical Institute. Instrumental constants were determined by calibration. Equations have been derived that connect Raman signals, fluorescence of oil products and chlorophyll in various spectral regions, and laser pulse energy with the concentration of dissolved organic matter and oil products, concentration of chlorophyll, and the value of the optical water type index. The distribution of the oil products and chlorophyll concentrations along the ship routes during research missions are mapped.

The study of light-absorbing and light-scattering substances in surface ocean water is of great interest for oceanology and, in particular, for evaluation of the ecological state and pollution of the seawater with anthropogenic pollutants, first of all, oil products. Among various measurement techniques, the methods of laser sensing from a moving vessel are most promising, since they allow underway measurements in different voyages: passenger, cargo, research, and others. Measurements (not requiring to stop a vessel) accompanied by underway sampling for following laboratory analysis were organized in the 53rd cruise of the RV *Akademik Kurchatov* around Europe (1994). Similar studies were also conducted in the 26th cruise of the RV *Vityaz* in the Atlantic Ocean (1991).

The technique of seawater sensing from a vessel with a UV laser and the corresponding equipment were developed at Shirshov Institute of Oceanology and Lenin Electrotechnical Institute. A shipborne lidar was mounted on a vessel deck. The radiation of this lidar at the wavelength of 347 nm induced Raman scattering in seawater near 397 nm, fluorescence of dissolved organic matter of natural origin (yellow substance) and oil products (hereinafter, DOM&OP) in the spectral region of 400–560 nm, and fluorescence of phytoplankton chlorophyll at 685 nm. The lidar was described in detail in Ref. 1 along with the tentative results of its use in the sub-satellite experiment in the 53rd cruise of the RV *Akademik Kurchatov*.

Starting from the 1970s, numerous experiments on laser sensing of seawater were conducted in order to determine optical properties of seawater, concentration of phytoplankton chlorophyll, dissolved organic matter, and oil hydrocarbons by lidar methods.^{2–6} etc. All the proposed fluorescent methods are based on normalization of fluorescent signals of substances to the Raman signal

of water itself. Our measurements showed and calculation confirmed (see below) that Raman signals are not stable at sensing of semi-infinite water medium, but they depend strongly on the type of water (its trophicity, pollution, etc.), varying up to ten and more times in different oceanic water areas. Therefore, the Raman signal with neglect of all other characteristics of water cannot serve a reference signal suitable for normalization. This causes the need to develop new theory and new algorithm for processing the data of shipborne seawater sensing. Consider derivation of the corresponding equations.

Let a short laser pulse having the energy N_0 and the wavelength λ_0 be incident vertically on the sea surface. The following assumptions will simplify the considered problem.

Assume that the medium is vertically homogeneous within a layer that forms the fluorescence response. This assumption is based on the fact that the wind-mixed layer in the open sea is almost always thicker than the layer forming the fluorescence response. We believe that the energy of a pulse reaching the depth z decreases according to the law found for the solar radiation field, i.e., corresponds to the optical classification developed in Ref. 7 with the coefficients refined in Ref. 8. It should be emphasized that here we deal with the pulse energy N reaching the depth z no matter whether the pulse spreads in any direction or not. Assume also that the echo is formed according to the two-flux approximation.⁸

Based on the above assumptions, we can realize that a water layer of thickness dz situated at the depth z is illuminated by a pulse with the energy

$$N = N_0 \exp(-\alpha_{\lambda_0} z), \quad (1)$$

and a Raman signal

$$dN = N_0 \exp(-\alpha_{\lambda_0} z) \gamma dz \quad (2)$$

is formed in it. Here α_λ is the coefficient of vertical extinction of radiation at the wavelength λ , in foreign literature this coefficient is often denoted by K_d ; γ is the constant of Raman scattering of radiation by water.

The Raman signal equal to

$$dN = N_0 \exp [- (\alpha_{\lambda_0} + \alpha_{\lambda_1}) z] \gamma G dz \quad (3)$$

passes from the water layer ($z, z + dz$) to the surface and then to a photodetector combined with the laser onboard a vessel at some altitude above the surface. Here λ_1 is the wavelength of Raman signal, G is a overlap factor depending on the lidar altitude above the surface and receiver's aperture, but constant for a given equipment, vessel, and lidar arrangement on its board. It is assumed that the angular aperture of the receiver completely covers the whole part of the water surface, through which the Raman signal comes out from the sea.

After integration of contributions from all layers over the depth, we can write the total energy of the Raman signal N_R received by the photodetector from the water medium as

$$\begin{aligned} N_R &= \int_0^\infty N_0 \exp [- (\alpha_{\lambda_0} + \alpha_{\lambda_1}) z] \gamma G dz = \\ &= N_0 \gamma G (\alpha_{\lambda_0} + \alpha_{\lambda_1})^{-1}. \end{aligned} \quad (4)$$

In the lidar used $\lambda_0 = 347$ nm, therefore $\lambda_1 = 397$ nm, and in our case:

$$N_R/N_0 = A (\alpha_{347} + \alpha_{397})^{-1}, \quad (5)$$

where $A = \gamma G$ is a constant for given equipment and a vessel, i.e., it keeps unchanged during the cruise.

Using the dependence of $(\alpha_{347} + \alpha_{397})$ on α_{500} , the above-mentioned classification from Ref. 7, and the refined coefficients given in Ref. 8, we obtain the empiric equation:

$$\alpha_{347} + \alpha_{397} = 4.1 \alpha_{500} - 0.06. \quad (6)$$

Thus, we have come to a simple method of contactless estimation of the optical water type index, m . Remind that by definition m is a dimensionless parameter proportional to α_{500} (Ref. 7):

$$m = k \alpha_{500}, \quad (7)$$

where α_{500} is the coefficient of vertical extinction of solar radiation (m^{-1}) at the wavelength 500 nm; $k = 43.43$ m.

Measuring N_R and N_0 at seawater sensing and having measured the calibration coefficient A , we can easily obtain the water type index m using sequentially Eqs. (5)–(7) and tabulated data.

It is extremely difficult to calculate the constant A from experimental conditions, therefore the value of A is determined at a chosen “calibrating” station (or several stations along the route), where the value of m is known. In the 53rd cruise, for calibration we selected the Ionian Sea, with the optical water type index $m = 1.59$ determined in other measurements. The value

of A was determined from N_R/N_0 obtained at stations in the Ionian Sea and then used for the whole route in water-type calculations. Then we used the equation

$$\alpha_{347} + \alpha_{397} = [A/(1-p)] [N_0/N_{397}], \quad (8)$$

where p is a “pedestal” (the value of p is estimated below).

The DOM&OP fluorescence signal at the wavelength λ was calculated by a similar model. The following equation for the energy of the DOM&OP fluorescence signal at the wavelength of 439 nm is derived similarly to Eq. (4), i.e., a band is chosen near the strongly blurred peak of the DOM&OP fluorescence spectrum under the exposure to a UV radiation ($\lambda = 347$ nm):

$$N_{439} = N_0 K_{\text{DOM\&OP } 347} \beta_{347 \rightarrow 439} G (\alpha_{347} + \alpha_{439})^{-1}, \quad (9)$$

where $K_{\text{DOM\&OP } 347}$ is the DOM&OP absorption coefficient at $\lambda = 347$ nm in water under study; $\beta_{347 \rightarrow 439}$ is the coefficient of conversion of the energy absorbed by DOM&OP to the spectral band at $\lambda_2 = 439$ nm, in which it is emitted.

In this paper, the concentration of DOM&OP in seawaters and its variability along the vessel trajectory are estimated directly in units of light absorption at the wavelength of 347 nm, i.e., by the values of $K_{\text{DOM\&OP } 347}$, in m^{-1} .

From Eqs. (5) and (9) we obtain the following equation for $K_{\text{DOM\&OP } 347}$:

$$\begin{aligned} K_{\text{DOM\&OP } 347} &= \frac{\gamma}{\beta_{347 \rightarrow 439}} \frac{(\alpha_{347} + \alpha_{439})}{(\alpha_{347} + \alpha_{397})} \frac{N_{439}}{N_R} = \\ &= B \psi_1 \frac{N_{439}}{N_R}, \end{aligned} \quad (10)$$

where $B = \text{const}$; $\psi_1 = (\alpha_{347} + \alpha_{439})/(\alpha_{347} + \alpha_{397})$ is determined by the optical classification (see Table).

Table. Vertical extinction coefficient in seawater depending on the water type index m

m	α_{500}, m^{-1}	α_{347}, m^{-1}	α_{397}, m^{-1}	α_{439}, m^{-1}	α_{685}, m^{-1}	ψ_1	ψ_2
1.2	0.027	0.033	0.024	0.021	0.48	0.95	9.08
1.5	0.034	0.050	0.036	0.032	0.49	0.94	6.26
2.0	0.046	0.073	0.055	0.049	0.50	0.94	4.44
3.0	0.069	0.138	0.10	0.087	0.51	0.93	2.71
4.0	0.092	0.178	0.13	0.12	0.53	0.93	2.29
5.0	0.12	0.230	0.17	0.15	0.55	0.93	1.94
6.0	0.14	0.29	0.21	0.19	0.57	0.93	1.79
7.0	0.16	0.34	0.26	0.23	0.59	0.93	1.55
8.0	0.18	0.39	0.30	0.26	0.61	0.93	1.45
9.0	0.20	0.44	0.33	0.30	0.63	0.93	1.38

Now let us define the pedestal p . It is that level of the energy of the DOM&OP signal at $\lambda = 397$ nm, on which the energy of the Raman signal lies (as on a background or pedestal). Let it be equal to ξN_{439} ($\xi < 1$). If p is determined in fractions of N_{397} , then

$$p = (\xi N_{439}) / (N_R + \xi N_{439}) = \xi (N_{439} / N_{397}); \quad (11)$$

$$N_R = (1 - p) N_{397}. \quad (12)$$

Then, substituting Eq. (12) in Eq. (10), we obtain the equation

$$K_{\text{DOM\&OP } 347} = B\psi_1 / (1 - p) N_{439} / N_{397}. \quad (13)$$

The algorithm for processing the experimental data is as follows. First, we determine p by Eq. (11). Using the literature data,⁹ we then estimate ξ as $\xi \approx 0.25$. Then, using Eq. (13), we calculate the concentration of natural organic matter plus oil products in the sensing zone in optical units m^{-1} – the value of the absorption coefficient in the UV spectral region at $\lambda = 347$ nm.

Now turn to estimation of the chlorophyll concentration from the fluorescence signal at $\lambda = 685$ nm. Use the signal amplitude ratio N_{685} / N_{397} and take into account that

$$N_{685} / N_{397} = N_{685}(1 - p) / N_R. \quad (14)$$

Similarly to Eqs. (4) and (9), we can write

$$N_{685} = N_0 K_{\text{pig } 347} \beta_{\text{pig } 347 \rightarrow 685} G(\alpha_{347} + \alpha_{685})^{-1}, \quad (15)$$

where $K_{\text{pig } 347}$ is the absorption coefficient of phytoplankton pigments at 347 nm (in m^{-1}); $\beta_{\text{pig } 347 \rightarrow 685}$ is the coefficient of transfer of the energy absorbed by phytoplankton pigments inside cells to the red spectral band at $\lambda = 685$ nm, in which this energy is then emitted.

It is natural to assume that the Baire law:

$$K_{\text{pig } 347} = K_{\text{pig } 347}^* C_{\text{chl}} \quad (16)$$

is valid, in which C_{chl} is the chlorophyll concentration, in mg/m^3 ; $K_{\text{pig } 347}^*$ is the specific absorption by pigments in $\text{m}^{-1} \cdot \text{m}^3 / \text{mg}$, i.e., m^2 / mg . The chlorophyll concentration is determined in mg/m^3 .

From Eqs. (4) and (15) taking into account Eqs. (12) and (16), we obtain

$$C_{\text{chl}} = C (1 - p)^{-1} \psi_2 N_{685} / N_{397}, \quad (17)$$

where $C = \gamma / (K_{\text{pig } 347}^* \beta_{\text{pig } 347 \rightarrow 685})$ is a constant; its value is assumed independent of the species composition of plankton and time of day;

$$\psi_2 = (\alpha_{347} + \alpha_{685}) / (\alpha_{347} + \alpha_{397}). \quad (18)$$

The values of ψ_2 , as ψ_1 , following from the optical classification of water types are given in the Table as depending on the optical water type index m . The constant C , as A and B , is determined experimentally at several stations.

Below we present the order of measurements and calculations using the data of laser sensing of seawaters with a lidar of the type described above.

1) The lidar is calibrated in seawater with known m , $K_{\text{DOM\&OP } 347}$, and C_{chl} (at calibrating station/stations). Calibration consists in determining the constants A , B , and C by Eqs. (5), (13), and (17).

2) The pedestal p is calculated by Eq. (11) from laser sensing data for the cruise route.

3) The optical water type index m and then the concentrations of DOM&OP and chlorophyll are calculated by Eqs. (6)–(8), (13), and (17) from the data of laser sensing, i.e., experimental values of N_0 , N_{397} , N_{439} , and N_{685} .

Thus, the theory has been developed. The equations have been obtained that connect the measured parameters: Raman signals, DOM&OP fluorescence in different regions of the spectrum, and laser pulse energy, with the sought parameters: DOM&OP concentration, chlorophyll concentration, and the value of the optical water type index m – in the linear approximation with unknown coefficients A , B , and C . It is worth emphasizing here that by N_0 , N_{397} , N_{439} , and N_{685} we mean not the values of these parameters in joules, but some signals proportional to them and recorded with linear receivers; and the coefficients of proportionality are unknown and included in the calibrated values of the constants A , B , and C .

It is difficult to calculate the coefficients A , B , and C theoretically, and we should not expect high accuracy of these calculations. Therefore, a very important problem is lidar calibration under field conditions. The values of A , B , and C were determined directly in sea, once the device was installed in the operating position aboard the vessel, i.e., at the same geometry as in measurements. Calibration was conducted in water areas, where the values of m and the concentrations $K_{\text{DOM\&OP } 347}$ and C_{chl} were known from direct measurements using accepted procedures adequate to these characteristics. Thus, the chlorophyll concentration was determined by the UNESCO method in samples,¹⁰ m was obtained from measurements of the light field,⁷ the concentration of organic matter in units of light absorption $K_{\text{DOM\&OP } 347}$ (or $K_{\text{DOM\&OP } 390}$) was measured in samples with a dual-beam spectrophotometer with the water bidistillate in the reference cell. It is not necessary to know the lidar power (pulse energy) in absolute units, it is sufficient to direct a small part of laser radiation to the photodetector and provide for detector linearity.

In our case, the lidar was calibrated in the Ionian Sea (values of A and B were determined) and in the Sargasso Sea (the value of C). The value of m in the Ionian Sea was 1.59.

The calibration value of B was obtained in the following way. In 10 areas of the Ionian Sea (stations along the mission route), the measured values of N_{439} / N_{397} were, on the average, 0.0183 for the used device with the root-mean-square deviation of 0.0028. We believed that there were no oil products in this sea. The values of $K_{\text{DOM\&OP } 347}$ were determined as the difference between $K_{\text{DOM\&OP } 347}$ for water at $m = 1.59$

by extrapolation of data from Ref. 11 (0.027 m^{-1}) and the table data for the pure seawater $K_{\text{DOM\&OP } 347} = 0.011 \text{ m}^{-1}$, i.e., $K_{\text{DOM\&OP } 347} = 0.016 \text{ m}^{-1}$. Calculation by Eq. (13) with the use of the measured ratios N_{439}/N_{397} gave $B = 0.926$.

Similar procedure developed for homogeneous areas of the Sargasso Sea in order to calculate C (C_{chl} was determined in samples by the UNESCO method) with the use of Eq. (17) gave this value equal to 1.07.

Using the measurement results, we have drawn the maps demonstrating the distribution of the concentration of DOM&OP (organic matter of natural origin, i.e., phytoplankton and products of its vital functions, with the organic matter being mostly in the dissolved state (DOM) plus anthropogenic oil products) and phytoplankton chlorophyll along the mission routes. On the section New York – Cape-Blan – Las Palmas (Fig. 1) the DOM&OP concentration in optical units – values of the absorption coefficient at the wavelength of 347 nm – varied from 0.003 m^{-1} (Sargasso Sea) up to 0.92 m^{-1} (New York Bay), i.e., 300 times. The chlorophyll concentration on this section varied from 0.016 (Sargasso Sea) up to 3.3 mg/m^3 (in Canary upwelling), i.e., 200 times, with the rms deviation of 36% from the values measured by the standard method in samples. It was noticed that the DOM&OP concentration increased eastward from the Mid-Atlantic Ridge faster than the chlorophyll concentration. Possibly, this was connected

with the transport of Canary upwelling water to the west by the northern trade-wind current.

Figure 2 shows the DOM&OP concentration in seas surrounding Europe (measurements were conducted in the 53rd cruise of the RV *Akademik Kurchatov*). We can see that waters of Baltic Sea, Danish Straits, Northern Sea, and English Channel are strongly polluted. Waters of the Mediterranean Sea, except for areas near seaports, are relatively clean.

In waters of the Mediterranean Sea, the DOM&OP concentration varied from 0.013 m^{-1} (Ionian Sea) to 1.83 m^{-1} (Naples Bay). Thus, most polluted waters were detected as approaching the Naples Seaport.

The level of DOM&OP fluorescence in waters of the Sea of Marmora exceeds that for the Black Sea. This refutes with the hypothesis that the Sea of Marmora is polluted through Bosphorus. Likely, on the contrary, penetration of surface water of the Sea of Marmora through Bosphorus increases fluorescence of Black Sea water in the southwestern area adjacent to Turkey.

Measurements showed also that DOM&OP fluorescence near large seaports, such as New York, Naples, Rotterdam, Istanbul, Piraeus, Lisbon, Havre, and Las Palmas exceeds by tens and even hundreds times the natural level of seawater fluorescence. This means that the concentration of oil products in these waters many times exceeds the concentration of the light-absorbing fraction of natural organic matter being the product of phytoplankton vital functions.

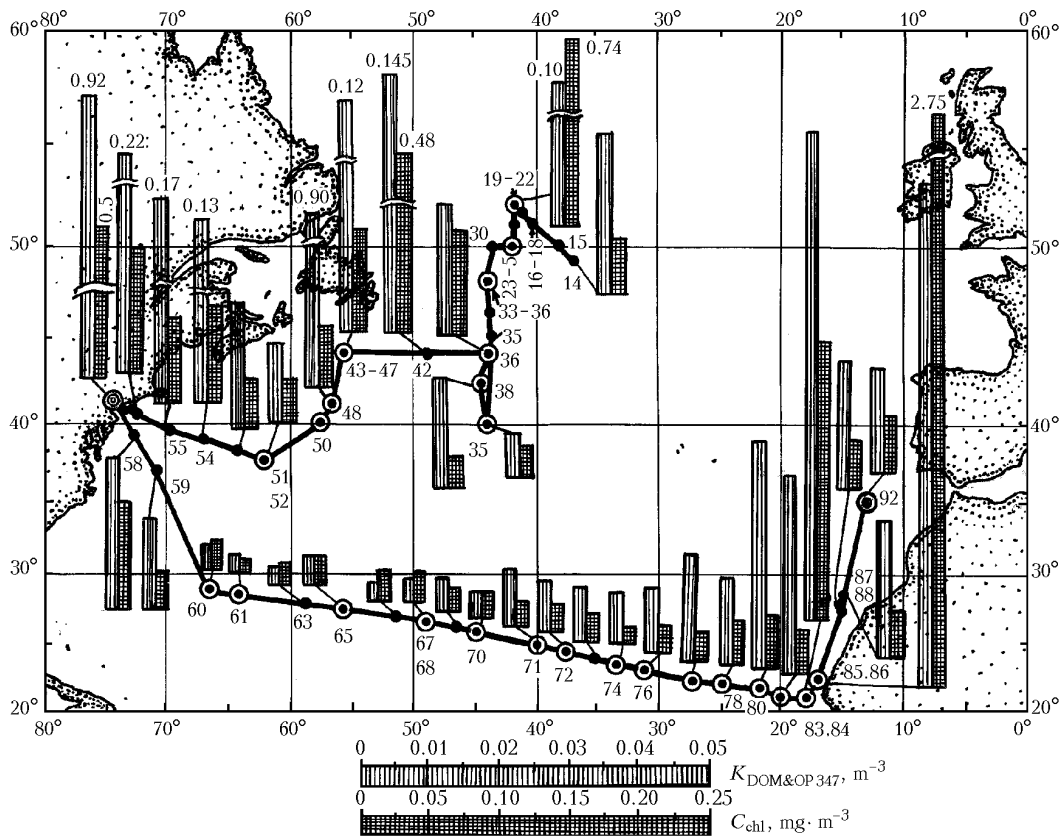


Fig. 1. Concentration of the dissolved organic matter (yellow substance) plus oil products $K_{\text{DOM\&OP } 347}$ and chlorophyll concentration C_{chl} as measured with a UV fluorescent lidar in the North Atlantic (26th cruise of the RV *Vityaz*, 1991).

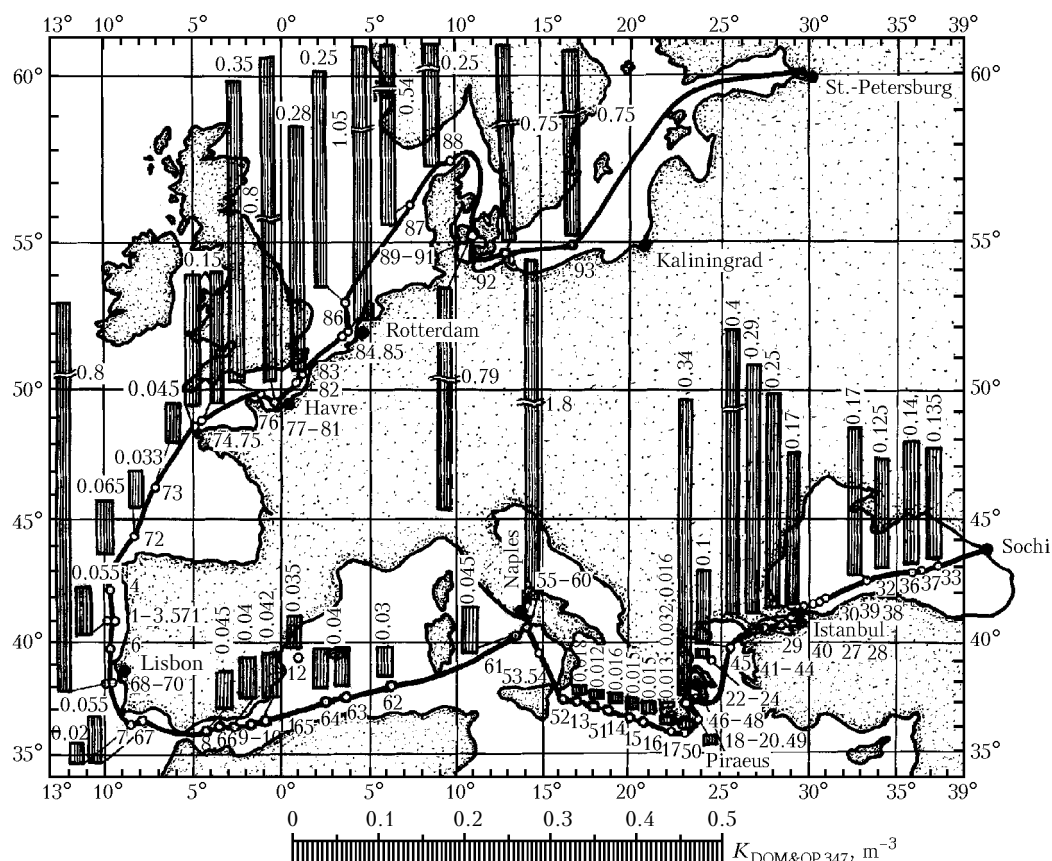


Fig. 2. Concentration of the dissolved organic matter (yellow substance) plus oil products $K_{\text{DOM\&OP } 347}$ and chlorophyll concentration C_{chl} as measured with a UV fluorescent lidar in cruise around Europe (53rd cruise of the RV *Akademik Kurchatov*, 1994).

The proposed technique and the results obtained demonstrate a realistic possibility of organizing ecological control over the state of seawater over vast water areas with the use of a shipborne fluorescent UV lidar.

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