LASER SPECTROMETERS FOR DIAGNOSTICS OF ORGANIC ADMIXTURES IN NATURAL WATER

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In this paper we deal with the problems of laser diagnostics of organic admixtures in water. In this connection we show that development of a multipurpose compact laser spectrometer is an urgent problem of such a diagnostics approach. We present a version of such spectrometer and discuss some results of its tests during the expedition along Volga river in June—July 1993 onboard "Il'ya Repin" ship.

INTRODUCTION

The analysis of natural water media for determining concentrations of different organic admixtures (OA) is needed in many scientific and practical problems, such as monitoring and protection of the environment, study of migration of organic matter in the World Ocean and their transfer through the boundary of "ocean—atmosphere" system, distribution of organic matter in soil water, monitoring of quality of potable water in water—supply systems, monitoring of super—pure and aggressive water media in technological cycles, etc. Due to a unique nature of water medium the number of such problems is not restricted and their solutions require not only the application of all of the available methods but also the development of new more efficient methods and instrumentation.

Global abundance of OA and unpredictable appearance of organic pollutants in water media make necessary continuous monitoring and obtaining results in real time. There exists now a lot of methods and facilities of passive sounding of water media which can be realized onboard the Earth's satellites. The program of satellite monitoring of water media if realized will provide, in particular, information about concentration of different admixtures and will start formation of a native data bank on their spatiotemporal distribution over the Earth. These programs also incorporate the development of highly efficient methods and facilities of active ground—based sounding of natural water for calibration and supplement of satellite—derived information. Among these are the methods of laser spectroscopy.

METHOD OF LASER FLUORIMETRY

In diagnostics of water media the optical methods become more attractive. One of the most efficient is the method of laser fluorimetry due to its high sensitivity and possibility to obtain results quickly and be used at a distance. Most of OA in natural water possess fluorescence properties that causes an extremely wide range of practical applications of this method.[1] Therefore a great deal of lidars for monitoring of organic admixtures in water media are fluorescence lidars (in scientific literature they are called flidars).

The application of the fluorimetric method is strongly limited by the dependence of the measurement results on experimental conditions and instrumentation parameters that makes it difficult to compare and intercalibrate the results obtained. Relativity of fluorimetric measurements does not allow one to perform remote quantitative diagnostics of natural water media due to uncontrolled parameters of the sounding path.

However, the decisive factor was that the OA fluorescence intensity (fluorescence cross section was 10^{-18}–10^{-20} cm^{2}sr^{-1}) with their concentration of the order of 10^{-8}–10^{-12} M in natural water turned out to be comparable, by the order of magnitude, with intensity of spontaneous Raman scattering (RS) of water ($\sim 10^{-29}$ cm$^2 \cdot$sr^{-1}). This enabled one to use RS of water (solvent) as an internal reference mark and thus to put fluorimetry of natural water media onto a quantitative base when conducting measurements both on samples and remotely.[2]

The disadvantage is weak selectivity of the fluorimetry method because of wide overlapping of the OA fluorescent bands. However, the intense development of numerical methods of processing the spectra of multicomponent organic mixtures will allow this difficulty to be overcome too.

The use of laser fluorimetry in diagnostics of natural water media is restricted due to a nonlinear effect of fluorescence saturation and photochemical decomposition of organic admixtures.[3] Even for photon current densities $F \sim 10^{24}$ cm^{-2}s^{-1}, which are sufficiently low for present pulsed lasers, the F dependence of fluorescence intensity becomes substantially nonlinear. The effect of fluorescence saturation complicates the procedure of determining the OA concentrations. However, this effect can be useful when identifying different OA in natural water.[4] The effect of photochemical processes appearing in OA exposed to laser radiation on the measurement result depends strongly on the specific object and observation conditions and must be taken into account.[3]

The interaction of such complicated natural systems as OA of natural water with laser radiation has not been studied yet. Hence it is necessary to accumulate experimental data and to elucidate empirical relations between the characteristics of objects and the parameters of recorded return signals. That is why the instrumental realization is significantly ahead of the methodical support.

FLUORESCENCE LIDARS FOR OIL POLLUTION MONITORING OF WATER MEDIA

Most of the "oil" lidars were constructed to detect oil films on the water surface and to carry out their quantitative and qualitative diagnostics (determination of the film thickness, identification of oil or oil products).

In the early studies a nitrogen laser (λ = 337 nm) or a doubled frequency ruby laser (λ = 347 nm) were used in the lidar as a radiation source.[5,6] In the receiving system a telescope with a 30–cm aperture, a set of interference filters, and a PM were used. Such systems allowed a reliable record of fluorescence spectra of oil pollutants (OP) to be made from a distance to 300 m.

In 1977 in Japan a field experiment was made[7] using a YAG:Nd^{3+} laser with the second (λ = 532 nm, 3 MW) and fourth (λ = 266 nm, 200 kW) harmonics with pulse duration of 8 ns, and pulse repetition rate of 30 Hz. A receiving system consisted of a telescope with a 50–cm aperture and a strobed optical multichannel analyzer of the OMA–1 type, firm PARC (USA). Different oil products were poured out on a water surface in a special container and were sounded from a 30–m distance. The study of different modes of diagnostics showed that at a distance of 10 m the signal–to–noise ratio for a kerosene film 20 μm thick at λ = 266 nm was 15, and for an oil film of the same thickness it was about 100 at λ = 532 nm.

An airborne lidar with a N$_2$ laser (1 mJ, 3 ns, 100 Hz), a telescope (30 cm), and a recording system based on strobed multichannel converters and a set of photodiodes was constructed and tested for identification of artificial spreads of oil products.[8] The 380–690 nm range was divided into 16 channels using interfilters with 20–nm spectral half–width. The system sensitivity was estimated at a level of 50 photons. This lidar makes it possible to conduct not only spectral but also kinetic measurements by strobing the 16 receivers. A similar lidar was used to measure a RS signal as a function of the sounding depth.[9] This result is extremely important for developing the methods of sounding using a RS signal as a reference mark.

The N$_2$ and KrF lasers were compared to find an optimal radiation source in lidars.[10] Different mixtures of oil products were sounded from a 43–m distance. In case of the KrF laser the fluorescence was recorded through a telescope to OMA–1 with a UV scintillator, and with the N$_2$ laser it was recorded through a telescope and PM. As the calculations showed the KrF laser could provide for a better signal–to–noise ratio for 150–m sounding altitude with equal energy per pulse.

A similar comparison of three TEA lasers, KrF (λ = 249 nm), XeCl (λ = 308 nm), and N$_2$ was made in Ref. 11. The mean values of energy of these lasers were normalized at a level of 1 mJ, and an analyzer OMA–2 of the firm PARC (USA) with a UV scintillator was used to record the spectra. During remote sounding of five different types of oil the authors found the XeCl laser to be the most efficient from the point of view of reliability and a number of shots per one charge of a gaseous mixture. The minimum detectable thickness of an oil film was 0.01 μm, and a 0.1 μm thick film was readily recorded with a single laser shot.

An interesting development of an oceanographic lidar system was made recently.[12] An excimer laser (λ = 308 nm, 10 MW, 12 ns, 10 Hz) and a dye laser (λ = 450 nm) were used as radiation sources. A recording system was constructed based on a 0.4–m telescope after which a light flux was divided with interfilters into seven high–rate PMs strobed individually. The information processing and the telescope–system rotation were controlled with a microcomputer LSI–11/23. The spectral range was divided into 7 channels of ~10–nm half–width: 344, 366, 380, 450/500, 533, 650, and 685 nm. The channels 344, 366, and 380 nm were chosen

to separate out RS on the background of fluorescence of the dissolved organic matter (DOM). This system was used according to the program MARPOL on artificial spreads from board the ships and, as the authors stated, enabled one to determine the film thickness in the range within 0.1–10 μm and to identify them. It was also noted that simultaneous measurements of films with a radar and UV/IR cameras failed to give any results.

The simultaneous use of spectral and kinetic information formed the basis for developing an onboard lidar.[13] A YAG:Nd^{3+} laser (λ = 355 nm, 4 mJ, 10 Hz) with a shortened laser pulse (~3 ns) served as a radiation source. An external objective was connected with laser and polychromator through a system of light–guides. The spectral range (350–700 nm) was divided into 4 channels of a 10–nm half–width capable to be recorded with high–speed PMs. In kinetic measurements the traps were installed on the light–guides between the PM and the polychromator. The lidar should be preliminary calibrated against films with known absorption coefficients. During the remote diagnostics (up to 30 m) the obtained two–dimensional set of data was compared to the its data bank for 50 spectra and the object was identified in real time.

Thus, the lidar systems based on laser fluorimetry for remote monitoring of oil films on a water surface has been further developed during the past several years. However, a set of problem to be solved for diagnostics of water media is much wider. Of paramount importance is the development of new methods and instrumentation for detection of OA in water thickness since the oil pollutants in the form of OA exist just in water over the longest period of time being the most toxic and so the most detrimental to a water ecological system. At the same time the development of the methods of oil pollution diagnostics in a water volume runs into much more serious problems than the film detection.[15,17]

UNESCO developed a preparational method of detecting oil pollutants (OP) based on extracting OP from water with the help of organic solvents and subsequent determination of OP concentrations in the extracts by the fluorimetric method.[14] During our experiments it was shown[17] that the YAG:Nd^{3+} laser (λ = 266 nm) used in the UNESCO method for exciting the radiation fluorescence enables one not only to increase the method sensitivity by one order of magnitude (up to the level of 1 μg/l) which is much lower than the maximum permissible concentration (50 μg/l) but also to make crude identification of OP.

However, the use of UV lasers for remote diagnostics of OA in the water column faces some problems. First, a foam on the water surface consisting of surface–active organic matters creates an intense fluorescence background and practically fully scatters the laser radiation. Second, when there is no foam, the strong absorption by surface water (of the order of 1 m^{-1} for sea water) mainly due to DOM does not allow one to measure deep water layers in the UV spectral range.

One of the ways out of this situation is to develop a laser analyzer with a flowing cell. Such an analyzer was constructed and used in the 13th mission of the "Professor Shtokman" research ship for continuous 24–hour monitoring of DOM fluorescence distribution along the 1800–mile run of the ship in different areas of the World Ocean.[16]

A light–guide cable towed behind the ship or imbedded at the stations can be used more efficiently, in our opinion, to determine spatiotemporal OA distribution in the water layer during the monitoring. Our industry now produces special light–guides of ~0.5 mm diameter with weak damping (less than 10 dB/km) up to 250–nm

wavelengths. Such light–guides, with branch pipes at different depths, would enable one to study stratification of natural water over almost the entire photic zone. The radiation of the onboard laser is directed into the light–guide and excites a water microvolume (~0.05 ml) at some depth. A return signal is detected with the onboard receiving optical system through the crossed backward light–guide.

These systems have considerable promise for monitoring OA in natural waters due to their small size and adaptability, and they may be constructed in the near future. A multipurpose laser spectrometer is described below not only as an independent tool for diagnostics of water media but also as a part of such a system.

MULTIPURPOSE COMPACT SPECTROMETER

When constructing a laser spectrometer we meant this sufficiently costly device to be multipurpose, i.e., to be able to determine as wide set of OA as possible in different forms of their existence in natural water at different regimes of monitoring.

The information collected by our laboratory during more than 20 marine expeditions makes it possible to formulate the principal requirements to this analyzer:

1. Availability of highly reliable small–size laser source with a set of frequencies in the UV and visible spectral ranges;

2. Recording system must provide:

a) spectral range of record no less than 250–800 nm;

b) sensitivity at a level of photon units;

c) dynamic range no less than 10^3 ;

d) possible strobing of pulses of no longer than 1 ns.

While the native YAG:Nd^{3+} lasers with frequency multipliers meets the requirements for a laser source (pulse duration must be somewhat shortened), the optical multichannel analyzer OMA–4 of the firm PARC (USA) joined with a stric–camera of the firm Hamamatsu (Japan) is now the only which meets the requirements for a recording system.

Nevertheless, on the order of the stock company "Ecological Systems", we have constructed a native small–size spectrometer with specifications close to the abovementioned: sensitivity is at the level of 10 photons, however the signal–to–noise ratio is by an order of magnitude lower than that of OMA–1; the dynamic range is 250 but it can be widened to 10^3 after some modernization; and the minimum duration of the strobe is ~ 50 ns.

The spectrometer is provided with algorithms and computational programs for determining concentrations of the most important organic admixtures in natural water: natural DOM, oil pollutants, some dyes, and proteins. The background of experience of our laboratory[15] enables us to supplement the methodical support of the spectrometer with algorithms and programs for determining some more parameters; chlorophyll "a" entering into the content of phytoplancton cells; temperature and salinity of water; partial concentrations of solid and liquid phases in heterophase water systems (ice, snow); a content of liquid technological media used in microelectronics (the Karo mixture, especially pure water, et al.); concentrations of weighted particles; and thickness of an oil film on a water surface.

The accomplishment of the aforementioned functions is based on measurements of intensities of the chosen spectral components in an optical response of the object to the laser excitation. All algorithms for extracting information about the object parameters are based on the method of an internal reference mark which provides for high accuracy of obtaining the data and standards for their measurements.[1]

The spectrometer operates in two modes:

– the mode of analyzing the samples placed into the cell or pumped through the cell with a peristaltic pump;

– the mode of remote sounding from the distance up to 50 m (the lidar mode).

The design of the instrument makes it possible to rearrange it for transforming from one mode to the other during some minutes.

The spectrometer consists of:

1. YAG:Nd^{3+} laser (10 ns, 5 Hz) with frequency multipliers: 532 nm (20 mJ); 355 nm (10 mJ); and 266 nm (5 mJ). An operating wavelength is established by changing the filters in the laser emitter. The weight of the emitter with a supply unit and a cooling unit does not exceed 7 kg. Its overall dimensions are 500×400×150 mm^3.

2. Spectrum analyzer MAS–22UF (512 channels, target of 0.5×12.5 mm^2), which is supplemented with an interface for coupling with the IBM–compatible computer and corresponding mathematical software for information exchange.

A built–up construction and small dimensions of the spectrometer facilitate its transportation and installation on an operating table of arbitrary size and configuration.

This spectrometer with a water–flow cell and a YAG:Nd^{3+} laser ($\lambda = 266$ nm) was used for diagnostics of OA during the "Il'ya Repin" ship expedition along Volga river in June–July 1993. The water from the river was pumped through a quartz cell using a peristaltic pump in a special hose dropped into a metallic tube which was fixed onboard the ship. Such a scheme provides for required frequency of water pattern sampling.

The spectrum was recorded with the analyzer MAS–22UF through a quartz capacitor and a polychromator. The obtained spectra were represented on the monitor display and, if required, were recorded onto a flexible disk both in an Apple–II and IBM formats. The time of spectrum record did not exceed 30 s.

The spectrum of a water return signal in the region of Ples is depicted in the Fig. 1. The programmed processing of the spectrum gives the fluorescence parameter $\Phi = A_{fl}/A_{RS}$, where A_{fl} and A_{RS} are the intensities in maxima of the bands of fluorescence and Raman scattering (RS), respectively. The transition is performed from the value Φ to a "nonsaturated" fluorescence parameter Φ_0 which is linearly related to concentration of an admixture under study.

The *in situ* tests made during this expedition enabled us to determine the difficulties which appear during the sounding of river waters.

First and foremost large concentrations of DOM account for a very intense wide band of fluorescence with maximum at 425 nm which slowly decays in the water RS range ($\lambda = 290$ nm) and creates a powerful background thus making the determination of oil pollutants concentration difficult.

I_{fl}, rel. units
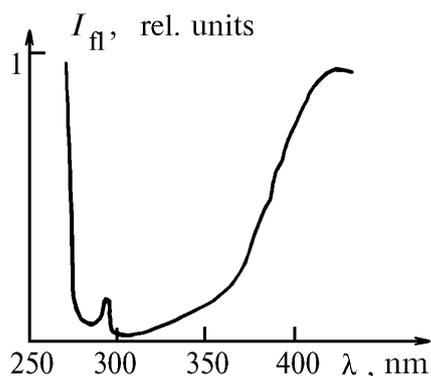
FIG. 1. *The intensity spectrum (I_{fl}) of the return signal of water of Volga river near Ples during excitation by* 266 nm *radiation.*

The constructive and software drawbacks of the MAS–22UF instrument which hinder realization of the spectrometer potentials have been found:

a) a poor ratio between the MAS–22UF target size and the dispersion region of the used small–size polychromator operating in high orders of diffraction;

b) the software did not involve the mode of spectrum overintegration, i.e., storage of the spectrum was terminated automatically when the signal reached maximum in any of 512 channels. This did not allow us to separate out a weak fluorescence signal of oil pollutants in the 320 nm range in the presence of intense lines of Mie scattering and DOM fluorescence.

TABLE I. *Measurement results of the total organic carbon (C_{org}, mg/l) and fluorescence parameter Φ_0 (reflecting DOM content) during the expedition of the "Il'ya Repin" ship (June–July 1993).*

N	Date	Time	Distance from Moscow, km	Orienteer	C_{org} (mg/l)	Φ_0	$\alpha = C_{org}/\Phi_0$
1	30.06	19.15	555	Kostroma	13.0	24.3	0.53
2	30.06	21.40		Ples	10.4	18.1	0,57
3	1.07	8.00	806	Gorodets	13.7 (12.5*)	—	—
4	1.07	10.40		Balakhna	12.1	21.5	0.56
5	2.07	19.15	861	Nizhny Novgorod	14.6	29.6	0.49
6	2.07	23.40		Lock	—	63.5	—
7	3.07	17.00	614	Ples	—	16.3	—
8	3.07	21.15	614	Ples	13.4	20.7	0.64
9	3.07	22.15	—	Ples	13.8 (13.7**)	29.8	0.46
10	4.07	18.40	—	Yaroslavl	14.9	17.6	0.84
11	4.07	19.50	—	Podosenovo	18.3	17.1	1.07
12	5.07	18.30	190	Novookatovo	17.1	31.0	0.55
13	6.07	10.30	233	Tver	14.5	—	—
14	6.07	18.15	—	Tver	13.9	18.6	0.74
15	30.06	(water sample from the ship water pipe)			10.6	—	—

* Measurement of the sample N 3 one day later (without conservation).

** Repeated measurement of the sample N 9.

At a later time, after the expedition, the polychromator was substituted with a specially designed monochromator MUM–1 with a concave Rowland grating (300 grooves/mm) and the software was further improved.

Nevertheless, the values of the Φ_0 parameter for DOM listed in the table were obtained during the measurements in different water areas of Volga river. The values C_{org} measured using the Lyutsarev carbon analyzer are given here as well, the water for determining C_{org} being sampled from the hose of the spectrometer water–flow cell.

As follows from the table, the values of the coupling coefficient $\alpha = C_{org}/\Phi_0$ were close to each other. This makes it possible to expect a sufficiently large value of coefficient of correlation for a data array provided for statistics. It should be noted that the problem on correlation between C_{org} and DOM fluorescence is still far from understanding and calls for integrated investigations.[17]

For these reasons a direct diagnostics of OP in water had failed. Therefore, the water samples taken near Nizhny Novgorod and Yaroslavl were extracted with pure hexane for subsequent measurements by the developed scheme.[15] However when extracting the water samples with hexane in the dividing funnel at the interface there formed a steady foam which did not disappear during two days. This testified to very high concentrations of surface–active substances (detergents) in water. Taking into account this fact the parameter Φ_0 was not measured in hexane extracts because of impossibility to determine correctly the volume ratio between an initial sample and an extract.

Thus the laser diagnostics of OA in water such as that of Volga river (with its disastrous ecological state), in contrast to marine waters, has its specific properties determined by large concentration of a complex mixture of different OA of domestic sewages. However, this is beyond question that with further instrumentational and methodological development, which we have started, these difficulties will be resolved, and the described laser spectrometer will be used in diagnostics not only of marine but also river water.

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