

ECOLOGICAL MONITORING IN THE CASPIAN SEA (MOUTH ZONE OF THE RIVER VOLGA) WITH A SHIPBOARD LASER SPECTROMETER

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ABSTRACT

Some peculiarities and results of ecological monitoring of the Caspian Sea coastal zone and the mouth zone of the river Volga are discussed. A shipboard laser spectrometer, elaborated by the authors, was included in the measuring complex of the new ecological patrol vessel *Russia* belonging to the Foreign Economic Association *Zarubezhgeologia* of the Ministry of Natural Resources of the Russian Federation. Emission spectra with laser excitation at 532 and 266 nm were registered both in motion of the ship and at stations, containing the Mie scattering line, the Raman scattering (RS) band from water, the fluorescence bands of dissolved organic matter (DOM), oil pollution (OP) and phytoplankton. For this specific aquatic region special attention was given to the determination of OP concentrations from the spectra. It is shown that the direct fluorescence method allows the OP concentration to be determined without sample preparation in all types of water down to 10 µg/l using a new water-soluble standard. A very high variability of the intensity of the above-mentioned spectral bands was detected in the investigated area. The results demonstrate the practical application of the methods and tools of laser spectroscopy to the ecological monitoring of aquatic systems with complex structures and dynamics.

Keywords: laser monitoring, fluorescence, oil, Caspian Sea.

INTRODUCTION

Since 1972, possibilities of laser monitoring of sea and inland water were demonstrated in many publications (see bibliography in (1)), in particular, in papers of our group (2,3,4,5,6,7,8,9). Now, it is necessary to pass from demonstration of possibilities to practical use of laser methods and means in real ecological projects. Our paper presents such practical work, which was carried out within the ecological monitoring project of the Caspian Sea coastal zone.

At present strong emphasis is placed on the investigation of the Caspian Sea region. The Caspian Sea is a unique marine basin with rich mineral and biological resources. This region has excellent perspectives to further intensive industrial development. Ecological monitoring of the Caspian Sea coastal zone and mouth zone of the river Volga (10) is one of the most important scientific problems. There are significant spatial and temporal variations of the ecological situation for this zone. The region is characterized by strong heterogeneous spreading of admixtures of anthropogenic (for example, oil pollution OP) and natural origin (dissolved organic matter DOM, phytoplankton, suspended matter) (10). Therefore, for this region it is especially important to use express methods and means of monitoring. The methods and tools of laser spectroscopy belong to them. In connection with the specific character of the Caspian Sea as a region of intensive oil output and at the same time as a unique region of valuable fish species location, effective methods and tools of oil pollution monitoring have special significance. This is not restricted to oil films on the water surface, but includes the emulsified-dissolved form of oil in the water volume as well. This OP fraction is the main threat for the ecological situation because of its high toxicity and long residence time in the water column. For the Russian fish industry the maximum permissible OP concentrations were determined to be 50 µg/l. At present, there are no alternatives to fluorescent methods with lamp and laser excitation for *in situ* and remote monitoring of OP at these concentrations. The choice between lamp and laser spectrometers depends on concrete tasks and conditions of monitoring.

In 2002 an ecological expedition was carried out in the Caspian Sea coastal zone and mouth zone of the river Volga with the new ecological patrol vessel *Russia*, which belongs to Foreign Economic Association *Zarubezhgeologia* of the Ministry of Natural Resources of the Russian Federation. A laser spectrometer was elaborated and mounted aboard of the ship. Equipped with a flow-through cuvette, the instrument could be used for a direct analysis without sample preparation. The applicability of direct fluorescence measurements, and of measurements on sample extracts for determination of OP concentrations in emulsified-dissolved form in different types of water was investigated. Both from the ship in motion and at stations, 850 spectra with laser excitation at 266 and 532 nm were obtained and processed. The data reveal the structure of spreading of organic admixtures in the subsurface water layer. This structure is of great interest to ecological services.

METHODS

In our work, the method of laser fluorometry, using the water Raman scattering signal as the intrinsic standard, is the basic method for determining different organic admixtures in natural water (2,3,4,5,6,7,8,9,11,12,13). This method has also been applied for the determination of fluorescent admixtures in other types of organic solvents (for example, hexane) which show Raman scattering (3,12).

A portable laser spectrometer was elaborated to apply this method for water area monitoring with the ship underway. The water analysis is carried out with a special quartz flow-through cuvette with laser excitation wavelengths at 266 nm (for diagnostics of DOM, oil pollutants, suspended organic matter) and 532 nm (for diagnostics of phytoplankton and suspended organic matter). A multi-channel optical spectral analyser, interfaced with a notebook, is used to detect emission spectra from the samples.

Typical spectra from water with laser excitation wavelengths at 266 (A) and 532 nm (B) are shown in Figure 1. Their spectral bands and lines are the following: a) lines of elastic scattering (the intensity depends on suspended matter); b) the bands of water Raman scattering, which are used as intrinsic standards (11,12,13); c) the DOM fluorescence band (this band may be overlapped by the OP fluorescence band); d) the fluorescence band of light oil fractions and protein-like compounds in the spectral region between 300 and 360 nm (with 266 nm excitation); e) the fluorescence band of chlorophyll *a* of phytoplankton with its maximum at 685 nm (fluorescence spectra of blue-green algae show another band with a maximum at 600...650 nm, which is caused by phycobilin pigments).

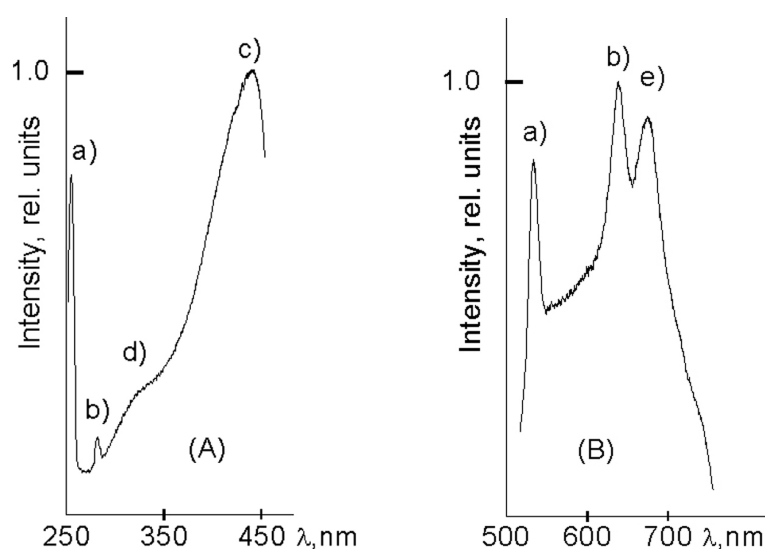


Figure 1. Typical emission spectra of water under laser excitation wavelengths at 266 nm (A) and 532 nm (B). An explanation of the spectral bands (a)...(e) is given in the text. The spectra shown here and in the other figures are not corrected for the spectral sensitivity of the spectrometer.

The following normalised fluorescent parameters are used as quantitative characteristics for estimating admixtures concentrations in the water: $\Phi_o^{DOM} = N_{FL}^{DOM} / N_{RS}$; $\Phi_o^{OP} = N_{FL}^{OP} / N_{RS}$ and $\Phi_o^{PP} = N_{FL}^{PP} / N_{RS}$, where N_{FL}^{DOM} , N_{FL}^{OP} and N_{FL}^{PP} are the photon numbers of DOM, oil pollution and phytoplankton fluorescence, correspondingly, N_{RS} is the photon number in the spectral band of Raman scattering. The subscript o denotes the absence of fluorescence saturation (2).

The possibilities of standardization of these parameters, as measures of the content of organic admixtures in water, are discussed in (11). However, the settlement of this problem remains a matter of the future. At present, the main task is to transform these parameters to concentrations ($\mu\text{g/l}$) of admixtures. This problem should be solved with standards, which can be used without extensive sample treatment and well approximate the fluorescence of admixtures. Until recently there were no such standards available. Therefore, long procedures of calibration are carried out: for DOM by DOM oxidation (14), for phytoplankton chlorophyll a by sample filtration and acetone extraction of pigments (15), for OP by hexane extraction (16). These procedures are not the universal methods: the obtained coefficients of relations between Φ_o and concentrations depend on the peculiarities of the water under investigation.

In this work, we applied an express calibration method (now only for determination of Φ_o^{OP}), which uses a new water-soluble standard. Let us consider the direct method of OP analysis in water using this calibration. Figure 2 shows spectra with 266 nm excitation from water samples without OP (B) and with comparatively high concentrations of OP (A). When the spectrum is normalized to the maximum of the fluorescence band, deformations of the DOM spectrum can be distinctly seen in the spectral region of 300...400 nm, if $C^{OP} > 10 \mu\text{g/l}$. As is known, fluorescence in this spectral region is produced by polyaromatic hydrocarbons with two and three benzene rings, which are compounds of light oil products such as diesel fuel or some refined oils. The application of differential spectra method allows the spectral components of oil products to be obtained and to be normalized to Raman scattering (if $C^{OP} > 10 \mu\text{g/l}$). The minimum threshold of OP determination in this case is determined by the spectral noise value of the background band of DOM. In case of very low concentrations of OP ($C^{OP} < 10 \mu\text{g/l}$), when the differential spectra method does work properly, one can apply the artificial neural networks technique (9).

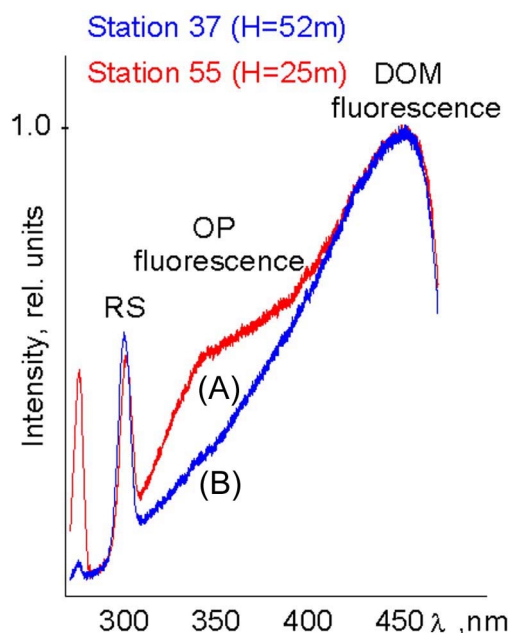


Figure 2. Spectra of water with very low concentration of OP (B) and with high ($\sim 200 \mu\text{g/l}$) concentration of OP (A) with 266 nm laser excitation (cruise of R/V Russia, Aug-Sept 2002). H is the sampling depth.

To convert the parameter Φ_o to OP concentration, it is necessary to use a standard. In this work we used the state OP standard (passport 7117-94) as a water-soluble standard.

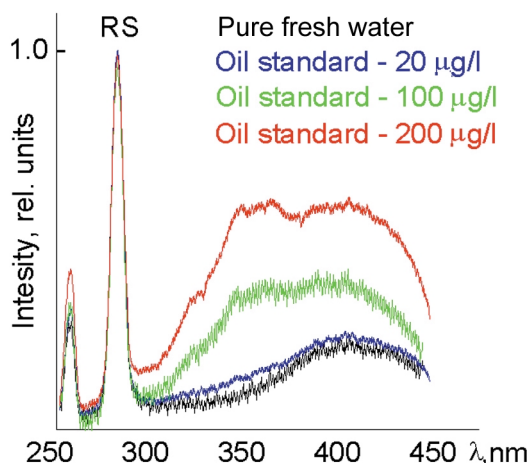


Figure 3. Spectra of different concentrations of oil standard solutions (passport 7117-94) in pure fresh water. Laser excitation wavelength is 266 nm.

Spectra of different concentrations of standard (passport 7117-94), dissolved in pure fresh water, are shown in Figure 3. This special standard was elaborated by the Moscow A. A. Bochvar Institute of Non-organic Materials for determining OP in natural water for purpose of arbitration. This standard uses turbine oil (TP-22) as a representative of OP in natural water. The standard sample is a tablet, soldered in a glass ampoule. Tablets with different concentrations of OP are dissolved in definite volumes of water. The relative error of the certified value does not exceed 0.8% with a probability of 0.95.

It was tried to carry out an intercalibration of the direct method and the method of extraction. A modified variant (3) of the UNESCO method (16) was used, recommended to determine OP in seawater. In this method the oil product is extracted from seawater by an organic solvent (hexane) and then the fluorescence of the oil product in hexane is related to the fluorescence of a standard dye (chrysene for example) (16). As shown in (3), using the fourth harmonic of the Nd:YAG laser at 266 nm increases the sensitivity of the OP determination in hexane extracts. In our experiments the threshold of sensitivity was 0.1 $\mu\text{g/l}$ for light OP in hexane solution (see Figure 4).

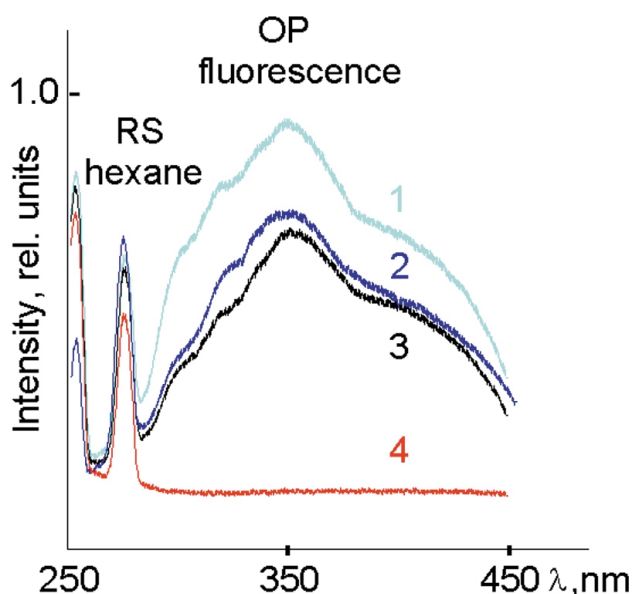


Figure 4. Spectra of hexane OP solution under laser excitation at 266 nm (cruise of R/V Russia, Aug-Sept 2001): 1: hexane extract of water escapes of vessel "Russia"; 2: hexane solution of diesel oil MC16B2 (2 $\mu\text{g/l}$) of tugboat OTR-715; 3: hexane solution of diesel oil BP-HV32 (1 $\mu\text{g/l}$) from the engine of the vessel "Russia"; 4: pure hexane.

RESULTS

The spectra of suspended matter, DOM with OP, phytoplankton under laser excitation at 266 and 532 nm wavelength are shown in Figures 2 and 5-7. There are shown spectra for water samples with minimum and maximum values of parameters Φ_o^{SUSP} , Φ_o^{DOM} , Φ_o^{OP} and Φ_o^{PP} , measured in the region of monitoring. This region includes the part of river Volga from Astrakhan to the mouth zone and the Northern part of the Caspian Sea to latitude 43°20'N. In this water area the salinity is less than 4 (10). In each figure we accentuated one of the peculiarities of the spectra: In Figure 5 one can see the variability of the elastic scattering band intensity; in Figure 6 the variability of DOM fluorescence; in Figure 7 the variability of phytoplankton fluorescence; in Figure 2 the variability of the OP fluorescence.

Using the direct method with the water-soluble standard we determined that in the investigated region the OP concentration variability range was from 10 $\mu\text{g/l}$ (the threshold for our direct method) to 200 $\mu\text{g/l}$.

We investigated the applicability of the UNESCO hexane method of measuring the OP concentrations for the area of monitoring. We concluded that the UNESCO method is not applicable to river water. Extraction of OP from river water by hexane does not show the border between water and hexane (to obtain heterogeneous phases) distinctly enough because of bubbles and a considerable amount of organic mucilage, even settling of the extracts during a month.

In the expedition, we obtained 850 spectra similar to the spectra shown in Figures 2, 5-7. On the basis of these data we made maps of the parameter F_o spatial distributions. The distributions represent the spatial structure of suspended matter, DOM, phytoplankton, OP in surface layer of water, and also vertical profiles of these characteristics at stations. Steady survey at ship motion provided high resolution and revealed a fine spatial structure of fields. The survey was carried out during four cruises from 28 August to 17 September 2002. We discovered evident changes of the field structure from one cruise to another. Thus, laser methods provide a new level of ecological monitoring for the northern part of the Caspian Sea and the mouth zone of the river Volga with their complicated spatial structure and fast variability of fields. The discussion of ecological conclusions to be drawn from the obtained data is a matter of ecological service in this region and exceeds the frame of this publication.

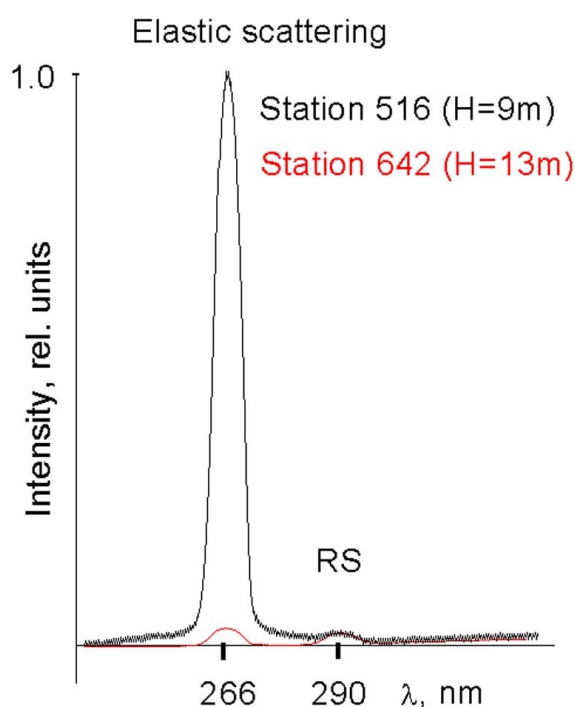


Figure 5: Spectra of water samples with different contents of suspended matter, cruise of R/V Russia, Aug-Sept 2002. Laser excitation wavelength is 266 nm here and in Figures 6 and 7.

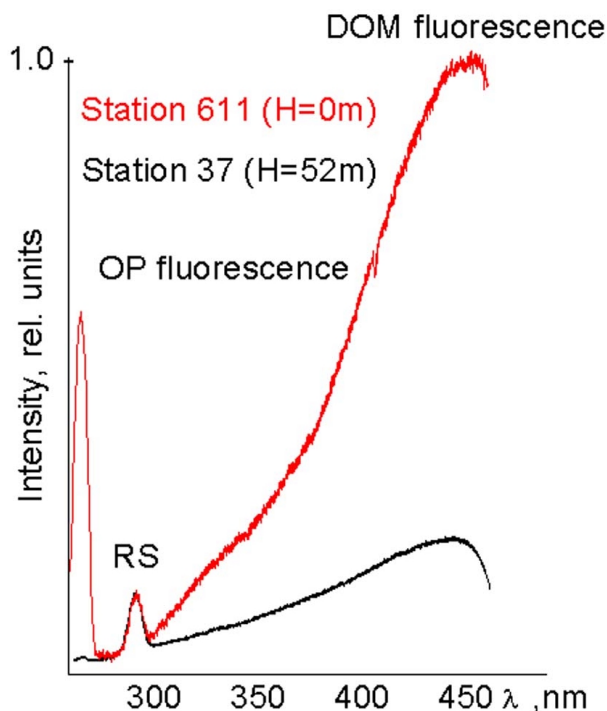


Figure 6: Spectra of water samples with different contents of DOM, cruise of R/V Russia, Aug-Sept 2002.

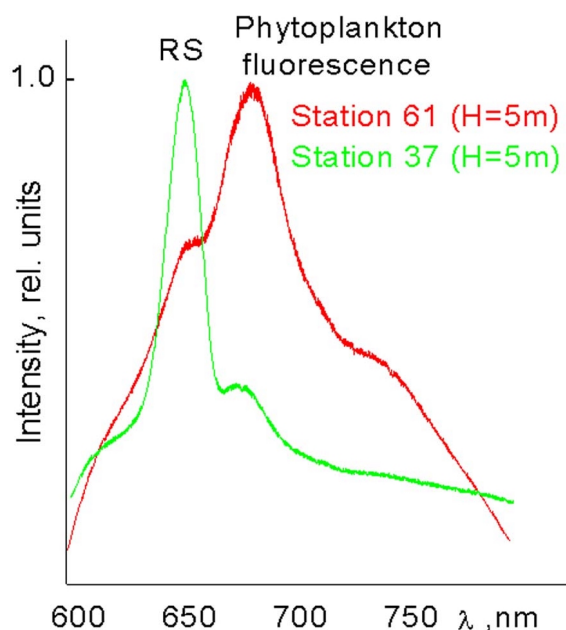


Figure 7. Spectra of water samples with different contents of phytoplankton, cruise of R/V Russia, Aug-Sept 2002.

CONCLUSION

The obtained results show benefits of methods and apparatus of fluorescence spectroscopy of natural water. Perspectives of their application are demonstrated in projects of ecological monitoring, in particular, of oil pollution monitoring. The project of ecological monitoring of the Caspian Sea coastal zone and the mouth zone of the river Volga ranges among the most important of such projects. This region has specific hydrological, hydrochemical, and hydrobiological features that determine strict demands for monitoring technology. The results of the work show an agreement of the permanent laser monitoring from the ship in motion with these demands.

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