SPECIFIC FEATURES OF THE FLUORESCENCE SPECTRA OF OIL PRODUCTS

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Crude oil and oil products (OP) are most widely spread among organic pollutants of water. Development of the fluorescence–based methods for identification and quantitative analysis of oil and OP including remote laser sounding techniques, needs for knowledge of their luminescence spectra for the cases of surface films and water mixtures as well as distinctions from such spectra of dissolved organic matter of natural origin. We investigated some features of fluorescence of oil and OP both in films (from 1 *to* 100 μm *thick) and in the bulk of water to reveal their distinctions from fluorescence spectra of dissolved organic matter (DOM).*

1. INTRODUCTION

Crude oil and OP are most widely spread organic pollutants of water. OP find their way into seas and oceans as a result of effluent of unrefined industrial waters, wrecks of tankers, losses of crude oil at oil productive shelf zones and from sea transport. The annual ingress of oil and OP into seas and oceans reaches 10 million tons, what approximately equals to the total amount of hydrocarbons that are formed as a result of natural decomposition of vegetable and animal remainders.[1]

Having got on the water surface oil spreads very rapidly into a thin film. A typical thickness of an oil film on the ocean surface is estimated at 20 μm two hours after spilling oil.[2] Some oil components (light fractions) fairly quickly evaporate, others come into water (so called dissolved–emulsified fraction). Physico–chemical and biological utilization of OP proceeds rather slowly. Under favorable conditions only 50% oil spilled is decomposed during the first week. The process of utilization is strongly retarded at temperatures below 10°C, so, for example, in Arctic waters the oil can remain in the initial form for decades.

Development of the fluorescence methods for identification and quantitative analysis of oil and OP (including remote laser sounding techniques) needs for knowledge of the spectral–luminiscence characteristics of oils both in the bulk of water and in form of oil films and their distinctions from such spectra of dissolved organic matter (DOM) of natural origin.[3]

We have investigated some features of fluorescence of oils and OP in films and in water to reveal their difference from spectra of DOM fluorescence in water in order to provide quantitative analysis of oil pollution with relevant information.

Difficulties in the interpretation of experimental results on oil fluorescence are in the fact that crude oils is a complicated mixture of hydrocarbons, oxygenous, nitrous, and other compounds. Different oils are composed of different components, so getting into the water they form various fractions. To construct a model of oil fluorescence vast experimental material is needed.

We think that our experimental results may be used for constructing a model of physico–chemical transformations that occur at OP penetration from film into water.

2. EXPERIMENT

The aim of the experiments was studying the spectra of fluorescence emission and excitation in thin films (from 1 to 10 μm). An oil film was imitated by a layer of OP of known thickness between two quartz plates. We investigated several types of OP, i.e., gasoline, diesel fuel, samples of Saratov, Georgian, Shaim, and Libyan oils as well as their water fractions and samples of DOM in water. Absorption spectra were measured with a "Specord M40" spectrophotometer and fluorescence spectra were recorded with a "Jobin Yvon 3CS" device with a xenon lamp as a source of an exciting radiation. A spectrofluorometer provided a correction of the fluorescence spectra for the intensity of exciting radiation and sensitivity of a photomultiplier. Wavelengths of exciting radiation chosen for making experiments on studying emission spectra of fluorescence were 222, 248, 266, 308, 337, 400, and 532 nm, i.e., close to laser wavelengths.

3. BEHAVIOR OF THE ELECTRON SPECTRA IN DEPENDING ON THE OIL FILM THICKNESS

Figure 1 shows absorption spectra of OP. As is seen from the figure only a gasoline sample has a distinct maximum in the absorption spectrum (solid curve). This sample can be referred to the category of "the weakly absorbing" samples (the thickness of the cell for gasoline was 100 μm) while the rest of the absorption spectra were recorded with the cell of 1 μm thickness. Figure 1 shows also the absorption spectrum of DOM in natural water (water from Moskva–river with high content of organic substances, a hundred times diluted with distilled water) obtained in a 3 cm thick cell (dashed–dotted curve in Fig. 1).

Investigation of the fluorescence spectra of OP and their behaviors depending on the thickness of a sampling cell allowed us to divide all the OP studied into two groups.

For gasoline and diesel fuel excited with a short–wave radiation the maxima of the emission spectra $l_{\text{fl}}^{\text{max}}$ are in the UV region (290 and 355 nm, respectively) and do not depend on a cell thickness (Fig. 2).

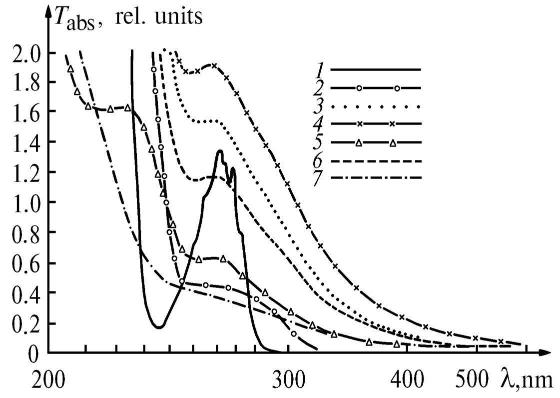

FIG. 1. The absorption spectra of oil products: gasoline (1), diesel fuel (2), Saratov oil (3), Georgian oil (4), Shaimskaya oil (5), and Libyan oil (6).

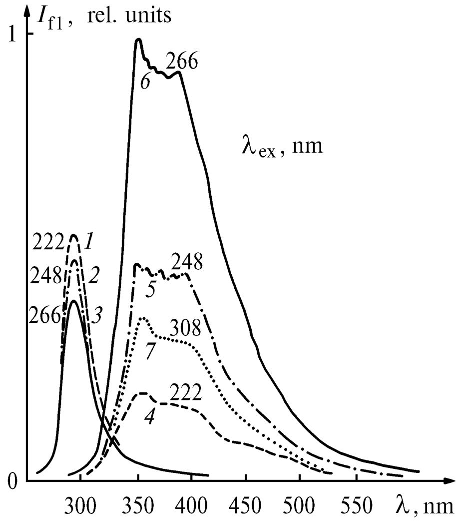

FIG. 2. The spectra of fluorescence of gasoline (curves 1–3, the cell thickness is 10 μm*) and diesel fuel (curves 4–7, the cell thickness is* 1 μm*) at different wavelengths of excitation.*

For samples of crude oils with all possible wavelengths of excitation the maxima of the emission spectra of the fluorescence are in the visible region and its position depends on the cell thickness. Thus at an increase of the cell thickness from 1 to 100 μm the maximum shifts to the long waves by 10–40 nm depending on the oil type.

Such a behavior of the spectra of crude oils is obviously explained by the effect of multiple reabsorption of the fluorescence emission.[4] For wide structureless bands of the fluorescence the difference of the absorption coefficient within the fluorescence profile leads to the redistribution of intensities within the spectrum and therefore to a long–wave shift of the maximum in the fluorescence emission spectrum.

The dependence of the position of the fluorescence maximum on the thickness of an oil film does not allow this spectral feature to be used for identifying the type of a crude oil, since the spread in values $l_{\rm fl}^{\rm max}$ for different oils is overlapped by variations of this feature depending on the film thickness. Figure 3 shows the fluorescence spectra of Libyan and Saratov oils. The spectra of fluorescence excitation as well as of the absorption ones for all the OPs, except for gasoline, are structureless bands with a monotonic fall off of the intensity toward the long wavelengths. Variation of a cell thickness does not lead to a marked change in the spectra shapes.

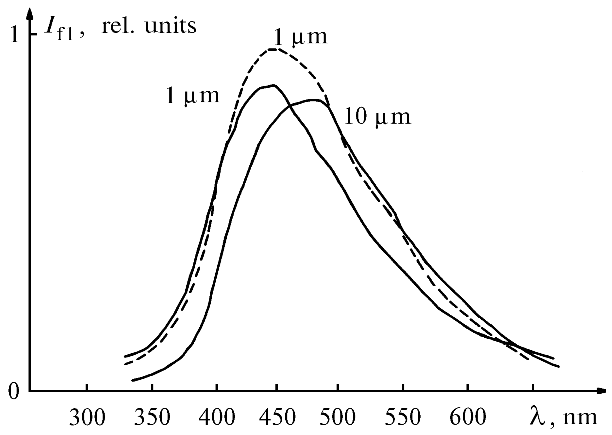

FIG. 3. The fluorescence spectra of the Libyan oil (solid curve, the cell thickness is 1 *and* 10 μm*) and Saratov oil (dashed curve, the cell thickness is* 1 μm*).* $\lambda_{\rm ex}$ = 308 nm.

Note that in the case of 1 μm thick cell (an optically thin layer) no effect of the fluorescence reabsorption occurs and the variation of the quantum efficiency of the fluorescence for different samples of crude oils ($\lambda_{\rm ex}$ = 266 nm) can reach 60 times whereas the variations of the absorption coefficient do not exceed 3 times.

4. SPECTRA OF FLUORESCENCE EXCITED BY RADIATION OF DIFFERENT WAVELENGTHS

As known oils are a complex of organic molecules with different structures and therefore one could expect that the excitation of the fluorescence by radiation of different wavelengths would yield strongly different fluorescence emission spectra. However, our researches showed that for any fixed thickness of a cell, for all the samples of OP the position of the maximum and the shape of the fluorescence spectrum are independent of $\lambda_{\rm ex}$. Earlier (see Ref. 5) the independence of the position of the maximum of the fluorescence band on $\lambda_{\rm ex}$ was observed for 5 samples of crude oil when changing the wavelength of excitation from 249 to 420 nm. It should be noted that the fluorescence spectra of crude oils studied in Ref. 5 had a distinct spectral structure consisting of 3 bands. We explain this structure in the fluorescence spectra[5] by the fact that the authors investigated not the crude oils themselves but their solutions in benzene. As a matter of fact OPs, in many organic solvents, have fluorescence spectra with a distinct structure when excited by short–wave radiation. Such structures are used for OP identification by means of contact luminescence methods.[6]

At the same time the comparison of the luminescence spectral features of the OP samples in water (a dissolved–emulsified fraction) and oil films showed their essential difference. The change of OP films for OP in water is followed not only by the change of the fluorescence intensity, number of maxima and their spectral position, but also by the change of the maxima behavior depending on the wavelength of exciting radiation. The fluorescence spectra (the number of bands in spectrum, their intensities and position) strongly depend on λ_{ex}. Figure 4 shows the fluorescence spectra of a sample of a crude oil in the form of a 1 μm thick film (solid line) and in water (dashed line) excited by radiation at the wavelengths 266 and 337 nm.

Figure 4 also shows the fluorescence spectrum of DOM in water (dashed curve). An interesting behavior of the fluorescence spectra of DOM is observed depending on the excitation wavelength. The shape of the band and the position of the maximum remain constant to some wavelength (approximately to 330 nm) but at further wavelength increase the band is shifted to the long waves, its width remains constant and difference between λ_{ex} and $1_{\text{fl}}^{\text{max}}$ keeps constant no less than 80 nm. Such a behavior is rather unusual for molecules of organic compounds and is not explained as yet. A model conception of the character of the fluorescence band of DOM can be found in Refs. 7–9.

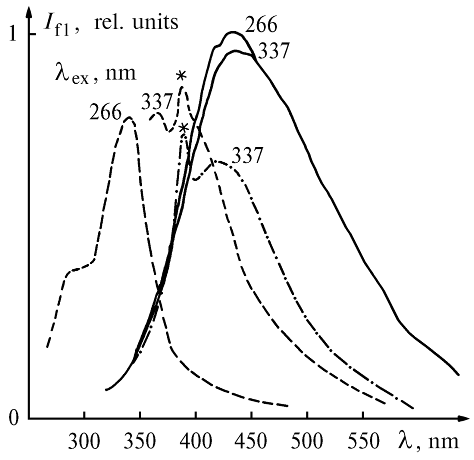

FIG. 4. The fluorescence spectra of Libyan oil. The line of the Raman scattering at λ_{ex} = 337 nm *is marked by asterisk.*

5. PROBLEM OF IDENTIFICATION OF THE OIL POLLUTION

Identification of oil pollution on the water surface may be both an independent task, for example, for trial, and as a part of the problem of quantitative diagnostics. To estimate the thickness of an oil film it is necessary to know spectroscopic parameters of OPs. For estimating the thickness of a film by the fluorescence method[10] there is a formula $d = -1/(k_e + k_f)\ln(F/F_0)$, where k_e and k_f are the attenuation coefficients of light by a film at the wavelength of excitation and at the wavelength of fluorescence, F and F_0 are the intensities of the fluorescence of a d thick film and of an optically thick layer of OP. In order to estimate the thickness of an oil film it is necessary to know the values k_e, k_f, and F_0.

Note that identification of OP is not the determination of individual chemical compounds of a given oil, but a comparison of "fingerprints" observed in the spectrum of oil spilled with the supposed ones.

There is a number of contact spectral–luminescent methods[6] for identification of oil pollution: spectroscopy of excitation and emission at room and low temperatures, synchronous spectroscopy, spectroscopy of derivatives, TLS–diagrams (total luminescence spectra), etc. These techniques are applied to the OP samples that are dissolved in certain proportion by organic solvents and then the obtained results are compared with the spectra of standard samples.

The following spectroscopic characteristics are recommended in the literature to be used for remote identification of oil:

– position and shape of the emission and excitation bands of fluorescence and the TLS–diagrams;[11]

– kinetic of the fluorescence decay;[12]

– "conversion efficiency" – the ratio of the intensity of fluorescence of an optically thick layer of OP to the intensity of exciting radiation;[13]

– the lines of Raman scattering of OP (see Ref. 14).

The first three characteristics strongly depend on the thickness of an oil film and therefore their use for films is too problematic. The lines of Raman scattering of OP can very exactly define its individuality but in application of this method to crude oils and heavy OPs it is hardly possible to resolve Raman lines of OP against the background of wide and intense band of fluorescence. Our research showed that the spectra of emission and excitation of the fluorescence can be used only for rough classification of oil pollutions rather than their identification.

6. SEPARATING THE FLUORESCENCE SPECTRA OF OP IN FILM AND IN WATER

Such characteristics of OP fluorescence as the intensity and position of the bands are essentially different when OP is in film and in water. In the remote fluorescence methods of the pollution it is believed that the fluorescence intensity at a specific wavelength or the integral over the spectrum can be a measure of quantity of the impurity under study. However, the coupling coefficient between the fluorescence intensity and the quantity of oil pollution will be different for OP in the film and in water. So, to estimate the contents of OP it is necessary to separate the contributions from OP in the film and that from the bulk of water into the fluorescence spectra. Although this problem is very important no results of such studies by other groups were found in the literature. We think that this is caused by a very complicated character of the physicochemical processes occurring in OP when it comes from film to water. The OP fraction in water is called a dissolved–emulsified one in order to emphasize ambiguity of the process of the OP dispersal in water.

Figure 4 shows the emission spectra of OP fluorescence in a film and water. Let us consider their distinctions.

OP films yield a single band of fluorescence, the maximum of which depends on the wavelength of the exciting radiation. For the case of OP in water the number of bands in the spectrum, their intensities and positions of the maxima depend on λ_{ex}, but for all the OP studied in water the fluorescence spectrum for $\lambda_{ex} \leq 308$ nm contains necessarily the band with the maximum at about 340 nm. So, we propose to use the intensity of fluorescence at this wavelength as a quantitative characteristic of OP content in the bulk of water. This band appears to be due to the OP components soluble in water.

7. SPECTRAL SEPARATION OF THE FLUORESCENCE SIGNALS OF NATURAL DISSOLVED ORGANIC MATTER AND OIL PRODUCTS

Analysis of real sea and river waters by methods of fluorescence arises the problem on spectral separation of the fluorescence signals from DOM of natural origin and an OP. There exist contact methods of the separation to which we can refer, for example, the extraction of a sample by an organic solvent (most often hexane) to extract OP with the following recording of the fluorescence of the hexane extracts of OP and the water sample after extraction.[3] In the case of a remote application one has to find another way of separating DOM and OP, for example, the spectral one. In Refs. 15 and 16 OPs were studied directly in water and in the hexane extracts. To separate DOM and OP it was proposed to excite the fluorescence by radiation at 222 and 250 nm. In this case the light and water–soluble fractions of OP have the fluorescence band that lies in the other spectral range as compared to that of DOM. At the same time heavy fractions of OP yield the fluorescence spectrum similar the DOM spectrum. There exists a method[17] of separating the spectra of DOM and OP in water under excitation by two wavelengths: $\lambda_1 = 337$nm and λ_2 that lies within the interval 337–370 nm. The method is based on different spectral relation of the excitation spectra of OP and DOM in this range. However, this method needs for preliminary identification of OP, since different OPs have different spectra of excitation.

As our research showed all the OPs in water have a band with maximum at about 340 nm which can surely be recorded in the presence of DOM in water having the maximum of the band at about 420 nm (see Fig. 4). However, the field tests in water showed that the organic substances of biological origin (amino acids, phenol compounds) yield also the fluorescence band with the maximum at 330–340 nm, whose width and shape are similar to those of the fluorescence band of OP in water.

We propose a different approach to separation the contributions from DOM and OPs. Studies of the excitation spectra of fluorescence showed that near the maximum of the emission spectrum of DOM fluorescence (400 or 425 nm) there is a peak for OP in water in the region of wavelengths from 230 to 260 nm against a background from the wide structureless band. Intensity of this peak may serve as an indicator of the oil pollution in water and a quantitative measure of their content. No such peaks are observed for DOM.

The problem on separating the fluorescence responses of oil films and DOM is much more complicated. For the case of crude oils in the form of a film $l_{\text{fl}}^{\max}$ lies in the region from 420 to 490 nm for any wavelength of the excitating radiation and the spectrum in shape and width is only slightly different from the fluorescence spectra of DOM. The excitation spectra of fluorescence of OP and DOM films are also similar in shapes. So, their separation is not so simple.

8. CONCLUSIONS

The main results of this work are:

1. An increase of the film thickness from 1 to 100 μm, for crude oils, shifts the maximum of the fluorescence spectrum toward long waves because of the fluorescence reabsorption. In the case of the light OPs no such shift is observed in this range of thickness.

2. Separation of the fluorescence signals from OP in a film and in water, OP in water and DOM, and rough classification of OPs are possible based on fluorescence spectra ($\lambda_{\text{ex}} \le 308$ nm). For the case of OP in a film the difference of the fluorescence spectra of excitation and emission from corresponding spectra of DOM is much smaller, so their separation is more problematic.

3. The precise identification of oils in a film for this fluorescence spectra is difficult, for these spectra depend not only on the oil type but also on the film thickness.

4. The spectral characteristics presented in this paper may be used in developing remote methods for measurement of the thickness of oil films on water surface by means of the fluorescence spectroscopy and the spectroscopy of the Raman scattering.

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