

## THE EFFECT OF TEMPERATURE AND ULTRAVIOLET RADIATION ON THE LUMINESCENCE SPECTRUM CHARACTERISTICS OF DISSOLVED ORGANIC SUBSTANCE

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The specific features of the fluorescent response of dissolved organic substance (DOS) in water to optical excitation are examined: reversible and irreversible changes in the fluorescence spectra and in the fluorescence excitation and absorption spectra, induced by ultraviolet radiation and temperature variations. The results obtained are used to develop methods for diagnosing DOS, which is one of the most abundant components of natural media.

Fluorescence spectra of natural dissolved organic substance (DOS) are successfully used in solving such important problems as monitoring of natural aqueous ecosystems and technological aqueous media. The band parameters (intensity and position of the peak, spectrum half-width) are affected by ions of various metals [1], acidity of the medium [2], UV radiation of various continuous sources of light [3, 4], emission of a pulsed nitrogen laser [5], etc. Determination of the true parameters of the DOS fluorescence band and the use of these parameters for solving applied problems, as well as investigation of the nature of this band, cannot be accomplished unless the entire multitude of factors affecting the spectrum are studied in detail. The present paper is concerned with the effect of temperature and UV radiation on the fluorescence spectrum characteristics of DOS.

The temperature dependence of the fluorescence spectra (FS) and fluorescence excitation spectra (FES) was investigated in a thermostated quartz cell by means of a Jobin Yvon 3CS lamp fluorimeter with subsequent computer processing; the absorption spectra were studied on a SPECORD M40 spectrophotometer. The temperature of water samples in the range of 0 to 80°C was maintained with an accuracy of  $\pm 2^\circ\text{C}$ . The fluorescence spectra were recorded using two excitation wavelengths  $\lambda_{\text{exc}}$  of 266 and 337 nm (which correspond to the emission of two UV lasers frequently used in applied studies). The fluorescence excitation spectra were recorded at  $\lambda = 425$  nm and then corrected. It should be noted that in the literature one often encounters uncorrected FES (see, e.g., [6]); these spectra proved to differ strongly from the true ones. The temperature dependence curves of the FS and FES are shown in Fig. 1. Figure 1 demonstrates that as the temperature increases, the intensity in the peak of the FS and FES of the DOS drops from 1 at 20°C to 0.6 at 80°C. Lowering of the temperature from 20°C to 0°C leads to an increase in the peak intensity by 15% for the FES and by 20% for the FS of the DOS, compared with the corresponding intensity values at 20°C.

However, even considerable changes in the intensity of the fluorescence bands do not lead to changes in the shape of the spectra: normalized with respect to the spectral maximum, the FS of the DOS coincide at different temperatures. The position of the maximum,  $\lambda_{\text{max}}$ , in the FS and FES does not change within the entire range of temperature variations and is equal to  $420 \pm 2$  nm and  $312 \pm 2$  nm, respectively (for the FES the local maximum is meant, see Fig. 1 b). The fluorescence band half-width remains constant within the measurement errors:  $110 \pm 2$  nm.

Furthermore, in the processing of experimental data we have noticed that the temperature dependence of the intensity in the maxima of the fluorescence and fluorescence excitation spectral bands of the DOS are described fairly well by the law  $I = I_0 \exp\{\alpha(t - t_0)\}$ , the subscript "0" denoting the temperature  $t = 20^\circ\text{C}$ . Figure 2 shows the dependences  $\ln(I/I_0) = \alpha(t - t_0)$ ; the straight lines are drawn by the least squares method. The  $\alpha$  coefficient obtained is  $-0.0082 \text{ deg}^{-1}$  for the FS and  $-0.0078 \text{ deg}^{-1}$  for the FES.

It has also been found that the temperature dependence of the spectral band intensity is a reversible effect. As the sample temperature returns to  $t = 20^\circ\text{C}$ , the intensities in the FS and FES maxima return to the former value with an accuracy of  $\pm 4\%$ , this being within the limits of measurement errors.

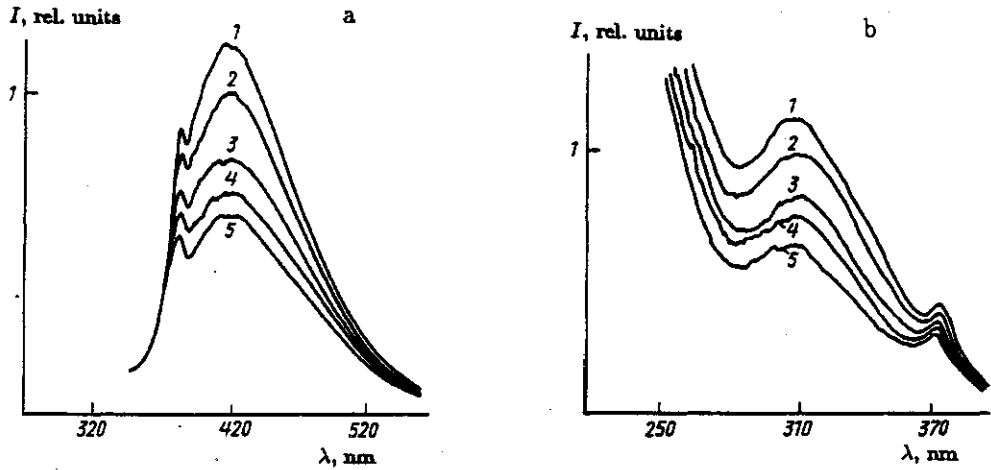


Fig. 1

Temperature dependence of the DOS fluorescence spectra (a) and fluorescence excitation spectra (b):  $t = 0^\circ\text{C}$  (1),  $20^\circ\text{C}$  (2),  $40^\circ\text{C}$  (3),  $60^\circ\text{C}$  (4), and  $80^\circ\text{C}$  (5).

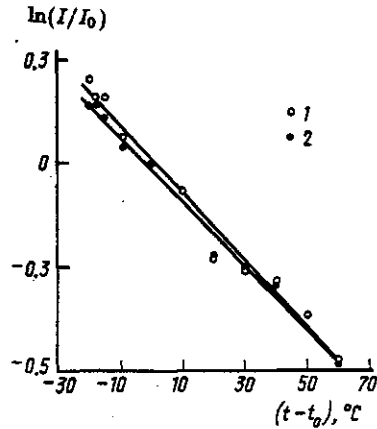


Fig. 2

Temperature dependence of the intensity of the fluorescence spectra (1) and fluorescence excitation spectra (2) maxima ( $t_0 = 20^\circ\text{C}$ ).

When studying the effect of the UV radiation on the FS, FES, and absorption spectra of the DOS, we relied on the data reported in the literature [3, 4]. The authors of these publications investigated the effect of the solar UV radiation and of the UV radiation of the xenon lamp on the fluorescence and absorption spectra of the DOS in sea water. Irradiation of sea water with continuous light in the spectral range of 290-340 nm for several hours brings about a diminution of the DOS fluorescence intensity ( $\lambda_{\text{exc}} = 337$  nm), and also a diminution of the optical density in the 290-340 nm region and its increase in the 340-390 nm region. Irradiation in the spectral range of 340-390 nm produces an opposite effect: the optical density and fluorescence intensity grow in the 290-340 nm region. The magnitude of the effect is 20-30%. In the present paper we investigated changes occurring in the FS, FES and absorption spectra of the DOS upon its exposure to continuous radiation of a Model PRK-7 mercury lamp.

DOS was sampled from natural water of the Baltic Sea. The samples were irradiated uniformly throughout the volume in a one centimeter quartz cell. Different regions of the UV spectrum were selected by means of filters made from optical colored glass (BS-4, UFS-1, BS-4+UFS-5, BS-5+UFS-5), while individual narrow

sections of the mercury lamp spectrum ( $\Delta\lambda = 5$  nm) were cut out by interference filters ( $\lambda = 226, 313, 334,$  and  $366$  nm).

The entire radiation spectrum from the mercury lamp was subdivided into sections (Fig. 3) *A*, *B*, *C*, and *V* in accordance with the pass-band half-widths of the filter combinations. The most intensive lines in the mercury lamp spectrum are indicated in Fig. 3 by arrows.

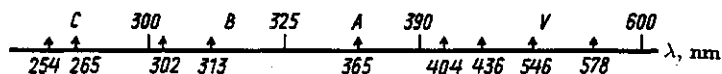


Fig. 3

Mercury lamp radiation spectrum.

The region *B* cannot be separated from the spectrum by means of a simple combination of filters. Therefore, we investigated the effect of the region *A* + *B* and the region *A*, and the difference in the results obtained enabled us to draw a conclusion about the effect produced by the region *B* on the FS, FES, and absorption spectra of the DOS.

Using the reported data [7] on the light energy distribution over the spectrum of the PRK-7 mercury lamp, it is possible to find the percentage of energy related to different spectral regions. The respective figures are 18% of the total integral value of the radiation energy for the regions *A* and *B*, and 20 and 42% for the regions *C* and *V*.

Analysis of the experimental data obtained suggests the following conclusions.

(1) Irradiation of the samples with the whole spectrum of the mercury lamp and with selected portions of the spectrum in the regions *A*, *B*, and *C* always brings about a decline of the intensity in the maximum of the FS and FES of the DOS; in some cases a change in the spectrum shape and a shift of the maximum take place (Fig. 4).

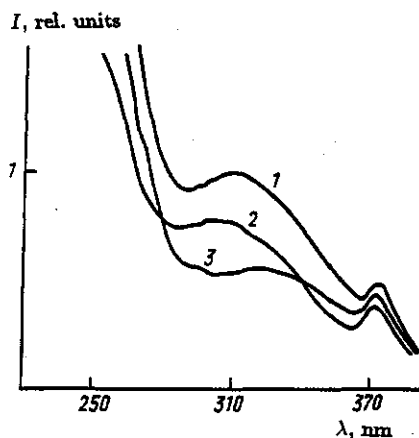


Fig. 4

Fluorescence excitation spectra: prior to exposure to UV radiation (1); after exposure to UV radiation for 1 h in the *A* region (2) and in the *A* + *B* region (3).

(2) The distribution of the mercury lamp radiation energy among the regions *A*, *B*, and *C* is nearly uniform, but the strongest effect on the spectra is produced by hard UV radiation with  $\lambda < 325$  nm (*C* and *B* regions).

Under the effect of radiation in the region *C*, the FS and FES maxima shift to the long wavelength range ( $\Delta\lambda \leq 10$  nm for the FS and  $\Delta\lambda \leq 15-25$  nm for the FES, the magnitude of the shift depending on the

exposure time). Irradiation of the DOS in the region *B* results in a similar tendency but to a smaller extent. Irradiation with a greater wavelength (region *A*) leads to a reduction of the DOS FS intensity, an increase of the half-width of the spectra, but the spectral peaks do not shift in this case. According to our results and to the data reported in [3, 4], irradiation in the *V* region produces no effect on the spectral characteristics of the DOS.

The range of maximum changes in the FES approximately coincides with the irradiation range (Table 1).

Table 1

Range of irradiation, nm	Range of maximum changes in FES, nm
Total spectrum of PRK-7 mercury lamp	220-340
300-390	280-350
325-390	300-375

Thus, irradiation in the *C* and *B* regions induces a "burnout" of a portion of the DOS; the irradiation proves to be particularly effective in the short wavelength region (to 325 nm), and this irradiation causes the shift of the FS and FES maxima to the long wavelength region.

3. In our investigations of the UV radiation effect on the absorption spectra of the DOS we could not find any definite pattern in the behavior of the spectra, and, consequently, the data reported in [3, 4] were not confirmed. It was noted that there exists no correlation between the behavior of the absorption and fluorescence spectra for the given type of the DOS, this being consistent with the data reported by other authors [8]. This suggests that the fraction of the DOS having a luminescent capacity makes an insignificant contribution to the absorption band of the entire DOS.

4. UV radiation brings about changes in all the spectral characteristics of the DOS, which do not disappear in the course of time (observations lasted for three days).

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