

LASER FLUORESCENT DIAGNOSTIC OF DISSOLVED
ORGANIC MATTER IN NATURAL WATER.

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ABSTRACT:

Important problems of environment control demand elaboration of remote methods for dissolved organic matter (DOM) diagnostics in natural water. Currently fluorescent methods using Raman scattering signal as an internal standard are widely applied for environment control DOM in water.

In this paper temperature variations and ultraviolet irradiation (both lamp and laser sources) influence on fluorescence excitation and emission spectra of water samples have been investigated. Photo chemical processes under laser excitation and effect of fluorescence saturation have been studied. The obtained results give a chance to support the hypothesis of the nature of fluorescence band of dissolved organic matter in water.

KEY WORDS: Remote Sensing, Water, Fluorescence Spectra.

1. INTRODUCTION.

The dissolved organic matter is a significant ingredient of natural water systems and determines its ecological state. That is why the creation of the precise and sensitive methods to control the presence of DOM total quantity in water is now as the actual problem as before. One of such method is the fluorescent analysis based on the hypothesis that the correlation between fluorescent intensity (I_{f1}) and DOM concentration (C) exists. However, more careful investigation of DOM spectral characteristics led us to conclusion that the relation between I_{f1} and C is practically much more complex that one could anticipate a priori. There are many factors which break this correlation. These factors are:

- 1) random changes of the fluorescent source intensity;
- 2) dependence of fluorescent signal level on the experimental conditions and as well as the conditions of the waves propagation;
- 3) temperature changes of the water;
- 4) changes of pH values in water;
- 5) presence of metal ions in water;
- 6) ultraviolet (UV) radiation from the Sun and excitation radiation of laser or lamp sources.

The first two factors can be removed using the method with calibration of fluorescent signal according to Raman scattering (RS) signal of water and parallel detection of these signals (Fadeev, 1983). Parameter $F=I_{f1}/I_{RS}$ doesn't depend on fluctuations of radiation source power, experimental conditions and is used in our case as a parameter correlating with concentration of organic pollutions (DOM in our case).

It is important to emphasize that the use of RS signal as an internal standard is the basic principle for remote sensing, when some parameters can not be controlled.

Influence of metal ions on fluorescence spectra of DOM has been studied in (Safronova, 1989). Changes of the fluorescent intensity connected with variations of pH values and temperature (in range 8...42°C) have been investigated in detail in (Smart, 1976). Influence of UV sunlight radiation on fluorescence spectra of DOM are described in (Samokhina, 1989).

The goal of this paper is to study the general appropriateness of the spectral characteristic of DOM under temperature variations (in wide range 0...80°C) and UV radiation excitation by both lamp and laser sources. During these experiments we supposed to estimate an influence of factors mentioned above on the spectral characteristics of DOM (to correct fluorescence spectra obtained *in situ*). Moreover new experimental results extend our knowledge about the nature fluorescence band of DOM.

2. INSTALLATION.

In this paper the samples of DOM from Baltic Sea have been investigated. The water samples with different concentration of DOM have been obtained by means of dilution of the most concentrating sample by different volumes of distilled water.

Emission and excitation fluorescence spectra were detected by the lamp spectrofluorimeter "Jobin Yvon 3CS" with computer data handling and correction for instrumental spectral sensitivity. Absorption spectra were detected by spectrophotometer "Specord M40".

The experimental installation to study influence of UV laser irradiation included N_2 -laser ($\lambda_{exc} = 337$ nm, $t = 8$ ns, with power of one pulse $P = 20$ kWt, frequency of pulse repetition $f = 1 \dots 1000$ Hz), 1 cm diameter quartz cell with water sample pumping by peristaltic pump (speed of pumping up to 1 l/s), polychromator and optical multichannel analyzer Plasma Monitor (512 channels, model 1451, PARC). Wavelength dispersion was 0.37 nm per channel.

3. TEMPERATURE INFLUENCE ON FLUORESCENCE SPECTRA OF DOM IN WATER

1. At temperature rise from 0°C to 80°C intensity both for excitation and emission DOM fluorescence spectra decreases. Temperature decrease leads to inverse effect (see Fig.1)

2. Valuable changes of fluorescence intensities don't lead to spectral shape changes (location of spectral maxima and spectrum width).

3. Temperature dependence of spectral intensity is a reversible process with accuracy +4%.

4. Temperature dependence of maximum intensity both for emission and excitation spectra is well described by the formula $I = I_0 \exp(-a(t-t_0))$ where sign "o" corresponds to temperature $t = 20^\circ\text{C}$. Coefficient $a = 0.0082$ has been obtained for emission spectra and $a = 0.0078$ for excitation spectra.

Thus temperature influence on DOM fluorescence spectra in natural water is enough small and may be easy taken into account during *in situ* measurement of DOM concentration using correction factor.

4. ULTRAVIOLET IRRADIATION INFLUENCE ON DOM FLUORESCENCE SPECTRA

In this paper samples of DOM were irradiated evenly in volume in 1 cm quartz cell by Hg-lamp and Xe-lamp with different color glass filters and inter filters.

1. The strongest influence on spectra appears as a result of shortwave UV radiation ($\lambda = 200 \dots 300$ nm): spectra are distorted by shape, maxima of excitation and emission spectra shift to longer wavelengths ($\Delta\lambda$ for emission spectra < 10 nm and $\Delta\lambda$ for excitation spectra $< 15-25$ nm, depends from irradiation time). UV light in $300 \dots 325$ nm range effects on DOM fluorescence spectra like as shortest UV light, but with less efficiency (see Fig.2). Radiation with longer wavelength ($325 \dots 400$ nm) leads to intensity and width decrease but doesn't effect any spectrum maxima shift. Visible light doesn't affect any DOM spectral characteristics.

2. The spectral range of maximal intensity changes in excitation spectra approximately equals to that of irradiation. Thus if water sample is irradiated by sun light ($\lambda > 300$ nm) changes of fluorescence maximum intensity with $\lambda_{exc} = 337$ nm would be much

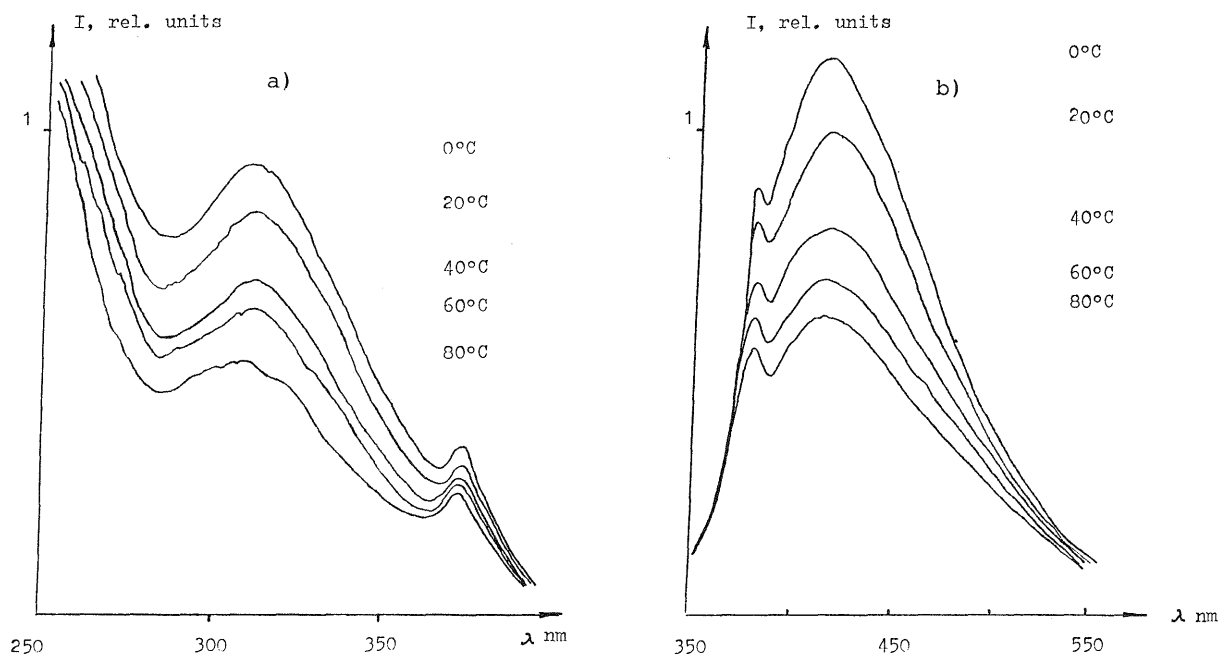


Fig. 1. Temperature dependence of excitation (a) and emission (b) DOM fluorescence spectra.

than with $\lambda_{exc} < 300$ nm.

3. Absorption spectra failed to reveal any correlation with UV irradiation. It was obtained also that there is no correlation between absorption and fluorescence spectra behavior, it is in accordance with other studies (Safronova, 1989). This permits us to think that responsible for luminescence part of DOM does not contribute much in absorption spectrum.

4. UV radiation affect irreversibly all spectral characteristics (investigation time was 3 days). During *in situ* monitoring UV sun irradiation of surface water leads to errors of DOM concentration measurement, yet we can not calculate this natural factor. The exception of influence of laser excitation radiation on the fluorescence spectra will be studied at the next section.

5. INFLUENCE OF UV LASER IRRADIATION ON DOM FLUORESCENCE SPECTRA

Currently laser fluorescent methods are widely applied for environment control including organic pollutions measurement in water. The basic principle of remote fluorescent sensing is the use of Raman water scattering signal as an intrinsic standard (Fadeev, 1983; Chubarov, 1984).

But the influence of laser UV irradiation on DOM fluorescence spectra and effect of fluorescence saturation have not been studied yet. In this section some photochemical processes under laser excitation and effect of DOM fluorescence saturation have been investigated.

5.1 Influence of photochemical processes on DOM fluorescence spectra.

Spectral changes of DOM fluorescence depend on number of laser pulses n , which irradiate the same volume of water sample.

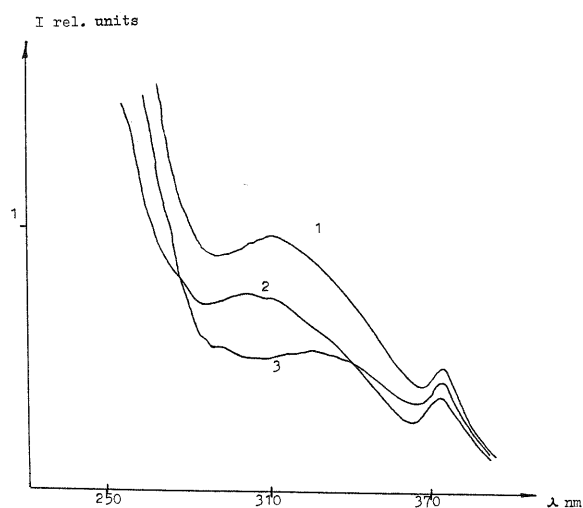


Fig. 2. Continuous UV radiation influence on corrected excitation fluorescence spectra: 1 - initial spectrum, 2 - after one hour of UV irradiation at spectral range 325...390, 3 - after one hour of UV irradiation at spectral range 300...390.

1. With the maximal speed of water pumping and $f=2.5$ Hz each laser pulse irradiates new volume of sample ($n=1$).

2. $n=1...30$. The spectral shape and I_{fl}^{max} are practically constant. Intensity of maximum decreases not more than for 10% comparatively with "uninfluenced" sample with $n=1$.

3. $n > 30$. λ_{fl}^{max} shifts to longer wavelengths and spectral intensity decreases for 10...50 %. These spectra with various f differ by intensity (see Fig.3).

4. After irradiation without water pumping the fluorescence intensity never was the same as before irradiation.

5. The relaxation process of photochemical changes in fluorescence has been investigated in experimental conditions without water pumping with various frequency of laser pulse repetition $f = 10...1000$ Hz. First, the sample was irradiated by laser light with $f=1$ kHz during 5 min (total number of laser pulses was about $3 \cdot 10^5$), the spectral intensity decreased for 50 %. Then fluorescence spectra from previously irradiated sample were detected. One can suppose that there are some relaxation processes for DOM, characterized by different relaxation time from 1 ms to 0.1s (according to $f = 10...1000$ Hz).

Thus the regime with $n=3$ is the best regime of spectra investigation *in situ*. Intensity of maximum doesn't decrease more than for 3% and the duration of fluorescence detection decreases comparatively with "uninfluenced" sample ($n=1$).

5.2 The effect of saturation of DOM fluorescence.

The effect of fluorescence saturation is caused by limited lifetime of organic molecule in excited state and appears as a nonlinear dependence of fluorescence intensity on exciting power. In this work the fluorescence spectra with various degree of laser power attenuation and also saturation curves have been obtained in optimal experimental conditions with maximal speed of pumping to minimize photochemical effects.

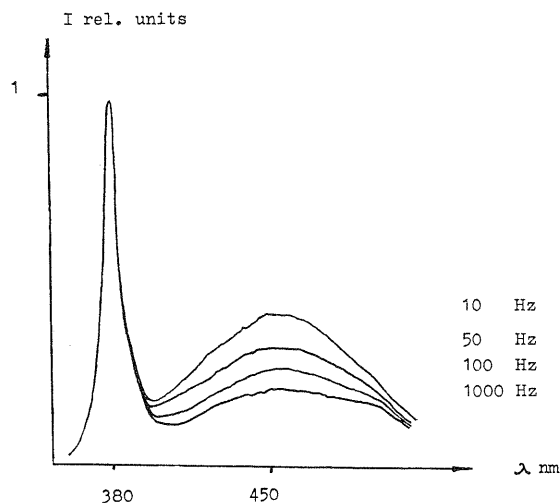


Fig. 3. The DOM fluorescence spectra with various frequency of laser pulse repetition f .

The spectral shape is independent on laser pulse power. But relative fluorescence intensity decreases with the increasing of pulse power (see Fig.4).

On the Fig.5 there are saturation curves - dependencies of fluorescence intensity I_{f1} on excitation intensity F , which is normalized by $I_{f1}(F=1)$. They are not linear, the degree of nonlinearity decreases with DOM concentration increasing.

6. CONCLUSION.

1. These experimental results permit us to estimate influence of temperature variation and UV radiation excitation on fluorescence spectra of DOM and permit us to correct spectra obtained *in situ*. Optimal regime of fluorescence detection for remote control of sea-water pollutions are proposed.

2. The obtained results give evidence that there is no relation between absorption and fluorescence spectra behaviour. This fact led us to the conclusion that the different parts of DOM participate in absorption and fluorescence processes. In all probability there exist some special fluorescent groups of fluorofors in natural organic matter. These groups form the fluorescence band and constitute small part of DOM. Fotophysical processes of intra- and inter-molecular interactions of these fluorofors are complex and in need of subsequent study.

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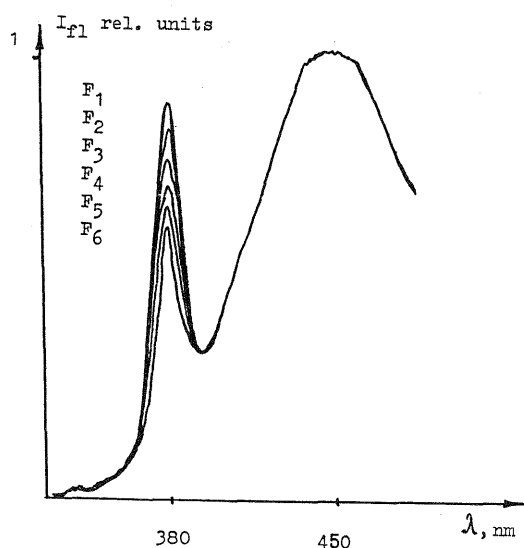


Fig. 4. The DOM fluorescence spectra with various attenuation of laser pulse power ($F_1:F_2:F_3:F_4:F_5:F_6=1:0.75:0.55:0.21:0.1:0.05$).

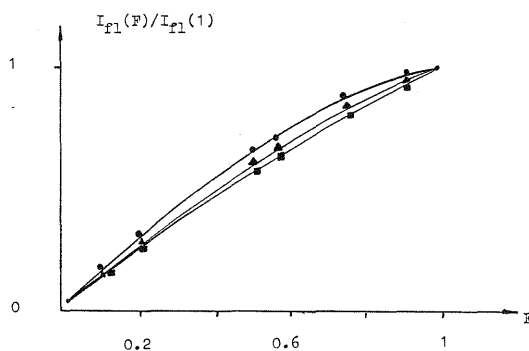


Fig. 5. The dependence of DOM fluorescence intensity I_{f1} on excitation intensity F (the saturation curve), which is normalized by $I_{f1}(F=1)$, for various DOM concentration in water ($C_1(\blacksquare) > C_2(\blacktriangle) > C_3(\bullet)$).

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