Laser-induced fluorescence of organic impurities in drinking water

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We present in this paper the spectra of laser-induced fluorescence (LIF) of organic impurities in drinking water excited by the fourth harmonic of a Nd:YAG laser radiation at $\lambda = 266$ nm. We propose to assess the degree of water pollution using the intensity ratio between the fluorescence of an impurity and the Raman band of water (F/R). Water samples, taken at different stages of the technological cycle of water cleaning being employed at the Chistaya Voda Company, convincingly demonstrate the decrease in the content of organic impurities in drinking water during its processing.

The purity of drinking water will undoubtedly become a problem in the forthcoming millennium. The reserves of pure water are limited; therefore, the technologies of its purification attract the primary attention. Up to now, great variety of systems and methods for water purification and control have been devised.

Formerly it was considered that the bioluminescent methods are most sensitive in detecting low concentrations of organic molecules. They allow detection of a matter at concentrations of 10^{-18} mol/l in a sample.[1] It seems reasonable that this value is their limiting sensitivity bounded by the "biochemical noise," that is, spontaneous nonfermentative oxidation of substrates. The bioluminescent tests are commonly used in the control over pollution of the waste and industrial water.[2,3]

Recently the same level of sensitivity was reached by use of the methods based on measuring the laser-induced fluorescence (LIF).

The LIF detectors are actively used in high-performance liquid chromatography and capillary electrophoresis.[4–6] They allow detection of substances with low quantum yield of fluorescence at concentrations of $10^{-11} - 10^{-15}$ mol/l. In some cases, the detection of individual molecules with high quantum yield is possible.[7] High sensitivity and simplicity make the method of laser-induced fluorescence very attractive both for analytical and control purposes.

This paper presents some experimental results on the LIF studies of drinking water exposed to the radiation of forth harmonic of a Nd:YAG laser at 266 nm wavelength. It is shown that the laser together with the systems of data accumulation and processing form a high-sensitive spectroscopic complex, which can successfully be used in monitoring the organic impurities at all stages of the processing cycle of the drinking water purification.

Experimental setup

It is the laser used that primarily determines the LIF-detector's sensitivity. The fluorescing organic impurities in water have intense absorption bands in the spectral range 220–280 nm (see Table). There are very few lasers emitting the UV radiation at the wavelengths within this range. We have to choose between the excimer lasers (for example, KrF, $\lambda = 248$ nm), solid-state lasers with the frequency conversion of the emission (e.g., the forth harmonic of a Nd:YAG laser radiation at $\lambda = 266$ nm), and a combined laser (for example, frequency-doubled, to $\lambda = 280$ nm, radiation of a dye laser pumped by an excimer laser).

The features of the excimer laser are short pulses (< 10 ns) and their low repetition frequency. The traditional way of recording the short pulses is based on the processing (accumulation and averaging) of analog signals with the help of expensive gated integrators. These integrators are able to abate spurious dark noises and other asynchronous noises, subtract averaged noises, and perform other real-time arithmetic and sorting operations. Besides, the necessity of using high-purity and toxic gases makes the maintenance of such lasers rather expensive and dangerous, particularly, in analytical studies.

The problem of measuring the fluorescence signal is easily resolved, when using, as the excitation source, the forth harmonic of a Nd:YAG laser radiation at 150–200 ns pulse duration and 2–3 kHz repetition frequency. In this case, inexpensive analog-to-digital converters can be applied to the processing of the digitized signals (output and accumulation).[8]

The optical arrangement of the experimental set-up for recording the LIF spectra at excitation by the forth harmonic of Nd:YAG laser radiation is presented in Fig. 1.

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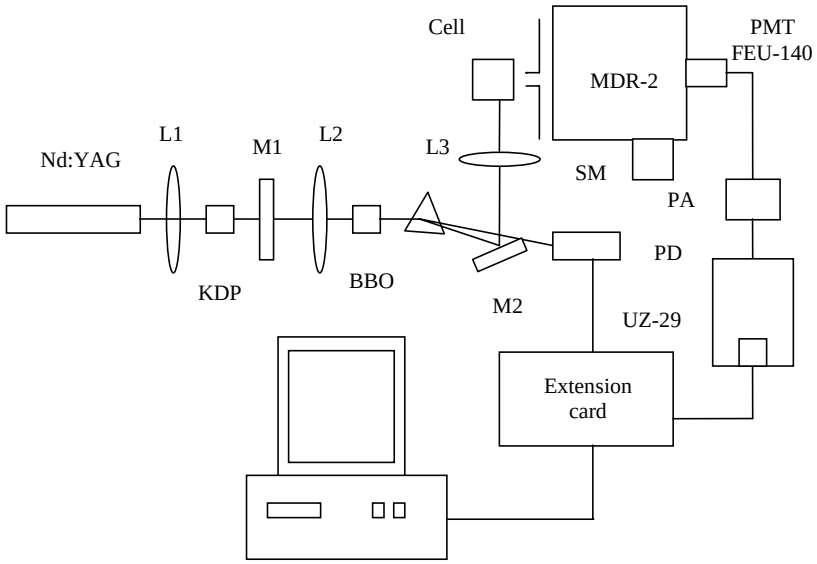

Fig. 1. The optical arrangement of the setup: Nd:YAG is the laser; L1, L2, and L3 are the lenses; M1 and M2 are the dichroic mirrors.

The Nd:YAG laser radiation is sequentially converted into the second and then forth harmonic by means of KDP and BBO crystals installed outside the cell. The routine control over the second harmonic radiation power is made with a high-speed photodiode of FD16 type. The power of the forth-harmonic radiation is measured with the liquid-phase ferrioxalate actinometer by the method described in Ref. 9.

The laser used generated the pulses of 200 ns duration at 3 kHz repetition frequency. The mean power of the forth-harmonic radiation is 40 mW. The forth-harmonic radiation is separated out by a prism and then directed to the quartz cell with a sample. The fluorescence is recorded through the cell's side located in front of the input slit of an MDR–2 monochromator. We have equipped the monochromator with a stepper motor (SM) and a potentiometric sensor of the wavelength. The stepper motor control and reading the data from the wavelength sensor are performed by the IBM PC board of the data accumulation and control. The control over the laser acoustooptics Q-switch and synchronization of the measurement process are also performed using this board.

The fluorescence signal is recorded with the photomultiplier FEU–140. A preamplifier (PA) on the basis of an operational amplifier (OA) AD811 is located inside the PMT's housing. It allows transmitting the pulsed signals with minimum distortions along sufficiently long cable line. After amplification with a wide-band amplifier UZ–29 (the emitter follower for matching signals is located at the amplifier output), the pulsed signal comes to the accumulation board, where it is memorized by the peak detector for the time necessary for its digitizing.

The high repetition frequency of pulses of the Nd:YAG laser, comparative to the excimer laser, allows the accumulation of 10000–30000 pulses at each wavelength for a relatively short time, as well as their averaging in order to improve the S/N ratio.

Objects of investigation and experimental results

Figure 2 presents the LIF spectrum of the running water (curve *1*) obtained at U_{PMT} = 1400 V with 10000 pulses stored at each wavelength at 2 nm step. The intense narrow line at 294.3 nm wavelength is the Raman signal R from water (the value of the Q-branch frequency shift relative to the excitation frequency for water is 3440 cm^{-1} (Ref. 10)), which can be used as the internal reference signal[11] for normalizing the fluorescence signal F. There is a correlation between the magnitude of the F/R ratio and total content of organic impurities in water samples.

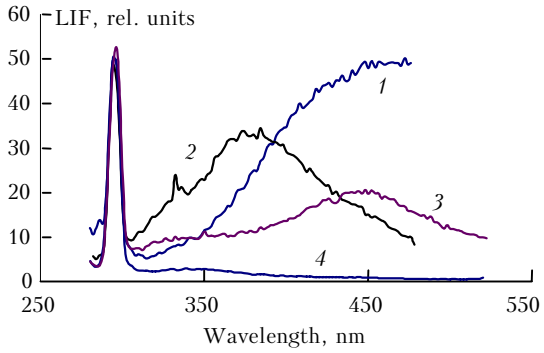

Fig. 2. The LIF spectra: running water (*1*); distilled water (*2*); the spring water (*3*); bidistilled water (*4*).

The LIF spectrum of the running water is characterized by the wide fluorescence band with the maximum near 430 nm. This is so called "blue" fluorescence of water, the nature of which is still not completely understood, but it is caused by the organic impurities of technogenic origin.[12] Typical F/R ratio for the running water is equal or exceeds unity (in our case $F/R = 1.01$). We have noticed significant variations of this ratio for running water sampled in different districts of Novosibirsk, as well as its increase in the spring–summer period and after heavy rains.

The ultra pure water samples do not fluoresce under exposure to UV radiation.[13]

Curve *2* in Fig. 2 depicts the LIF spectrum of the distilled water, obtained under the same conditions. It distinctly shows a shift of the maximum to the wavelength of 375 nm and a decrease of the ratio F/R down to 0.71.

By convention, the organic impurities in water may be divided into two types: 1) "low-molecular organic" primarily absorbing in the range 250–300 nm (UV-fluorescence in the range of 330–360 nm) (see Table) and 2) "high-molecular organic" absorbing mostly in the range of 300 to 380 nm ("blue" fluorescence at 400–450 nm).

Table. Spectral features of the main organic impurities and their content in the water at the system input (0th stage), after softening (4th stage), and after osmosis (5th stage)

Substance	Mol. mass	Content,* ng/l	λ_{abs}, nm (log ε)**	λ_{fl}, nm
Low molecular				
Phenol	94.11	0–25.0 4–11.0 5–3.0	210(3.8) 270(3.2)	300
Naphthalene	128.16	0–1.2 4–n/d 5–0.4	220(5.0) 275.5(3.8)	336
High molecular				
Acenaphthene	154.21	0–0.3 4–0.2 5–0.1	228(4.9) 289(3.8) 321(3.2)	365
Fluorene	166.21	0–5.4 4–1.8 5–1.6	206(4.6) 260(4.3) 301(4.0)	310
Anthracene	178.22	0–0.7 4–0.5 5–0.1	251(5.3) 338(3.7) 357(3.9) 375(3.9)	402
Phenanthrene	178.24	0–16.0 4–3.0 5–1.1	250(4.7) 293(4.1) 330(2.5) 346(2.5)	373
Pyrene	202.26	0–0.2 4–0.2 5–n/d	241(4.9) 272(4.6) 333.5(4.7)	372 394

* According to data of ecological study and chromatographic analysis made at the Institute for Organic Chemistry by an order from Chistaya Voda Company.

** ε is the molecular extinction coefficient, l/(mol. · cm).

At high concentration of the high-molecular organic, the "blue" fluorescence will dominate in the LIF spectrum, because the UV fluorescence of the low-molecular organic overlaps with the absorption band of the high-molecular organic and is efficiently quenched there, as in the case of the running water, for example.

The concentration of the high-molecular organic in the distilled water is significantly lower, therefore only the UV-fluorescence signal of the low-molecular organic is observed in its LIF spectrum (Fig. 2, curve *2*).

Figure 2 also presents the LIF spectrum of spring water (curve *3*). Of particular interest is the noticeable decrease in the fluorescence intensity relative to the Raman signal. Two fluorescence maxima are seen in this curve: at $\lambda = 332$ nm ($F/R = 0.19$) and at $\lambda = 446$ nm ($F/R = 0.39$). One may conclude that the amounts of both low-molecular and high-molecular organic are small in this water.

The LIF spectra of bidistilled water are shown in Fig. 2 by curve *4*. It is characterized by a very weak maximum at $\lambda = 338$ nm ($F/R = 0.059$). The quality of the bidistilled water deteriorates with time and the ratio F/R increases somewhat. We assume that bidistilled water is best purified from organic impurities. The ratio F/R of the order of 0.10–0.25 corresponds to quite pure water. The ratios less than 0.10 are indicative of a high degree of purification.

The LIF spectroscopy may be applied to control over processing stages of the drinking water purification. So, for example, the Chistaya Voda Company makes thorough purification of water using the equipment and technology of the company "Universal Aqua Technologies." The purification process includes the following stages: (1) water filtration through a combined filter; (2) birm-filtration; (3) carbon-filtration; (4) softening; (5) osmosing; (6) mineralization; and (7) ozonization.

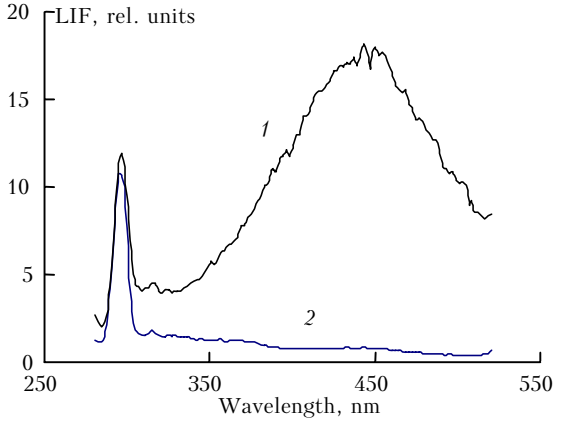

Fig. 3. The LIF-spectra of water of the Chistaya Voda Company: input water (*1*); water at the output after ozonization (*2*).

The LIF spectrum of the "input" water is presented in Fig. 3 (curve *1*). Its F/R ratio is equal to 1.52. At the setup output after ozonization (Fig. 3, curve *2*) this ratio falls to 0.17. The high-molecular organic signal is hardly seen in this spectrum, and that from low-molecular organic is extremely weak.

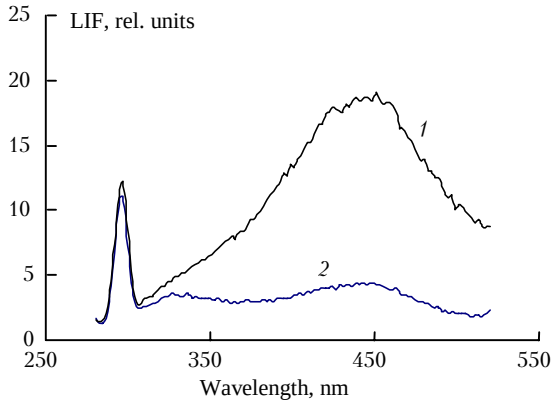

Fig. 4. The LIF spectra of water after the combined filter (*1*) and after the carbon filter (*2*).

Figure 4 (curve *1*) demonstrates the LIF spectrum of water passed through the combined filter (the first stage of purification). Its F/R ratio is also equal to 1.52 (like for the "input" water), because the principal purpose of the combined filter is to remove solid impurities. The ratio of the carbon-filtered water (after the 3rd stage) is 0.40 (Fig. 4, curve *2*). Figure 5 demonstrates the LIF spectra of the water washed off the osmose (F/R = 1.00, curve *1*) and the water, which has passed the osmose purification (F/R = 0.41, curve *2*).

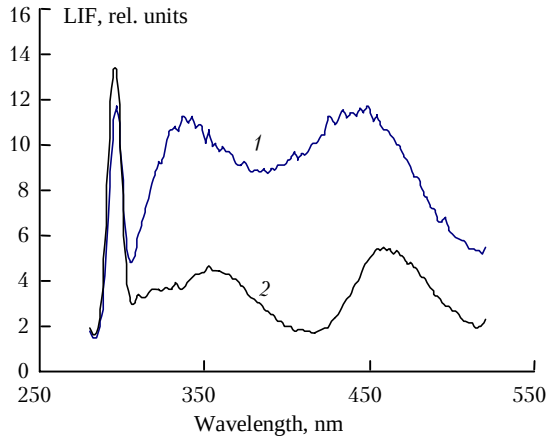

Fig. 5. The LIF spectra of water obtained for the control over the purification technology: the washing off the osmosis (*1*); the water after the osmosis stage of purification (*2*).

Comparing the LIF spectra for different water samples with that of the distilled water, we can draw a conclusion on the total concentration of organic impurities in the sample under study.

When devising the apparatus for laboratory monitoring of liquid-phase products, the proposed structure of the spectral complex can be simplified by replacing the monochromator with a polychromator and adding the flow-through cell. For further relation of the F/R ratio with the standard measuring units of water quality, we intend to conduct additional measurements following all basic technological stages using thorough screening by commonly accepted controlling methods. In this case the F/R ratio becomes a completely objective parameter allowing very accurate estimation of the degree of raw material purification based on the total content of the organic impurities.

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