Laser diagnostics of humic substances as natural detoxicants and fluorescent indicators of the pollutants in water

Peter A. Volkov[1], Vasiliy A. Kravtsov[1], Natalia Yu. Grechischeva[3], Natalia S. Scherbina[2], Victor V. Fadeev[1]

[1] Moscow State University, Physics Department, Russian Federation
[2] Moscow State University, Chemical Department, Russian Federation
[3] Russian Gubkin University of Oil and Gas, Russian Federation

Role of humic substances

In remote laser sensing of water medium there are a lot of problems concerning the investigation of the fluorescence of the humic substances (HS). HS are present in different concentrations in all natural water reservoirs and have many ecological functions – **concentration of chemical elements** and **energy**, **heat conditions regulation**, **chemical solutions transfer**. One of the most important functions of HS – **combining with** different **solutions and elements harmful for** the living **organisms**.

Main targets of the work

- **To define the molecular photophysical parameters** of the chosen toxicants and HS fluorophores using the nonlinear and kinetic laser fluorimetry methods.
- **To find out the possibility of using HS as a fluorescent indicator** of the toxicant presence in natural waters.
- **To try to distinguish different types of toxicants,** there for we used the representative of polyaromatic hydrocarbons - pyrene, and the representative of the heavy metal salts – uranyl.

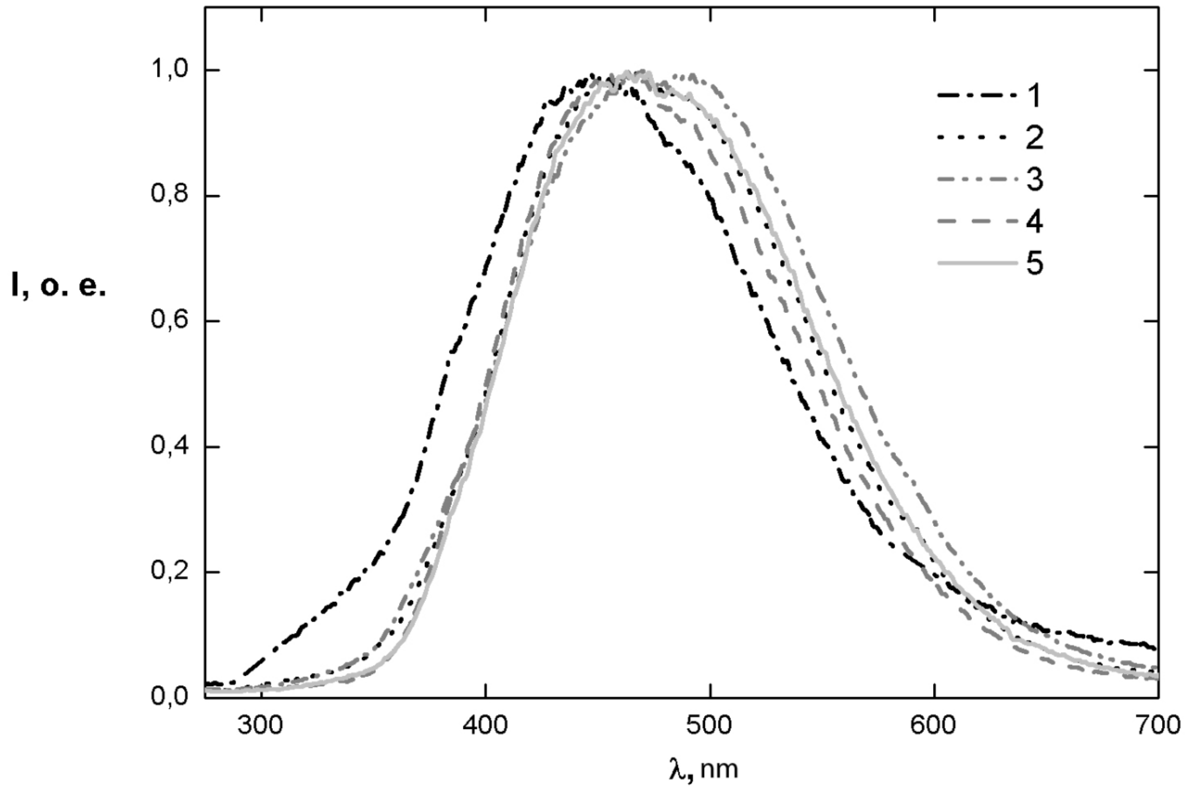
Equipment

- The photophysical parameter's measurements of HS and toxicants were made on a laser spectrometer. For excitations was used the **4-th harmonic** of **Nd^{3+}: YAG** laser radiation. Wavelength – **266 nm**. Duration and frequency of the impulses reiteration are **10 ns** and **10 Hz** correspondingly. Impulse energy is **0.3 mJ**, the photon flux density of the excitation radiation on **266 nm** can be changed in the range **$5\ 10^{23}$ - 10^{26} $cm^{-2}s^{-1}$** not taking into account the distribution of intensity in time and cross-section of the beam.
- For the corrected spectra's measurements we used the lamp spectrofluorometer **FluoroMax 4** (Jobin Yvon).

HS preparations

- - CHP, CHPm, LHS – preparations isolated from the coil and the leonardite;
- - RF – preparation isolated from the peat;
- - SR – preparation isolated from the river water dissolved organic matter;
- - POW – commercial preparation «Powhumus»;
- - THS - commercial preparation «Tekhnoexport».

Photophysical parameters of HS Fluorescence spectra



Gr.1 The corrected fluorescence spectra of HS preparations obtained with FluoroMax4 spectrofluorometer. 1-RF, 2-POW, 3-SR, 4-CHP, 5-CHPm

Photophysical parameters of HS

Preparation	$\sigma \cdot 10^{16}$, cm^2	τ, ns	$\eta \cdot n/C$, mol/g
RF	0.65 ± 0.05	2.5 ± 0.5	8 ± 2
POW	2.7 ± 0.2	2.4 ± 0.5	6 ± 2
SR	3.5 ± 0.3	2.5 ± 0.5	4 ± 1
CHP	0.5 ± 0.04	3.0 ± 0.5	37 ± 5
CHPm	0.35 ± 0.03	2.7 ± 0.5	66 ± 8

σ , τ – absorption cross-section and the lifetime of the excited state of the HS fluorophore

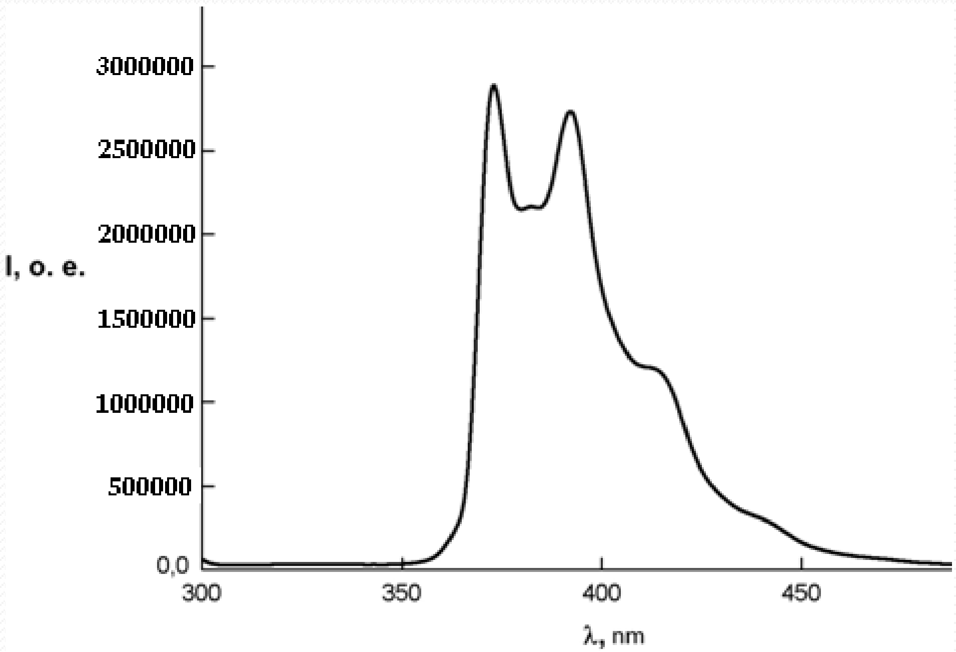
η , n – the fluorescence quantum yield and the fluorophores concentration.

C – mass concentration of HS

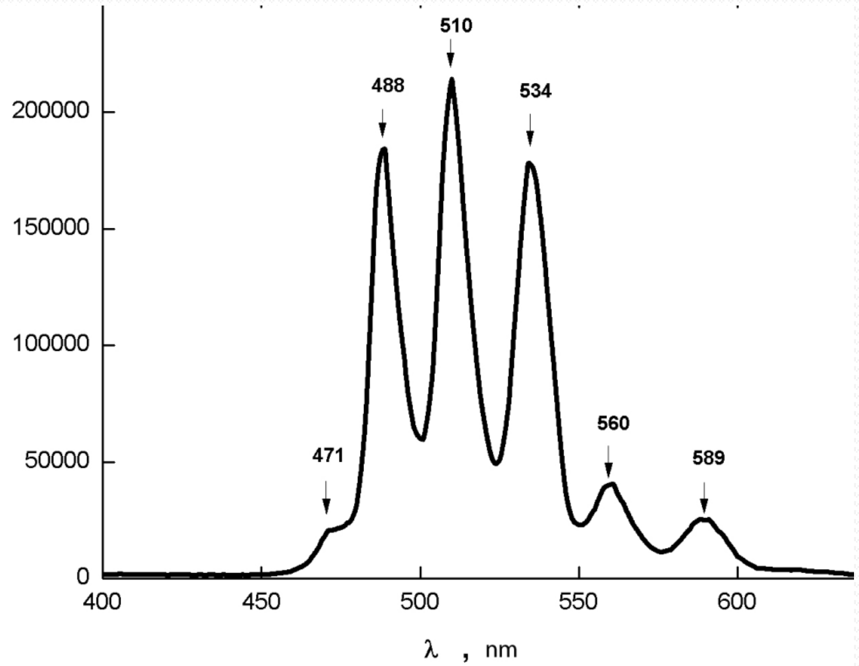
Measured by nonlinear and kinetic fluorimetry method

Photophysical parameters of pyrene and uranyl

The fluorescence spectra of pyrene and uranyl while excited with **266 nm** wavelength



Gr.2 Pyrene fluorescence spectra.



Gr.3 Uranyl fluorescence spectra.

Photophysical parameters of pyrene and uranyl

Parameter	Pyrene	Uranyl
σ	$(0.7 \pm 0.1) \cdot 10^{-16}$ cm^2	$(3.0 \pm 0.3) \cdot 10^{-17}$ cm^2
τ	85 ± 3 ns	1.8 ± 0.1 μs

Obtained with the nonlinear and kinetic fluorimetry methods.

The difference from HS – fluorophore **excited state lifetime is much longer than the laser pulse:**

$$\boldsymbol{\tau >> \tau_p}$$

HS and pyrene interaction

Chaining constant:

The fluorescence intensity of pyrene decreases (pyrene concentration is 60 ug/l) while the HS concentration rises from **1** mg/l to **10** mg/l.

Thus we calculate the chaining constant $\mathbf{K_{oc}}$:

$$F_0/F = 1 + \mathbf{K_{oc}} \cdot C_{HA.}$$

F_0 и F – pyrene fluorescence intensity with and without HS.

$\mathbf{K_{oc}}$ = (3.2   0.3)x 10^5 l/kg   for LHS sample;
$\mathbf{K_{oc}}$ = (3.6   0.4)x 10^5 l/kg   for THS sample.

HS and pyrene interaction

Photophysical parameters HS (3mg/l), obtained with the nonlinear and kinetic fluorimetry methods.

$\sigma = (3.5 \pm 0.2) \cdot 10^{-16}\ cm^2$ – without pyrene

$\sigma = (2.1 \pm 0.3) \cdot 10^{-16} cm^2$ – with pyrene (60 ug/l)

$\tau = 3 \pm 0.5$ ns – without pyrene

$\tau = 5 \pm 0.5$ ns – with pyrene (60 ug/l)

HS and uranyl interaction

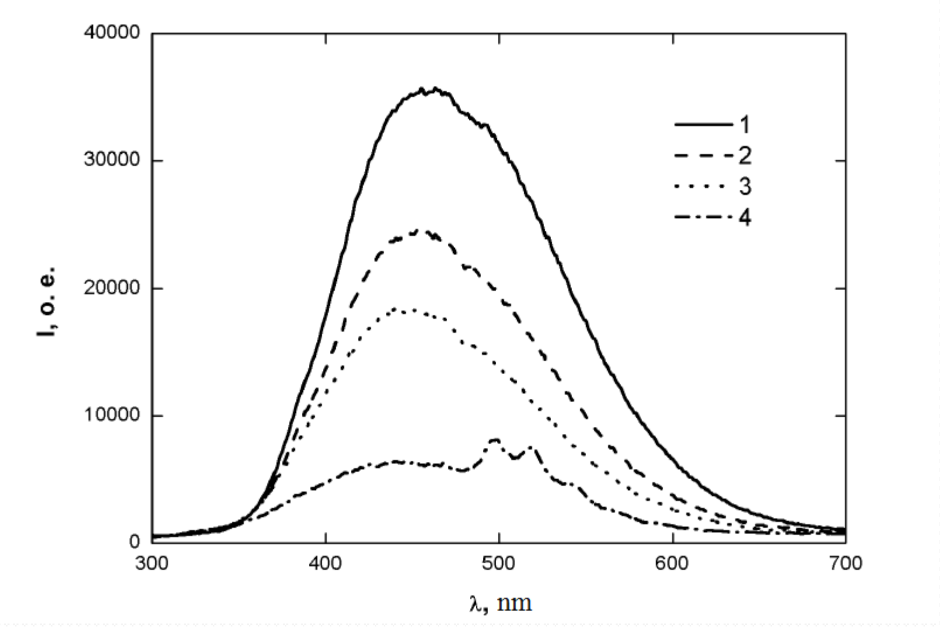
Content of functional groups in HS

Preparation	-COOH, mmol/g	-ArOH, mmol/g
CHP	4.2 ±0.2	1.1± 0.1
CHPm	3.6±0.1	4.4± 0.2

Two –COO⁻ groups can bind with the uranyl UO_2^{2+}. There for can be calculated the concentrations of uranyl and humic substances at which the interaction between them take place. A good fluorescent signal from uranyl is noticeable at concentrations of about 10^{-5} mol/l. So the concentration of –COOH- groups should be about 2 10^{-5} mol/l, which means mass concentration of CHP - 5mg/l.

HS and uranyl interaction

Influence of uranyl on fluorescence of HS.



Gr. 4 The samples with concentration of HS 50 mg/l (concentration –COOH-groups 2 10^{-4} mol/l) and concentrations of uranyl **1** -10^{-5}, **2** - 5 10^{-5}, **3** - 10^{-4}, **4** - 5 10^{-4} mol/l were used. The ratio of uranyl ions to concentration of –COOH- groups couples was there for 1:10, 1:2, 1:1, 5:1. Type of HS used: **CHP**.

HS and uranyl interaction

Influence of uranyl on photophysical parameters of HS (concentration of –COOH- groups 2 10^{-4} mol/l).

UO_2 concentration	$1 \cdot 10^{-5}$ mol/l	$1 \cdot 10^{-4}$ mol/l	$5 \cdot 10^{-4}$ mol/l
σ_{CHP}, cm^2	$(0.50 \pm 0.03) \cdot 10^{-16}$	$(1.0 \pm 0.1) \cdot 10^{-16}$	$(1.5 \pm 0.2) \cdot 10^{-16}$
τ_{CHP}, ns	3.0 ± 0.5	3.7 ± 0.5	2.5 ± 0.5
σ_{CHPm}, cm^2	$(0.70 \pm 0.04) \cdot 10^{-16}$	$(1.3 \pm 0.1) \cdot 10^{-16}$	$(1.4 \pm 0.2) \cdot 10^{-16}$
τ_{CHPm}, ns	2.7 ± 0.5	3.7 ± 0.5	3.5 ± 0.5

During measuring of the saturation curve signal was registered in detector's strobe - width 50ns with zero delay from laser pulse.

Conclusion

- With growth of uranyl concentration HS fluorescence intensity is decreasing and simultaneously fluorophor absorption cross section is increasing. Mechanisms are under investigation now.
- Thou not as strong as uranyl, pyrene influences the photophysical parameters of HS too.
- There for another property of HS is proposed – **the ability to use it as a fluorescent indicator for definition of toxic substances in water**. Difference of behavior in HS fluorescence in cases of pyrene and uranyl is connected with the chemical properties: uranyl exists in solution as an ion, while pyrene isn't charged (electro neutral). Interaction with uranyl leads to coagulation of HS; in case of pyrene coagulation doesn't take place.