The Fluorescence Characteristics and the Photophysical Parameters of the Humic Substances and their Relationship to the Chemical Structure

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1. INTRODUCTION

A relation of the fluorescence characteristics and the photophysical parameters of the humic substances on the one hand with their chemical structure on the other allows to solve the problem of express diagnostic of the humic substances in water and to propose a theory concerning the humic fluorescence.

The principal possibility of solving such problems have discussed in (1,2).

The following fluorescence characteristics were investigated : the fluorescence parameter normalized by the concentration of the humic substance, $\Phi_0 = \frac{N_{fl}}{N_{rs}C}$, were N_{fl}, N_{rs} - amount of the fluorescence photons and the Raman scattering photons correspondingly, c – mass concentration of the humic substances ; the parameter characterizing the form and position of the fluorescence band – the wavelength of fluorescence maximum λ_{max} and the width of the fluorescence band $\Delta\lambda$; the molecular photophysical parameters: σ and τ, which are lifetime of an exited state and the and the effective excitation crossection of the flourophore correspondingly.

The selection of such a set of parameters have proved in a number of articles, it's review is in (3). Under the current circumstances the choice of these parameters is caused by the expected relation of these parameters with the

chemical structure and by the presence of proved and tested experimental methods of their determination (3,4).

The objective of this work is to find the relation between fluorescence characteristics and the molecular photophysical parameters with the chemical structure of the humic substances.

2. MATERIALS AND METHODS

Twelve humic materials isolated from coal, soils, peats, and river waters used in this study are listed in (Tab. 1). Coil, peat and podzolic soil humic substances presented by different fractions: Fulvic Acid (FA), Humic Acid (HA), and non-fractionated mixture of HA and FA (HF); chernozems (mollisols) presented by FA and HA; and water humus substanses presented only by HF.

Table 1: Humic substances samples preparation.

I	PHA-T5	Peat humic acid
II	PFA-T5	Peat fulvic acid
III	PHF-T5	Peat HF
IV	CHA-GL	Coal humic acid
V	CFA-GL	Coal fulvic acid
VI	CHF-GL	Coal HF
VII	SHA-PW	Podzol soil humic acid
VIII	SFA-PW	Podzol soil fulvic acid
IX	SHF-PW	Podzol soil HF
X	SHA-CTK	Chernozem humic acid
XI	SFA-CTK	Chernozem fulvic acid
XII	AHF-IsX2	Water HF

The samples were prepared id a distilled water with a phosphate buffer (Ph 6.8) The humic substances concentration is 1 mg/L.

The preparations were chosen to make their characteristics the most contrast to each other. The molecular photophysical parameters were measured and the chemical structure characteristics for them were gained.

Equipment: Laser fluorimeter with the third harmonic of Yag:Nd laser (355 nm), with the optical multichannel analyzer, that allows to measure the fluorescence from 250 to 700 nm. The fluorimeter allows to obtain a kinetic and a

fluorescence saturation curves. A kinetic curve is the dependence of the amount of the fluorescence photons in the receiver strobe (10 ns) on the shift of the strobe from the laser pulse (with a step of 2.5 ns). A saturation curve – the dependence of the amount of the fluorescence photons on the power of the laser pulse.

3. RESULTS AND DISCUSSION

The optical spectral responses on a laser pulse, containing the Raman scattering band and the humic substances fluorescence band, were measured. Three fluorescence parameters were obtained: λ_{max}, $\Delta\lambda$ and Φ_0.

The kinetic and the saturation curves were calculated and the molecular photophysical parameters were restored under the conditions of the most simple one flourophore model.

All the information is shown in (Tab. 2). The chemical structure parameters are listed there also.

Table 2: The combined experimental data: fluorescent, photophysical and chemical structural parameters.

№		Max. position	Half band width	Φ_0 for 3 mg/L	Car-C,H 108-145	CarO 145-165	Tau	Sigma
I	Pha-T5-98	457	39	13	32	7	4.85384	--
II	Pfa-T5-98	456	35	21	24	8	4.67993	1.8
III	Phf-T5-98	451	34	9	25	8	3.62259	2.1
IV	Cha-GI-02	466	46	31	47	14	3.18242	2.1
V	Cfa-GI-02	450	33	47	32	11	3.71799	1.7
VI	Chf-GI-02	453	54	18	46	15	2.85663	--
VII	Sha-Pw-04	455	58	9	19	6	3.016	2.3
VIII	Sfa-Pw-04	456	35	24	21	7	2.97247	--
IX	Shf-Pw-04	453	36	10	10	2	3.51716	1
X	Sha-Ctk-04	463	42	18	33	8	2.91215	2.6
XI	Sfa-Ctk-04	460	40	15	22	4	3.26393	--
XII	Ahf-IsX2-04	456	39	37	19	7	2.92866	3.7

The analysis of the data in Table 2 shows that in basic the changes of the fluorescence and photophysical parameters corresponds to the parameters that characterize the aromaticity and the size of the fluorophore.

4. CONCLUSIONS

The simultaneous measurement of the three fluorescence and two photophysical parameters of the humic substances and their comparison with the chemical structure have been performed for the first time.

The obtained results shows that the photophysical parameters of the different humic substances are very contrast and are in close relation with their chemical characteristics and structure. Finding out of such relations makes possible to prove the method of the express analysis of the humic substances in water using the laser fluorimetry methods and also makes possible to propose a theory of the structure of the humic fluorophore.

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