

# Investigation of Polydispersion Characteristics of Humic Acid Molecules by Means of Luminescence Spectroscopy

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## Abstract

A simple method of discrimination for the molecules of humic acids (HA) with respect to their dispersion states is proposed. The method is based on non-uniformity of the contour of HA luminescence spectra and involves the determination dependence of the position of maximum in the fluorescence spectrum  $\lambda_{\text{obs}}$  on the wavelength in the maximum of fluorescence excitation spectrum  $\lambda_{\text{exc}}^{\text{max}}$  or determination of the dependence of  $\lambda_{\text{exc}}^{\text{max}}$  on  $\lambda_{\text{obs}}$ . The applicability of the method is demonstrated with several samples of aqueous solutions of HA.

Humic acids (HA), independently of their origin, are high-molecular nitrogen-containing organic acids; their molecules contain aromatic groups. The analysis of results obtained by a number of procedures allowed creating a general image of the structure of humic acid macromolecule: the presence of a nucleus (aromatic hydrocarbon framework) and periphery (polysaccharide–polypeptide chains) [1, 2]. It is assumed that the molecular fragments of the nucleus and periphery of one HA molecule are connected by chemical bonds. A characteristic feature of the humic acid macromolecules is their dispersion [1, 2], which is exhibited in substantial variations in the size of HA macromolecules isolated from the soil at one site, which is due to the variability of the quantity (and quality) of chemical fragments comprising it. The determination of HA dispersion is an important problem because this parameter is used to differentiate soil kinds [1, 2]. Till recently, the data on dispersion of HA were obtained from the chromatographic data [1, 2].

Publications dealing with the luminescence spectroscopy of HA lack any special discussion of dispersion, though there are some considerations that this parameter should be expressed in luminescence spectra [3–5]. A model status

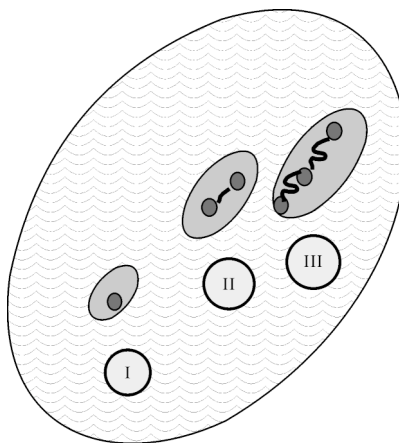


Fig. 1. Model of the positions of luminophor groups in HA molecules placed in a liquid solution. Hatched region depicts a solvent, gray colour marks the HA macromolecules, black circles are luminophor groups. For details, see the text.

of luminophor groups in HA molecules placed in a liquid solution is shown in Fig. 1. (For simplicity, we limit our consideration to the case when the HA solution contains three macromolecules.) One can see that, along with the dispersion of HA due to the variability of the geometric size of macromolecules, additional dispersion will take place for the luminophor groups (even if they are fully identical for all the molecules), which is due to differences in chemical structure (micro surroundings) of the molecules containing those luminophors. Thus, one should expect that the luminescence spectrum observed experimentally is to give an overall information concerning the state of luminophors not only in different macromolecules but also in each of the HA molecules. However, according to Kasha's rule (or the 1st Vavilov law), for organic molecule of any complexity in liquid solution, luminescence always occurs from the zero vibration level of the first excited state independently of the excitation wavelength [6]. This means that the luminescence spectrum of a specific HA molecule (in particular, the position of the maximum of luminescence band  $\lambda_{fl}$ ) should be independent of the excitation wavelength  $\lambda_{exc}$ . So, if several kinds of HA molecules are present in solution (see Fig. 1), the luminescence of II and III molecules, as well as that of I molecule, will be characterized by only one spectrum. Therefore, experimentally observed luminescence spectrum  $I_{exc}$  under photo-excitation of the liquid HA solution will be a sum of the luminescence spectra of each HA macromolecule  $I_i$ :

$$I_{lum} = \Sigma I_i \quad (1)$$

One can see that the position of the maximum in the total luminescence spectrum will depend on relative contributions from each of the  $I_i$  constituents, which, in turn, is determined by the absorption efficiency and quantum yield [6]. Hence, using the dependence of  $\lambda_{fl}$  on  $\lambda_{exc}$ , that is, providing sequential excitation of an  $i$  kind of HA molecule one can obtain information on the disperse state of HA samples with respect to fluorescence groups. (It should be noted that the first attempt to obtain quantitative information about the state of HA dispersion was likely to be the applica-

tion of temporal transformation of the spectra of T-T absorption [7].)

The information on the dispersion of HA samples can also be obtained from the luminescence experiments when analyzing the dependence of the position of excitation band maximum  $\lambda_{exc}^{max}$  on the wavelength of fluorescence observation  $\lambda_{obs}$ , that is, in the experiments with the observation of excitation spectra of HA molecules.

The published communications on the luminescence of HA solutions did not provide any systematic consideration of quantitative links between the dependences of  $\lambda_{fl}$  on  $\lambda_{exc}$  and the dependences of  $\lambda_{exc}$  on  $\lambda_{obs}$ . Meanwhile, it seems reasonable that these dependences are able to gain comparative information about the disperse characteristics of HA. The goal of the present work is the investigation of disperse properties of HA samples isolated from different kinds of soil by means of the procedures proposed above.

The positions of the maxima of luminescence bands of HA molecules isolated from three different kinds of soil are shown in Fig. 2 plotted *versus*  $\lambda_{exc}$  according to the data of [8]. One can see that each kind of HA can be confronted with an individual dependence of  $\lambda_{fl}$  on  $\lambda_{exc}$ . Quantitative, a measure of dispersion (dispersion coefficient) can be accepted to be the tangent of the slope of the observed de-

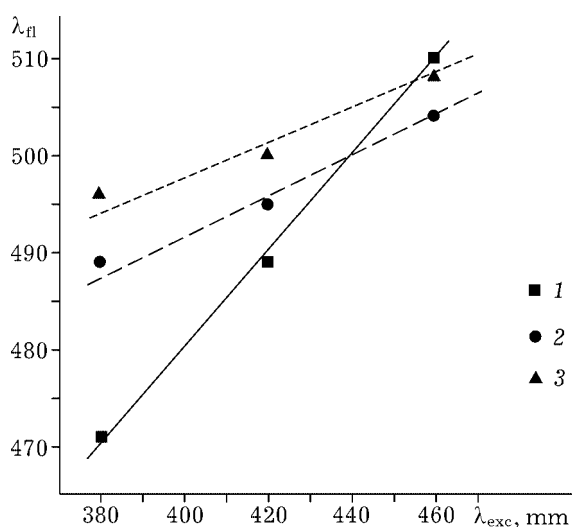


Fig. 2. Dependence of the position of maximum of fluorescence of HA  $\lambda_{fl}$  macromolecules isolated from black earth (1), ferrazole (2), ranker (3) and the wavelength of excited light  $\lambda_{exc}$  [8].

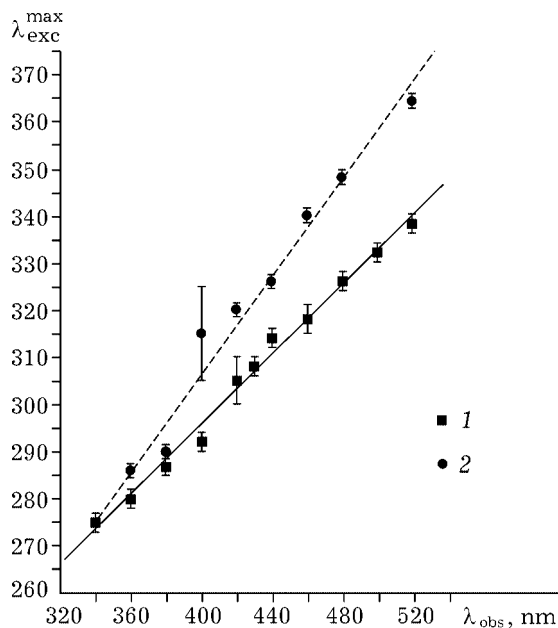


Fig. 3. Dependence of the positions of maximum of excitation spectrum on the wavelength of luminescence observation for twice distilled water (1) and for water from water-pipe (2). The continuous line:  $\lambda_{exc}^{max} = (156 + 0.37\lambda_{obs})$  nm, dash line:  $\lambda_{exc}^{max} = (110 + 0.51\lambda_{obs})$  nm.

pendences. These tangents are 0.49, 0.19 and 0.175 for the HA isolated from black earth, ferrazole and ranker, respectively. Therefore, the HA isolated from the black earth is characterized by maximal dispersion. This means that the HA from the black earth has the largest number of molecular fragments differing in luminescence properties, while other HA samples are more uniform. Maximal dispersity of the HA samples isolated from the black earth is likely to be connected with the maximal number of microorganisms and maximal (in comparison with other kinds of soil) level of biological activity [1, 2].

The dependences of  $\lambda_{exc}^{max}$  on  $\lambda_{obs}$  of luminescence for the residues of HA in water from water-pipe (Novosibirsk, Akademgorodok, upper territory) and in twice distilled water\* are shown in Fig. 3.

The tangent of slope of the obtained dependences within the studied spectral region is

only slightly larger for the fluorescence of water from water-pipe than for the twice distilled water. So, it follows from the data obtained that distillation has rather weak effect on the dispersion of HA residues. This is likely to be due to rigid treatment of water at the purification works (chlorination, ozonization, etc.), which causes substantial destruction of HA. Therefore, a substantial difference between the slope tangents for the systems under consideration should mean that the water from water-pipe is poorly treated. So, the proposed method for the analysis of luminescence spectra can be used to analyze the degree of water purification.

It seems that the proposed fluorescence methods of determining HA dispersion will allow obtaining additional useful information for solving numerous tasks of the theory of structure and origin of HA, as well as for a number of practical problems.

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\*The spectra of luminescence and excitation of water samples were recorded with Hitachi instrument at a temperature of 22 °C.