Optimization of electrospray ionization conditions for more informative mass spectra in structural research of HS for applications in medicine

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Humic substances (HS) represent products of postmortal decomposition of living organisms and compose one of the largest reservoirs of organic carbon of global ecosystem. HS possess non-stocihiometric compositions and heterogeneic structures representing natural polyfunctional macromolecular compounds. Comprehension and quantitative description of HS structure belong to one of the most challenging tasks of modern structural analysis. This task is of particular virtue given the prospective pharmacological properties shown both by HS and metal-HS complexes in antiviral, anti-inflammatory, anti-tumor, and other activities. However, a directed use of HS in medicine is greatly hindered due to a lack of single structure which can be prescribed to those compounds for creating quantitative structure-activity relationships (QSAR). New approaches are needed for developing structural descriptors for the compounds of this complexity. Considerable progress in the area of understanding of the molecular structure of HS is currently reached due to application of Fourier transform ion cyclotron mass spectrometry (FTICR MS) in combination with electrospray ionization (ESI). Recently it has been shown by our group that change of electrospray ionization conditions significantly influences on effectiveness of ionization of HS isolated from water [1]. The task of the current work was optimization of electrospray ionization conditions for HS isolated from peat, coal and soil with the goal to obtain the most informative FTICR mass spectrum during relatively short time.

ESI FTICR mass spectra were acquired on the hybrid mass spectrometer LTQ FT Ultra (Thermo Electron Corp., Germany) with 7T superconductive magnet. The instrument was equipped with Ion Max (Thermo Electron Corp., Germany) ion source. Mass spectra processing was performed by original software, developed at the laboratory, which included: solving of Diophantine equations, calculation of total mass difference statistics, determination of charge states.

Dependence of signal intensity on the choice of the solvent, ESI voltage and the sample concentration was studied. The signal intensity was calculated as a summary intensity of 6 peaks from mass spectra, which were reproduced for each solvent and had high enough intensity even at not optimal conditions. As the solvent, methanol, water-methanol mixture (1:3) and acetonitrile were used. For each of chosen solvents the optimal ESI voltage was determined. For the optimal solvent the dependence of the signal from concentration of the sample was studied.

At the result the most informative ESI FTICR mass spectra was acquired for HS dissolved in acetonitrile. For each of measured samples the optimal ESI voltage had been established.

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[1] E.V. Kunenkov, A.S. Kononikhin, I.V. Perminova, A.V. Garmash, I.A. Popov, E.N. Nikolaev. Vestnik Moskovskogo Universiteta. Khimia. 2010. Vol. 51, No. 5, p. 364-368.