Metal Binding by Humic Substances – Characterization by High-Resolution Lanthanoide Ion Probe Spectroscopy (HR-LIPS)

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In ultra-low-temperature experiments at 4.7 K the luminescence of Eu(III) bound to different hydroxy- and methoxybenzoic acids and to humic substances (HS) was investigated. The benzoic acid derivatives were used as simple model compounds for common metal-binding structures in HS. The Eu(III) luminescence was directly excited by means of a pulsed dye laser, scanning through the $^5D_0 \leftarrow {}^7F_0$ transition of Eu(III) and subsequently high-resolution total luminescence spectra (TLS) were recorded. Based on the thorough analysis of the high-resolution TLS conclusions were drawn with respect to the number of different complexes formed and to the symmetry of the complexes. The crystal-field strength parameter $N_v(B_{2q})$ was dependent on the electrostatic forces induced by the ligands as well as on the symmetry of the complexes. The formation of thermodynamically stable complexes was found to be slow even for small model ligands such as 2-hydroxybenzoic acid. Comparison between the model compounds and HS clearly revealed that the carboxylate group is the dominant binding site in HS. Indices for the formation of chelates, e. g. similar to 2-hydroxybenzoic acid, were not found for HS.

Key words: Humic Substances; Europium; Benzoic Acids; Low-Temperature Luminescence.