

CE-DAD-ICP-MS for determination of complex formation constants for the complexation of lanthanides and actinides with humic substances

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The investigation of complex formation constants for the humic acid complexation of actinides and, as model substances, lanthanides, is of interest with respect to the deep geological disposal of radioactive waste. In most aquatic systems and also in clay formations, natural organic matter such as humic substances (HS) is present. These HS can act as ligands for metal ions and thus have an influence in the speciation and migration of radionuclides.

In earlier studies, it has been shown that the CE-ICP-MS (1) as well as CE-DAD-ICP-MS (2) coupling can be applied for the investigation of the complexation behaviour of metal ions with HS. The different species are separated by CE and detected by DAD and ICP-MS. By application of pressure onto the CE capillary during the separation it is possible to detect both the cationic and anionic species at the exit of the capillary. The free metal ions and metal containing HS species can be measured with a low limit of detection by ICP-MS, whereas the HS as well as some EOF markers can be detected by DAD due to their light absorption. For calibration purposes and to identify the species, iodine marked humic acid can be used and easily detected by both detectors.

Due to the dissociation of the metal-humate complex, the interpretation of resulting electropherograms is complicated. Besides the cationic free metal ions and the anionic metal humate complex, there is another species consisting of initially complexed metal. It is supposed that these metal ions are dissociated from „weak binding sites“ of the humic substance caused by the high electric field under CE separation conditions. By lowering the concentration of metal ions, the complexation at „weak binding sites“ is likely to play a minor role. Thus, a more precise determination of complex formation constants should become possible.

For a standard (Aldrich) humic acid, a combination of ultrafiltration to determine the loading capacity LC as a function of pH, with CE is being used to obtain reliable $\log \beta$ values. For fulvic acid, ultrafiltration is not feasible and the aim of the present study is to determine both the loading capacity and $\log \beta$ values by CE.

(1) R. Kautenburger, K. Nowotka, H. P. Beck, *Anal. Bioanal. Chem.* **2006**, *384*, 1416-1422.

(2) E. Gromm, diploma thesis, Johannes Gutenberg-University, Mainz **2008**.