

Abstract No. Schä0082

Functional Group Analysis of Natural Gorleben Fulvic Acid using C(1s) Spectra Deconvolution

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Beamline(s): X1A

Introduction: In natural aquifers, organic and inorganic colloids are ubiquitous and take part in geochemical solid-water-interface reactions. Due to their strong interaction with multivalent metal ions humic colloids exert a crucial influence on the mobility of actinides in natural [1] and anthropogenic influenced aquifer systems [2]. The isolated fulvic acid (FA) used in this study origin from the Gorleben aquifer (Lower Saxony, Germany) representing the far-field of a potential deep geological final storage site for heat-generating high level radioactive waste in Germany. The aim of this study is to demonstrate the possibility of functional group quantification in complex natural organic matter by comparison of high resolution C(1s) NEXAFS spectra with ^{13}C -NMR measurements.

Methods and Materials: The detailed description of the groundwater composition, the Gorleben site and the isolation and characterization of the FA present in Gorleben groundwater is described in [3,4]. For spectra deconvolution two ionization thresholds (IP) were used to generate the continuum spectrum. FWHM of Gaussian peaks were set to 0.4 eV and 5 Gaussian functions representing the main $1s\text{-}\pi^*$ transitions were used (Fig. 1). Details on spectra deconvolution are given in [5]. For quantitative analysis ^{13}C NMR spectra were acquired with a Bruker DMX 500 NMR spectrometer (Rheinstetten, Germany). For details on the principle and the analytical setup it is referred to [6, 7].

Results & Discussion: The isolated Gorleben groundwater fulvic acids show in the C(1s) spectra deconvolution a significant variation of phenol, aromatic carbon and aliphatic content (Fig. 1). Furthermore a slight variation in carbonyl groups and almost no variation in the carboxyl group content could be observed. Isolated FA of the re-charge dominated areas show thereby the highest aliphatic content with the lowest aromatic and phenol content. A good linear correlation ($r^2 > 0.9$) of aromatic C=C and C-H, phenol, aliphatics and carbonyl groups between the ^{13}C -NMR and C(1s) NEXAFS (Fig. 1) results were found. Due to the low variation in the carboxyl group content of the samples no linear correlation coefficient could be determined. Overall the results clearly demonstrate that C(1s) NEXAFS deconvolution can be used in the Gorleben system to quantify functional group content of highly complex natural organic material. The transferability of these procedure to other natural systems however is under investigation.

References:

- [1] Kim, J.I., G. Buckau, H. Rommel, B. Sohnius, *Mat. Res. Soc. Symp. Proc.* **127** (1989) 849-854.
- [2] Vilks, P., H.G. Miller, D.C. Doern, *Appl. Geochem.* **6** (1991) 565-574.
- [3] Buckau, G., R. Artinger, P. Fritz, S. Geyer, J.I. Kim, M. Wolf, *Appl. Geochem.* **15** (2000) 171-179.
- [4] Artinger, R., G. Buckau, S. Geyer, P. Fritz, M. Wolf, J.I. Kim, *Appl. Geochem.* **15** (2000) 97-116.
- [5] Schäfer, T., Hertkorn, N., Artinger, R., Claret, F., Bauer, A. *J. de Physique IV* (submitted)
- [9] Hertkorn, N., A. Permin, I. Perminova, D., Petrosyan, A. Kettrup, *J. Environ. Qual.* **31** (2002) 375-387.
- [10] Hertkorn, N., T. Schäfer, R. Artinger, P. Schmitt-Kopplin, *Org. Geochem.* (in prep.)

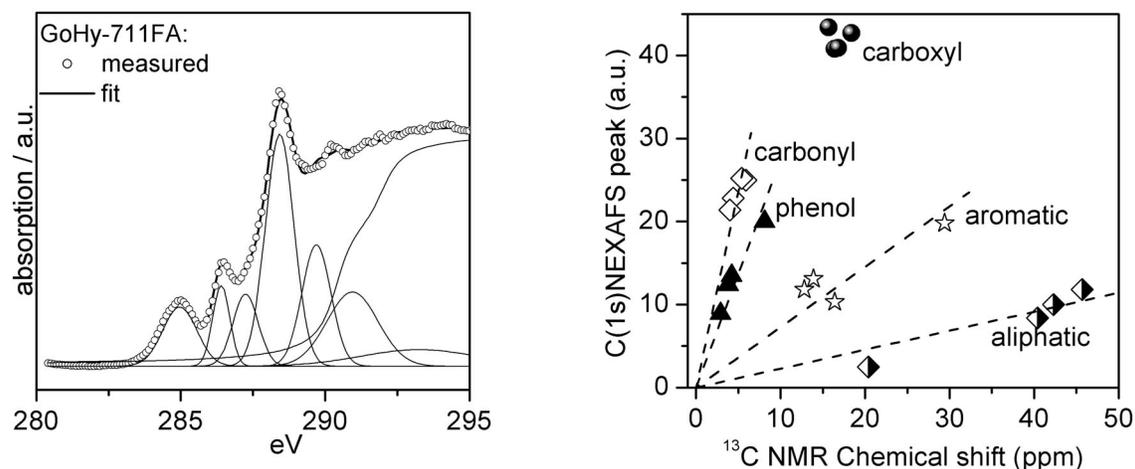


Figure 1: Left: C(1s) spectra deconvolution of sample GoHy-711 isolated fulvic acid showing the main π^* -transitions, the two σ^* transitions and the arctangent step function. $1s\text{-}2\pi^*$ transitions not shown. Right: Correlation of C(1s) NEXAFS peak areas and ^{13}C -NMR chemical shift.