NEXAFS spectroscopy with a laser plasma x-ray source on soil samples

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Abstract. Humic substances are post-mortal organic substances without an exact chemical structure. Their large specific surface is important for transport processes, especially in soils. We analyzed the NEXAFS spectra of humic substances, from which the amount of certain chemical compounds such as aromatic and aliphatic groups can be verified by the resonances of their binding energy. For the experiments, a compact table-top setup working with a laser plasma source was used. NEXAFS makes it possible to distinguish between samples, even if they contain the same composites, because information about the specific functional groups in the sample is supplied.

The evaluation was carried out using the program SpecFit. It was developed on IDL within our group and allows to fit the NEXAFS-data with a combination of arctangent, Gaussian and Lorentzian curves.

1. Introduction
Humic substances make up a major part of the natural organic matter (NOM), not only in soils, but also in water (rivers, lakes, oceans and their sediments) and organic deposits (peat, brown coals and shale). They can be divided into humins, humic acids and fulvic acids, according to their color or to their solubility depending on the pH of the solution [1].

Humic substances are also the reason for the characteristic brown color of decaying plants. They have an amorphous macro-molecular structure of high molecular weight. Thus, since humic substances do not have an exactly defined chemical structure, it is of key importance to find reliable ways to measure their properties.

2. NEXAFS-spectroscopy and SpecFit
With near edge x-ray absorption fine structure spectroscopy (NEXAFS) it is not only possible to characterize humic substances from different origins, even if they contain the same composites, but also to easily distinguish between the operationally defined fractions fulvic acid, humic acid and humins [3]. This stems from the fact, that NEXAFS reveals the binding forms within a sample by measuring the sum over all possible final states of the electrons and so yields information about the specific functional groups [2]. Thus, NEXAFS-spectroscopy is a powerful means to especially characterize environmental samples.

Because of the lack of an exact structure, it is more suitable (compared to linear combination methods) to fit the spectra with a combination of arctangent, Gaussian and Lorentzian curves.
using the evaluation program SpecFit, which was developed within our group using Interactive Data Language (IDL) [4]. Figure 1 shows an example of the evaluation with SpecFit on the basis of a data set we gained from a fulvic acid. The arctangent function simulates the absorption edge, whereas the Gaussian curve denotes the resonance peak [5] [2]. The Lorentz curve takes the broadening of the resonance into account, which is an intrinsic feature of the experimental apparatus.

![Figure 1. a) NEXAFS-spectrum of fulvic acid evaluated with a combination of Gauss-, Lorentz- and arctan- curves using the program SpecFit. b) Comparison of the areas under the first three Gauss-peaks.](image)

The assigned peaks can then be related to the values of the resonances of certain binding energies, for instance single or double bond between two C-atoms. We decided to assign a peak and an absorption edge to every resonance over the method of defining one general arctangent function to approximate the absorption edge and several Lorentz-Gaussian curves to fit the peaks. That way, the real peak heights are acquired, especially for the important peaks before and right at the absorption edge. The parameters were chosen in a way to find the optimal fit for the data curve.

3. Materials and Methods

We analyzed two different sample groups. The first group consisted of four samples from the area around Göttingen, representing the different fractions of humic substances. The second group was one sample of humic substances (purchased from Sigma Aldrich), which was extracted using three different solvents. All humic substances have been mixed with Millipore-water. We used 1% standard solutions, which would be diluted further, if necessary. The basic procedure was the following: The glass vessels (2ml, Eppendorf) containing the solutions of humic substances and water were treated with ultrasound for several minutes and afterwards 1-2μl were dropped on a Si₃N₄-foil. The water evaporated and the foil with the dry sample was mounted on the sample holder and installed in the table-top NEXAFS-spectrometer (Laser Laboratorium Göttingen), which is explained in reference [6]. The Si₃N₄-foils (100nm thick, frame 5×5mm², window 1.5×1.5mm²) were purchased from Silson Ltd., Northampton, England.

4. Results and Discussion

First, we compared four samples containing different amounts of humic substances with each other, see figure 2. The three parts, which humic substances can be divided into, can clearly be differentiated. Humins in the very humus-rich chernozem contains the highest amount of aromatic carbon. This sample was from a chernozem-soil [7]. Humic acid, here in the form of its salt (Ka-humate) is a frequently used fertilizer. The fulvic acid was of aquatic origin. Both acids contain significantly less carbon than the chernozem. The smallest content of humus could be found in the luvisol-sample. Luvisol is a soil, which contains clay minerals and calcite and normally is poor in nutrients (humus). As the aromatic content decreases, the carboxylic groups become more and more observable in the spectrum. Another feature, which is also growing, is the amount of potassium, observable by the increasing peaks of the LIII and LII peaks. The second series of humic substances samples characterized the influence of the extraction solvent on the humic fraction. We analyzed one reference sample of humic acid and the same sample after three different extraction methods (figure 3). The measurements reveal, that the
choice of the solvent influences the chemical composition of the sample. This should be taken into account, when analyzing soil samples or other specimens that need to be extracted.

Figure 2. Normalized NEXAFS-spectra of the four different soil-samples. The evaluation has been done with SpecFit. However, the difference in peak heights of the aromatic, carboxylic and potassium peaks is clearly visible.

Figure 3. Normalized NEXAFS-spectra of the reference sample and the result of the three different extraction methods. The evaluation has been done with SpecFit. Again, the different peak heights of the aromatic, carboxylic and potassium peaks are clearly visible.

5. Conclusion
We analyzed two groups of soil samples regarding their carbon-content. One group consisted of different fractions of humic substances, whereas the other group was made up of one humic substances sample (reference) and the result of the extraction of this sample using three different solvents. The experiments show, that the spectrometer operating with a laser-driven plasma source is a good alternative to synchrotron-based spectro-microscopes, if spatial resolution is not necessary.

All of the samples were clearly distinguishable concerning the three major carbon-binding groups (aromatic, phenolic and carboxylic) and more; where the information was derived from the fitting method. This evaluation, using a combination of Lorentzian, Gaussian and arctangent curves, is an improvement to methods using only one general arctangent curve to approach the absorption edge, especially when working with samples without exactly specified content such as biological and environmental specimens.

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