XANES Studies of the Effect of pH on Complexation of Copper(II) with Humic Substances

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Introduction: This work was carried out to quantify structural changes of the inner complexation shell of Cu\(^{2+}\) in its complexes with natural organic matter (NOM) and model compounds in a wide range of pH. The non-uniformity of copper-binding sites in NOM [1,2] manifests itself through a gradual change of XANES spectra associated with increased copper doses.

Methods and Materials: The fraction of Suwannee River NOM retained by XAD-4 resin and eluted by acetonitrile was used. A model polymer (polystyrenesulfonic-co-maleic acid, PSM) was also used in this study. As a reference compound, Cu-EDTA complex was also measured at different pH. X-ray absorption measurements were carried out at the X16-C beamline of the NSLS at BNL.

Results: The first derivatives of the XANES spectra indicated a variety of structural processes associated with the increase of pH. Among those, the position of the zero of the first XANES derivatives (that is, the position of the maximum of the absorption coefficient) exhibited a graduate shift towards higher energies with the increase of pH (Fig. 1). After comparing these results with those of the XANES measurements of Cu-EDTA complex where, even at pH 10, no shift was observed, it was hypothesized that the location of this feature may be affected by both the tetragonal distortion of the inner shell in the Cu\(^{2+}\) complexes and the total charge of the central cation and surrounding functional groups.

Conclusions: It was concluded that the observed effect is consistent with the incorporation of hydroxyls into the inner shell at pH>9. This process is likely to be accompanied by the expulsion of the organic ligands and eventually formation of either insoluble hydroxides or, at very high pHs, soluble polyhydroxy-species.


Figure 1. Shift of the position of the zero value in the first XANES derivatives for Cu-NOM and Cu-PSM complexes vs. pH.