COMPLEXATION OF TETRAVALENT METALS BY HUMIC SUBSTANCES DETERMINED BY CAPILLARY ELECTROPHORESIS-INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (CE-ICPMS) AND EQUILIBRIUM DIALYSIS EXCHANGE

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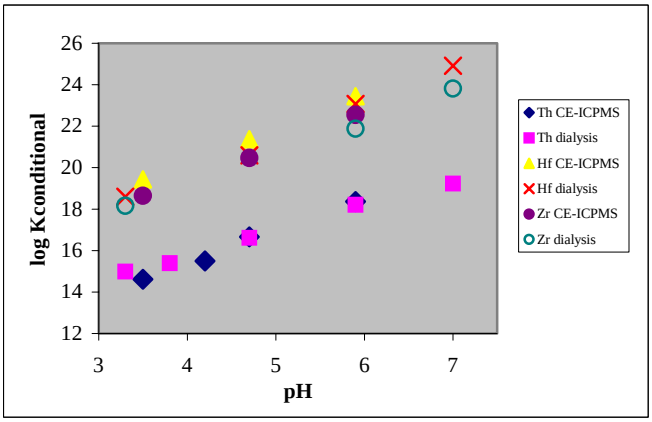
Introduction

The presence or absence of humic substances in the water column can determine whether trace metals will be present in limited quantities as a nutrient, or in surplus quantities as a toxicant. Metal binding in trivalent cations has been extensively studied, but less data exists for the actinides and tetravalent metals. Studies of trivalent metals have shown that even at low HS concentrations found in groundwater, metal-humate complexation takes precedence over hydrolysis and carbonate complexation (Glaus 1995). Concentration of tri- and tetravalent trace metals in groundwater can be directly related to concentration of HS. This makes metal-HS interactions important to account for in assessing transport of radionuclides in groundwater from nuclear repository sites.

Capillary electrophoresis coupled with ICP-MS has been shown to be an extremely useful tool in quantifying how effective HS are in complexing trace metals. High detection levels of ICP-MS allow experiments to be carried out under natural conditions of very low metal concentrations. The ligand competition approach used in Sonke and Salters, 2004 allows accurate measurements to be taken despite the fact that CE is a disequilibrium speciation technique, where the original equilibrium of the system is disturbed to separate the species (M, L, and ML) in time and/or space in order to measure them. By using two strong ligands, HA/FA and EDTA, kinetically stable complexes are formed that are resistant to dissociation and can be measured accurately (Sonke & Salters 2004). In order to validate the results obtained by CE-ICP-MS, equilibrium dialysis exchange was used to determine the binding constants of Th, Hf, and Zr. These experiments were performed at the same ionic strength and over the same pH range as the CE-ICP-MS experiments.

Results and Discussion



Conditional stability constants were calculated for Th, Hf, and Zr humic complexes at pH 3.5, 4.7, 6, and 7 at ionic strength of 0.1. Dialysis exchange experiments produced conditional binding constants similar to CE-ICPMS. Overall, the conditional stability constants of the tetravalent metal-HA complexes are several orders of magnitude higher than the lanthanide-HA complexes. CE-ICPMS experiments were also conducted comparing binding constants of REEs with various humic acids, including soil, peat, and aquatic HA. We found that all humic acids used in these experiments yielded similar binding constants when complexed with REEs.

Conclusions

This research provides conditional binding constants for tetravalent metal-HA complexes in the acidic to neutral pH range. Tetravalent metals appear to bind more strongly to HA than the trivalent REEs. In addition, this dataset can be used to assess predictive speciation models. The results obtained by CE-ICPMS are validated by equilibrium dialysis exchange, indicating that CE-ICPMS is a viable tool to study metal speciation.

References

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