

SPECIATION OF TETRAVALENT METALS THORIUM, HAFNIUM, AND ZIRCONIUM BY CAPILLARY ELECTROPHORESIS INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (CE-ICP-MS) AND EQUILIBRIUM DIALYSIS LIGAND EXCHANGE (EDLE)

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Introduction

Because thorium is often used as a proxy for the actinides, Th-humate interactions can allow us to assess the importance of tetravalent actinide-humate complexes in groundwater transport from nuclear repositories. To simulate metal-humate interactions in nature, experiments must be carried out using trace metal concentrations. Sensitive detection systems such as ICP-MS make working with small (nanomolar) concentrations possible. This study coupled capillary electrophoresis (CE) to ICP-MS to determine tetravalent metal partitioning between several different HA species and a reference ligand, EDTA. From this data, conditional binding constants for $M^{4+}HA$ species can be calculated. This method of separation was compared to more traditional dialysis membrane experiments (EDLE).

Experimental

CE-ICP-MS experiments were performed by coupling a homemade CE apparatus to the Finnigan MAT "ELEMENT" high resolution sector ICP-MS in the Geochemistry laboratory at NHMFL. The interface provided continuous sheath flow via syringe pump so as not to induce a siphoning effect due to nebulizer aspiration. More details can be found in Sonke & Salters, 2004. CE-ICP-MS and EDLE samples were prepared in the clean lab for pH range 3.5-7 and IS = 0.1. Metal species in EDLE experiments were separated by partitioning due to size exclusion via diffusion through a 1000 Da membrane.

Results and Discussion

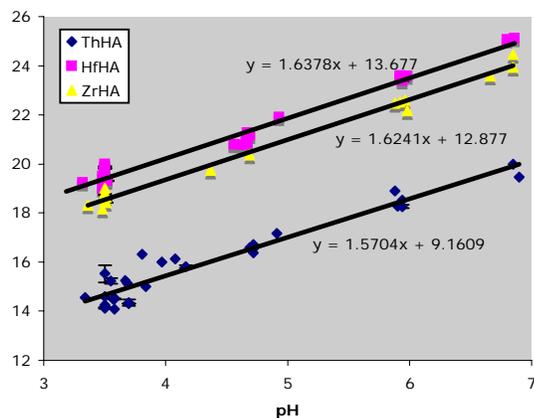


Fig. 1. Variation of $\log k_{\text{conditional}}$ as a function of pH.

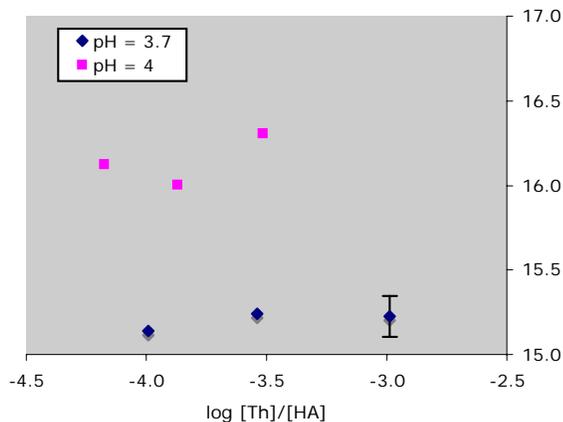


Fig. 2. Effect of free metal concentration on $\log k_{\text{conditional}}$.

Conclusions

Results of this research indicate that tetravalent metals strongly complex humic substances. It appears that the behavior of ThHA binding constants is responding to variations in pH, and not metal concentration. The variation of conditional binding constants over several orders of magnitude of $[M]/[HA]$ is no greater than the variation of replicate samples of the same $[M]/[HA]$ values. This data represents the first side by side study of CE-ICP-MS and a more traditional speciation method, and will provide important data to validate polyelectrolyte models.

Acknowledgements

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References

Sonke, J.E. and Salters, V.J.M., *Journal of Analytical Atomic Spectrometry*, **19**, 2, 235-240 (2004).