

DOE Problems Addressed

The goal of this task is to develop analytical methodology that can be used to understand the equilibria of organic complexants and their products in multicomponent mixtures. Knowledge generated by the success of this project can be used to address such DOE needs as: a) determining the concentration of organic complexants to meet waste acceptance criteria prior to disposal; b) aiding in waste treatment in which DOE EM-50 sponsors efforts to destroy chelators prior to removal of metal contaminants; and c) processing secondary waste streams in which chelating agents are introduced to decontaminate surfaces prior to decommissioning radioactive equipment and facilities.

Research Objective

The overall objective is to develop and enhance our understanding of chemical equilibria for major organic complexant species (chelators, chelator fragments, small organic acids and their products) in multi-component aqueous matrices such as the mixtures of DOE stored wastes. To progress toward this objective, organic complexants must be separated and speciated in mixtures of high ionic strength. HPLC employing zirconia-based stationary phases is being studied in order to understand the separation requirements for organic complexants and the products formed by complexants with metals in complex aqueous mixtures. Separated complexant species will then be characterized using positive and negative ion thermospray mass spectrometry (TSMS). The final goal is to develop the analytical capability needed to define chemical concentration and equilibria for complexant species in DOE waste streams.

Research Progress and Implications

Significant progress during the past twenty-eight months of the 3-year project has been made in understanding the effectiveness of zirconia-based stationary phases for separating complexing agents such as nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), citrate and oxalate. Each of these complexing agents has been used to solubilize radioactive metals from spent fuel rods and nuclear processing equipment, and now are components of high-level alkaline tank waste. Other chelators being studied are ethylenediamine-N,N'-diacetic acid (EDDA), imidodiacetic acid (IDA), N-2-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA) and N-(2-hydroxyethyl) imonodiacetic acid (HEIDA), which may be present as degradation products and are potential complexers of strontium and cesium, the primary fission products found in DOE tank waste.

Separation investigation initially employed bare zirconia particles with an average diameter of 3 μ m as the stationary phase in HPLC separation. The zirconia is known to have Lewis acid sites that coordinate hard Lewis bases such as carboxylates very strongly. The stationary phase also exhibits Brönsted acid/base character that can provide fixed charge sites for anion or cation exchange depending on the pH of the eluant. However, it is the coordination chemistry of zirconia that has been exploited to separate the chelators. A variety of elution conditions were tested. Two approaches were applied. The first used gradients of increasing hydroxide or increasing fluoride concentration to provide competing ligand to displace the complexants. However, even at very high pH, the complexants were either irreversibly sorbed or the band width of complexant profiles was so great that this approach was deemed impractical. In a second approach low pH gradients or low pH buffers with a gradient of increasing ionic strength of acetate or fluoride were used. The rationale was that at low pH the chelators would be partially protonated in free solution and the formation constant for the zirconium-chelator complexes would be less favorable, allowing elution of the complexants. Results indicate that if the pH is too low or if the fluoride concentration is greater than 10 mM, the chelators elute as a group with virtually no retention. Even with moderate pH or fluoride gradients, the solutes do not elute in well-formed bands, presumably due to very slow desorption kinetics.

In contrast, work with zirconia coated with quaternized polyethyleneimine (QPEI) effected the separation of IDA, NTA and EDTA quite well under a variety of elution conditions. The separation of these complexants on QPEI-zirconia falls into three general groups: 1) IDA, EDDa, and HEIDA are weakly retained; 2) NTA, EDTA, HEDTA, and DTA show moderate retention and can be separated under a variety of eluting conditions; and 3) oxalate and citrate are strongly retained and can be eluted

with gradients in pH or bicarbonate. Further investigations are being pursued to optimize complexant separation on QPEI-coated zirconia.

HPLC separations followed by thermospray mass spectrometry have been utilized to develop positive ion mass spectra of organic complexants related to EDTA. These spectra have been defined at different source temperatures in water:methanol solvent systems containing different buffering components. Mass spectra show a peak at mass $[M+1]^+$ when vaporized from solvent media at low pH.

As the pH increases the relative amount of mass $[M+1]^+$ appears to decrease in favor of a mass at $[M + \text{adduct}]^+$. This tendency to form an adduct in the gas phase can be related to the relative proton affinity of these complexants in the vapor phase. A lower proton affinity in the vapor phase should be consistent with greater acidity in the solution phase. Such characteristics may aid in defining behavior in solution. Accordingly interpretations of TSMS spectra should be useful in the characterization of DOE mixed waste solutions.

As a caveat to the study of bare zirconia as an HPLC stationary support, the material is also being evaluated as a sorbent for the selective removal of complexants or complexed metals at the head end of a waste treatment flowsheet. To simulate a waste treatment process, batch tests were performed in which bare zirconia was added to process water containing ^{90}Sr and ^{137}Cs in the presence and absence of citrate. Results indicate that neither the radionuclides nor citrate were sorbed on bare zirconia. Batch tests simulating high alkaline tank wastes containing EDTA still need to be performed.

Planned Activities.

Within the remaining eight months of the project the following activities will be accomplished: 1) optimization of chelator separation on QPEI-coated zirconia; 2) conclude predictive capability of proton affinity (or gas phase acidity from TSMS characteristics); 3) complete TSMS studies of known chemical species of complexants and metal ions; 4) detail project results in a manuscript for the open literature. [There will be a no-cost extension of the chromatography development at the University of Minnesota in order to accommodate the availability of a post-doctoral research worker.]

Information Access

Results from these investigations will be published in the open literature. At this point in time the following presentations have been given at national scientific meetings:

1. Separation and speciation of organic complexants in DOE wastes using HPLC on zirconia-based stationary phases and thermospray mass spectrometry . American Chemical Society, Fall Meeting, New Orleans, LA, August 22-26, 1999.
2. HPLC separation of chelating agents on quaternized polyethyleneimine coated zirconia . Eastern Analytical Symposium, Somerset, NJ, November 16, 1999.