

Project ID: **59978**

Project Title: **Thermospray Mass Spectrometry Ionization Processes Fundamental Mechanisms for Speciation, Separation and Characterization of Organic Complexants in DOE Wastes**

Lead Principal Investigator:

Dr. John E. Caton
Research Staff Member
Chemical and Analytical Sciences Division
Oak Ridge National Laboratory
Mail Stop 6120
P.O. Box 2008
Oak Ridge, Tennessee 37831--6120
Telephone: 423-241-5189
e-mail: jec@ornl.gov

Co Principal Investigators:

Debra T. Bostick
Research Staff Member
Chemical Technology Division
Oak Ridge National Laboratory
Mail Stop 6201
P. O. Box 2008
Oak Ridge TN 37831 6201
USA
Telephone: (423)576-7956
e-mail: dab@ornl.gov

Peter W. Carr
Professor
Department of Chemistry
University of Minnesota
207 Pleasant Street SE
Minneapolis MN 55455 0431
USA
Telephone: (612)624-0253
e-mail: carr@chem.umn.edu

Gary Mabbott
Visiting Scientist
Department of Chemistry
University of Minnesota
207 Pleasant Street SE
Minneapolis MN 55455 0431
USA
e-mail: mabbott@chem.umn.edu

RESEARCH OBJECTIVES

The overall objective of this research is to develop and enhance our understanding of the chemical equilibria for major organic complexant species and their products with metals in aqueous mixtures such as those found in DOE radioactive tank wastes. Our approach to achieving this objective is a series of incremental studies involving cooperative efforts at Oak Ridge National Laboratory (ORNL) and at the University of Minnesota. Investigations at ORNL are characterizing soft ionization mass spectrometry processes for the complexant species by developing and interpreting positive and negative ion thermospray mass spectrometry (TMS) of some organic complexants and their decomposition products and relating the spectral distributions to gas phase chemistry. Subsequently this knowledge of the gas phase chemistry will be related to known solution chemistry behavior. At the University of Minnesota liquid chromatography separations on zirconia-based chromatographic supports are being studied in order to understand the separation of organic complexants and the products formed by complexants with metals in complex aqueous mixtures; and thereby define the conditions needed to introduce a simplified chemical stream into the mass spectrometer. Ultimately the knowledge gained from these parallel efforts will be combined at ORNL to characterize the complexant species in a multi-component aqueous mixture with the final objective being to develop the analytical capability needed to define chemical equilibria for complexant species in DOE waste streams.

RESEARCH PROGRESS AND IMPLICATIONS

This annual report summarizes the progress achieved during the previous twelve months (June, 1998 through May, 1999) of this three-year project, which started on October 1, 1997. The subcontract with the University of Minnesota has been in place for about fourteen months; and during this period much progress has been made in understanding the effectiveness of zirconia-based stationary phases for separating chelators by HPLC. The chelators that have been studied are nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), citrate and oxalate which are reagents that have been used to solubilize radioactive metals from spent fuel rods and nuclear processing equipment. Other chelators being studied are ethylenediamine-N,N'-diacetic acid (EDDA), imidodiacetic acid (IDA), N-(2-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA) and N-(2-hydroxyethyl)iminodiacetic acid (HEIDA) which may be present as degradation products and are potential complexers of strontium and cesium.

This project purchased an evaporative light scattering detector (ELSD) for the liquid chromatography developmental studies at the University of Minnesota. An ELSD can detect solutes such as the chelators that lack strong solute chromophores required for detection by UV absorption. Another important advantage of the ELSD is the relative insensitivity of the detector to changes in the mobile phase composition so that gradient elution separations on zirconia sorbents are easier to monitor. In addition, the ELSD requires volatile mobile phases; thereby making the ELSD an ideal detector for methods to be adapted to liquid chromatography-thermospray mass spectrometry (which also requires volatile mobile phases).

Initial separation investigations using bare zirconia particles as the stationary phase were carried out on a column 5 cm in length containing particles with an average diameter of 3 μm . Table 1 in the Appendix of this report shows the various mobile phase conditions that were employed. These results seem to indicate that bare zirconia is not the stationary phase of choice for the separation of these chelators.

QPEI (quaternized polyethyleneimine-coated zirconia particles) is a strong anion exchange stationary phase that effected the separation of IDA, NTA and EDTA quite well under a variety of elution conditions. Table 2 (in the Appendix of this report) shows the conditions that have been studied at this time. In general the separation of the complexants of interest fall into three groups. IDA, EDDA and HEIDA are poorly retained under most conditions and have not been separated from each other. NTA, EDTA, HEDTA, and DTPA show strong retention and have been separated under several eluting conditions. The chromatographic characteristics of this second group are strongly influenced by the pH of the mobile phase and also by the concentration of fluoride or bicarbonate in the mobile phase. The third group of solutes, oxalate and citrate, are very strongly retained. This third group can be eluted with gradients in pH or bicarbonate, but their peaks often exhibit tailing or excessive band broadening.

Positive ion TMS spectra of seven different organic complexants related to EDTA have been defined in water:methanol solvent systems containing different buffering components. The water content of the water:methanol eluting system has ranged from 50 % to 95 % (by volume): but most successful studies have utilized an elution solvent containing equal volumes of water and methanol (1:1). Buffer components have been combinations of ammonium acetate, ammonium fluoride, and ammonium trifluoroacetate. The total concentration of buffer components has generally been 0.1 M. Buffer pH's of 2.2, 4.8, 6.7, and 7.9 have been investigated. Mass spectra of all these complexants showed a peak at mass $[M+1]^+$ when vaporized from solvent media at lower pH's. As pH increases the relative amount of mass $[M+1]^+$ appears to decrease in favor of a mass of $[M + \text{adduct}]^+$. This tendency to form an adduct in the gas phase can be related to the relative proton affinity of these complexants in the vaporized phase. A lower proton affinity in the vapor phase should be consistent with greater acidity in the solution phase. Such characteristics observed after thermospray vaporization may aid in defining behavior in solution. Accordingly, interpretations of TMS spectra should be useful in the characterization of DOE mixed waste solutions.

PLANNED ACTIVITIES

- 10/99: Evaluate predictive capability of proton affinity (or gas phase acidity) from TMS characteristics
- 12/99: Complete study of chromatographic properties of QPEI-coated zirconia.
- 04/00: Complete TMS studies of some known chemical species of complexants and metal ions.
- 09/00: Complete manuscripts for open literature describing results of these studies.

INFORMATION ACCESS

Results from these investigations will be published in the open literature. At this point in time two abstracts have been accepted for presentations 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, Monchanin, DE, November 16, 1999.

APPENDIX (59978, page 1 of 2)

Tables showing methods investigated for the separation of complexants on zirconia-based liquid chromatography stationary phases.

Table 1. Mobile Phase Conditions Used with Bare Zirconia Stationary Phase.

Mobil Phase	Elution	Comment
0.02 M NH ₄ OH	Isocratic	Too strong
0.3 M Acetic acid, pH 4.2	Isocratic	NTA does not elute
0.3 M Acetic acid, pH 4.2 0.1 M NH ₄ F	Isocratic	One peak observed for mixture near t _m
0.15 M Acetic acid, pH 3.2	Isocratic	NTA does not elute
3 M Acetic acid, pH 3.2	Isocratic	NTA does not elute
3 M Acetic acid, pH 3.2 0.025 M NH ₄ F	Isocratic	Too strong
3 M Acetic acid, pH 3.2 0.010 M NH ₄ F	Isocratic	Too strong
3 M Acetic acid, pH 3.2 0.005 M NH ₄ F	Isocratic	Too strong
0.3 M Acetic acid, pH 5 0.005 M NH ₄ F	Isocratic	Too strong
0.2 M ammonium acetate, pH 8.3	Isocratic	Too weak
0.2 M ammonium acetate, pH 9.5	Isocratic	Too strong
pH 7.5 to pH 12 0.02 M to 0.4 M Buffer	Gradients	EDTA elutes only in very broad band at very high pH or with void volume if initial pH is high.
pH 8 to pH 9.6; 0.2 M NH ₄ F	Gradient	NTA elutes in void volume
pH 8.3; 0.0 M NH ₄ F to pH 9.6; 0.2 M NH ₄ F	Gradient	After initial injection NTA elutes near t _m
pH 4.2; 0.002 to 0.040 M NH ₄ F	Gradient	One peak near t _m ; broad band near 12 min; steep background
pH 4 to pH<1	Gradient	Two peaks; later peak asymmetric
pH 3; 0.3 M to 3 M acetic acid	Gradient	Some resolution of early eluting components; others show very broad bands

Gradients: indicates that various gradient elutions within these conditions were tested.

Tables showing methods investigated for the separation of complexants on zirconia-based liquid chromatography stationary phases.

Table 2. Mobile Phase Conditions Used with Commercial QPEI Coated Zirconia Stationary Phase.

Mobile Phase	Elution	Comment
0.3 M acetic acid; 0.24 M NH ₄ F; pH 4.0	Isocratic	Dicarboxylates elute near t _m , others do not show peaks
.075 M acetic acid; 0.25 M NH ₄ F; pH 4.0	Isocratic	After treatment of column with 0.1M phosphate NTA not observed.
0.01 to 0.060 M CO ₃ ²⁻ ; 0.3 M ammonium acetate; pH 9.4	Isocratic	All elute near t _m
0.01 to 0.050 M HCO ₃ ⁻ ; 0.2 M ammonium acetate; pH 8.5	Isocratic	Resolution of 3 groups of chelators
0.1 M HCO ₃ ⁻ ; 0.2 M ammonium acetate; pH 8.0	Isocratic	All elute near t _m
0.020 M HCO ₃ ⁻ ; 0.1 M NH ₄ F; 0.2 M ammonium acetate; pH 8.5	Isocratic	4 peaks for 5 chelators in mixture
0.0 to 0.1 M NH ₄ HCO ₃ ; 0.2 M ammonium acetate; pH 8.5	Gradients	4 peaks for 5 chelators in mixture; citrate broad
0.0 to 0.1 M NH ₄ HCO ₃ ; 0.2 M NH ₄ F; 0.2 M ammonium acetate; pH 8.5	Gradients	4 peaks for 5 chelators in mixture; citrate broad
0.0 to 0.4 M NH ₄ HCO ₃ ; 0.2 M ammonium acetate; pH 8.0	Gradients	4 peaks for 5 chelators in mixture; citrate broad
0.02 M NH ₄ HCO ₃ ; 0.2 M ammonium acetate; pH 7.9 to pH 9.5	Gradients	4 peaks for 5 chelators in mixture; citrate broad
0.01 to 0.1 M NH ₄ HCO ₃ ; 0.2 M ammonium acetate; pH 7.9 to pH 9.5	Gradients	4 peaks for 5 chelators in mixture; citrate and oxalate co-elute
0.01 to 0.1 M NH ₄ HCO ₃ ; 0.2 M ammonium acetate; pH 5.0 to pH 9.5	Gradients	4 peaks for 7 chelator mixture

Gradients: indicates that various gradient elutions within these conditions were tested.