

FINAL REPORT
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**Therospray Mass Spectrometry Ionization Processes:
Fundamental Mechanisms for Speciation, Separation and Characterization
of Organic Complexants in DOE Wastes**

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1.0 EXECUTIVE SUMMARY

The overall objective was 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. High performance liquid chromatography (HPLC) employing zirconia-based stationary phases was 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 were then characterized using positive and negative ion thermospray mass spectrometry (TMS). The final goal was to develop the analytical capability needed to define the identity and, ultimately, the chemical equilibria for complexant species in DOE waste streams.

To this end organic complexant species were employed as models in these investigations; selected compounds included ethylenediaminetetraacetic acid (EDTA), compounds related to EDTA, and decomposition products of these complexants. At Oak Ridge National Laboratory (ORNL) studies were directed toward characterizing soft ionization mass spectrometry processes that would elucidate the chemical nature and structure of complexant species. Efforts at the University of Minnesota investigated liquid chromatographic separations of organic complexants on zirconia-based chromatographic supports in order to understand the conditions needed to introduce a simplified chemical stream into the mass spectrometer. The combined efforts have led to the development of an analytical procedure in which an aliquot of tank waste is pretreated to reduce the alkalinity and level of carbonate in the sample. The modified waste is then introduced into a commercial column of quaternized polyethyleneimine (QPEI)-coated zirconia particles. Using eluant gradients in pH and bicarbonate, complexants contained in the waste are individually separated. HPLC separations followed by thermospray mass spectrometry are used to develop positive ion mass spectra of organic complexants related to EDTA. These spectra were defined at different source temperatures in water:methanol solvent systems containing different buffering components.

2.0 RESEARCH OBJECTIVES

The overall objective of this research was to develop and enhance our understanding of the identity of 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 was a series of incremental studies involving cooperative efforts at ORNL and at the University of Minnesota. Investigations at ORNL characterized 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. This knowledge of the gas phase chemistry can be related to known solution chemistry behavior. At the University of Minnesota liquid chromatography separations on zirconia-based chromatographic supports were studied in

order to understand the separation of organic complexants and the products formed by complexants with metals in complex aqueous mixtures. This information was used to define the conditions needed to introduce a simplified chemical stream into the mass spectrometer. Ultimately the knowledge gained from these parallel efforts were combined at ORNL to characterize the complexant species in a multi-component aqueous mixture. The final objective was to develop the analytical capability needed to identify complexant species and to define chemical equilibria for these species in DOE waste streams.

3.0 METHODS AND RESULTS

This report summarizes the progress achieved in investigations that we have been pursuing under EMSP Project 59978 over the time frame of October 1, 1997 through December 31, 2001. The studies were a cooperative effort carried out in the Department of Chemistry at the University of Minnesota and at ORNL. The emphasis of the task was designed to develop the analytical methodology that could be used to understand and define chemical equilibria for major organic complexant species and their products with metals in aqueous mixtures of high ionic strength. The organic complexant species employed as models in these investigations were ethylenediaminetetraacetic acid (EDTA), selected compounds related to EDTA, citric acid, oxalic acid, and decomposition products of these complexants. At ORNL studies have been directed toward characterizing soft ionization mass spectrometry processes that may elucidate the chemical nature and structure of complexant species. Efforts at the University of Minnesota have been investigating liquid chromatography separations of organic complexants on zirconia-based chromatographic supports in order to understand the conditions needed to introduce a simplified chemical stream into the mass spectrometer. Subsequently, the knowledge gained from these parallel efforts will be combined to characterize the complexant species in a multi-component aqueous mixture. The resulting knowledge of the identity and distribution of complexant chemical species in aqueous mixtures of high ionic strength can then be used to define chemical equilibria for complexant species in such multi-component mixtures

Liquid chromatography studies at the University of Minnesota. The complexants, whose structures are illustrated in Fig.1 in the Appendix, were employed in studying the effectiveness of zirconia-based stationary phases for separating chelators pertinent to DOE waste needs by HPLC [1]. EDTA, HEDTA, NTA, DTPA, citrate and oxalate are some of the reagents that have been used to solubilize radioactive metals from spent fuel rods and nuclear processing equipment. Others, such as IDA, HEIDA, and EDDA, might be present as degradation products and are potential chelators for strontium and cesium.

In order to develop a chromatographic separation that would link easily to the mass spectrometer, an evaporative light scattering detector (ELSD) was purchased and dedicated to these investigations. The ELSD is ideal for the detection of solutes such as these chelators that have no chromophores (other than the carbonyl group). The lack of strong solute chromophores renders detection by UV absorption unsuitable for monitoring the separation of these chelators. Another important advantage of the ELSD

is its relative insensitivity to changes in the mobile phase composition so that gradient elution separations are easier. However, the ELSD does share with the mass spectrometer the limitation that the mobile phase must be volatile. This constraint eliminates many mobile phase additives, such as phosphate ions, that can be very effective in improving the efficiency of separations with zirconia-based stationary phases. It also means that the detector will be blind to some solutes, such as acetate and glycolic acid that are volatile at the temperatures needed to vaporize the aqueous solvent.

Bare Zirconia as a Stationary Phase. A promising chromatographic system that was applied to this task is either coated or uncoated zirconia. Microparticulate zirconia (3 – 10 microns) can be produced with a narrow particle diameter distribution (better than 1 micron) [2–5]. These monodisperse particles have a large fraction of pores between 60 - 1000 Å which allow for rapid transport of solutes to the chromatographically active surface (surface area $\sim 170 \text{ m}^2/\text{cm}^3$). In addition, when compared to most common chromatographic supports, zirconia has greater thermal stability [6, 7], can withstand pressures up to 9000 psi, and is not subject to swelling or shrinking with changes in mobile phase [8].

The surface chemistry of zirconia is unique because it is the only unmodified (non-mixed) metal oxide which possesses four distinct types of chemical moieties. It has acidic and basic sites as well as oxidizing and reducing sites [9]. All sites can be used to optimize separations, especially when bare zirconia is used in a normal phase mode or when the surface has been coated with poly(ethylene imine) [PEI] in an anion exchange mode. The active site which is often most responsible for the selectivity displayed by the zirconia surface is the *hard* Lewis acid site. Binding sites of this nature, which are not found on silicas but are found on alumina supports, arise because of interruptions of binding at a surface [10]. At these surface sites full coordination of zirconium (IV) ions by oxygen is not possible; therefore Lewis acid sites are left which can accept electron pairs from a variety of hard Lewis bases depending upon the composition of the solution in equilibrium with the surface. Hard Lewis bases include species such as hydroxide, fluoride, acetate, chloride and phosphate but do not include nitrogen and sulfur type ligands. The Lewis acid sites strongly retain oxyanions such as carboxylates and phosphates. A postulated interaction between the carboxylate component of EDTA and bare zirconia is presented in Fig. 2 of the Appendix.

Initial studies attempted the separation of a simple mixture of IDA, NTA and EDTA on bare zirconia particles. These solutes represented the range of ligands that differed in terms of increasing relative binding strength (di-, tri-, and tetra-carboxylates, respectively). A column (5 cm in length) was packed in-house by the upward slurry process (at 5000 psi) with 3 micron particles of bare zirconia. The zirconia was obtained from ZirChrom Separations where it was prepared by polymerization-induced colloid aggregation. It was expected that the carboxylate groups would coordinate well with the Zr(IV) on the surface and could be eluted with fluoride or hydroxide. Table 1 in the Appendix shows the various mobile phase conditions that were employed. Results of these initial studies are discussed in the following paragraphs and indicate that bare zirconia is not a good choice for this separation.

In general, both fluoride and hydroxide are hard Lewis acids and can displace most ligands from the zirconia surface. The influence of fluoride is illustrated in Fig. 3 of the Appendix. Fluoride was expected to be most effective as a displacing eluent at pH's near its pKa (~3.2). When no fluoride was present in the mobile phase (0.3 M acetic acid adjusted to pH 5 with concentrated ammonia) only a very small, unretained peak was observed at ~0.9 minutes upon injection of the mixture of three chelates. When 25 mM fluoride was included in the mobile phase, the three complexants co-eluted with the unretained solute peak as shown in Fig. 3b of the Appendix. Some resolution of EDTA from the other two solutes could be obtained by lowering the fluoride concentration to 5 mM as shown in Fig. 3c (Appendix). However, no improvement in resolution was realized for a variety of fluoride gradients at this pH. It also appeared that the fluoride on the zirconia desorbs rather slowly. After exposing the column to 25 mM fluoride followed by a 10 minute rinse of buffer without fluoride, an injection of the complexant mixture gave a single peak at the time for the unretained solute in a manner similar to what was observed when 25 mM fluoride was present in the running buffer. A conditioning procedure was adopted as a means of eliminating this "history" effect. Before changing mobile conditions, the column was rinsed with 20–30 mL of 0.1 M ammonia to displace all adsorbates with hydroxide ion. Then the column was rinsed with 20–30 mL of 0.1 M nitric acid to neutralize the surface of the zirconia (convert the hydroxide ligands to water). Finally a minimum of 20 mL of running buffer was rinsed through the column before injecting any sample.

Several different mobile phase pH ranges were investigated. Neither NTA nor EDTA eluted in mobile phases of acetic acid (from concentrations of 0.03 to 3.0 M) at pH 3.0. In isocratic runs in buffer prepared by mixing trifluoroacetic acid and ammonia to give equal concentrations of trifluoroacetic acid and its conjugate base (presumably at pH ~0.7) all three chelators eluted without retention. Gradient elution in which the mobile phase changed linearly from a 0.1 M acetic acid buffer (pH 4.0) to a 67 mM trifluoroacetate buffer (pH ~0.7) did lead to retention of NTA and EDTA. However, these two solutes eluted together in small, broad peaks.

In basic solutions up to ~ pH 8.3 NTA and EDTA were strongly retained. If the column was equilibrated at a higher pH before injecting, NTA was eluted in the void volume. It was possible to elute EDTA using a gradient from pH 7.5 to ~pH 11.5 (50 mM morpholine to 50 mM diethyl amine) but the peak was so broad that this approached seemed impractical. (See Appendix, Fig. 4.) The very broad bands for NTA and EDTA and the bimodal retention behavior depending on the initial pH (either no retention or very strong retention) suggested that the rate of desorption for these two solutes was very slow. Although other work has shown that fluoride can enhance the desorption kinetics for solutes on zirconia-based media, it seemed unlikely that the addition of fluoride to the mobile phase would narrow the peaks enough to permit the separation of more than a few solutes at a time. Accordingly it was concluded that stationary phases other than bare zirconia should be investigated.

Quaternized Polyethyleneimine (QPEI). Quaternized polyethyleneimine is a strong anion exchange resin commercially available as a chromatographic medium. We have found that a mixture of IDA, NTA and EDTA separates well under a variety of conditions using this stationary phase. Table 2 (Appendix) shows the conditions that have been investigated in these studies. Separations of more complicated mixtures of complexants showed that the solutes of interest generally fall into three groups. IDA, EDDA and HEIDA were poorly retained under most conditions and were not separated from each other. A second group (NTA, EDTA, HEDTA, and DTPA) showed strong retention. Members of this group were strongly influenced by the buffer pH and concentration of fluoride or bicarbonate in the mobile phase and were partly or completely resolvable under some conditions. Two other solutes, oxalate and citrate, were very strongly retained. They could be eluted with gradients in pH or bicarbonate, but their peaks often exhibited tailing or excessive band broadening. The influence of pH and eluents on retention with this column type is discussed in the following paragraphs.

Preliminary work was performed with a column packed in house using an early generation of QPEI-coated (6 micron) zirconia particles. Although promising separations were obtained on this column, concerns about comparisons with commercial columns led us to switch to a 4.6 mm diameter X 10.0 cm strong anion exchange (SAX) column from ZirChrom Separations, Inc. This column was packed with QPEI-coated 3 micron zirconia particles. Liquid chromatography on this column with an ammonia buffer (with 3 mM carbonate ion) at pH 9.0 resulted in a mixture of 5 complexants (IDA, NTA, EDTA, oxalate, and citrate) being eluted together in the void volume. At slightly lower pH's bicarbonate was an effective eluent. Fig. 5 (Appendix) shows the influence of bicarbonate on the retention of the same mix of five complexants. Both citrate and oxalate yield very broad peaks that are hard to distinguish from the baseline under these conditions. Some slight improvement in peak shape was obtained with the addition of high levels of fluoride.

Elution by gradients in pH, bicarbonate (or a combination of the two) provided better resolution. Fig. 6 (Appendix) shows a separation using a combination pH and bicarbonate gradient. The resolution is good although the peaks for EDTA and oxalate tend to be broad at low bicarbonate concentrations. This response suggests that they might be interacting with bare spots of the zirconia support.

The best separation of chelators was obtained using bicarbonate and pH conditions presented in Fig. 7. Seven chelators were separated by flowing Buffer A (0.13 M ammonium acetate/0.02 M NH_4CO_3 , pH 8.0) through the QPEI-coated zirconia for 3 min. This was followed by a linear gradient starting from 100% Buffer A to 100% Buffer B (0.15 M NH_4HCO_3 , pH 9.3) over a 10 min time span. The resolution of individual chelators is good although the peaks for EDTA and oxalate tend to be broad at low bicarbonate concentrations. This response suggests that they might be interacting with bare spots on the zirconia support.

Ammonium bicarbonate was chosen as an eluant because of its volatility. We expected the bicarbonate anion would displace the carboxylate-containing solutes from the strong

anion exchange sites on the QPEI. However, the behavior of these chelators suggests that the primary mode of separation is not ion exchange. Consider the influence of charge and pH. Since the stationary phase contains a quaternary amine, the charge on the coating is independent of pH. Therefore, an ion exchange mechanism would not be influenced by pH unless it coincided with a change in the degree of ionization of the solutes. Consequently, one would predict for an anion exchange mechanism that the higher the pH, the more negative the effective charge on the solute and the greater the retention.

The order of elution for most of the chelators in this study does follow the order of effective charge as would be predicted for an anion exchange retention mechanism. For example, Table 3 shows that retention time (for an isocratic separation at pH 8.0) increases in the order IDA, NTA and EDTA following the order of their increasingly negative effective charges of -1 , -2 , and -3 . However, there are some important exceptions. Oxalate, which has a charge of -2 , elutes after EDTA.

In Table 3 the retention factor, k' , is a measure of the time that a chelator spends attached to the stationary phase compared to the time that it spends in the mobile phase. Numerically, it is calculated from the total time, t_R , that the chelator takes to elute from the column and the time, t_m , that a solute that has no affinity for the stationary phase takes to move through the column.

$$k' = (t_R - t_m)/t_m$$

In the case of the EDTA-like chelators only a small fraction of the molecules are in the most negatively charged (completely deprotonated) form at pH 8. The effective charge is calculated from the weighted average of the different species that exist for a given chelator at that pH.

$$\text{Effective charge} = \sum (\alpha_i Z_i),$$

where α_i is the fraction of the population of a chelator molecule with charge Z_i at the specified pH. These α -values can be calculated from acid dissociation equilibrium constants for a given chelator and the pH of solution. [See, for example, Daniel C. Harris, Quantitative Chemical Analysis, 5th ed., W. H. Freeman, NY, page 254 and following.] As the pH increases the effective charge becomes more negative (or remains at its most negative value). The table shows that retention (affinity for the stationary phase) generally increases with effective charge on the solute. One would expect that trend for an anion exchange mechanism of retention. However, oxalate is an important exception. Also at low bicarbonate levels (< 30 mM bicarbonate, but 0.15 M ionic strength maintained by acetate) malate, tartarate, oxalate and citrate were so well retained that their peaks were not observed. Simple ion exchange can not account for such behavior.

Furthermore, the behavior of these solutes at other pH's is inconsistent with an ion exchange mechanism of retention. Fig. 8 shows the retention factor for these solutes

decreases with increasing mobile phase pH. Clearly the retention for these chelators decreases as the pH increases despite the fact that the effective charge for these solutes remains constant or becomes more negative over the same pH range. (See the effective charge at pH 10, for example, in Table 3.) In this experiment isocratic chromatograms were recorded at different pH values in an ammonium acetate mobile phase (0.15 *M* ionic strength) containing 10 *mM* bicarbonate ion. In other experiments with fluoride and acetate buffers at pH 4 (where the charge on these solutes is closer to zero than at pH 8) no elution peak was observed for NTA, EDTA, or oxalate even using a fluoride eluent concentration as high as 250 *mM*. Again, this is contrary to an ion exchange mechanism which would predict weaker retention at low pH than at high pH.

Retention is very weak at high pH even though this column has a fixed positive charge. This observation suggests that anion exchange is, at most, a minor factor in the retention of these chelators. What other mechanisms could be contributing to the retention? A strong possibility is that the solutes are interacting with bare spots on the zirconia support material. The column manufacturer [11] recommends using small amounts of phosphate in the mobile phase to block any exposed zirconium sites. Carboxylates, carbonate and hydroxide ions are known to bond strongly with zirconia by complexation [10]. For the chelators in this study retention decreased as the bicarbonate level increased at the same level of ionic strength. Fig. 9 shows the influence of bicarbonate in the mobile phase on retention. In fact the chelators did not elute in a morpholine/acetate buffer (at pH 8.8, 0.15 *M* ionic strength) without bicarbonate in the mobile phase. These observations support the hypothesis that bicarbonate is acting as a displacing ligand.

There is strong evidence that chelation with the zirconia support material is a principal mechanism for retention. Note that solutes such as citrate, oxalate, tartarate, malate and malonate can form stable 5- or 6-member chelate rings with metals and show longer retention than solutes such as succinate and glutarate which can not form stable chelates. Models of the surface of zirconia indicate that two thirds of the zirconium atoms on the surface will have two d-orbitals that are not occupied by bonds to network oxygen atoms[9]. Consequently, these orbitals will be available to bind multiple ligands from solution. It is also well known that zirconium is a hard Lewis acid. Hard Lewis acids prefer to coordinate with hard Lewis bases such as oxygen-containing ligands rather than nitrogen-containing ligands. This preference may explain why solutes, such as oxalate and citrate, that can offer two oxygen containing coordination sites in forming a 5- or 6-member ring with the same zirconium atom are retained longer than NTA or EDTA. Even though NTA and EDTA form stronger chelates with a metal in solution, they must employ a nitrogen ligand in any 6-member ring. Since a surface bound zirconium atom can offer only two coordination sites, it will prefer the chelator that has two oxygens to form ring over a chelator with an oxygen and a nitrogen. The increased retention of EDTA over other chelators is likely a result of its ability to reach simultaneously more than one zirconium atom on the surface. Again, refer to Fig. 2 to view the different ways in which the chelators might interact with exposed zirconia.

It is somewhat surprising that ion exchange appears to play such a minor role in the separation of these organic ions on this column. The column does, indeed, exhibit anion

exchange properties under these conditions as evidenced by the retention of nitrate ion. (Data not shown.) Why, then, is the electrostatic interaction between these chelators and the quaternary nitrogen groups in this stationary phase so weak? Quite likely the answer lies in how closely the chelator ions can approach the charge sites on this resin. There are four long chains in a tetrahedral arrangement about each charged nitrogen atom in the QPEI. The organic ions are too bulky to approach as closely as small inorganic ions do. Furthermore, the charge on these chelators is not localized in a single functional group, but rather on separate branches of the molecule. Even if one end of the chelator were able to squeeze in close to the charge site, some steric hindrance might be expected in squeezing a second branch of the same molecule in close as well.

With the same stationary phase McNeff and Carr [12] showed that ion exchange does play a role in the retention of several derivatives of benzoic acid. However, they also demonstrated that hydrophobicity strongly influenced the retention of these ions. This stationary phase is nearly as hydrophobic as ODS. Anions of benzoic acid derivatives are attracted both by the cation charge site and by the non-polar side chains of the stationary phase. Compact inorganic ions may be small enough to avoid the hydrophobic chains of the stationary phase and bond electrostatically with the charge site, but bigger, polar structures such as EDTA are too large to avoid the side chains and are excluded.

Evaluation of bare zirconia as a scavenger for citrate. As a caveat to the study of bare zirconia as an HPLC stationary support, the material was also evaluated as a sorbent for the selective removal of complexants or complexed metals at the head end of a waste treatment flowsheet. Citrate ion is often added as a complexing agent to solutions used to reclaim radioactively contaminated surfaces. Citrate has also been used in past liquid extraction processes to improve the recovery of soluble metal radionuclides. Once introduced into solution, the same chemical characteristics that aid decontamination efforts make the treatment of secondary radioactive wastes containing citrate difficult. Citrate can bind with radioactive species in spent wash solutions so that they can not be removed by standard sorption methods. Alternately, citrate can also passivate the surfaces of sorbents used to remove radionuclides from secondary waste. Therefore, conditioning of spent wash solutions containing citrate will be required upstream prior to standard processing of radioactive waste solutions. Because the HPLC development work at the University of Minnesota had observed that bare zirconia under certain eluting conditions strongly retained citrate, a series of experiments were carried out to ascertain whether or not bare zirconia might be a candidate for conditioning spent wash solutions containing citrate before further waste processing.

One mechanism for conditioning spent wash solutions containing citrate is to incorporate a sorbent that is selective for citrate or metals complexed by citrate at the head end of the process flowsheet. Because zirconia is an effective solid phase for the chromatographic separation of complexants containing carboxylic acid functional groups, it was tested as a possible pretreatment method for citrate-containing wastes. To simulate a waste treatment process, batch tests were performed in which bare zirconia powder was added to process water containing ^{90}Sr and ^{137}Cs . Removal of the radionuclides was observed in solutions in the presence and absence of 0.01 M sodium citrate. Decontamination

results were compared to batch testing using crystalline silicotitanate (CST), a sorbent specific for ^{90}Sr and ^{137}Cs uptake. A series of samples also contained a mixture of zirconia and CST to determine whether the secondary waste could be treated using a mixed sorbent bed.

The MINTEQA2 geochemical model was used to calculate the percentage of strontium and the competing wastewater cations, magnesium and calcium, that would be complexed in the presence of 0.01 M citrate ion. Calculated results indicate that approximately 60% Mg and 98% Ca would be present as citrate species; Sr remains as the free, doubly charged cation. If zirconia successfully removed citrate, it was anticipated that ^{90}Sr and ^{137}Cs uptake on CST would be similar to results of process water free of complexants. If zirconia removed complexed competing cations or played no role in the sorption of complexed citrate species, radionuclide uptake on CST would be enhanced.

Batch test results indicated that neither ^{90}Sr or ^{137}Cs are significantly sorbed onto bare zirconia in the presence or absence of 0.01 M sodium citrate. Typical sorption coefficients (K_d) for ^{90}Sr or ^{137}Cs on CST are 2×10^5 and 5×10^6 L/kg, respectively, for a 140 h contact time. Sorption of the radionuclides on CST was unaffected by the presence of bare zirconia in mixed-sorbent batch samples. The complexation of the competing cations, Ca and Mg, by citrate did not lead to the anticipated elevation in the K_d for ^{90}Sr in samples containing only CST. For contact times greater than 70 hours, citrate depressed the sorption of both ^{90}Sr and ^{137}Cs by 10-fold. Bare zirconia, thus, did not enhance ^{90}Sr sorption by removing soluble Ca- and Mg-citrate species. Additionally, citrate appears to progressively reduce the sorption efficiency of CST for radionuclides, leading to the conclusion that bare zirconia does not sorb free citrate ion competitively in the presence of CST.

Liquid Chromatography/Thermospray-Mass Spectrometry. HPLC separations followed by thermospray mass spectrometry (TMS) was utilized to develop positive ion mass spectra of organic complexants related to EDTA. These spectra were defined at different source temperatures in water:methanol solvent systems containing different buffering components. Mass spectra showed a peak at mass $[\text{M}+1]^+$ when vaporized from solvent media at low pH. As the pH increased the relative amount of mass $[\text{M}+1]^+$ appeared to decrease in favor of a mass at $[\text{M} + \text{adduct}]^+$. This tendency to form an adduct (water in this case) 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.

Studies combined HPLC with thermospray mass spectrometry to develop mass spectra for EDTA and six related compounds (NTA, IDA, HEDTA, HEIDA, DTPA and EDDA): The complexants were initially separated on a deactivated C8 reversed phase column. The aqueous eluting solution, which was buffered to a pH between 2.2 and 2.5 with trifluoroacetic acid and ammonium hydroxide, was monitored by a standard diode array detector and by positive ion thermospray mass spectrometry placed in series with the

diode array detector. Table 4 in the Appendix summarizes the operating conditions of the TMS. The chromatographic profile (Fig. 10 in the Appendix) generated by monitoring the ultraviolet absorbance of this seven-component synthetic mixture does not appear to be well resolved because the buffer components in this eluent absorb ultraviolet light just as well as the chelators. In contrast extracted ion profiles from positive ion thermospray mass spectra generated during this chromatogram showed much better resolution and peak shape. A comparison of the chromatographic profiles generated by the two detectors in series illustrates the enhanced information that can be obtained from the thermospray monitor for aqueous eluting streams moving at high flow rates (1 mL/min).

The positive ion thermospray mass spectra of EDTA and six related complexants were determined in the eluents from the HPLC system. The thermospray positive ion spectra are shown (Figs. 11–17) of the Appendix. These spectra were recorded in an online instrument library which served as a reference point for the ongoing work in these studies. An examination of these spectra shows that $[M+1]^+$ ion appeared for all compounds. Other ions which appeared in many of the spectra were $[M-17]^+$ (presumed to be $[M-\text{water}+\text{H}]^+$), $[M+18]^+$ (presumed to be $[M+\text{NH}_4]^+$) and $[M+15]^+$.

The positive ion thermospray mass spectra of EDTA and the six related compounds were defined at different source temperatures in water:methanol solvent systems containing different buffering components at several pH's. One such solvent system utilized a water:methanol (1:1 by volume) mixture that was buffered with 0.1 *M* ammonium acetate (pH = 6.7). Mass spectra of all seven complexants showed a peak at mass $[M+1]^+$ when vaporized from this solvent medium. Only NTA showed a significant peak at mass $[M+18]^+$ which was interpreted as the formation of an adduct with an ammonium ion from the buffered solvent medium. This observation for the vaporized NTA is consistent with the measured acidity in aqueous solution where the first acid dissociation for NTA has a lower pK value than those reported for EDTA, HEDTA, and IDA (1). This tendency to form an ammonium adduct in the gas phase would indicate that NTA has a lower proton affinity than the other complexants in the vaporized phase. This lower proton affinity in the vapor phase would be consistent with the greater observed acidity in the solution phase. Accordingly, this observation provides an indication that characteristics observed after thermospray vaporization should aid in defining behavior in solution.

Progress has also been made in developing thermospray mass spectra at source temperatures of less than 170 °C. Such lower source temperatures reduce the amount of thermal degradation for labile species. Pressures in the analyzer chamber of the mass spectrometer tend to elevate as the thermospray source temperature is reduced; however, the instrument has been operated for up to 8 hours at a source temperature of 175 °C and a solvent flow of 1 mL/min. This time interval is of sufficient duration to analyze multiple liquid chromatography separations.

4.0 RELEVANCE, IMPACT, AND TECHNOLOGY TRANSFER

4.1 DOE PROBLEMS ADDRESSED

Hundreds of tons (1) of organic complexants were utilized in various DOE activities. Now a significant portion of these complexants are a part of mixed waste streams and the very properties that made them so useful can solubilize heavy metals and make them environmentally mobile. The methods and techniques developed in this work generate information needed:

- to characterize wastes prior to their disposal;
- to determine the relative quantities of the metals that may not be removed in DOE treatment processes;
- to design strategies to counteract the effect of these organic complexants in DOE waste streams; and
- to aid in determining off-site migration patterns of complexed contaminants from burial grounds.

More specifically the knowledge and capabilities generated by these studies are directly applicable to several documented DOE needs for the environmental management of nuclear wastes: i) in waste disposal where the content of organic complexers must be established to meet waste acceptance criteria; ii) in waste treatment where DOE EM-50 programs currently sponsor tasks both to destroy organic chelators and to remove metal species from highly alkaline wastes; and iii) in decontamination and decommissioning work using chelating agents which then must be removed from the resulting waste stream. This work will support recently publicized DOE needs for waste characterization tools (Hanford Site Science Need: RL-WT038-S) and for determining the effect of organic constituents on waste processing (Hanford Site Science Need: RL-WT058-S).

5.0 PROJECT PRODUCTIVITY

As indicated previously, the time frame for the availability of a postdoctoral investigator at the University of Minnesota has dictated that separation studies at the University of Minnesota were carried on for approximately fifteen months beyond September 30, 2000, under a no-cost extension of the original award. These extended studies built upon the information developed prior to September, 2000. More gradient work was performed in which a systematic study determined the potential for resolving the target complexants. Studies to enhance the understanding of the retention mechanism were carried out. Work to further delineate the mechanism for complexant anions in DOE waste matrices would aid in optimization of the HPLC separation of these components.

6.0 PERSONNEL SUPPORTED

1. Debra T. Bostick, Nuclear Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6181.
2. John E. Caton, formerly of Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6120.
3. Prof. Peter W. Carr, University of Minnesota, 207 Pleasant Street SE, Minneapolis, MN 55455-0431.
4. Gary Mabbott, University of Minnesota, 207 Pleasant Street SE, Minneapolis, MN 55455-0431.
5. Jung Hag Park, University of Minnesota, 207 Pleasant Street SE, Minneapolis, MN 55455-0431.
6. Bin Chen, University of Minnesota, 207 Pleasant Street SE, Minneapolis, MN 55455-0431.

7.0 PUBLICATIONS

Results from these investigations were 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.

8. INTERACTIONS

Gratis samples of PREP ZirChrom-Phase powder and accompanying character data were contributed by ZirChrom Separations, Inc. Additionally, a commercially-packed strong anion exchange (SAX) column containing QPEI-coated zirconia particles was also donated by the company.

9 TRANSITIONS

Acquisition of actual waste or recipes specific for the preparation of simulants representing waste from individual tanks at either the Hanford or Savannah River sites would be the next step in implementing this technology at DOE waste facilities. Because the character of the waste varies from tank-to-tank, the HPLC separation of chelators may have to be tailored for each site to optimize the performance of the separation scheme.

10 PATENTS

None.

11. FUTURE WORK

Waste samples will only need a simple pretreatment, at most, prior to injection onto the HPLC column. In fact, mixtures of chelators in 0.1 M NaOH have been successfully separated by injecting 5 μ L samples directly onto the QPEI-coated zirconia column. The results showed only small changes in retention times. Although the level of NaOH that is present in some tanks is much higher, a smaller sample size and/or diluting the sample will be a practical way of dealing with it, since the TMS is a much more sensitive detector than the ELSD that was used for this experiment. Presence of carbonate anion in tank waste may also affect the performance of the HPLC separation scheme. Again, the most practical solution to this problem will be to dilute the waste sample with acid such that both the NaOH and carbonate content of the sample is reduced by neutralization prior to injection into the HPLC.

The other experiment yet to be performed is a separation of chelators in the presence of metal ions such as aluminum and strontium. Here again, we would predict only a small effect on the retention time of the chelators. At the start of the separation the eluant conditions (pH 8 and low bicarbonate level) favor a strong chelation with the zirconia. Even though the column that we chose to use is actually a quaternary polyethylenimine coated zirconia (designed with anion exchange in mind), we have strong evidence that the mechanism of retention is chelation with the underlying zirconia. (If necessary, one could start the gradient at a lower pH in order to favor the retention of the chelators even more.) We would expect that chelator bound to a metal ion in the solution would release it in favor of binding with the zirconia.

The tendency of chelators to gain or lose a proton during the thermospray ionization process allows the calculation of the relative proton affinity for individual chemical species. Subsequently this knowledge of the gas phase chemistry can be related to known solution chemistry behavior. A more complete database of TMS spectra would provide the basis for this extended study.

12. LITERATURE CITED

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12. C. McNeff and P. W. Carr, "Synthesis and Use of Quarternized Polyethylenimine-Coated Zirconia for High-Performance Anion-Exchange Chromatography", *Anal. Chem.* **67**, 3886-3892 (1995).

12. FEEDBACK

None.

APPENDIX

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

MOBILE 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 and 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.

**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
0.075 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	Gradient	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	Gradient	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	Gradient	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	Gradient	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	Gradient	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	Gradient	4 peaks for 7 chelator mixture

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

Table 3. Retention on QPEI-coated Zirconia and Solute Effective Charge

Solute	Retention Factor (k')	pH 8		pH 10	
		Deprotonated fraction*	Effective charge	Deprotonated fraction*	Effective charge
IDA	0.104 ± 0.0082	0.02	-1.0	0.61	-1.6
HEIDA	0.120 ± 0.038	0.15	-1.1	0.095	-1.9
EDDA	0.129 ± 0.0035	0.03	-1.0	0.72	-1.7
succinate	0.338 ± 0.0066	1.0	-2.0	1.0	-2.0
NTA	0.460 ± 0.0410	0.02	-2.0	0.65	-2.7
HEDTA	0.579 ± 0.0039				
malonate	0.590 ± 0.012	1.0	-2.0	1.0	-2.0
malate	0.760 ± 0.040	1.0	-2.0	1.0	-2.0
tartrate	1.16 ± 0.046	1.0	-2.0	1.0	-2.0
EDTA	1.20 ± 0.089	0.01	-3.0	0.5	-3.1
DTPA	1.646 ± 0.0081				
oxalate	2.73	1.0	-2.0	1.0	-2.0
citrate	no elution	1.0	-3.0	1.0	-3.0

Column conditions for determination of k' : 60 mM bicarbonate, pH 8, 0.15 M ionic strength.

* Fraction in the completely deprotonated form.

Table 4. Instrumental Operating Parameters for the TMS

Parameter	Setting
Filament	ON
Discharge Electrode	OFF
Fragmentation Electrode	OFF
Electron Multiplier Voltage	2125 V
Source Temperature	226 °C
Analyzer Temperature	100 °C
Tip Temperature	235 °C
Stem Temperature	104 °C
Solvent	1:1 Methanol:water that was 0.1 M in ammonium acetate, pH = 6.6.
Flow Rate	1 mL/min

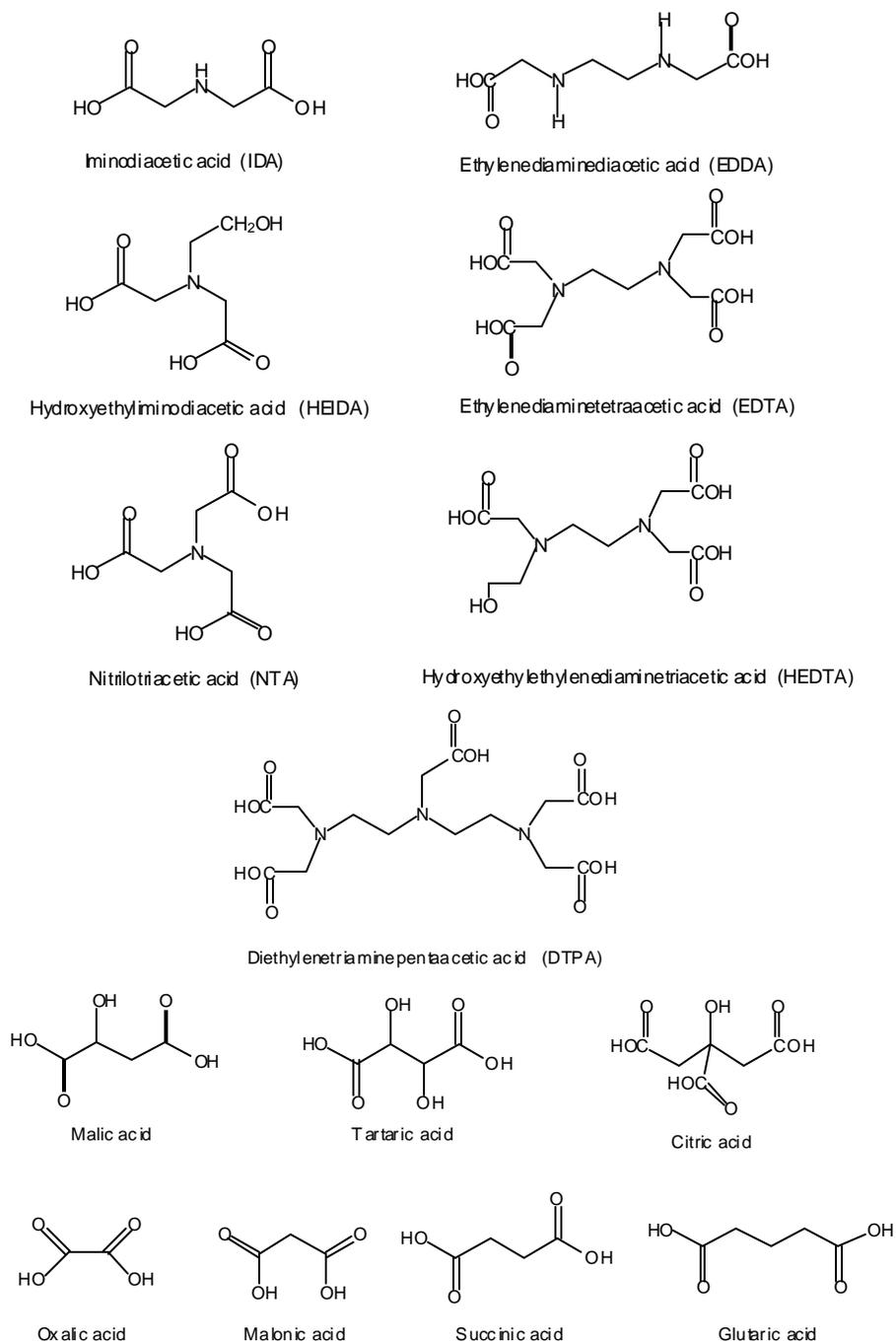
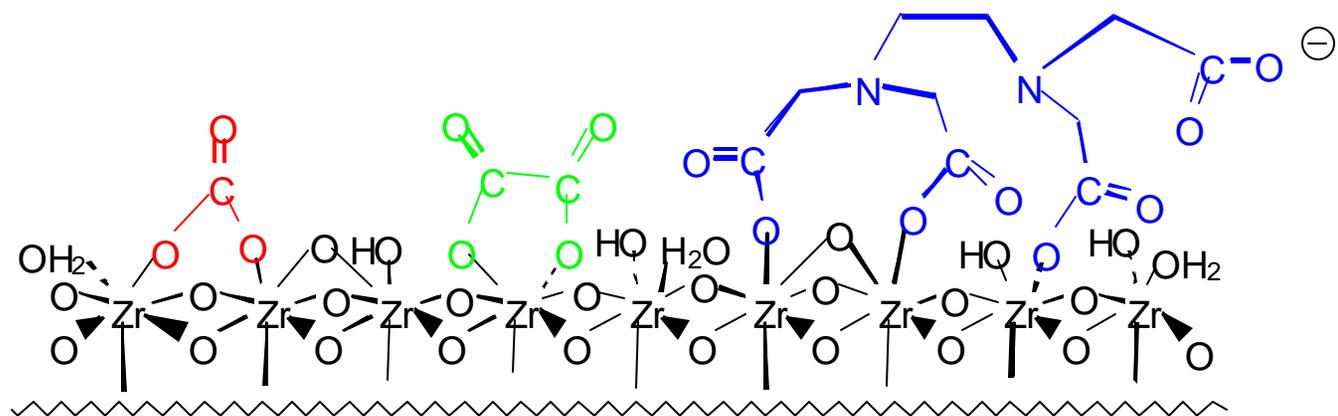


Fig. 1. Structures of chelators used in this study.



Zirconia Support

Fig. 2 Hypothetical model of interaction between chelators and bare zirconia.

[Bicarbonate may block very active binding sites. Chelators may form 5- and 6-member rings with a single zirconium center or bridge between zirconium atoms. Zirconium shows a preference for oxygen-containing ligands and little attraction for nitrogen-containing ligands.]

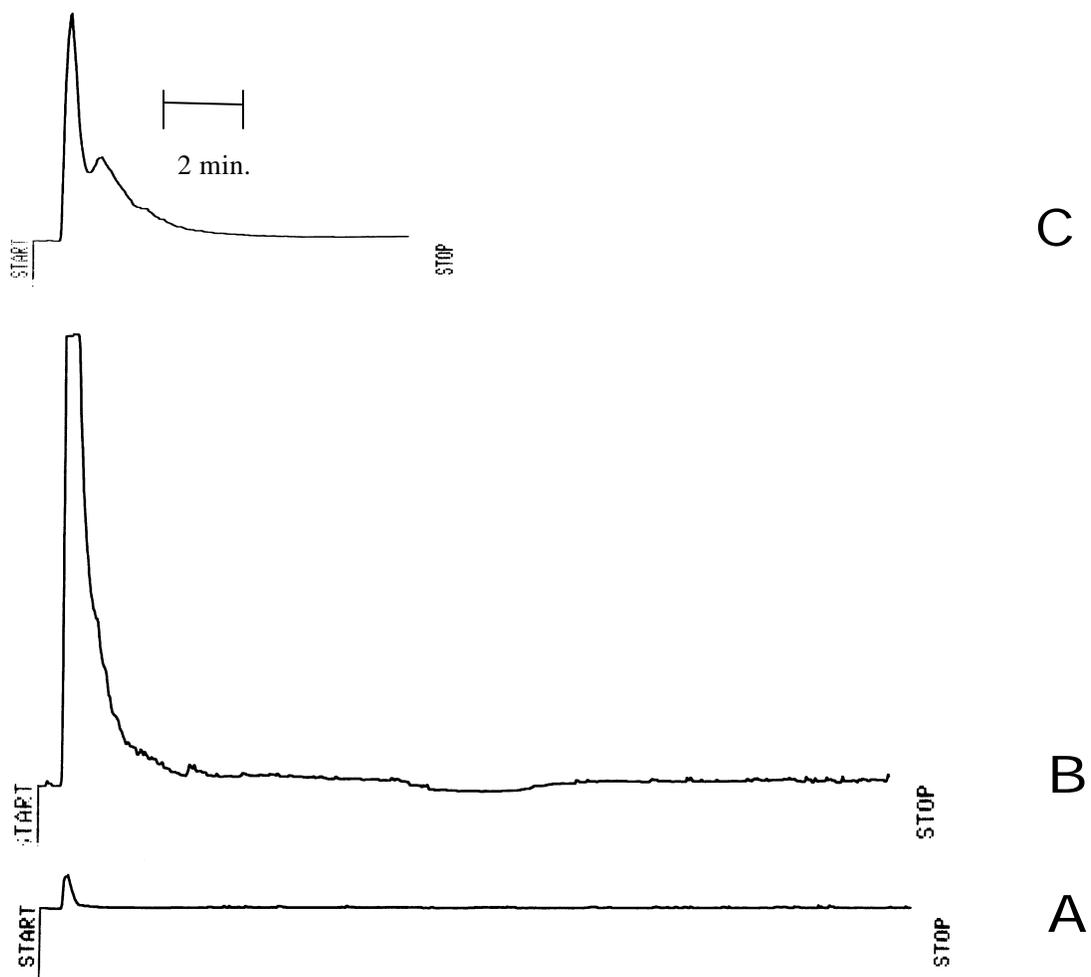


Fig. 3. The influence of fluoride in the mobile phase on the retention of a mixture of IDA, NTA, and EDTA onto a column of bare zirconia.

[A) 0.3 M acetate buffer at pH 5.0 with no fluoride. B) 25 mM fluoride in 0.15 M acetate buffer, pH 5.0. C) 5 mM fluoride in 0.27 M acetate buffer, pH 5.0.]

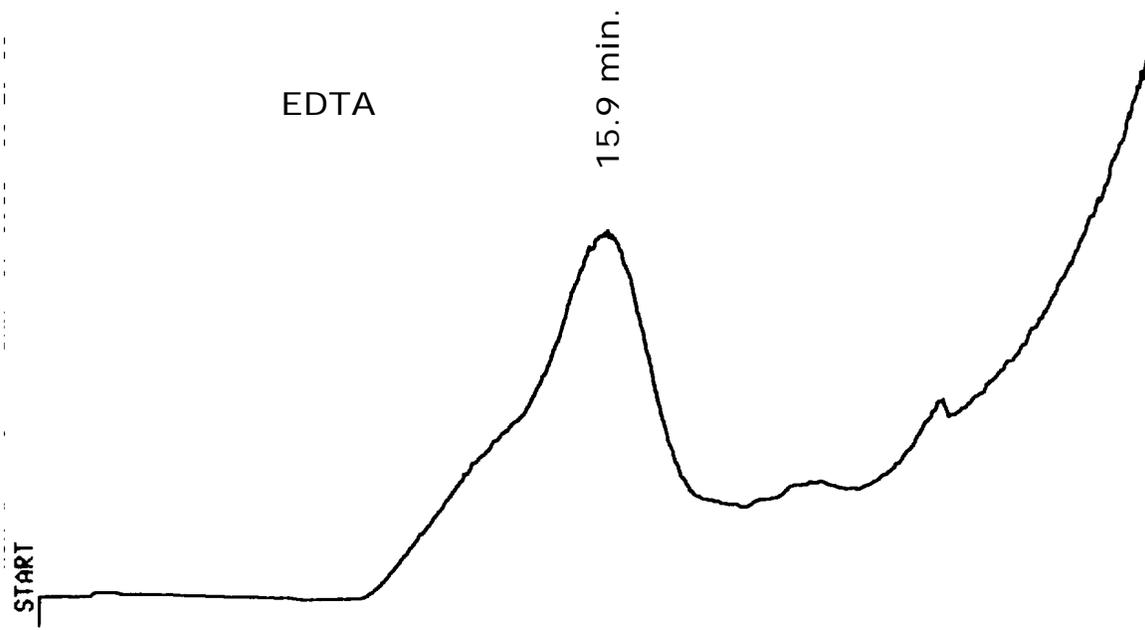


Fig. 4. Chromatogram of EDTA on bare zirconia using a gradient of 0.05 M morpholine acetate at pH 7.5 to 0.05 M diethylamine at ~11.5.

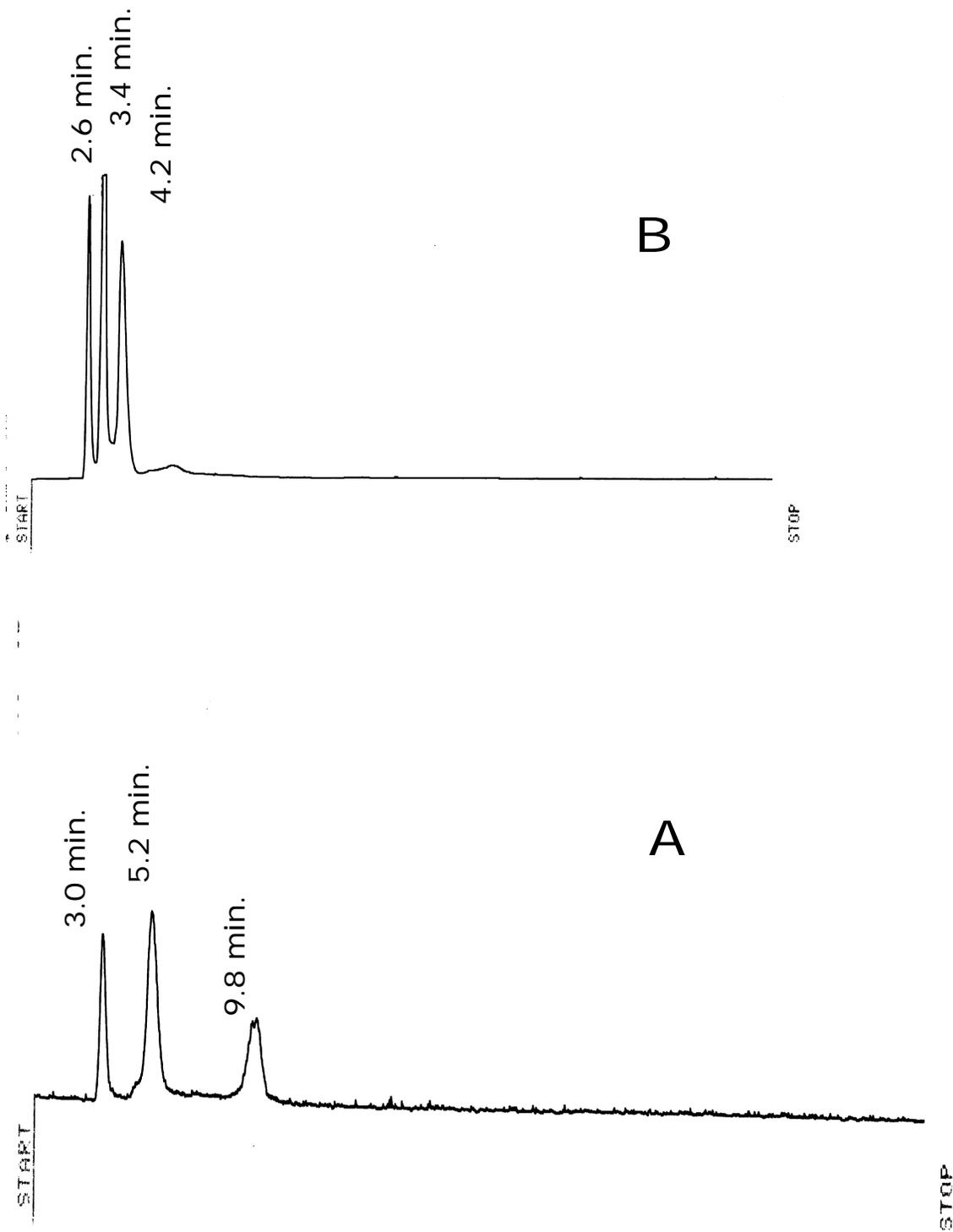


Fig. 5. Chromatograms of a mixture of IDA, NTA, EDTA, oxalate and citrate on QPEI-coated zirconia.

[A) 25 mM NH_4HCO_3 and 0.2 M ammonia at pH 8.5 and
B) 50 mM NH_4HCO_3 and 0.2 M ammonia buffer at pH 8.5.]

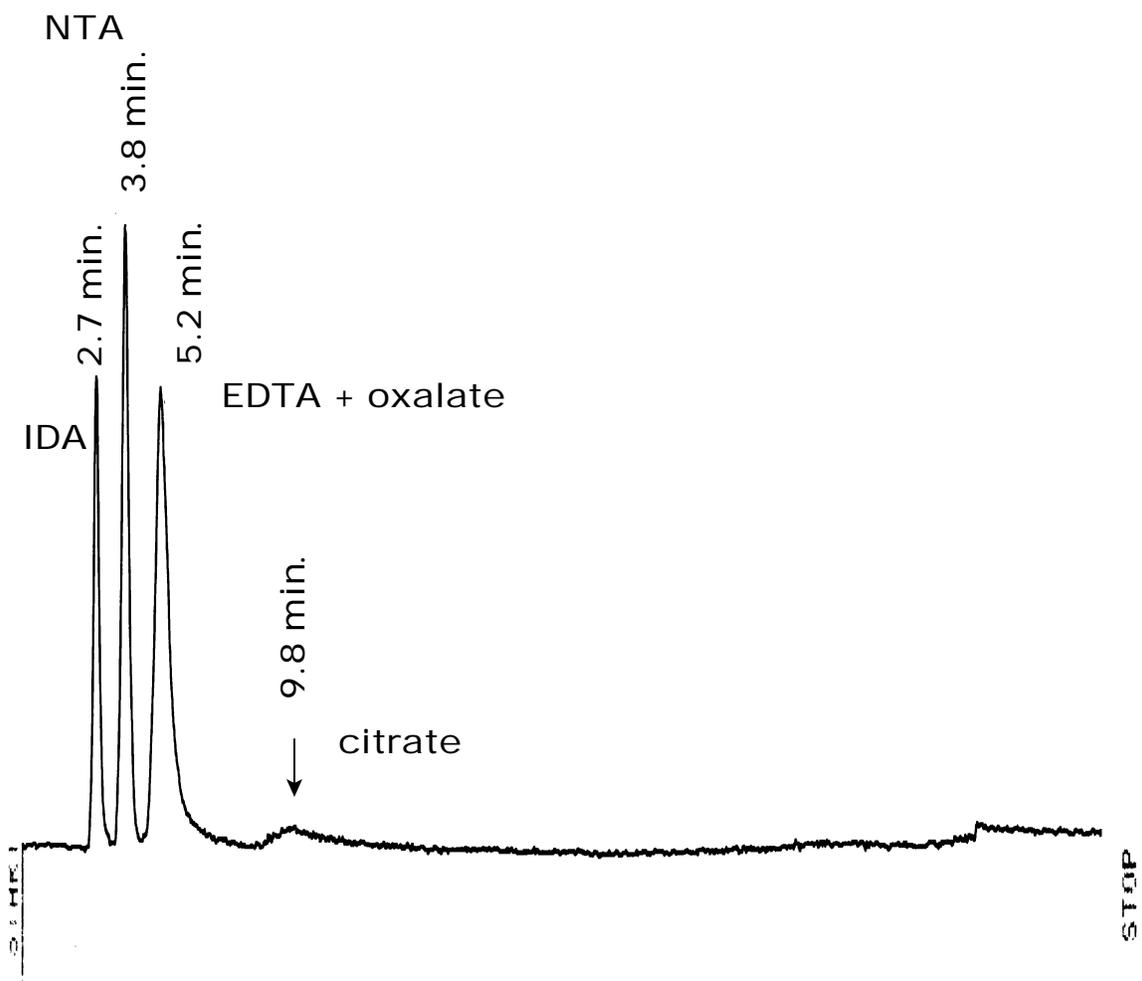


Fig. 6. Chromatogram of IDA, NTA, EDTA, oxalate and citrate on QPEI-coated zirconia in 20 mM NH₄HCO₃, 0.2 M NH₄F and ammonia buffer at pH 8.5.

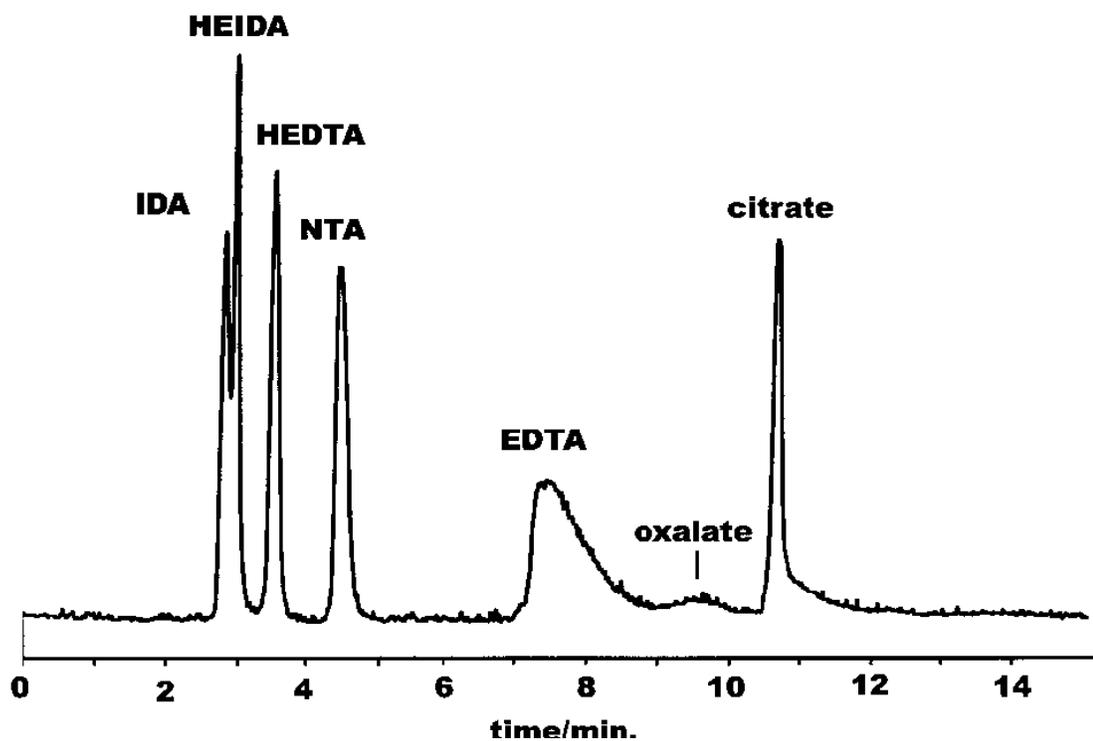
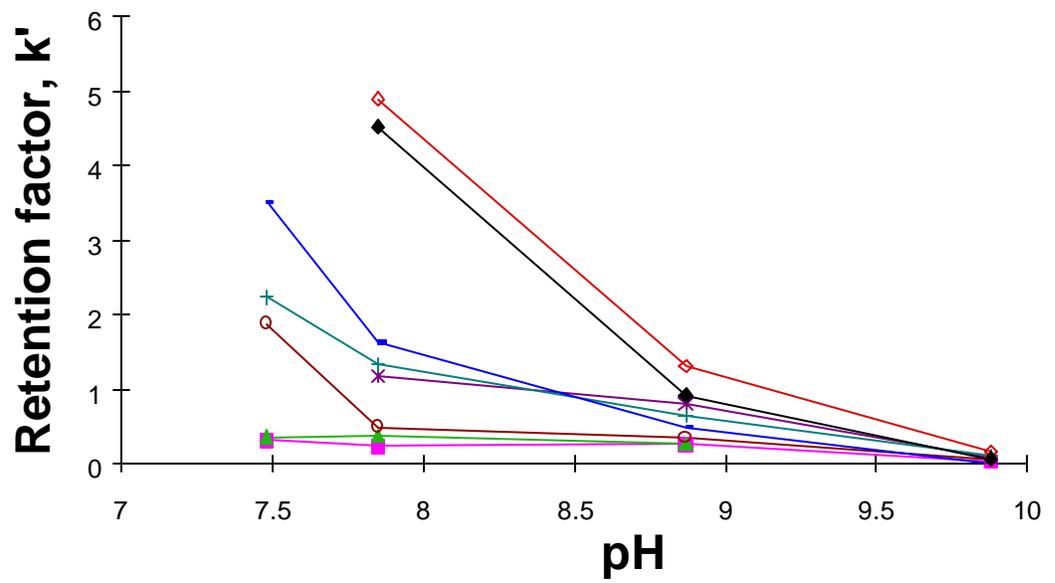


Fig. 7. Gradient elution of seven chelators on QPEI-coated zirconia.

[Gradient conditions: Buffer A = 0.13 M ammonium acetate/0.02 M NH_4CO_3 , pH 8.0. Buffer B = 0.15 M NH_4HCO_3 , pH 9.3. Starting at 100% Buffer A for 3 minutes followed by a linear ramp to 100% Buffer B at 10 minutes.]



—■— IDA —▲— HEIDA —○— HEDTA —*— glutarate —+— NTA —■— malonate

Fig. 8. Influence of pH on retention in the presence of 10mM bicarbonate.

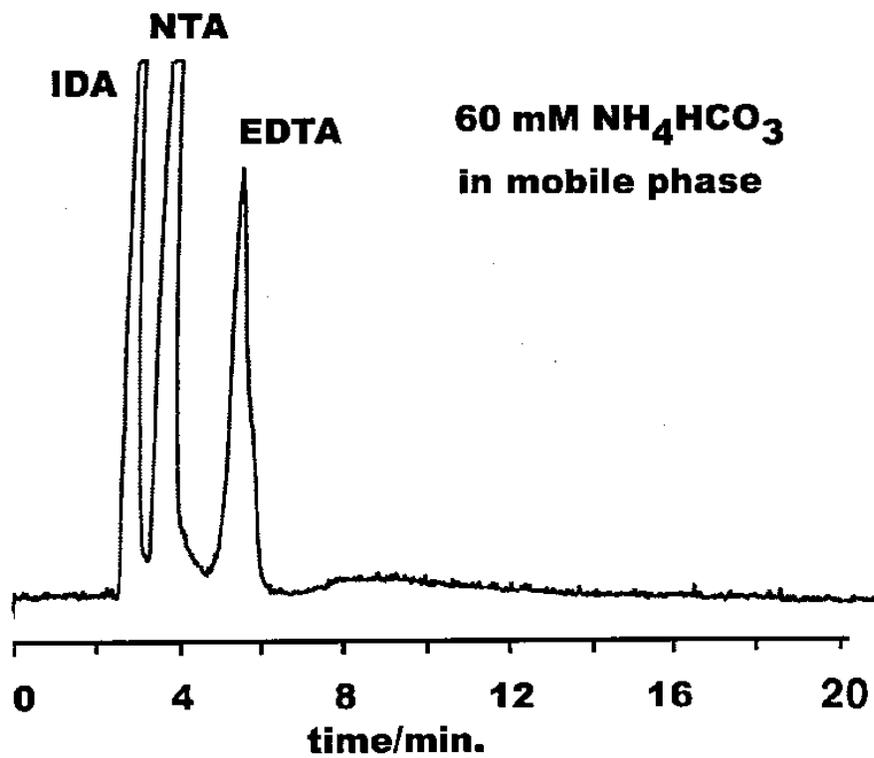
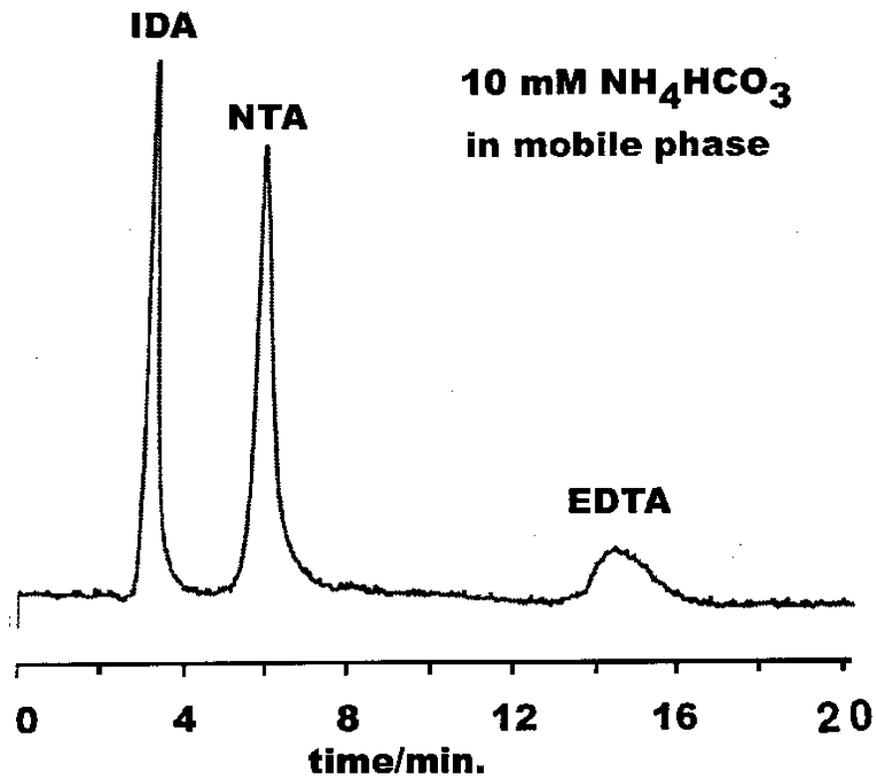


Fig. 9. Isocratic elution of chelators on QPEI-coated zirconia in morpholine acetate buffer at pH 8 and 0.15 M total ionic strength.

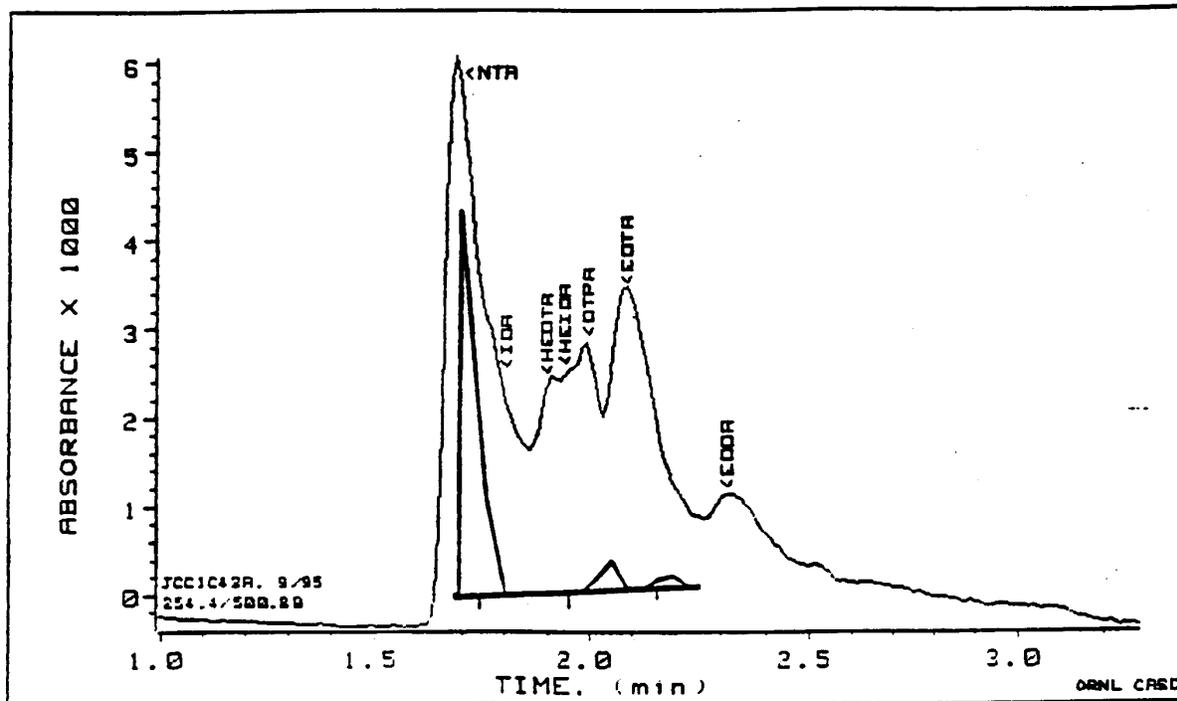


Fig. 10 Chromatogram of seven chelators/complexers monitored for ultraviolet absorbance at 254 nm.

[Isocratic elution with 98.5:1:0.5 water:acetonitrile:methanol solution that was adjusted to pH 2.4 with 0.06 M trifluoroacetic acid and 0.05 M ammonium hydroxide. The eluting solvent had a very high background caused by the buffer components. Inserted into this absorbance profile is the extracted ion profile for nm/e 191 to 193. {Nitrilotriacetic acid has a molecular weight of 191 and shows an $[M+1]^+$ ion at 192. See Fig. 14.

IMIDODIACETIC ACID

Entry Number 1 from C:\DATABASE\ANIONP1.L
CAS 000142-73-4
Melting Point 243
Boiling Point -300
Retention Index 0
Mol Formula C4H7NO4
Mol Weight 133.037
Company ID ORNL

Miscellaneous Information

SPECTRUM FROM DIRECT INJECTION OF 25 UL OF A 13.3 PPM SOLUTI
ON CARRIED BY 1/1 H2O/MEOH THAT WAS 0.1 M IN NH4Ac.

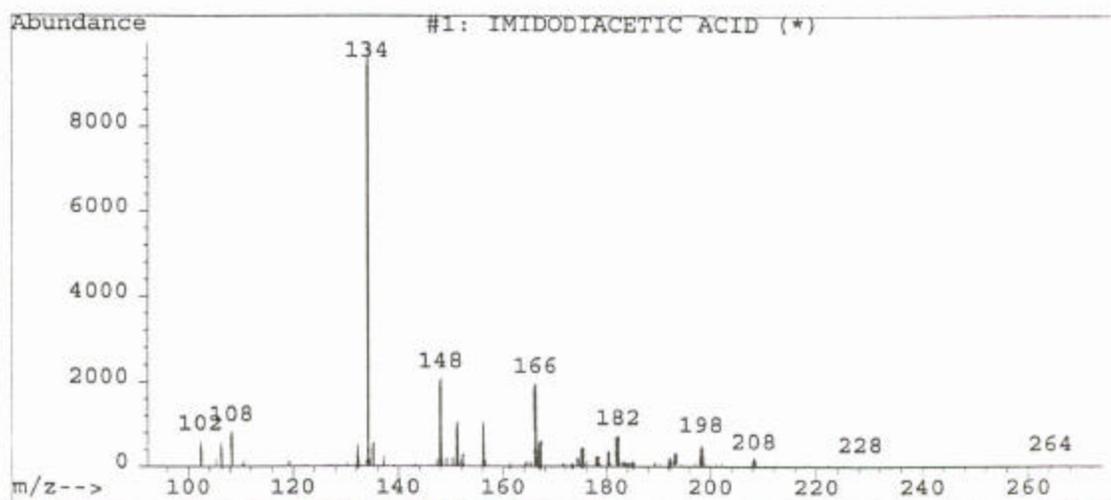


Fig. 11. Imidodiacetic Acid.

[Reference thermospray positive ion mass spectrum generated by direct injection (no column) into the thermospray probe from the liquid chromatographic injection system. Eluting solvent was 50:50 (by volume) water:methanol that was 0.1 M in ammonium acetate. Note the $[M+1]^+$ peak at 134.]

Ethylenediamine-N,N'-diacetic Acid

Entry Number 2 from C:\DATABASE\ANIONP1.L
CAS 005657-17-0
Melting Point 225
Boiling Point -300
Retention Index 0
Mol Formula C6H12N2O4
Mol Weight 176.079
Company ID ORNL

Miscellaneous Information

EDDA. Direct injection of 25 ul of a 17.6 PPM solution in
a stream of 1/1 MeOH/H2O that was 0.1 M in ammonium acetate.

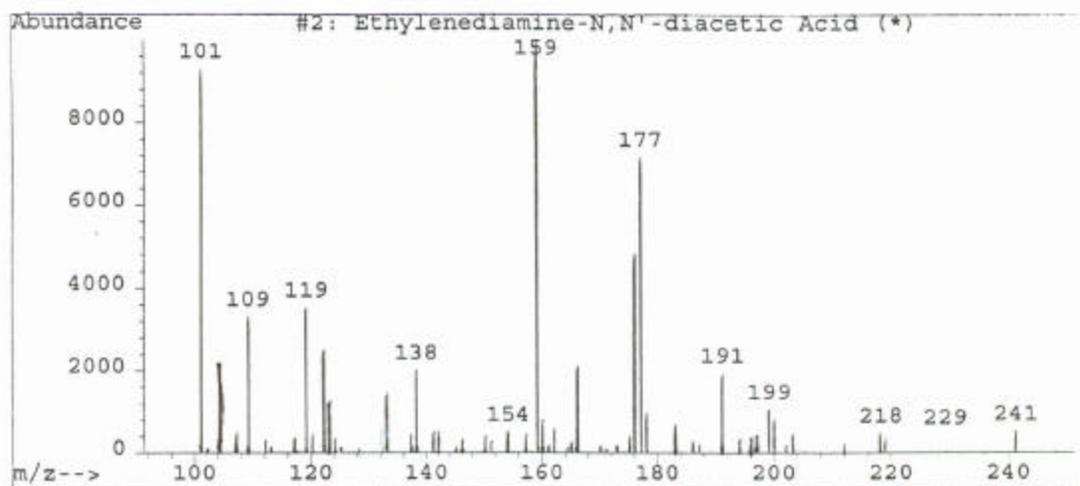


Fig. 12. Ethylenediamine-N,N'-diacetic acid.

[Reference thermospray probe from the liquid chromatographic injection system. Eluting solvent was 50:50 (by volume) water:methanol that was 0.1 M in ammonium acetate.

Note the $[M+1]^+$ peak at 177 and the $[M+1-18]^+$ peak at 159.]

N-(2-hydroxyethyl)ethylenediaminetriacetic Acid

Entry Number 5 from C:\DATABASE\ANIONP1.L
CAS 000150-39-0
Melting Point 212
Boiling Point -300
Retention Index 0
Mol Formula C10H18N2O7
Mol Weight 278.11
Company ID ORNL

Miscellaneous Information

HEDTA. Direct injection of 25 ul of a 27.8 PPM solution in
a stream of 1/1 MeOH/H2O that was 0.1 M in ammonium acetate.

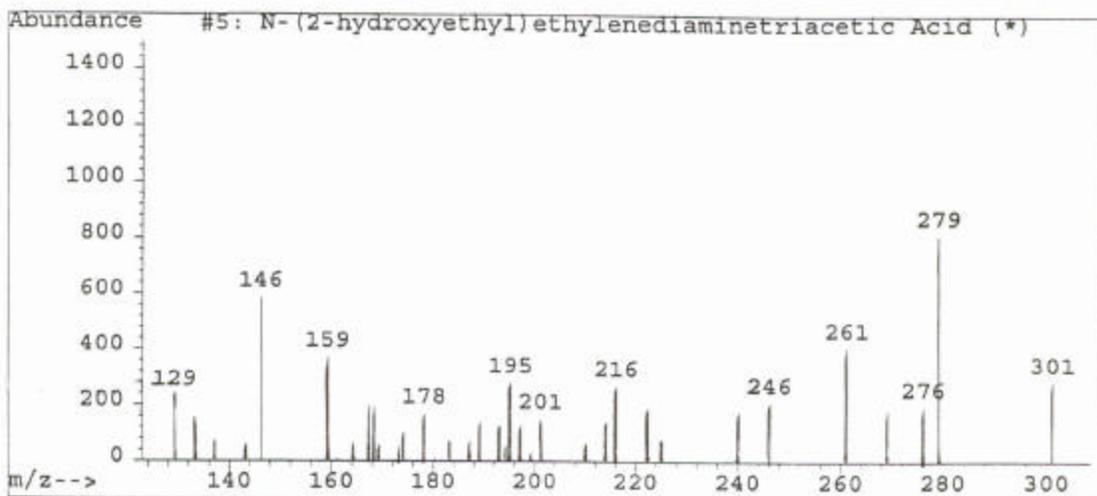


Fig. 13. N-(2-hydroxyethyl)iminodiacetic acid.

[Reference thermospray probe from the liquid chromatographic injection system. Eluting solvent was 50:50 (by volume) water:methanol that was 0.1 M in ammonium acetate. Note the $[M+1]^+$ peak at 178.]

Nitrilotriacetic Acid

Entry Number 4 from C:\DATABASE\ANIONP1.L
CAS 000139-13-9
Melting Point 246
Boiling Point -300
Retention Index 0
Mol Formula C6H9NO6
Mol Weight 191.043
Company ID ORNL

Miscellaneous Information

NTA. Direct injection of 25 ul of a 19.1 PPM solution in a stream of 1/1 MeOH/H2O that was 0.1 M in ammonium acetate.

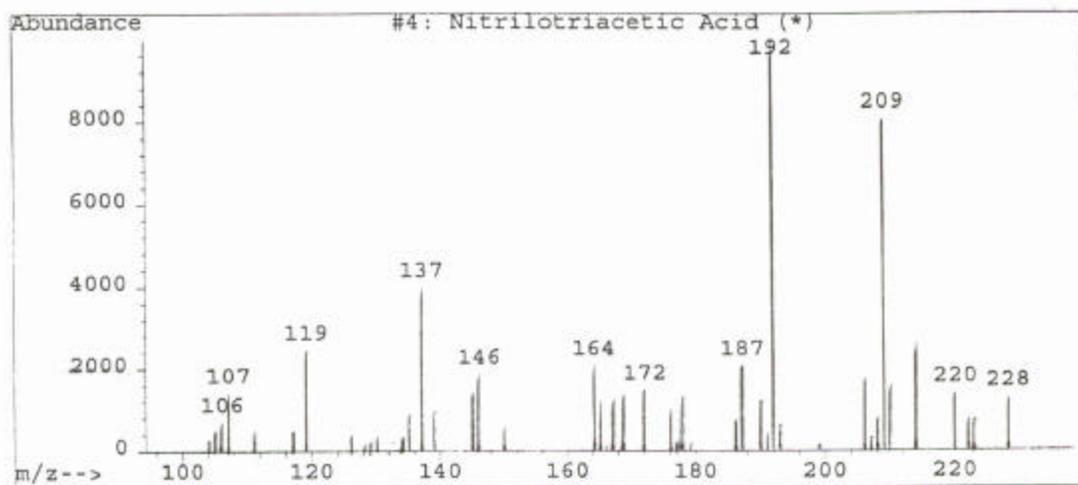


Fig. 14. Nitrilotriacetic acid.

[Reference thermospray probe from the liquid chromatographic injection system. Eluting solvent was 50:50 (by volume) water:methanol that was 0.1 M in ammonium acetate. Note the $[M+1]^+$ peak at 192 and the $[M+18]^+$ peak at 209.]

N-(2-hydroxyethyl)ethylenediaminetriacetic Acid

Entry Number 5 from C:\DATABASE\ANIONP1.L
CAS 000150-39-0
Melting Point 212
Boiling Point -300
Retention Index 0
Mol Formula C₁₀H₁₈N₂O₇
Mol Weight 278.11
Company ID ORNL

Miscellaneous Information
HEDTA. Direct injection of 25 ul of a 27.8 PPM solution in
a stream of 1/1 MeOH/H₂O that was 0.1 M in ammonium acetate.

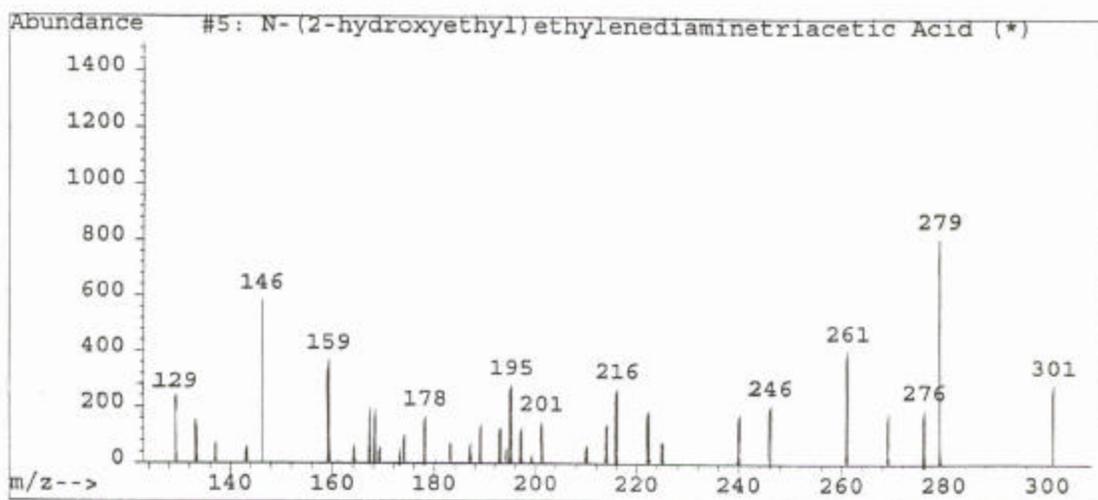


Fig. 15. N-(2-hydroxyethyl)ethylenediaminetriacetic acid.

[Reference thermospray probe from the liquid chromatographic injection system. Eluting solvent was 50:50 (by volume) water:methanol that was 0.1 M in ammonium acetate. Note the $[M+1]^+$ peak at 179 and the $[M+1-18]^+$ peak at 161.]

Ethylenediamine-N,N'-diacetic Acid

Entry Number 2 from C:\DATABASE\ANIONP1.L
CAS 005657-17-0
Melting Point 225
Boiling Point -300
Retention Index 0
Mol Formula C6H12N2O4
Mol Weight 176.079
Company ID ORNL

Miscellaneous Information

EDDA. Direct injection of 25 ul of a 17.6 PPM solution in
a stream of 1/1 MeOH/H2O that was 0.1 M in ammonium acetate.

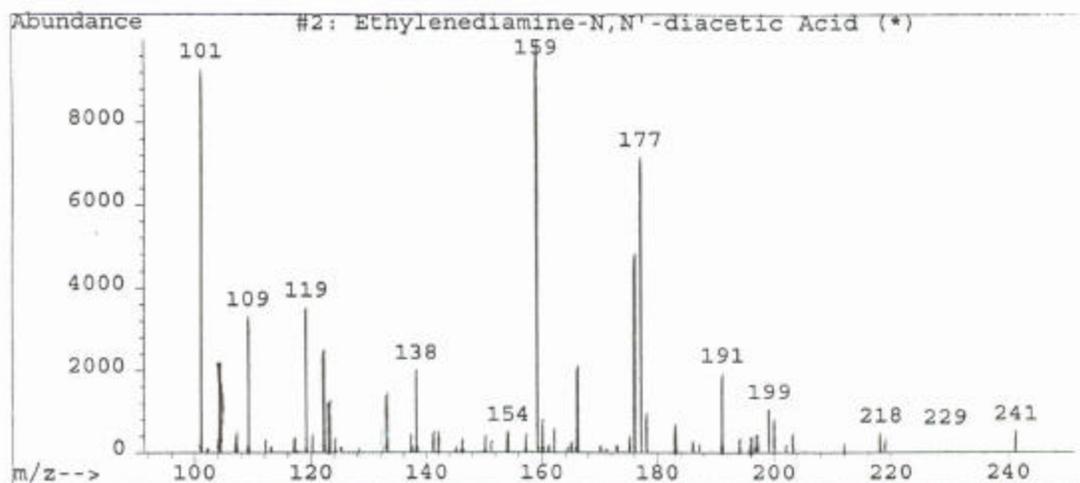


Fig. 16. Ethylenediaminetetraacetic acid.

[Reference thermospray probe from the liquid chromatographic injection system. Eluting solvent was 50:50 (by volume) water:methanol that was 0.1 M in ammonium acetate. Note the $[M+1]^+$ peak at 177 and the $[M+1-18]^+$ peak at 159.]

Diethylenetriaminepentaacetic Acid

Entry Number 6 from C:\DATABASE\ANIONP1.L
CAS 000067-43-6
Melting Point 219
Boiling Point -300
Retention Index 0
Mol Formula C14H23N3O10
Mol Weight 393.137
Company ID ORNL

Miscellaneous Information

DTPA. Direct Injection of a 25 ul of a 39.4 PPM solution in
a stream of 1/1 MeOH/H2O that was 0.1 M in ammonium acetate.

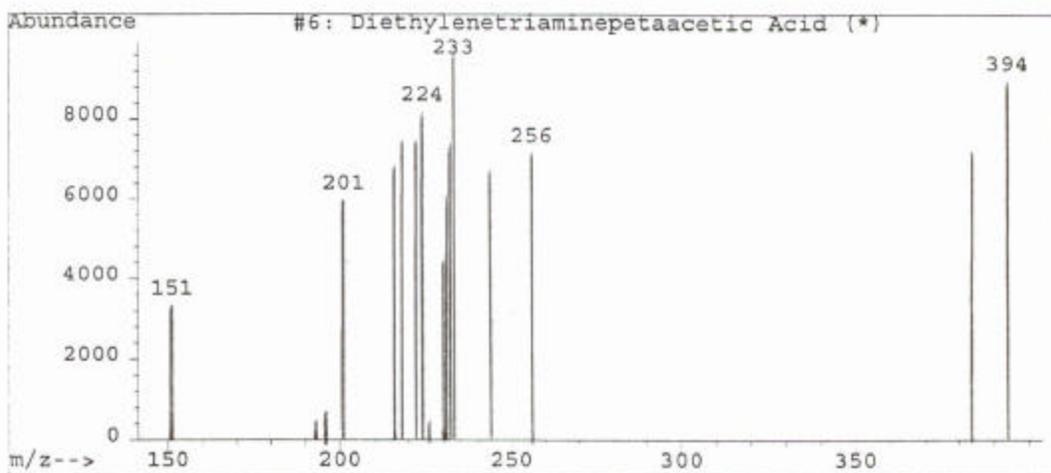


Fig. 17. Diethylenediaminetetraacetic acid.

[Reference thermospray probe from the liquid chromatographic injection system. Eluting solvent was 50:50 (by volume) water:methanol that was 0.1 M in ammonium acetate. Note the $[M+1]^+$ peak at 394. The $[M-10]^+$ peak at 384 is definitely associated with DTPA.]