Notice: The current controlled version of this document is on the LCODocs website (https://lcodocs.lanl.gov/). A printed copy of the document may not be the current version.

LOS ALAMOS NATIONAL LABORATORY
CARLSBAD OPERATIONS

LCO-ACP-39, Revision 0

Radiolytic Degradation of Organics – Progress Report

Effective Date: 12/18/24

Originator:

DAVID FAVELA MORALES (Affiliate) Digitally signed by DAVID FAVELA MORALES (Affiliate) Date: 2024.12.12 16:36:38 -07'00'

David Favela, LANL-CO ACRSP Date

JEAN FRANCOIS LUCCHINI (Affiliate) Digitally signed by JEAN FRANCOIS LUCCHINI (Affiliate) Date: 2024.12.12 16:46:38 -07'00'

Jef Lucchini, LANL-CO ACRSP Date

Approved by:

Jonathan Icenhower Digitally signed by Jonathan Icenhower Date: 2024.12.17 14:06:29 -07'00'

Jonathan Icenhower, LANL-CO ACRSP Team Leader Date

PRISCILLA YANEZ (Affiliate) Digitally signed by PRISCILLA YANEZ (Affiliate) Date: 2024.12.18 08:26:14 -07'00'

Priscilla Yanez, LANL-CO Quality Assurance Manager Date

DOUGLAS WEAVER (Affiliate) Digitally signed by DOUGLAS WEAVER (Affiliate) Date: 2024.12.18 08:51:54 -07'00'

Doug Weaver, LANL-CO Division Leader Date

History of Revisions

Revision Number	Effective Date	Pages Affected	Description of Revision
0	12/18/24	All	Original Release

ACRONYMS AND ABBREVIATIONS

α	Alpha particles
ACN	acetonitrile
Am	Americium
ATWIR	Annual Transuranic Waste Inventory Report
CBFO	Carlsbad Field Office
Da	Dalton
DOE	U.S. Department of Energy
DOTA	1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid
EDTA	Ethylenediaminetetraacetic acid
ESI	Electrospray ionization
Gy	Gray
HCl	hydrogen chloride
He^{2+}	helium ion
H_2O	water
HPLC-MS	high-performance liquid chromatography mass spectrometry
HR-MS	high resolution mass spectrometry
IBML	Ion Beam Materials Laboratory
LANL	Los Alamos National Laboratory
LC	liquid chromatography
LC-MS	liquid chromatography mass spectrometry
M	molar; moles/liter
min	minute
µL	microliter
µm	micrometer
mL	milliliter
mm	millimeter
mM	millimolar; millimoles/liter

ACRONYMS AND ABBREVIATIONS (cont.)

MeV	megaelectron volt
MV	megavolt
nA	nanoampere
NaCl	sodium chloride
NaOH	sodium hydroxide
pH	negative log of the hydrogen ion concentration
psi	pound per square inch
Pu	plutonium
QAPD	Quality Assurance Program Document
QL-1	Quality Level 1
qTOF	quadrupole time-of-flight
s	second
Ti	titanium
TRU	transuranic
U	uranium
V	volt
WIPP	Waste Isolation Pilot Plant

EXECUTIVE SUMMARY

Since March 26, 1999, a substantial amount of transuranic (TRU) waste has been shipped to the Waste Isolation Pilot Plant (WIPP). Commonly, this TRU waste contains organic constituents such as ethylenediaminetetraacetic acid (EDTA), citrate, acetate, and oxalate. These organic chemicals are by-products and reagents utilized during the processing of defense related nuclear material. All these carboxylate-based organic compounds are common ligands, which coordinate with metals ions, such as plutonium and uranium. These metal-ligand complexes have the potential to increase the solubility of the metal in brines. Degradation from radiolysis has been documented to effect the persistence of similar organic ligands, but more work is needed to investigate, specifically, the degradation of these organic compounds in the presence of alpha-emitting isotopes (e.g., ^{241}Am, ^{238}Pu, ^{239}Pu, ^{235}U, ^{238}U, etc.).

The experiments reported herein investigated the degradation of these organic ligands using a helium ion (He^{2+}) beam as the alpha (α) particle source. The results of these experiments further support that the radiolytic environment in which these organic ligands reside in the WIPP repository favors degradation over time from alpha emitting radioisotopes. These results are significant with respect to the persistence of these organic complexants and their ability to solubilize Pu complexes over time.

Preliminary results using EDTA and citrate suggest that 5.1 MeV alpha particles effect ligand degradation in water. For simplicity, the initial radiolysis experiments were performed in water. However, subsequent experiments will also include NaCl (3M and 5M) to reflect the WIPP brine conditions.

It is important to note that the data presented in this progress report are Non-Quality Level 1 (QL-1) data, per the Carlsbad Field Office (CBFO) Quality Assurance Program Document (QAPD), since the preliminary experiments described herein consisted in setting up and testing the experimental processes and instrumentation. Future experiments will be performed in a QL-1 setting, to confirm and expand these preliminary data.

TABLE OF CONTENTS

ACRONYMS AND ABBREVIATIONS 3
EXECUTIVE SUMMARY 5
1.0 INTRODUCTION 7
2.0 SUMMARY OF EXPERIMENTS 8
2.1 Solution preparation 8
2.2 Irradiation experiments 8
2.3 Mass spectrometry analyses 9
3.0 RESULTS AND DISCUSSION 10
3.1 Analysis of irradiated EDTA solution 10
3.2 Analysis of irradiated citrate solution 14
3.3 Comparison of organic ligand degradation 17
3.4 Additional experimental observations 18
4.0 CONCLUSIONS 18
4.1 Future Work 18
5.0 QUALITY ASSURANCE, DATA TRACEABILITY AND DOCUMENTATION 19
6.0 ACKNOWLEDGEMENTS 19
7.0 REFERENCES 20

1.0 INTRODUCTION

Several organic ligands can increase the mobility of dissolved metals (e.g., Ca^{2+}, Mg^{2+}, etc.) and radionuclides (e.g., Am, Pu, U, etc.) in solution by chelating metal ions to yield charged metal complexes (Hakem et al., 2001; Means and Alexander, 1981; Foreman and Smith, 1957). A higher solubility is expected for these ligand-metal complexes compared to radionuclides in the absence of organics. With respect to the WIPP, four chelating agents common to TRU processes generating waste destined for WIPP have the potential to increase the solubilization of the resident actinides. These complexing agents are ethylenediaminetetraacetic acid (EDTA), citrate, oxalate, and acetate. They are systematically quantified and updated annually in the Annual Transuranic Waste Inventory Report (ATWIR) by the Department of Energy Carlsbad Field Office (DOE-CBFO). Two of these complexants, EDTA and citric acid, and their respective degradation products following He-ion beam irradiation are investigated to assess the anticipable long-term persistence of these complexing agents.

Figure 1A displays the free ligand and the hexadentate metal chelate of EDTA. EDTA's amine and carboxylate functional groups possess electrons that can interact with the metal orbitals to form highly stable EDTA-metal complexes. While EDTA has been the focus of multiple gamma radiolysis experiments (Toste, 1998; Toste et al., 2005), there is a lack of studies involving the alpha irradiation of EDTA ligand. However, there is precedent for alpha radiolysis of EDTA's closely related congener, DOTA, a cyclic polydentate ligand (Fiegel et al., 2019). DOTA (free ligand) and its metal chelate are shown in Figure 1B.

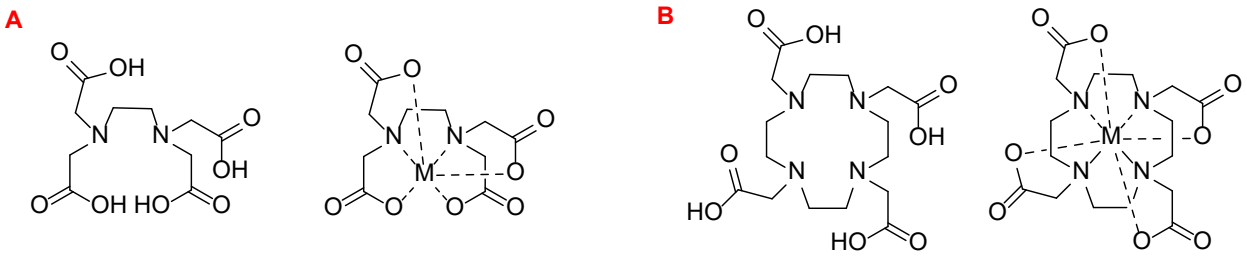

Figure 1. A) (left) Structure of fully protonated EDTA ligand and (right) EDTA-Metal chelate. B) (left) Structure of fully protonated DOTA ligand and (right) DOTA-Metal chelate.

The radiolysis experiments performed by Fiegel et al. (2019) indicated DOTA degradation occurred via different mechanisms such as decarboxylation and condensation. EDTA is predicted to undergo a comparable degradation akin to DOTA due to their similar chemical structure. Analogous to EDTA, there is also a lack of literature precedent involving the alpha radiolysis of citrate ligand.

The objective of this work was to determine how alpha radiolysis affects aqueous organic ligand solutions that mimic the predicted WIPP basicity (pH 9). Solutions containing either EDTA or citrate were prepared, irradiated, and then analyzed by high-performance liquid chromatography mass spectrometry (HPLC-MS) to quantify the extent of degradation of the starting organics.

2.0 SUMMARY OF EXPERIMENTS

2.1 Solution preparation

A stock solution of EDTA (0.05 M) purchased from Thermo Fisher was used to prepare calibration standards. A stock standard solution of citrate (0.05 M) was prepared by dissolving a weighed amount of trisodium citrate dihydrate (Millipore Sigma, 99.9% pure) in ultrapure deionized water. This stock citrate solution was diluted to prepare calibration standards. All stock and diluted solutions were adjusted to pH 9 using 1 M NaOH and 1 M HCl. A pH electrode was used to measure the pH of the prepared solutions. pH strips were also used because they were the only method we could use post-irradiation, since the volumes of solution were not sufficient to use a pH electrode. Standards were filtered through 0.45µm syringe filters before loading 1.5 mL autosampler vials.

2.2 Irradiation experiments

The irradiation of the solutions containing either EDTA or citrate was performed at the Los Alamos National Laboratory (LANL) Ion Beam Materials Laboratory (IBML), using a NEC 3.0 MV Tandem and an irradiation cell, specifically designed to irradiate fluids (Fig. 2).

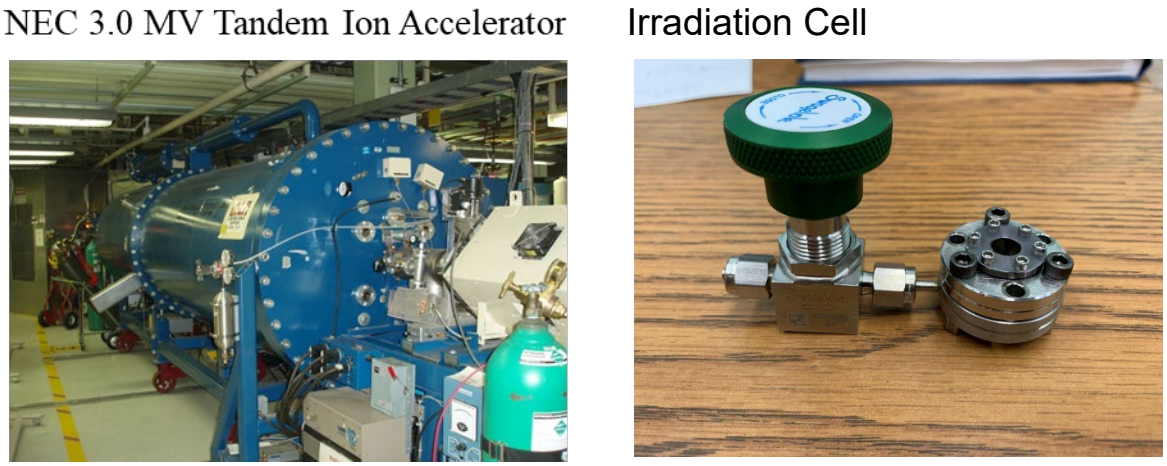

Figure 2. Left: a general view of the NEC 3.0 MV Tandem Ion Accelerator at the LANL IBML. Right: the irradiation cell used for these experiments.

A microliter syringe was used to introduce 850 µL of aqueous ligand solution into the stainless steel irradiation cell, equipped with Viton® o-ring and a 8-µm-thick titanium (Ti) foil. The irradiation cell was then mounted to the accelerator line, and the operator proceeded to perform ion beam adjustments and alignment.

When all the necessary settings were completed, the ion accelerator generated a linear beam of He^{2+} ions (i.e., α particles) by ionizing helium gas with an energy of 6.78 MeV before the titanium (Ti) foil (Fig. 3). The 4-mm diameter He^{2+} beam was directed to the Ti window, and penetrated the solution in the irradiation cell at a final energy of 5.1 MeV (which corresponds to the average energy of α particles emitted in TRU waste). At this energy, the projected range of α

particles in water is 38 µm. The He^{2+} flux was approximately 30 nA over a time period of 30 min which provided a dose of approximately 2×10^5 Gray (Gy) in solution and corresponded to about 2×10^{14} alpha particles being delivered into the solution. This corresponds to a radiation dose of at least two orders of magnitude higher than what can be anticipated in the WIPP.

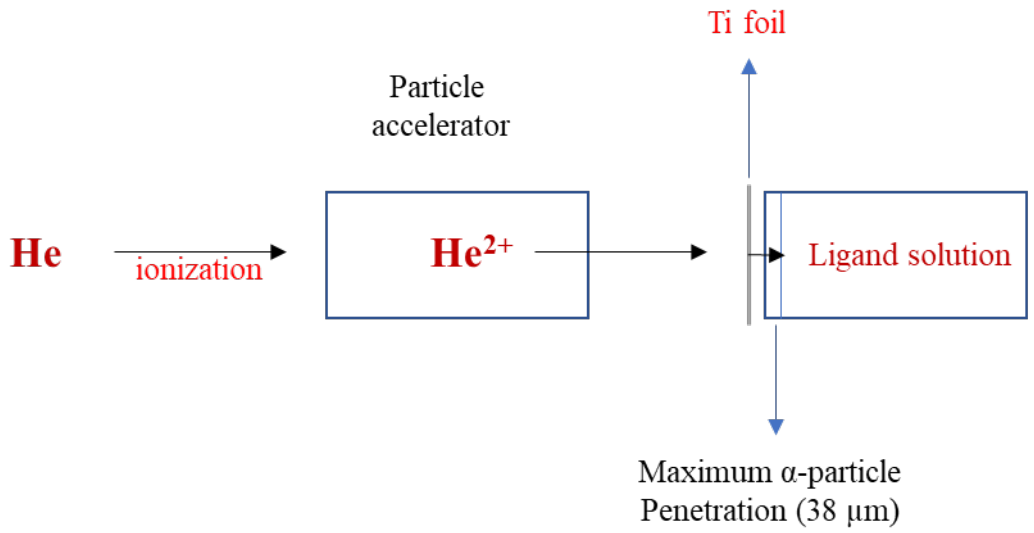

Figure 3. Schematic of the irradiation system. The irradiation cell (on the right of the Ti foil) is mounted to the ion accelerator (on the left of the Ti foil).

2.3 Mass spectrometry analyses

The analysis utilized a SCIEX X500R quadrupole time-of-flight (qTOF) mass spectrometer equipped with a Turbo V Ion Source and electrospray ionization (ESI) probe coupled to an ExionLC dual-pump liquid chromatography system suited for reverse-phase. Mobile phase solvents consisted of freshly prepared liquid chromatography mass spectrometry (LC-MS) grade water (VWR) and LC-MS grade acetonitrile (Fisher Scientific), for both positive- and negative-mode ESI runs. The column oven was held at 30°C across column types and the LC-qTOF system was equilibrated with their respective instrument method settings for at least five minutes prior to sample injection.

The qTOF instrument methods utilized Independent Data Acquisition using the maximum spray voltage available in each mode (5500 V in positive, -4500 V in negative) with a method duration equal to that of the LC. Curtain gas, ion source 1 (nebulizer) and ion source 2 (heater) gases were set to 30 psi, and the MS2 collision gas pressure setting of 7. Inlet gases all consisted of purified nitrogen produced from a Peak 1024 nitrogen generator (Peak Scientific). The mass range for detection in both the MS1 and MS2 (MS/MS) was 80-400 Da. All data were acquired using SCIEX OS (version 3.1) equipped with SCIEX LibraryView software (version 1.0) to utilize their commercial High-Resolution MS/MS spectral library (version 2.0) in addition to self-added high purity standards of EDTA and citrate that were prepared, collected, and analyzed on this instrument setup using these methods.

Instrument Method A (EDTA in ESI- mode): 1 µL of EDTA sample was injected via autosampler and delivered to an AccuCore C18 (4.6 mm × 150 mm, 2.6 µm) Reverse Phase column via an isocratic flow of 50:50 H_2O/ACN at 0.5 mL/min for ~10 min. The LC run time was subsequently reduced to 5 min. upon identifying the retention time of EDTA elution peak and optimizing its signal. The qTOF operated in negative mode (ESI-) with a source temperature set to 180 °C, MS1 and MS2 collision energies of 10 V ± 0V and declustering potentials of 50 V ± 0V, respectively. Accumulation times in the MS1 and MS2 were 0.25 s and 0.1 s, respectively. The acquisition software estimated these conditions yielded 231 cycles over a scan time of 1.301 s.

Instrument Method B (citrate in ESI+ mode): 10 µL of citrate sample was injected via autosampler and delivered to an Acclaim Organic Acid (4 mm × 150 mm, 5 µm) Reverse Phase column via an isocratic flow of 50:50 H_2O + 0.1% formic acid/ACN + 0.1% formic acid at 0.8 mL/min for 4 min. The qTOF operated in positive mode (ESI+) with a source temperature set to 200 °C, MS1 and MS2 collision energies at 10 V ± 0 V and 35 V ± 0 V respectively, and a declustering potential of 50 V ± 0V across both. Accumulation times in the MS1 and MS2 were 0.25 s and 0.1 s, respectively. The acquisition software estimated these conditions yielded 231 cycles over a scan time of 1.301 s.

3.0 RESULTS AND DISCUSSION

3.1 Analysis of irradiated EDTA solution

During method optimization it was found that the MS/MS analysis could not consistently quantify the EDTA mass peak below 0.1 mM. Additionally, concentrations above 5.0 mM tend to saturate the column and the detector, so a series of concentrations between 1.0 mM and 5.0 mM were utilized to establish a calibration curve (Fig. 4).

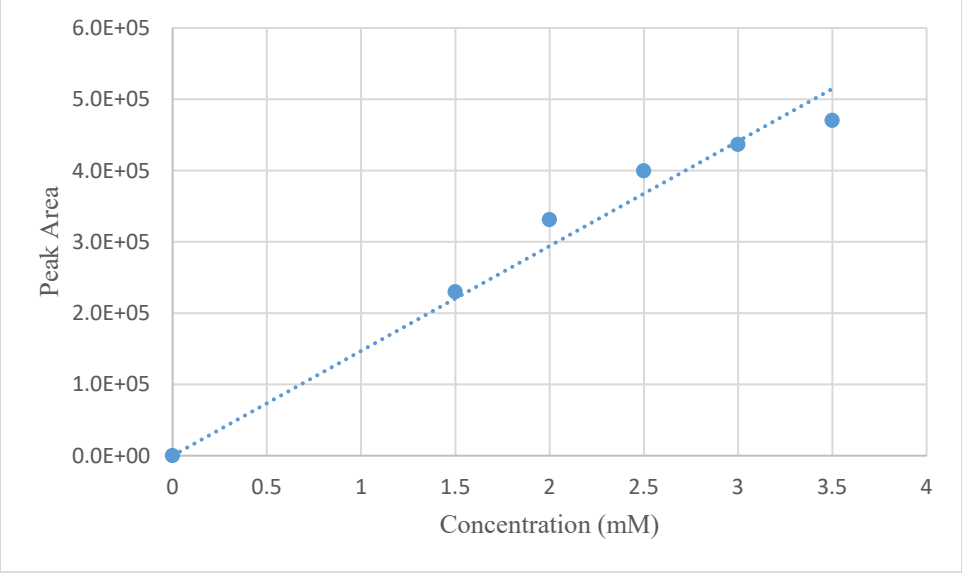

Figure 4. EDTA calibration curve. The data were regressed through the origin.

A 5.0 mM EDTA solution was used for the first irradiation experiment. The recovered irradiated sample was diluted to 2.5 mM (calculated by starting concentration) and analyzed by HPLC-MS. HPLC chromatograms of EDTA standard solution and irradiated EDTA solution are shown on Figure 5. The EDTA standard produced a single, well-defined peak, while the irradiated solution displays a broad asymmetric peak. The peak splitting pattern present in chromatogram B is evidence that new products, analogous in polarity to EDTA, formed during alpha radiolysis.

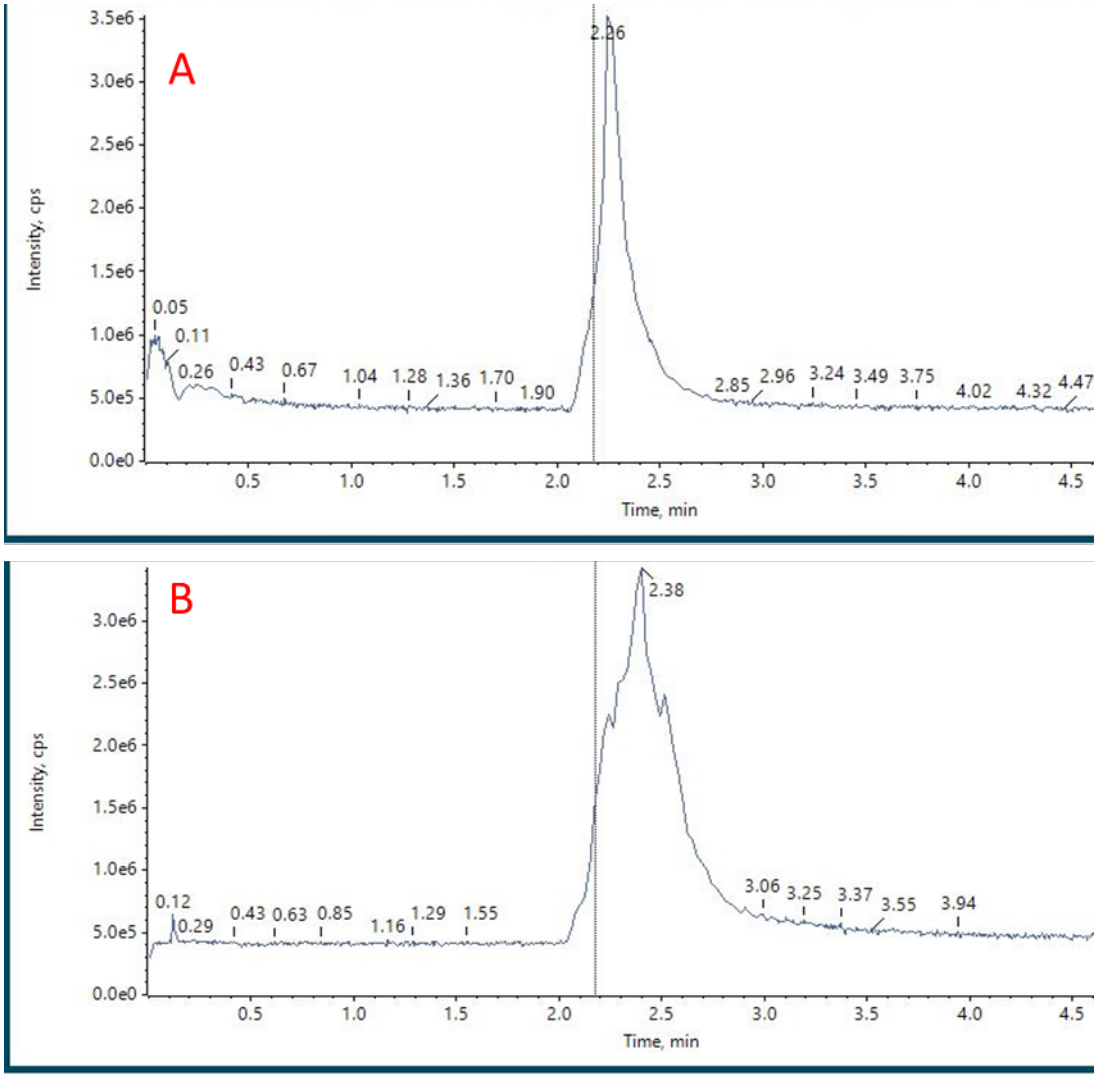

Figure 5. HPLC chromatograms of A) 3.5 mM EDTA standard and B) irradiated 5.0 mM solution diluted to 2.5 mM.

EDTA degradation was quantified by plotting the alpha-irradiated sample peak area along the calibration curve (Fig. 6). The area of the irradiated data point is only 62.5% of the area of the EDTA standard at the same concentration, indicating a significant amount of degradation occurred.

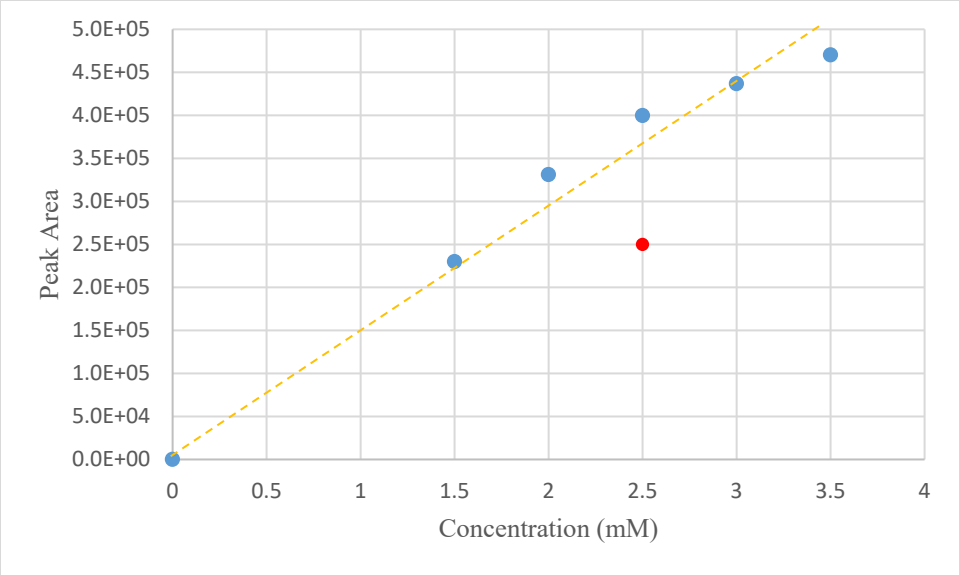

Figure 6. EDTA calibration curve with diluted 2.5 mM irradiated data point (red data point). The data were regressed through the origin.

It was hypothesized that a higher degree of degradation would be expected from a more concentrated solution. It is presumable that higher concentrations of reactive intermediates lead to an increase of intermolecular (chemical) reactivity with the organic ligand, thus increasing observed rate of degradation. To test this theory, a 50 mM EDTA solution (10× the first experiment's concentration) was irradiated. Figure 10 shows the chromatogram of EDTA standard compared to the 50 mM irradiated solution (diluted to 5 mM). Besides the subtle formation of a shoulder peak on the left side of the EDTA peak, a new, prominent signal appeared at the polar region of the chromatogram. At first glance, the new peak appears to be the same impurity that is visible in Figure 7A. However, it possesses a different retention time, which suggests that it could be a new degradation product.

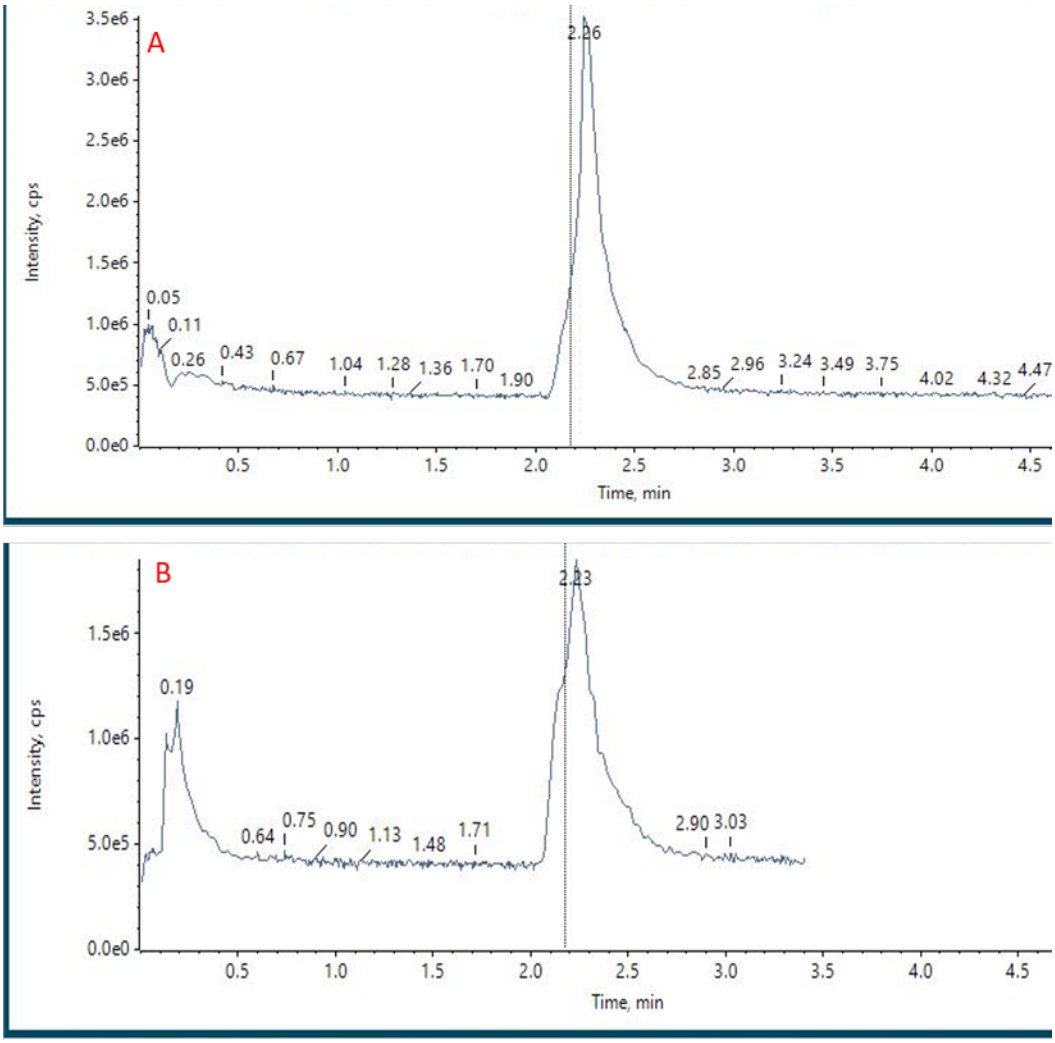

Figure 7. HPLC chromatograms of A) 3.5 mM EDTA standard and B) irradiated 50.0 mM solution diluted to 5.0 mM.

Fresh EDTA standards were prepared so the second irradiated EDTA solution (50 mM) was quantified using a new calibration curve (Fig. 8). EDTA degradation is more obvious for the higher concentration experiment. The irradiated data point is about 70% lower in intensity than the standard at the same concentration, resulting in more than half of the EDTA degraded during alpha irradiation. This was consistent with Fiegel et al. (2019) that a more concentrated ligand solution leads to higher overall degradation.

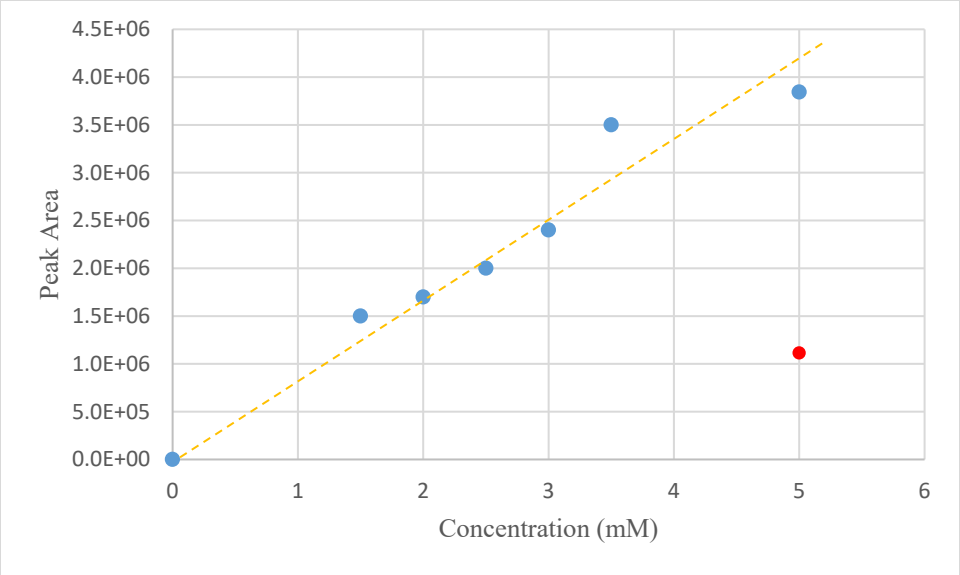

Figure 8. EDTA calibration curve with diluted 5.0 mM irradiated data point (red data point). The data were regressed through the origin.

3.2 Analysis of irradiated citrate solution

He^{2+}-induced degradation of citrate solution occurred in a similar fashion to EDTA. HPLC chromatograms of a citrate standard solution and an irradiated citrate solution are shown on Figure 9. The peaks at 1.20 (m/z: 294.9407) and 2.15 (m/z: 193.0355) min belong to sodium citrate and citric acid, respectively. HPLC chromatogram of irradiated citrate solution indicates a reduction in citric acid mass peak, as well as the appearance of degradation product peaks at 1.73 and 1.98 min.

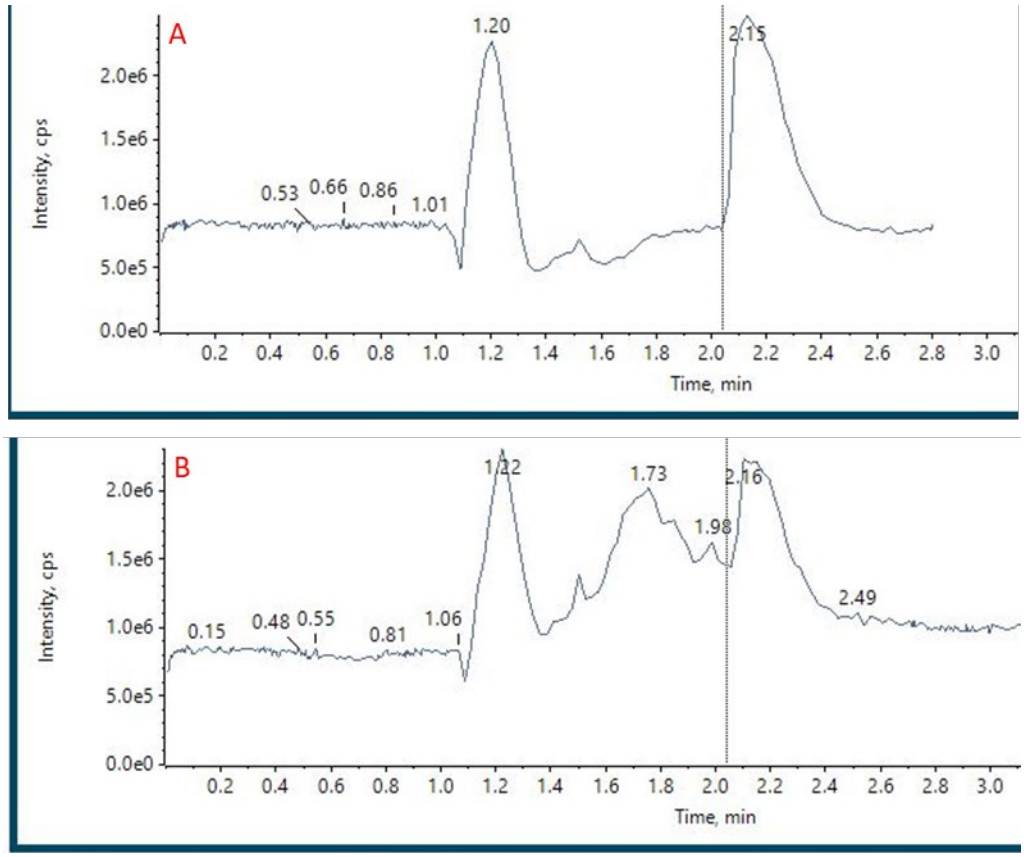

Figure 9. HPLC chromatograms of A) 3.0 mM citrate standard and B) irradiated 1.79 mM solution.

The irradiated 1.79 mM citrate solution shown above was plotted along a calibration curve to determine the degree of degradation (Fig. 10). Approximately 35% of citrate was degraded by alpha radiolysis.

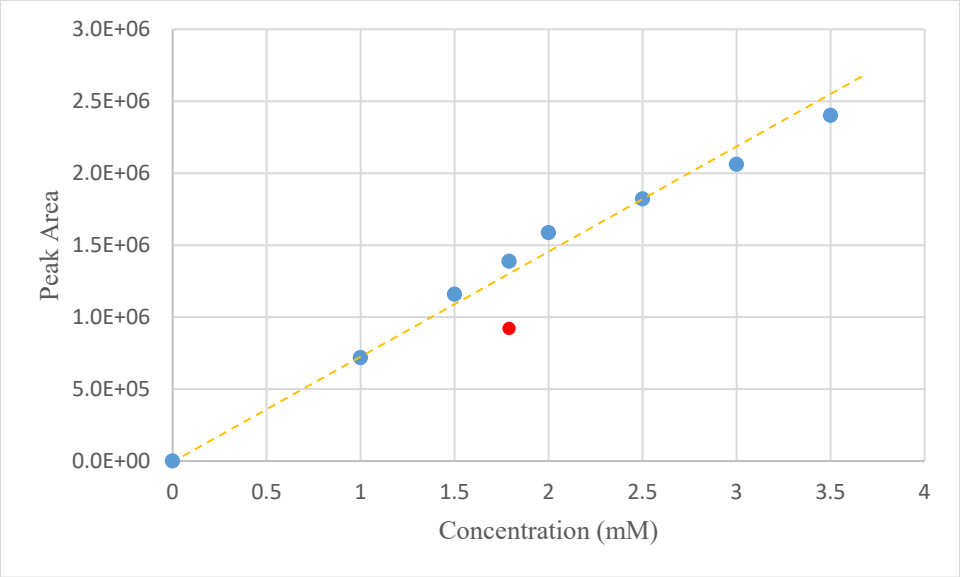

Figure 10. Citrate calibration curve with 1.79 mM irradiated data point (red data point). The data were regressed through the origin.

To test if citrate follows the same concentration-dependent pattern, a 10× more concentrated solution was irradiated. The recovered 17.9 mM sample was diluted to 1.79 mM (calculated by starting concentration) and analyzed by HPLC-MS. Unsurprisingly, a higher amount of ligand degradation (43%) was observed (Fig. 11).

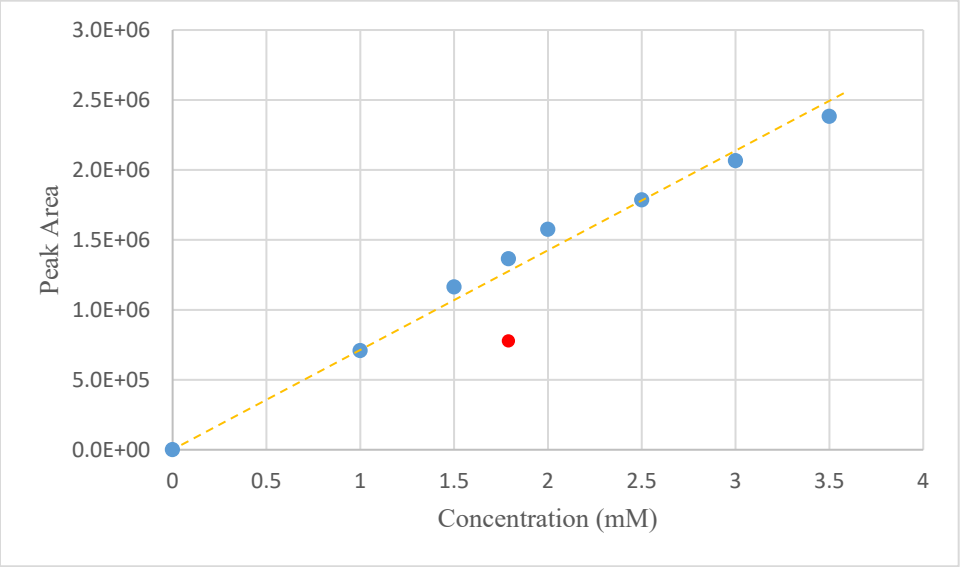

Figure 11. Citrate calibration curve with diluted 1.79 mM irradiated data point (red data point). The data were regressed through the origin.

Enhanced degradation of 50 mM citrate ligand is analogous to the results found in EDTA (Fig. 12). Approximately 60% of the citrate was degraded using the same conditions as the preceding citrate irradiations.

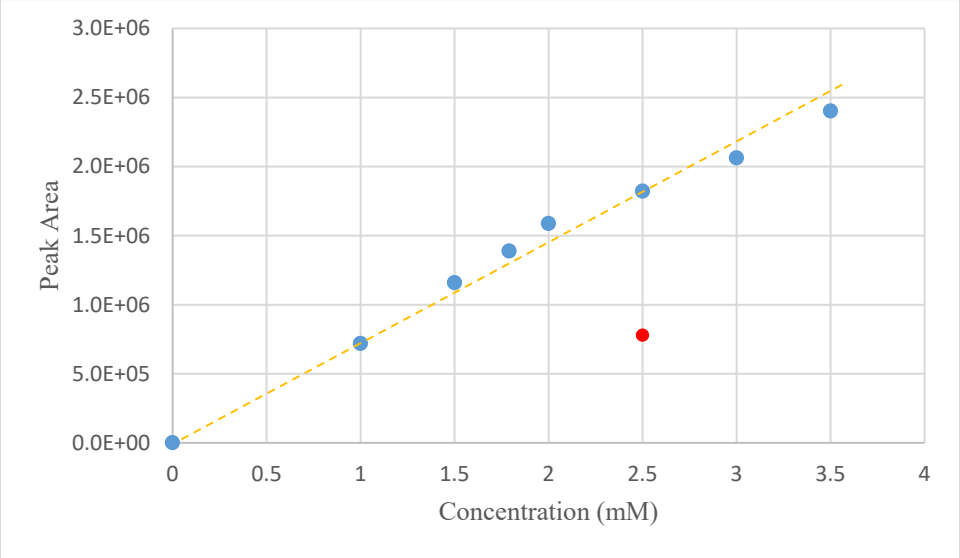

Figure 12. Citrate calibration curve with diluted 2.5 mM irradiated data point (red data point). The data were regressed through the origin.

3.3 Comparison of organic ligand degradation

While the chemical structure of EDTA and citrate are quite different, their degree of alpha-induced degradation is comparable. Table 1 summarizes the degradation of EDTA and citrate ligands at different concentrations. EDTA degradation nearly doubled as the concentration increased from 5 mM to 50 mM. Interestingly, a 10-fold increase in citrate concentration, from 0.179 mM to 1.79 mM, only achieved a 2% increase in degradation. However, an additional 10×increase in the solution concentration to 17.9 mM further degraded to 43%. Finally, radiolysis of the 50 mM solution degraded nearly 60% of the citrate ligand, a similar result to EDTA at the same concentration. Further studies are needed to determine if degradation rate increases linearly or exponentially with respect to ligand concentration.

Table 1. Summary of alpha radiolysis experiments for EDTA and citrate ligands.

Organic Ligand	Concentration of irradiated solution (mM)	Ligand degradation (%)	Ratio of concentration of irradiated solution to projected concentration in WIPP
EDTA	5.00	38	118
EDTA	50.0	70	1180
Citrate	0.179	32	0.1

Table 1. Summary of alpha radiolysis experiments for EDTA and citrate ligands (cont.).

Organic Ligand	Concentration of irradiated solution (mM)	Ligand degradation (%)	Ratio of concentration of irradiated solution to projected concentration in WIPP
Citrate	1.79	34	1
Citrate	17.9	43	10
Citrate	50.0	58	28

In the last column in Table 1, the ratios of concentration of irradiated solution to projected concentration in WIPP are provided. The expected concentrations of EDTA and citrate in WIPP are 4.22×10^{-5} M and 1.79×10^{-3} M, respectively (Domski, 2023). When tested at the concentration projected in WIPP, 34% of citrate ligand in aqueous solution decomposes in the conditions of the irradiation experiments (i.e., high alpha radiolysis dose).

3.4 Additional experimental observations

It was observed that the Ti foil in the radiolysis cell was bulged out because of gases that formed during alpha radiolysis of both EDTA and citrate (likely He). The solution was retrieved using a microliter syringe and placed in a new scintillation vial. pH strips were used to estimate the pH of the irradiated solution. In most cases, the pH values of the irradiated solutions decreased to roughly pH 6-7. Acidification of irradiated solutions was also observed in experiments performed at high alpha particles flux reported in the literature (Lucchini, 2001).

4.0 CONCLUSIONS

This report demonstrates that alpha radiolysis is capable of degrading EDTA and citrate ligands in aqueous solution at initial pH 9. HPLC-MS/MS analysis determined the degree of degradation effected by He^{2+} ions. Significant ligand degradation occurs at concentrations expected at WIPP and enhances further at higher ligand concentrations. All of the alpha-radiolysis experiments reveal a trajectory in reducing the availability of organic complexing agents at WIPP. This is relevant for future evaluations regarding solubilization and potential migration of the actinides at WIPP.

4.1 Future Work

Acetate and oxalate will be included using the same conditions as citrate and EDTA to account for all complexing agents tracked in the ATWIR. All four complexants will be irradiated in 3 M and 5 M NaCl solutions to better mimic the WIPP brine environment.

Certain by-products can be ascribed to specific degradation mechanisms such as decarboxylation or deacetoxylation. Therefore, future post-irradiation analysis will focus on the chromatographic peak separation, identification, and quantification of radiolysis by-products. It is important to

determine if degraded products can bind and increase the environmental mobility of actinides as efficiently as their parent ligand.

5.0 QUALITY ASSURANCE, DATA TRACEABILITY AND DOCUMENTATION

The experiments described in this report were initiated under the test plan, "Radiolytic Degradation of Organics – Focus on EDTA and Citrate" (LCO-ACP-35). However, all of the data presented in this report were generated in developmental experiments, which consisted in setting up and testing the experimental processes and instrumentation. Therefore, the data presented herein are considered as Non-QL-1 data, in accordance with the CBFO QAPD.

Even though obtained following best laboratory practices, the experimental results in this report are preliminary. They can inform about the trend and likely conclusions of the study, but they will have to be repeated and confirmed as QL-1, in accordance with the CBFO QAPD. A detailed description of the experiments presented herein can be found in the developmental scientific notebook assigned to the test plan LCO-ACP-35.

6.0 ACKNOWLEDGEMENTS

The authors wish to thank Katharine Orr (LANL – MST 7) for the immense help and knowledge regarding the use and maintenance of the HPLC-MS. The authors are also extremely grateful to Matt Chancey and Yongqiang Wang (LANL – MST 8) for all their guidance and experience with the helium ion beam.

7.0 REFERENCES

ATWIR - U.S. Department of Energy (DOE) 2023. Annual Transuranic Waste Inventory Report – 2023 (Data Cutoff Date 12/31/2022), DOE/TRU-23-3425, February 2024. Carlsbad Field Office, Carlsbad, NM.

Domski, P.S. 2023. Prediction of Baseline Actinide Solubilities for the Replacement Panels Plan Change Request (RPPCR) Performance Assessment. Sandia National Laboratories Report. ERMS 579503.

Fiegel, V., Berthon, C., Costagliola, A., Blain, G., Vandenborre, J., Vermeulen, J., Saint-Louis, G., Guerin, L., Sauvage, T., Fattahi-Vanani, M., Venault, L., Berthon, L. 2019. Alpha Radiolysis of DOTA Ligand in Aqueous Solutions with Helium Ion Beams. Radiation Physics and Chemistry. 165; 108409.

Foreman, J. K., Smith, T. D. 1957. The Nature and Stability of the Complex Ions formed by Ter-, Quadri-, and Sexa-valent Plutonium Ions with Ethylenediaminetetraacetic Acid. Journal of the Chemical Society. 1758-1762.

Hakem, N. L., Allen, P. G., Sylwester, E. R. 2001. Effect of EDTA on plutonium migration. Journal of Radioanalytical and Nuclear Chemistry. 250, 47−53.

Lucchini, J.F. 2001. Influence of Alpha Radiolysis of Water Alteration of the UO_2 Matrix of Used Nuclear Fuel. Thesis, University of Paris XI Orsay (in French).

Means, J. L., Alexander, C. A. 1981. The environmental biogeochemistry of chelating agents and recommendations for the disposal of chelated radioactive wastes. Nuclear and Chemical Waste Management. 2, 183.

QAPD, 2023. Quality Assurance Program Document, DOE/CBFO-94-1012, Rev. 14.

Toste, A. P. 1998. Gamma Radiolysis of EDTA in a Simulated, Mixed Nuclear Waste. Journal of Radioanalytical and Nuclear Chemistry. 235, 213-219.

Toste, A. P., Polach, K. J., Ohnuki, T. 2005. Chemodynamics of EDTA in a Simulated, Mixed Waste: Chemo-degradation vs. Gamma-radiolysis. Journal of Radioanalytical and Nuclear Chemistry. 263, 559-565.