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COMPLEXANT IDENTIFICATION IN HANFORD WASTE SIMULANT Sr/TRU FILTRATE (U)

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Complexant Identification in Hanford Waste Simulant Sr/TRU Filtrate

Final Report

Prepared

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List of Abbreviations

AAS	Atomic Absorption Spectrometer
Al	Aluminum
AMMS-ICE	Ion exclusion suppressor
BIDA	N-butyliminodiacetic acid
Ca	Calcium
Cd	Cadmium
Citr	Citrate
Cr	Chromium
Cu	Copper
EDTA	Ethylenediaminetetraacetic acid
Eh	Oxidation-reduction potential
F	Fluoride
Fe	Iron
F.R.	Flow rate
γ	Gamma radiation
Glu	Gluconate
Gly	Glycolate
Glyox	Glyoxylate
HEDTA	N-hydroxyethylethylenediaminetriacetic acid
HIBA	Hydroxyisobuteric acid
HPLC-MS	High Performance Liquid Chromatography – Mass Spectrometer
hr	Hour
HFBA	Heptafluorobuteric acid
IDA	Iminodiacetic acid
IC	Ion Chromatography
IC-MS	Ion Chromatograph - Mass Spectrometer
M	Molarity
Mg	Magnesium
Mn	Manganese
MW	Molecular Weight
NaOH	Sodium hydroxide
ND	Not Detected
NH_4OH	Ammonium hydroxide
Ni	Nickel
NIDA	N-(nitroso)iminodiacetic acid
NTA	Nitrilotriacetic acid
O	Oxygen
Oxal	Oxalate
Pb	Lead
pH	-log hydrogen ion activity
pKa	-log acid equilibrium constant
Phos	Phosphate
ppm	Part per million
QAPjP	Quality Assurance Project Plan
R	Retained on the column
rpm	Revolution per minute
SRTC/WTT	Savannah River Technology Center / Waste Treatment Technology
Sr	Strontium
Tart	Tartrate
TBAH	Tetrabutylammonium hydroxide
Th	Thorium
TRU	Transuranic element(s)
UV	Ultraviolet
Zn	Zinc

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Abstract

This project was designed to characterize the available multidentate ligand species and metal ion complexes of iron (Fe), strontium (Sr) and manganese (Mn) formed with the parent chelators, complexing agents and their fragment products. Complex identification was applied to AN-102 and AN-107 filtrate simulants for Hanford waste after an oxidation reaction with sodium permanganate to create a freshly precipitated manganese dioxide solid for adsorption of transuranic (TRU) elements. Separation efficiency of different ligands was investigated based on the exchange capability of different ion exchange and ion exclusion analytical columns including Dionex IonPac AS-5A, AS-10, AS-11 and AS-6. The elution programs developed with different mobile phase concentrations were based on the change in the effective charge of the anionic species and therefore the retention on the stationary phase. In the present work, qualitative and quantitative assessments of multidentate ligands were investigated. Identification methods for the metal ion complexes responsible for solubilizing Fe, Mn and Sr were applied to aged and fresh simulant waste filtrates.

The IC and AA analyses of the stoichiometric metal complexes showed that the carboxylate anions that are responsible for solubilizing iron and manganese in the filtrate obey the following corresponding sequences:

Fe(III): Tartrate >> Glyoxylate > Glycolate > Oxalate

Mn: EDTA >> Citrate > Tartrate

Therefore, the predominant metal complexes in the filtrate at high pH are Fe(III)-tartrate and Mn-EDTA.

Although concentration measurements of both fresh and 3-week aged filtrates showed that the degradation process occurs mainly due to the harsh chemical environment, it was found that the concentration of iron and manganese did not increase, within the error of the analytical measurements, after three weeks when compared with fresh filtrate.

1.0 SUMMARY OF TESTING

1.1 Objectives

A) Assess both qualitative and quantitative multidentate ligand species present in the filtrate solutions.

B) Identify the metal ion complexes responsible for solubilizing manganese, iron and other metal ion species.

C) Analyze aged and fresh simulant waste filtrates, based on the optimized analytical methods, to monitor the chemical behavior of the available multidentate ligands and their complexes, which will lead to increased process control.

1.2 Conduct of Testing

Based upon recipes supplied by Savannah River Technology Center / Waste Treatment Technology Department (SRTC/WTT) [1], two nonradioactive simulants for Hanford complexant wastes (241-AN-102 and 241-AN-107) were diluted to 6M sodium and adjusted to 1M sodium hydroxide by the addition of 17M NaOH. Following caustic adjustment, the two samples were treated at base case conditions to achieve a concentration of 0.075M of strontium(II) and 0.05M added manganese at 50±2 ^{0}C and allowed to digest for four hours. The reaction mixtures were cooled to room temperature in a re-circulating water bath to avoid localized over cooling. The mixtures were filtered with 0.1-micron nylon filter then kept under nitrogen in the dark. Complex identification in the fresh simulant filtrate for Hanford complexant wastes (241-AN-102 and 241-AN-107) were analyzed promptly following filtration. To follow the reaction behavior of the identified complexes, aliquots of the two-filtrate samples were re-filtered after three weeks and then subjected to IC analysis for complex identification.

1.3 Results and Performance Against Objectives

The first objective was to identify multidentate ligand species that are present in the filtrate solution. In this respect, qualitative and quantitative assessments of multidentate ligand species were investigated based on the newly developed analytical methods. The developed methods were applied not only to separate the original ligand that was used to prepare the simulant filtrate but also to identify the expected degradation products.

The second objective was to identify the metal ion complexes responsible for solubilizing manganese and iron. This was tested by preparing the metal complexes of the corresponding detected ligands in the filtrate solution. The IC and AAS analysis of the stoichiometric metal complexes showed that the carboxylate anions that are responsible for solubilizing iron and manganese in the filtrate obey the following corresponding sequences:

Fe(III): Tartrate >> Glyoxylate > Glycolate > Oxalate

Mn: EDTA >> Citrate > Tartrate

Therefore, the predominant metal complexes in the filtrate at high pH are Fe(III)-tartrate and Mn-EDTA.

The third objective was focused on analysis of aged and fresh simulant waste filtrates to monitor the chemical behavior of the available multidentate ligands and their complexes. In this respect, concentration measurements of both fresh and 3-week aged filtrates confirmed that the degradation process occurs mainly due to the harsh chemical environment. It was also found that the concentration of Fe and Mn did not increase, within the limits of the analytical measurement uncertainty, after 3 weeks compared to the fresh filtrate. The organic content of simulant waste filtrate is dynamic and may need continuous analytical monitoring.

1.4 Quality Requirements

The task was performed in accordance with the quality assurance requirements contained in the Quality Assurance Project Plan (QAPjP) "Quality Assurance Project Plan- Complexant Identification in Hanford

Waste Simulant Sr/TRU Filtrate" as shown in reference [2] of this report. The contents of the report were checked and peer reviewed in accordance with applicable WSRC and SRTC QA requirements. These QA requirements include applicable program elements of NQA-1-1989 and NQA-2a-1990.

1.5 Issues

No programmatic issues were identified as a result of this work.

2.0 INTRODUCTION AND LITERATURE REVIEW

Chemical characterization of Hanford waste, which accumulated during the processing of irradiated nuclear fuels and waste management activities, is an analytical challenge. This analytical problem is not only a result of the different charge states of the complexants and their degradation products but also because they form many complexes with metal ions resulting in multiple species. Further complication arises because the Hanford waste is highly radioactive, high in ionic strength and high in hydroxide concentration [19].

In actual Hanford mixed waste, in addition to several complexing and chelating agents [e.g., ethylenediaminetetraacetic acid (EDTA), N-hydroxyethylethylenediaminetriacetic acid (HEDTA), nitrilotriacetic acid (NTA) and citrate], 38 chelate/complexant fragments have been identified, compared to only 11 in the original analysis [3].

In a non-radioactive simulant of the actual waste containing the parent organics (EDTA, HEDTA, NTA and citrate), 20 chelate/complexant fragments were identified along with several mono and dicarboxylate anions [3]. This confirmed that most of the chelate fragments are formed via chemical degradation in a harsh chemical environment even in the absence of radiation [4] or pretreatment processing.

2.1 Literature Review on the Degradation of Chelating/ Complexing Agents in Hanford Complexant Waste

Analysis of liquid waste from Hanford shows that chelate/complexant fragments have been formed via radiolysis, chemical and/or thermal degradation. The presence of these fragments indicates that the organic content of nuclear wastes is dynamic [5].

2.1.1 HEDTA

Most of the HEDTA (94.4%) in the simulant disappeared after 100 hr of γ-radiolysis ($7.5 \times 10^6 \pm 10\%$ R) [6]. Comparison of HEDTA degradation with that of other parent compounds yields the following order for a single chelate containing simulant:

NTA (100%) > HEDTA (94.4%) > EDTA (89.1%) > Citrate (58.8%).

Whereas in a multichelate simulant the order is:

HEDTA (99.8%) > EDTA (77.5%) > NTA (66.7%) > Citrate (51.1%)

The most abundant organic identified in HEDTA radiolysis was methyl dimethoxy acetate which is formed via methylation of glyoxylic acid. HEDTA radiolysis yielded lower concentrations of two other carboxylate anions, ethandioate (oxalate) and propandioate (malonate).[6].

2.1.2 EDTA

EDTA also shows extensive degradation in simulant. EDTA degradation accounts for 10 of the chelate fragments formed in simulant containing a mixture of complexing agents[3]. Included amongst the fragments was tartrate.

Irradiation of EDTA yielded six chelator fragments (MW 105-263) and four dicarboxylic acids, the most abundant were, glyoxylic acid and N-(nitroso)iminodiacetic acid (NIDA) [5, 6]. After 100 hr of radiolysis 89.1% of the EDTA had degraded. When EDTA was mixed with other chelating agents and citrate, only 77.5% of EDTA degraded due to competition for the free radicals generated by radiolysis [5].

The use of non-radioactive simulants permits the systematic study of chemodynamics. After 90 days in the dark and at ambient temperature [3, 7] without radiolysis (chemical degradation), the losses of chelating agents are:

EDTA (72.1%)> HEDTA (71.6%) > NTA (5.9%) > Citrate (3.4%).

The major cause of organic degradation of EDTA and HEDTA in simulant is chemical degradation. Thus, radiolysis or thermal degradation is not necessary to degrade EDTA and HEDTA [8, 9].

2.1.3 NTA

Chemical degradation of NTA in metal ion simulant began immediately upon its addition to the simulated waste, i.e., at zero hour, 20.7% NTA was degraded [11]. Only two chelator fragment, NIDA and glyoxylic acid are formed. Heating the simulant and extending its storage to 100 hrs yielded only 2.6% more NTA degradation. Chemical degradation revealed that the chemistry of the simulant waste caused NTA degradation while the heat generated by radiation sources had little additional impact to NTA degradation [6,11]. In a mixed chelate system containing four chelate ligands, NTA degradation of 29.2% was observed followed by a steady increases to 68% after 171 days [10].

Radiolysis of NTA yielded four chelator fragments. Two fragments were formed via recombination of smaller fragments rather than simple degradation of a single species. N-butyliminodiacetic acid (BIDA) was the most abundant whereas glyoxylic acid was the least abundant. [11]

2.1.4 Citric acid

Radiolysis of citrate in a single complexant simulant produced 58.6% degradation after 100 days and yielded only propanedioic acid (malonic acid) as a degradation fragment [7]. This is similar to the 57% degradation noted with a multicomplexant simulant [10]. The loss of total organic content was more rapid and pronounced (41.4% after 100 hrs) as a result of radiolysis than from chemical degradation (17.6%, on average, after 180 days) [7].

Chemical degradation of citrate in simulated waste was 64.0% after 180 days, however the rate of degradation was very slow for the first 28 days. The degradation yielded several complexant fragments including ethanedioic (oxalic), propanedioic and butanoic acids. Oxalic acid dominated in chemi-degradation (59.3%) while malonic acid was much less abundant (4.7%) [7].

2.2 Literature Review on the Complexation of Iron

The iron (III) EDTA complex has a strong tendency to hydrolyze and polymerize without the usual caustic conditions doing so even in acid media [10]. In neutral and basic media, binuclear iron(III) complexes or their aggregates are formed with amino polycarboxylic acids because of the direct reaction with the deprotonated carboxylate group. At pH 9.9 in a single chelate system, Al(III), Cd(II), Cu(II), Co(II), Mn(III), Ni(II), Pd(II) and Zn(II)-EDTA complexes are stable whereas complexes of Fe(III), Ca(II) and Mg(II) were not detected [12].

In oxalate complexes, the C-C bond strength in the oxalate ligand decreases in the series Cr(III) < Co(III) < Mn(III) < Fe(III). Iron-oxalate is easily decomposed [13].

With citrate, the ferric complex is readily biodegradable while 1:1:2 Fe-U-citric complex is recalcitrant. At high pH, there are competitive reactions between hydroxy and citrate complexes of Fe(III) [14].

The presence of iron appeared to enhance the radiolytic stability of organic ligands, but decomposition was still significant. For example, a solution of 0.01M NTA with Fe(III) yielded only 10.0% degradation with a total dose of 4 X 10^6 R [15]. The decrease in decomposition was attributed to the presence of ascorbate, presumably because it competes for the free radicals generated by radiation [15]. Ferric ions may act as a stabilizer. Increasing the Fe(III) concentration from 2 $X10^{-4}$ to 9 $X10^{-4}$ M appeared to decrease the rate of radiolytic decomposition of EDTA, but above 9 $X10^{-4}$ M the decomposition appears to be independent of iron concentration. This could be interpreted as the of Fe-EDTA complex since it appears to be more resistant to free radical (H. or OH.) radiolysis [15]. Several possibilities for Fe(III) complexation with EDTA are reported [28].

The presence of iron and aluminum effectively dissociate Sr-EDTA complex in subsurface soils. Competition of Fe(III) and Al(III) for complex formation with EDTA was time dependant and controlled by the availability of iron and aluminum [16, 17]. In simulant (at high pH), Fe-EDTA and Fe-HEDTA complexes are not present [18]. The predominant complexes are Al-EDTA and Pb-EDTA as shown from the following series:

Al-EDTA > Pb-EDTA > Cr-EDTA > Ni-EDTA > Al-HEDTA > Pb-HEDTA > Cr-HEDTA > Ni-HEDTA

The EDTA and HEDTA complexes of Bi^{3+}, Cr^{3+}, $Cr_2O_7^{2-}$, UO_2^{2+}, Ni^{2+}, Fe^{3+} and Th^{4+} decompose in simulant because of the high hydroxide concentration and high ionic strength. When Fe-EDTA was treated with excess Pb^{2+} in simulant, a mixture of greenish crystals and brownish precipitate was observed, implying that Fe-EDTA decomposes in simulant. The analysis showed only Pb-$EDTA^{2-}$[18].

Gluconic acid has a tendency to form a stable Fe(III) gluconate complex, $Fe(OH)_2OCH_2(CHOH)_4CO_2H$, which is formed by iron bonding exclusively to the primary alcohol. Gluconate salts also have been used to sequester Fe (III) out of alkaline solutions [19].

2.3 Literature Review on the Complexation of Manganese

Kinetic and synthetic studies of Mn (III) with oxalate and malonate confirm that it has a particularly strong efficiency for oxygen-containing ligands [29-33]. Spectroscopic and crystal structure data support that the Mn(III) and Mn(IV) complexes are dimers containing bridging oxygen atoms [20, 21].

Mn (III) complexes with EDTA are metastable at high pH (pH = 10) [23]:

$$2\ \text{Mn-EDTA}^- + 2H_2O = MnO_2 + \text{Mn-EDTA}^{2-} + \text{EDTA}^{4-} + 4H^+ \qquad \Delta G = -10\ \text{Kj mol-1}$$

For pH < 6.5, Mn(III)-EDTA complexes are stable with respect to disproportionation, but not decomposition, reactions, $\Delta G > O$. Disproportionation of Mn(III)-EDTA is not linear with pH. The most rapid decomposition of Mn(III)-EDTA was shown at pH = 5-6. The rate of decomposition varied with excess [EDTA] at constant pH and inversely with pH [23]. Additionally, the authors observed no impact of light on the decomposition reaction.

With citrate, in neutral and alkaline solutions, the decomposition of Mn(III)-citrate can proceed spontaneously both by disproportionation and by reduction of Mn (III) by citrate [23]. The degradation rate with time was found to follow the sequence:

Mn(III)-Citrate > Mn(III)-EDTA.

Sodium gluconate was found to solubilize and form stable complexes with different oxidation states of manganese (II, III, IV) in strongly alkaline media. There are two forms of Mn(III)-gluconate complexes which are in slow equilibrium with each other. One of these species is the bis gluconate complex that is binuclear in manganese(III) and formed at low concentrations of sodium gluconate. The other species corresponds to a monomeric tris gluconate complex, which is predominant at high concentrations of sodium gluconate [22, 24]. Evidence indicates that the bisgluconatomanganese (III) complex, with bridging oxygen atoms, is the only species subject to oxidation by oxygen [22].

3.0 EXPERIMENTAL

3.1 Chemicals and Reagents

The chelating and complexing agents employed in this work were analytical reagent grade acid or sodium form. Standard acids were prepared in deionized distilled water as individual stock solutions and then combined to give a diluted working reference. The separation process was made at room temperature (20-22^{0}C). The eluent was maintained under a continuous flow of high-purity nitrogen gas to minimize baseline drift.

3.2 Chromatographic Instrumentation

The ion chromatograph used was a Dionex series DX-100 (Dionex Corp., Sunnyvale, CA) equipped with conductivity detector (Dionex Corp.), isocreatic pump (Dionex Corp.), 25 µL injection loop and a Dionex 4400 integrator. An anion micromembrane suppressor (ASRS- Ultra 4-mm) was used for suppression of the eluent conductivity to improve the signal-to-noise ratio and hence improve the detection limits. Dionex anion exchange columns tested in the method development included the 4-mm AS-5A/AG-5A, 4-mm AS-10/AG-10 and 4-mm AS-11/AG-11 columns. Ion exclusion column AS-6 coupled with ion exclusion suppressor (AMMS-ICE) was also used for separation of some inorganic acids. The analytical columns were regularly regenerated to remove strongly complexed anions that were retained on the columns.

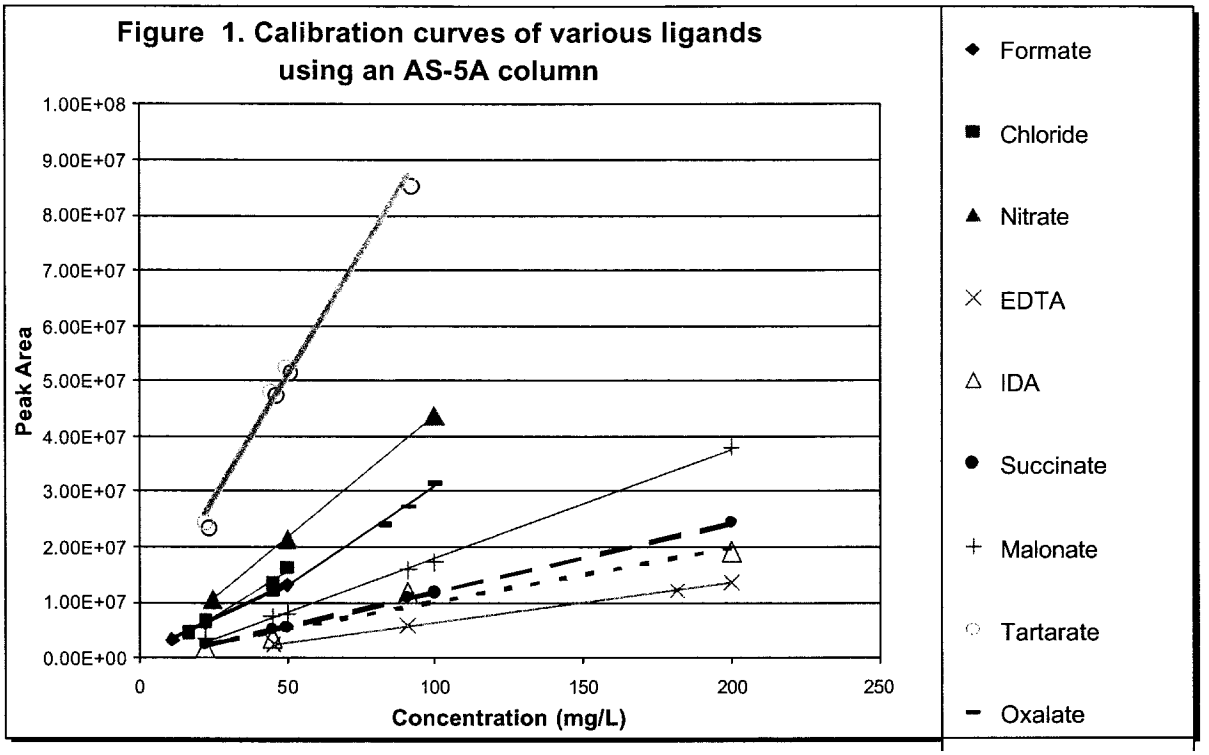
3.3 Calibration Curves for Quantification of Chelating and Complexing Ligands

Chromatograms were recorded using a model 4400 Dionex integrator to determine the retention time and peak area of each ligand. Peak area was used for quantification of the ligand concentration in standard and filtrate solutions. Concentrations in the filtrate samples were calculated from peak integrals compared to linear regression calibration curves established using varying concentrations of standards. In the first series of separation experiments, the chromatographic behaviour of 24 ligands was tested using the AS-5A analytical column. Based on their retention time, the ligands were classified into six sub-groups as shown in Table 1. Group 1-5 included all the original chelating and complexing agents (with the addition of tartrate, a breakdown product) that were used for preparation of the simulants AN-102 and AN-107 while Group-6 contained the predominant degradation products that formed from either chemical, radiolytic and/or thermal degradation of the original chelating and complexing acids. Four analytical columns were tested for all the chelating and complexing ligands. Calibration curves of the separated ligands on the corresponding analytical columns are shown in Figures 1-4. The overall experimental conditions will be discussed in more detail in the Results and Discussion Section.

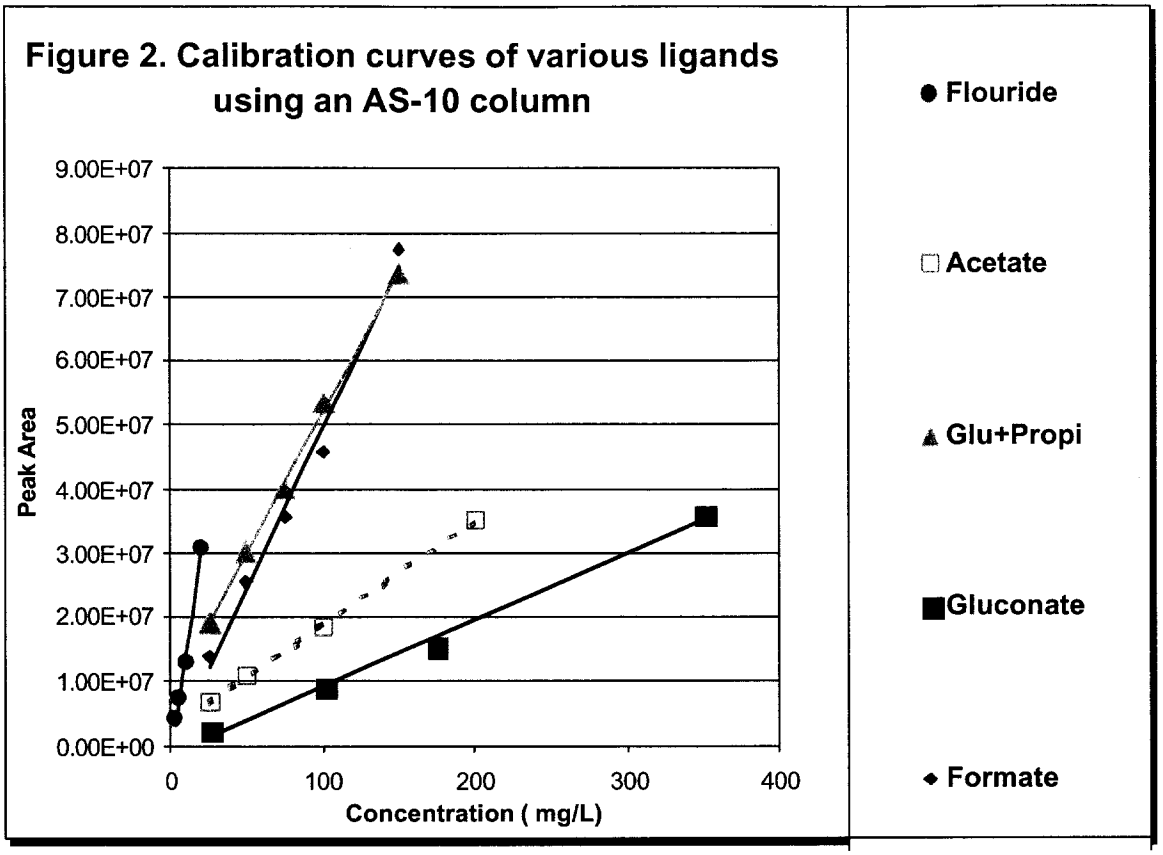
Table 1. Classification of chelating and complexing agents (AS-5A analytical column, F.R = 1.0 mL/min.)

Group	Analyte
G-1	Acetate
	Glycolate
	Gluconate
	Formate
G-2	Chloride
	Nitrate
	EDTA
	Phosphate
	Carbonate
	Nitrite
	Sulfate

Group	Analyte
G-3	IDA
	Succinate
G-4	Tartrate
	Oxalate
	Citrate
G-5	HEDTA
	NTA
G-6	Malonate
	Propionate
	HIBA
	Glyoxylate
	n-Butanate

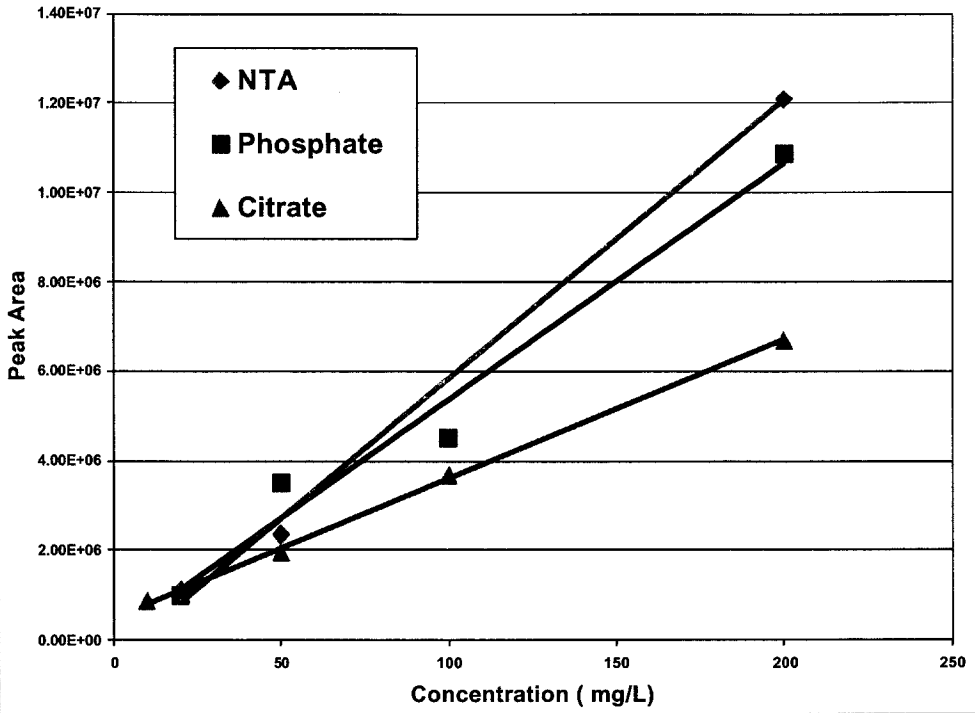


Species	Best Fit Line
Formate	y = 256,876x + 414,944
Chloride	y = 333,073x – 965,342
Nitrate	y = 442,713x – 698,466
EDTA	y = 71,549x – 775,330
IDA	y = 99,075x + 191,197
Succinate	y = 124,793x – 620,123
Malonate	y = 195,556x – 2,000,000
Oxalate	y = 355,538x – 5,000,000



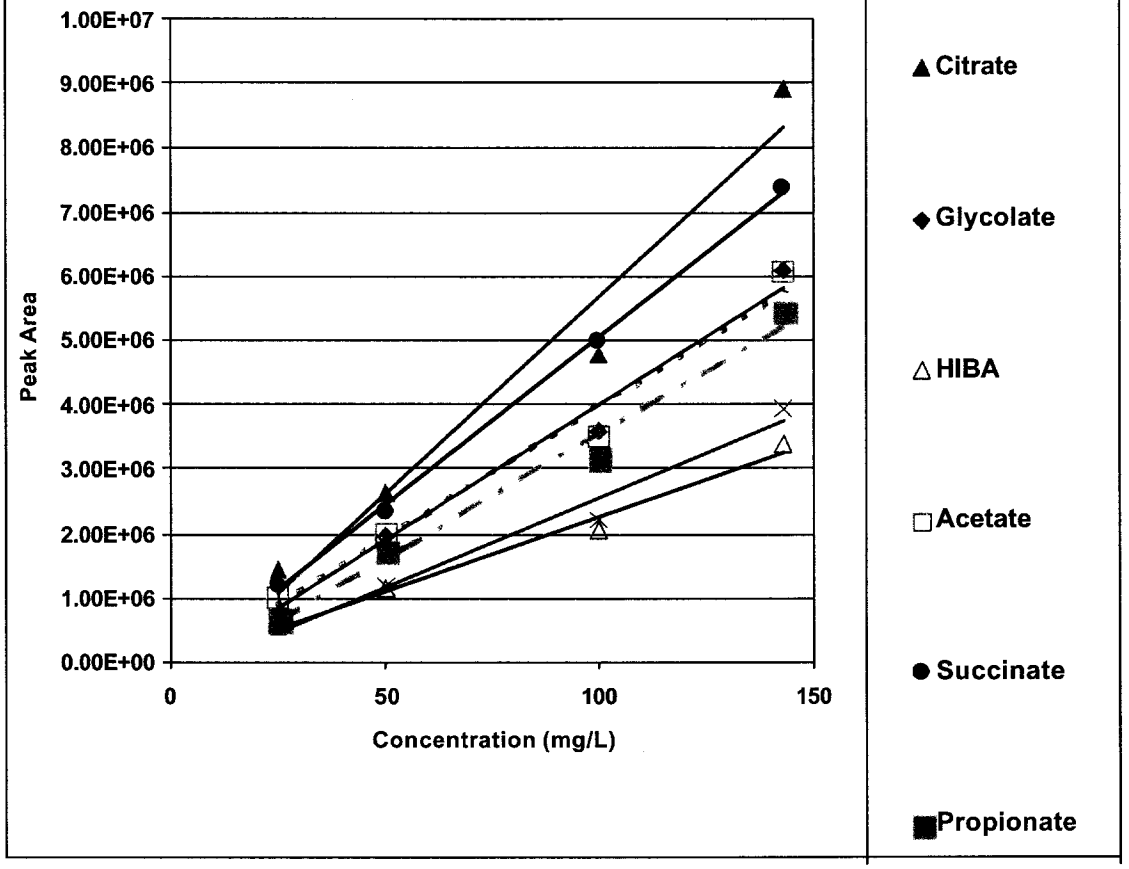
Species	Best Fit Line
Fluoride	y = 2,000,000x – 669,575
Acetate	y = 160,756x + 3,000,000
Gluconate + Propionate	y = 439,510x + 8,000,000
Gluconate	y = 103,913x – 1,000,000
Formate	y = 500,025x – 478,476

Figure 3. Calibration curves of various ligands using an AS-11 column



Species	Best Fit Line
NTA	y = 62,276x - 417,104 R2=0.9973
Phosphate	y = 52,587x + 104,686 R2=0.9733
Citrate	y = 30,841x + 516,337 R2=0.9991

Figure 4. Calibration curves of various ligands using an AS-6 column



Species	Best Fit Line
Glyoxylate	y = 27,547x – 196,091
Citrate	y = 61,400x + 446,241
Glycolate	y = 42,216x – 207,328
HIBA	y = 23,247x – 55,227
Acetate	y = 41,363x – 151,182
Succinate	y = 52,372x – 182,758
Propionate	y = 39,165x – 351,239

3.4 Preparation of the Proposed Complexes

In the present work, three different filtrate samples from simulant AN-107 were analyzed to identify the available ligands present in the aged filtrate. The aged filtrate samples included: base case, 0.0M OH^- added and 8-hr hold at 100^0C. Preparation of the base case sample was previously described in section 1.2. The second sample, 0.0M OH^- was similarly prepared using the base case conditions and kept at 0.0M NaOH (no further addition of sodium hydroxide). The third sample was also prepared at the base case conditions then held for 8-hr at 100^0C. These filtrate samples were selected to represent a high content of free ligands due to metal hydrolysis. Eleven common ligands were found in the aged filtrate samples. According to the scientific literature, metal-ligand complexes were prepared by mixing equimolar amounts of metal salt and ligand followed by pH adjustment with NaOH or NH_4OH to pH 7-9 [25, 26]. Another author recommended mixing the cation stock solution with an excess of ligand salt solution followed by neutralization [12, 27]. In the present work, metal complexes were prepared by mixing equimolar metal salts of Fe(III), Sr(II) and Mn(II) with each of the eleven ligands. For Fe and Sr complexes, 0.05M of each metal was mixed with 0.05M of each ligand. For Mn complexes, 0.01M solution of Mn was mixed with 0.01M of each ligand. The pH value of all the metal complexes was adjusted to be around pH 12 by adding NH_4OH. This is similar to the pH value of the actual filtrate samples.

All the metal complex solutions were centrifugated at 15,000 rpm for 20.0 minutes and then filtered using 0.1 μm, nylon filter paper. The filtrate of each metal complex solution was then subjected to UV spectrophotometer and IC analysis.

3.5 Stoichiometric Preparation of Metal Complexes

Metal complexes were prepared stoichiometrically with six chelating ligands that appeared to be responsible for solubilizing Fe, Sr and Mn. The stoichiometric ratios are shown in Table 2. The concentration of Fe(III), Sr(II) and Mn(II) was 0.01M in each metal complex solution to be relatively close to their concentration in the simulant waste filtrate. The more labile species Mn(II) was used instead of Mn(III) based upon the measured value of Eh in the simulant waste. Furthermore, excess amounts of the ligands were added to insure that the metal complexes were formed.

Table 2. Expected stoichiometric ratio of metal ion to ligand for Fe, Sr and Mn complexes

Analyte	Fe(III) (0.01 M)	Sr(II) (0.01 M)	Mn(II) (0.01 M)
Gly	1:4 S	1:2 S	1:2 S
EDTA	1:1 S	1:2 S	1:2 S
Tart	1:2 S	1:2 S	1:2 S
Oxal	1:4 S	1:3 ppt	1:4 S
Citr	NA	NA	1:2 S
Glyox	1:4 S	1:2 S	1:2 S

S: soluble complexes, ppt: precipitated complexes, NA: not analyzed

The pHs of all the metal complex solutions were adjusted to approximately 12 using NH_4OH to be similar to the simulant filtrate. The pH values of each metal complex solution are presented in Table 3.

Table 3. pH values of different metal complexes prepared stoichiometrically

Analyte	pH value		
	Fe (III)	Sr (II)	Mn (II)
Gly	12.6 brown ppt	12.4 soluble	12.1 brown ppt
EDTA	-	12.1 soluble	12.1 soluble
Tart	12.2 soluble	12.2 soluble	12.1 brown ppt
Oxal	12.1 brown ppt	-	12.0 brown ppt
Citr	-	-	12.0 dark brown ppt
Glyox	12.1 dark brown ppt	12.3 soluble	12.1 brown ppt

-: no information

A representative portion (10 mL) was taken from each solution at intervals of 1, 5, 7 and 9 days in order to monitor ligand degradation. The samples were centrifugated, filtered using a 0.1 μm nylon filter then subjected to IC and AA analysis.

3.6 Preparation of Fresh Simulant Filtrates

Based upon recipes supplied by SRTC/WTT, two nonradioactive simulants for Hanford complexant wastes (241-AN-102 and 241-AN-107) were diluted with water to 6M sodium. Following caustic adjustment to 1 M OH^- (17 M NaOH), the two samples were treated with 1 M strontium nitrate and 1 M sodium permanganate to achieve a concentration of 0.075 M of strontium(II) and 0.05 M permanganate at 50±2 ^{0}C and allowed to react for four hours. The reaction mixtures were cooled to 25 ^{0}C in a re-circulating water bath to avoid localized over cooling. The mixtures were filtered with 0.1 μm pore filter then kept under nitrogen in the dark. Complex identification in the fresh simulant filtrate for Hanford complexant wastes (241-AN-102 and 241-AN-107) were analyzed promptly following filtration. To follow the reaction behavior of the identified complexes, aliquots of the two-filtrate samples were re-filtered after three weeks and then reanalyzed by IC.

3.7 Experimental Limitations

- The lack of a gradient elution pump for the IC gave us some difficulties during the separation of strongly retained species on the analytical column; therefore, quantitative determination of the chelating and complexing acids is not precise.
- Unavailability of IC-MS or HPLC-MS methods did not allow us to determine the molecular weight of the separated metal ion complexes to confirm the chemical structure of the formed complexes.
- Alternative filtrate preparations for 241-AN-107 and 241-AN-102 using simplified ligand compositions were not investigated because complexed species present in the simplified simulant would not be indicative of complexed species present in the full waste simulant, due to likely synergistic reactions with the complex ligand mixture and the predominant metal cations. Instead, we looked at aged 241-AN-107 filtrates in which hydrolysis of metal cations in solution was more complete, thus maximizing the concentration of free ligands present in the filtrates. Knowledge of free ligands present in the aged filtrates could be used to predict possible complexed species in fresh filtrates.
- Radiolabeling experiments were not performed due to time constraints.
- Computer modeling was not performed due to time constraints.

4.0 RESULTS AND DISCUSSION

4.1 Methods Development for Separation of Carboxylate Anions by IC Columns

Simultaneous separation of anionic compounds has been performed by several chromatographic techniques [12, 26, 27]. Polycarboxylate agents and their complexes are polyvalent anions. As such, they are strongly

retained by a polymeric anion exchanger. The elution order of the polycarboxylate complexes in the IC mode depends on their ion-exchange affinity to the sorbants. In this respect, anion chromatographic separation of metal complexes in Hanford simulant filtrates has been reported on three anion exchange columns: AS-5A, AS-10 and AS-11. Another ion-exclusion column (AS-6) was explored specially to separate the weak carboxylate acids. Elution is in order of decreasing pKa.

Firstly, attempts to separate 24 carboxylate anions were tested using an AS-5A analytical column. To test the selectivity of the anion exchanger, isocratic elution of the uncomplexed ligands was investigated. Retention times for an Ion Pac AS-5A column at different mobile phase concentrations are presented in Table 4. Based on their retention time, the ligands were classified into six sub-groups as shown in Table 1. Group 1-5 includes all the original chelating and complexing agents that are used for preparation of the simulants AN-102 and AN-107, while Group-6 contains the predominant degradation products that formed from either chemical, radiolysis and/or thermal degradation of the original chelating and complexing acids. As shown in Table 4, serious overlap between all the carboxylate anions was observed using 50.0 mM NaOH. Dilution of the mobile phase to 25 mM leads to insignificant separation.

Table 4. Retention time (minutes) of polycarboxylate anions on AS-5A column

Group	Analyte	Mobile Phase Concentration (NaOH mM)				
		50	25	10	5	2.5
G-1	Acetate	1.3	-	Overlapped	2.4	3.36
	Glycolate	1.68	-	Overlapped	2.6	3.02
	Gluconate	1.7	-	Overlapped	2.75	2.97
	Formate	1.72	-	2.37	3.2	4.15
G-2	Chloride	2.34	2.93	4.53	6.18	7.14
	Nitrate	2.67	3.48	5.8	8.06	-
	EDTA	1.84	2.55	6.57	18.0	R
	Phosphate	6.64	-	14.46	41.8	R
	Carbonate	2.24	-	9.27	ND	ND
	Nitrite	4.85	7.32	15.65	22	-
	Sulfate	2.94	7.63	17.02	23	25
G-3	IDA	2.34	4.69	22.56	R	R
	Succinate	2.46	5.65	32.91	R	R
G-4	Tartrate	3.1	7.52	-	R	R
	Oxalate	3.3	9.18	34.86	R	R
	Citrate	9.0	ND	R	R	R
G-5	HEDTA	2.33, 5.2	-	R	R	R
	NTA	Many peaks	-	R	R	R
G-6	Malonic	-	5.89	24.5	-	-
	Propionic	-	1.83	2.05	-	-
	HIBA	-	-	1.95	-	-
	Glyoxylate	-	2.65	3.85	-	-
	n-Butanate	-	-	2.12	-	-

R: retained on the column, ND: not determined, -: no information

Table 5. Separation of group-1 using AS-5A column at different flow rates

Group	Analyte	1.0 mM NaOH		
		F.R.=1.0 mL/min	F.R.=0.5 mL/min	F.R.=0.3 mL/min
G-1	Acetate	3.07	5.57	8.16
	Glycolate	3.29	5.94	8.72
	Gluconate	3.29	5.94	8.72
	Formate	4.0	7.32	10.74

Further dilution of the mobile phase to 10 mM provided sufficient separation of the carboxylate anions in G-2, G-3, malonate in G-6, tartrate and oxalate in G-4. Severe overlap between carboxylate anions in G-1 was observed. Acids in G-5 were retained on the AS-5A column at 10 mM NaOH. Further dilution of the mobile phase to 5.0 , 2.5 and 1.0 mM did not improve the separation of carboxylate anions in G-1. Shown in Table 5 is a trial to separate G-1 analytes by lowering the flow rate of the mobile phase from 1.0 mL/min to 0.5 and 0.3 mL/min. Lowering the flow rate did not significantly improve the separation of G-1 compounds, especially glycolate and gluconate.

Attempts to separate the carboxylate anions in G-1 using an AS-11 analytical column at different NaOH concentrations were investigated at a constant flow rate of 1.0 mL/min. The retention time of the carboxylate anions are presented in Table 6. At 50.0 and 25.0 mM of NaOH, no significant improvement in the separation efficiency on AS-11 compared to AS-5A column was observed. Further dilution of the mobile phase to 15.0 mM shows a significant separation of phosphate, NTA and citrate. Both NTA and citrate were retained on the AS-5A column. Therefore, a high concentration of the mobile phase should be applied when using AS-5A column. Poor separation efficiency of G-1 on the AS-11 column was observed even by further dilution to 10 mM NaOH. A series of experiments were focused mainly to separate G-1 elements using the AS-10 column and different concentrations of eluent. The separation efficiency was evaluated by the difference in the retention time of two successive peaks. According to chromatographic theory, sufficient separation for quantitative measurement can be made between two adjacent peaks that have a difference in retention time $\geq$ 0.5 minute. As shown in Table 7, the difference in retention time between the subsequent compounds in G-1 was increased by decreasing the mobile phase concentration from 50 mM to 25 mM at a constant flow rate of 1.0 mL/min.

Table 6. Retention time (minutes) of polycarboxylate anions on AS-11 column

Group	Analyte	Mobile Phase Concentration (NaOH mM)			
		50	25	15	10
G-1	Acetate	Overlapped	1.87	Overlapped	-
	Glycolate	Overlapped	1.88	Overlapped	-
	Gluconate	Overlapped	1.87	Overlapped	1.93
	Formate	Overlapped	1.86	Overlapped	-
G-2	Chloride	-	-	2.4	-
	Nitrate	-	-	2.59	-
	EDTA	-	-	2.17	-
	Phosphate	2.10	-	13.5	-
	Carbonate	-	-	3.59	-
	Nitrite	-	-	3.6	-
	Sulfate	-	-	4.37	-
G-3	IDA	-	-	2.99	-
	Succinate	-	-	3.19	-
G-4	Tartrate	1.9	2.37	3.57	-
	Oxalate	1.99	2.76	4.38	-
	Citrate	2.17	-	22.06	-
G-5	HEDTA	1.98	2.53	2.58	-
	NTA	1.90	4.19	15.07	R
G-6	Malonic	-	-	3.4	-
	Propionic	-	-	2.0	-
	HIBA	-	-	1.95	-
	Glyoxylate	-	-	2.31	-
	n-Butanate	-	-	2.04	-

R: retained on the column, -: no information

Sufficient separation between G-1 elements on an AS-10 column was obtained using 25.0 mM of NaOH at flow rate of 0.5 mL/min. Separation of G-1 is highly deteriorated due to the overlap with G-6 elements (see Table 8).

Table 7. Separation of group-1 by ion chromatography using AS-10 column

[NaOH]	F.R. (mL/min.)	Analyte	R.T. (min.)	Difference
50.0 mM	1.0	Acetate	5.69	0.14
		Glycolate	5.85	0.31
		Gluconate	6.16	-
		Formate	6.91	Separated
		Chloride	17.18	-
		Sulfate	47.84	-
		HEDTA	R	-
40.0 mM	1.0	Acetate	6.06	0.2
		Glycolate	6.26	0.39
		Gluconate	6.65	-
		Formate	7.49	Separated
30.0 mM	1.0	Acetate	7.0	0.28
		Glycolate	7.18	0.51
		Gluconate	7.79	-
		Formate	8.89	Separated
25.0 mM	1.0	Acetate	7.63	0.32
		Glycolate	7.95	0.55
		Gluconate	8.5	-
		Formate	9.74	Separated
25.0 mM	0.5	Acetate	13.16	0.58
		Glycolate	13.74	1.66
		Gluconate	14.7	-
		Formate	16.98	Separated
1.0 mM	1.0	Acetate	R	-
		Glycolate	R	-
		Gluconate	R	-
		Formate	R	-

R: retained on the column, -: no information

Table 8. Separation of group-6 by ion chromatography using AS-10 column

Group	Analyte	25.0 mM NaOH, FR=0.5 mL/min.
G-6	Malonate	19.2
	Propionate	13.82
	HIBA	12.74
	Glyoxylate	13.5
	n-Butanate	4.88

Because of the importance of metal fluoro complexes at the time this work was conducted, the retention behavior of fluoride ion on an AS-10 column was investigated. As shown in Figure 5, fluoride ion and G-1 could probably be separated on an AS-10 column using 25.0 mM of NaOH at a flow rate of 0.5 mL/min.

Separation of the overlapped carboxylate anions, especially weak carboxylic acids that represent the degradation products (e.g. propionic and glyoxylic acid), was tested using an ion exclusion column (AS-6). Elution of carboxylate anions was carried out using 0.4 mM of HFBA at a flow rate of 1.0 mL/min. Suppression of the eluent background was performed using AMMS-ICE exclusion suppressor. The regeneration process of the exclusion suppressor was carried out using 5.0 mM of TBAH at a flow rate of 2.0 mL/min. Based on the obtained retention time of each carboxylate anion, as shown in Table 9, the AS-6 column yields sufficient separation for glyoxylate, citrate, glycolate, HIBA, acetate, succinate and propionate (Figure 6).

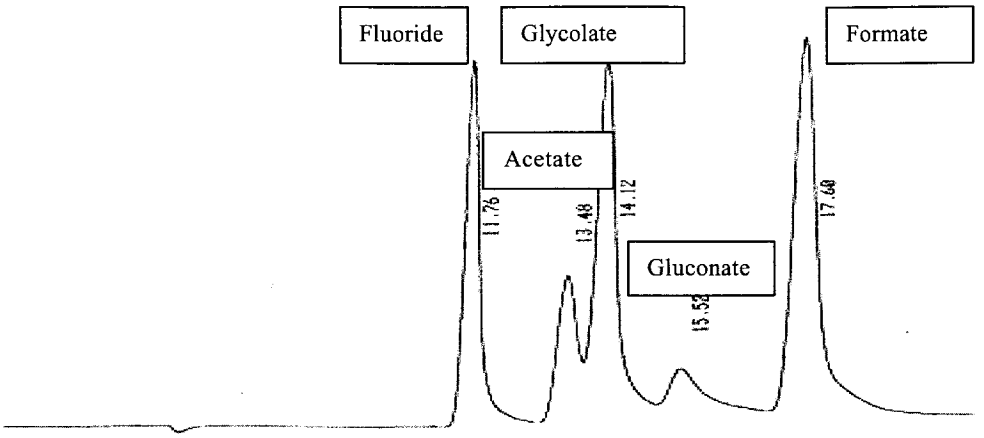


Figure 5. Separation of fluoride and G-1 using an AS-10 column and 25 mM NaOH at 0.5 mL/min flow rate.

Table 9. Retention time of polycarboxylate anions using AS-6 ion exclusion column

Group	Analyte	R.T. (min.)
G-1	Fluoride	7.66
	Acetate	15.94
	Glycolate	10.4
	Gluconate	7.56
	Formate	11.66
G-2	Chloride	5.1
	Nitrate	5.11
	EDTA	ND
	Phosphate	-
	Carbonate	-
	Nitrite	5.11
	Sulfate	ND
G-3	IDA	ND
	Succinate	16.49
G-4	Tartrate	7.31
	Oxalate	5.66
	Citrate	8.32
G-5	HEDTA	ND
	NTA	12.0
G-6	Malonate	7.52
	Propionate	27.04
	HIBA	14.33
	Glyoxylate	6.97
	n-Butanate	ND

ND: not detected, -: no information

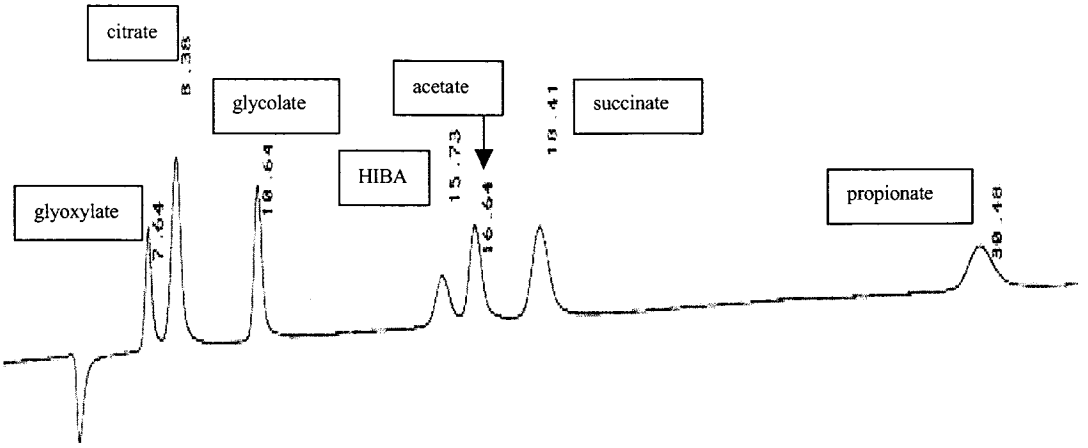


Figure 6. Ion exclusion chromatogram for the separation of glyoxylate, citrate, glycolate, HIBA, acetate, succinate and propionate with an AS-6 column

Based on the previous data, the proposed ion chromatographic protocols for the separation and quantitative determination of the chelating and complexing polycarboxylate anions we determined may be present in Hanford simulant waste filtrate of 241-AN-102 and 241-AN-107 can be summarized as follows:

- Use 10.0 mM NaOH (F.R. = 1.0 mL/min) and AS-5A to separate G-2, G-3, and tartrate, oxalate and malonate.
- Use 15.0 mM NaOH (F.R. = 1.0 mL/min) and AS11 to separate phosphate, NTA and citrate.
- Use 25.0 mM NaOH (F.R. = 0.5 mL/min) and AS10 to separate fluoride, gluconate and formate.Use 0.4 mM HFBA (F.R. = 1.0 mL/min), 5.0 mM TBAH regenerate (F.R. =2.0 mL/min) and AS-6 to separate glyoxylate, citrate, glycolate, HIBA, acetate, succinate, and propionate.

4.2 Analysis of the Proposed Metal Complexes

Referring to the stability constants of the detected ligands with Fe(III), Sr(II) and Mn(III) as presented in Table 10 [28], nine common ligands are expected to form complexes with these metal ions. These ligands including fluoride, acetate, glycolate, formate, EDTA, tartrate, oxalate, citrate and glyoxylate. IC analysis of each metal complex solution at pH 10 showed two peaks with the strong ligands such as EDTA, tartrate, oxalate and glucolate. The first peak has the same retention time as the free ligand while the second peak may correspond to the complexed species. Metal complex solutions of fluoride, acetate, formate, citrate, and glyoxylate showed only one peak at the same retention time of the free ligand. The formation of metal ion complex in each solution was evaluated semi-quantitatively by calculation of the percent complexation of each ligand. See equation {1} below. The mass balance calculation was done to determine the remaining concentration of ligand available for metal ion complexation. The original concentration of the ligand that was used to prepare the metal ion complex is presented in Table 11.

$$\% \text{ Complexation} = 100 \left[1 - \frac{[ligand]_{IC}}{[ligand]_{init}}\right] \qquad \{1\}$$

Table 10. Stability constants of Fe(III), Sr(II) and Mn(III) complexes

Group	Analyte	Sr(II)	Fe(III)	Mn(III)
G-1	Fluoride	8.5	13.7	1.3
	Acetate	1.1	9.6	0.8
	Glycolate	1.2	23.8	1.6
	Gluconate	1.0 a	-	-
	Formate	1.39	20 (20.0°C, *I*=0.1)	-
G-2	Chloride	20 (20.0°C, *I*=0.1)	1.48 (25.0°C, *I*=0.0)	1.12 (25.0°C, *I*=3.0)
	Nitrate	0.8 (25.0°C, *I*=0.0)	1.0 (25.0°C, *I*=0.0)	-
	EDTA	14.9	33.8	19.1
	Phosphate	4.2 (20.0°C, *I*=0.1)	8.3 (25.0°C, *I*=0.5)	-
	Carbonate	-	-	-
	Nitrite	-	-	-
	Sulfate	2.55 (25.0°C, *I*=0.0)	4.04 (25.0°C, *I*=0.0)	1.63 (25.0°C, *I*=4.0)
G-3	IDA	2.23(25.0°C, *I*=0.1)	10.72 (25.0°C, *I*=4.0)	-
	Succinate	-	-	-
G-4	Tartrate	0.91	9.5	2.49
	Oxalate	1.7	18.6	18.42
	Citrate	4.1	13.5	9.4
G-5	HEDTA	6.8	19.8	22.7 (25.0°C, *I*=0.2)
	NTA	4.97	15.9	20.25 (20.0°C, *I*=1.0)
G-6	Malonate	1.3 (25.0°C, *I*=0.1)	-	-
	Propionate	-	-	-
	HIBA	-	-	-
	Glyoxylate	-	-	-
	n-Butanate	-	-	-

a: temperature not stated, -: no information

Table 11. Original concentration of ligands in the proposed metal complexes

Analyte	M.W.	Fe(III) Complex (0.05 M)	Sr(II) Complex (0.05 M)	Mn(III)Complex (0.01 M)
Acetate	59.04	2952	2952	590
Glycolate	75.04	3752	3752	750
Formate	45.01	2250	2250	450
EDTA	288.2	14410	14410	2882
Tartrate	171.08	8554	8554	1711
Oxalate	88.01	4400	4400	880
Citrate	189.1	9455	9455	1891
Glyoxylate	73.05	3652	3652	730

The concentration of ligands is expressed in ppm.

A semi-quantitative determination of the remaining free ligand in each metal complex solution was made. The percentage of complexation of each ligand was tabulated based upon the original and remaining concentrations of each ligand as shown in Table 12.

Table 12. The percentage of metal ion complex formation

Analyte	Fe(III) Complex (%)	Sr(II) Complex (%)	Mn(III)Complex (%)
Acetate	4.0	8.0	-
Glycolate	21.0	14	35.0
Formate	2.0	zero	zero
EDTA	65.0	46.0	100
Tartrate	99.0	51.0	100
Oxalate	28.0	zero	17.0
Citrate	21.0	18.0	16.0
Glyoxylate	100	100	100

As shown in Table 12, there was a high possibility for complex formation of Fe(III), Sr(II) and Mn(III) metal ions with strong ligands such as EDTA, tartrate and glyoxylate. While moderate complex formation was observed with oxalate and citrate, a low degree of metal ion complex formation was observed with acetate and formate.

4.3 Analysis of the Stoichiometric Metal Complexes

Variation in metal complex formation is not only dependent on the stoichiometric ratio of the metal and ligand but also on the pH of the solution. In this respect, stoichiometric preparation of Fe(III), Sr(II) and Mn(II) with the strongly complexed ligands was carried out according to the recommended ratios as shown in Table 3 [28, 34, 35]. Six ligands were selected to represent the most strongly chelating/complexing agents for Fe(III), Sr(II) and Mn(II) metal ions. The variation in the concentrations of the six investigated ligands during the investigated period re presented in Table 13. Quantitative measurements show that the concentrations of some metal ion complexes decreased significantly with time (from day 1 to 9). These complexes include Fe-tartrate, Fe-oxalate, Mn-EDTA, Fe-glycolate, and Sr-glycolate. This is mainly due to chemical degradation of both free and complexed ligand and /or metal ion hydrolysis at high pH. Measuring the metal ion concentration by AA also tested the degree of complex formation in each metal complex solution as a function of time. The individual concentration of both Fe and Mn are tabulated in Tables 14 and 15, respectively. Based upon the average concentration of Fe(III) in different metal ion complex solutions, it could be observed that the concentration of Fe(III) obeys the following sequence:

Fe: Tartrate >> Glyoxylate > Glycolate > Oxalate

According to the average concentration of Mn, it could be observed that the concentration of Mn obeys the following sequence:

Mn: EDTA >> Citrate > Tartrate

The previous observation shows that the carboxylate anions that are responsible for solubilizing iron and manganese in the filtrate follow the corresponding sequences. Therefore, the predominant metal complexes in the filtrate at high pH are Fe(III)-tartrate and Mn-EDTA. In fresh solution (at day 1), Fe-tartrate and Mn-EDTA are prevalent compared with a competing reaction with OH^-. After long-term storage, metal hydrolysis is expected to predominate.

Table 13. Concentration of carboxylate anions in equimolar metal ion complexes

Analyte	Conc. (ppm)	Analyte	Conc. (ppm)
Tartrate		**Glyoxylate**	
Fe-Tartrate Day-1	2675	Fe-Glyoxylate Day-1	2518
Fe-Tartrate Day-5	2747	Fe-Glyoxylate Day-5	2088
Fe-Tartrate Day-7	2651	Fe-Glyoxylate Day-7	1920
Fe-Tartrate Day-9	2007	Fe-Glyoxylate Day-9	2611
Sr-Tartrate Day-1	2950	Sr-Glyoxylate Day-1	291
Sr-Tartrate Day-5	2925	Sr-Glyoxylate Day-5	157
Sr-Tartrate Day-7	2913	Sr-Glyoxylate Day-7	294
Sr-Tartrate Day-9	2859	Sr-Glyoxylate Day-9	260
Mn-Tartrate Day-1	2549	**Citrate**	
Mn-Tartrate Day-5	2624	Mn-Citrate Day-1	609
Mn-Tartrate Day-7	2787	Mn-Citrate Day-5	617
Mn-Tartrate Day-9	2657	Mn-Citrate Day-7	574
Oxalate		Mn-Citrate Day-9	593
Fe-Oxalate Day-1	3331	**Glycolate**	
Fe-Oxalate Day-5	3005	Fe- Glycolate Day-1	3387
Fe-Oxalate Day-7	3223	Fe- Glycolate Day-5	2071
Fe-Oxalate Day-9	2520	Fe- Glycolate Day-7	2590
Mn-Oxalate Day-1	3286	Fe- Glycolate Day-9	2163
Mn-Oxalate Day-5	3194	Sr- Glycolate Day-1	1570
Mn-Oxalate Day-7	2571	Sr- Glycolate Day-5	1187
Mn-Oxalate Day-9	2870	Sr- Glycolate Day-7	1215
EDTA		Sr- Glycolate Day-9	1270
Sr-EDTA Day-1	1059	Mn- Glycolate Day-1	590
Sr-EDTA Day-5	873	Mn- Glycolate Day-5	916
Sr-EDTA Day-7	1499	Mn- Glycolate Day-7	809
Sr-EDTA Day-9	1283	Mn- Glycolate Day-9	701
Mn-EDTA Day-1	1447	[cell intentionally left blank]	
Mn-EDTA Day-5	1029		
Mn-EDTA Day-7	624		
Mn-EDTA Day-9	906		

Table 14. Fe concentration in the stoichiometric metal complexes as determined by AAS

Metal Ion-Complex.	Day-1	Day-5	Day-7	Day-9	Ave. Conc. (ppm)
Fe-Gly	0.160	0.131	0.144	0.119	0.138
Fe-Tart	129	683	189	206	301
Fe-Oxal	0.117	0.111	0.102	0.115	0.111
Fe-Glyox	4.46	5.20	5.81	9.28	6.19

Table 15. Mn concentration in the stoichiometric metal complexes as determined by AAS

Metal Ion-Complex.	Day-1	Day-5	Day-7	Day-9	Av. Conc. (ppm)
Mn-Gly	0	0	0	0	0
Mn-EDTA	290	458	431	385	391
Mn-Tart	0.092	0.112	0.110	0.112	0.090
Mn-Oxal	0	0	0	0	0
Mn-Glyox	0	0	0	0	0
Mn-Citr.	8.72	0.045	1.07	0.076	2.47

4.4 Analysis of Aged and Fresh Simulant Filtrates

Based on the previous protocols, quantitative determination of carboxylate-containing and other anions in Hanford simulated waste was applied to three select filtrates of 241-AN-107 (Base case, 8-hr hold and 0.0 M OH^-). The selection was based on the high availability of different carboxylate anions due to potential metal hydrolysis in these samples. This hydrolysis will promote the dissociation of the metal ion complex and formation of the free ligand. The detected ligands in the three-filtrate samples are shown in Table 16. These ligands included fluoride, acetate, glycolate, formate, chloride, nitrate, EDTA, phosphate, tartrate, oxalate, citrate and glyoxylate. Quantitative measurement of nitrite and sulfate is restricted due to serious overlap arising from the high concentration of nitrite.

Table 16. Quantitative determination of carboxylate anions in Hanford simulated waste filtrates by IC

Group	Analyte	Concentration (mg/L)		
		Base Case	8 Hr Hold	0.0 M OH
G-1	Fluoride	173	138	165
	Acetate	1041	1055	1138
	Glycolate	12437	12680	12701
	Gluconate	ND	ND	ND
	Formate	13807	10270	13488
G-2	Chloride	595	3902	3954
	Nitrate	68977	87899	72284
	EDTA	3888	ND	ND
	Phosphate	2498	2654	1046
	Carbonate	ND	ND	ND
	Nitrite	Overlapped	Overlapped	Overlapped
	Sulfate	Overlapped	Overlapped	Overlapped
G-3	IDA	ND	ND	ND
	Succinate	ND	ND	ND
G-4	Tartrate	1881	2063	2237
	Oxalate	ND	ND	3629
	Citrate	9004	9338	18216
G-5	HEDTA	ND	ND	ND
	NTA	<10	<10	116
G-6	Malonate	ND	ND	ND
	Propionate	ND	ND	ND
	HIBA	ND	ND	ND
	Glyoxylate	16074	1118	ND
	n-Butanate	ND	ND	ND

ND: not detected

Table 17 shows the concentration of carboxylate anions in fresh simulant filtrates of AN-102 and AN-107. Concentration measurements in both fresh and 3-week aged filtrates confirmed that the degradation process has occurred mainly due to a harsh chemical environment. On the other hand, as shown in Table 18, it was found that the concentration of Fe and Mn increased significantly in AN-107 after 3 weeks compared with the fresh filtrate. This observation is probably due to a matrix effect in the AA caused by the loss of ligand material in the solution. Free metal ion species will precipitate later due to metal hydrolysis.

Table 17. Concentration (mg/L) of carboxylate anions in fresh simulant filtrates

Analyte	AN-102		AN-107	
	Initial	3 Week	Initial	3 Week
Gly	3633	3493	11375	5730
EDTA	ND	ND	2593	ND
Tart	20434	18453	11880	12584
Oxal	ND	ND	6328	403
Citr	2819	2172	5325	2337
Glyox	1690	ND	ND	ND

ND: not detected

Table 18. Concentration (mg/L) of Fe and Mn in fresh simulant filtrates

Analyte	AN-102		AN-107	
	Initial	After 3 Weeks	Initial	After 3 Weeks
Fe	0.369	0.372	3.317	3.728
Mn	0.135	0.111	0.680	0.920

5.0 CONCLUSIONS

Four different optimized protocols were applied successively for separation of multidentate ligand species based on the exchange capability of different ion exchange and ion exclusion analytical columns including Dionex IonPac AS-5A, AS-10, AS-11 and AS-6. The developed methods were applied not only to separate the original ligand that was used to prepare the simulant filtrate but also to identify the expected degradation products of the original polycarboxylate anions.

Quantitative determination of inorganic ligands and polycarboxylate anions in Hanford simulated waste filtrates of 241-AN-107 (Base case, 8-hr hold and 0.0 M OH) shows that the available ligands included fluoride, acetate, glycolate, formate, chloride, nitrate, EDTA, phosphate, tartrate, oxalate, citrate and glyoxylate.

Referring to the stability constants of the detected ligands with Fe, Sr and Mn, nine common ligands are expected to form relatively stable complexes with these metal ions. These ligands including fluoride, acetate, glycolate, formate, EDTA, tartrate, oxalate, citrate and glyoxylate.

A high possibility for complex formation of Fe, Sr and Mn was observed with strong ligands such as EDTA, tartrate and glyoxylate while the moderate complex formation was observed with oxalate and citrate. Less metal ion complex formation was observed with acetate and formate.

The IC and AAS analysis of the stoichiometric metal complexes showed that the carboxylate anions that are responsible for solubilizing iron and manganese in the filtrate obey the following corresponding sequences:

Fe(III): Tartrate >> Glyoxylate > Glycolate > Oxalate
Mn: EDTA >> Citrate > Tartrate

Therefore, the predominant metal ion complexes in the filtrate at high pH are Fe(III)-tartrate and Mn-EDTA.

Although concentration measurements of both fresh and 3-week aged filtrates confirmed that the degradation process occurs mainly due to a harsh chemical environment, it was found that the concentration of iron and manganese increased after three weeks compared with the fresh filtrate for AN-107. This is probably due to a change in the matrix effect on the AAS measurements. Free metal ion species would be expected to eventually precipitate due to metal ion hydrolysis. These observations indicate that generalizations cannot be made or calculated based on theory without analytical measurements.

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