

## ANALYSIS OF HANFORD TANK WASTES

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### ABSTRACT

Ethylenediaminetetraacetic acid (EDTA) and N-(2-hydroxyethyl)- ethylenediaminetriacetic acid (HEDTA) were used in defense-related activities at the Hanford Site in southeastern Washington. These chelators are now part of the complex mixed wastes found in large storage tanks at Hanford. The chelators form water-soluble complexes with most metals, thereby enhancing the migration of heavy metals in soils. After approximately 50 years of storage under radiolysis and favorable conditions for chemical degradation, other chelator fragments may have formed with equivalent or more complexing capability than the starting materials.

The Hanford Site has 177 high-level waste storage tanks. Several tanks contain high concentrations of complexants. One tank in particular, Tank 241-SY-101 (Tank SY-101), has exhibited episodic releases of flammable gas mixtures since its final filling in the early 1980s. It has been postulated that the organic compounds present in the waste may be precursors to the production of hydrogen.

Analytical techniques have been developed for sample preparation and the analysis of organics in tank waste. For water soluble organic components, a method for reducing the radioactivity level of tank waste samples without introduction or reduction of the organic content of the sample using cation exchange was developed. This technique allows the sample to be removed from the hot cell. Derivatization gas chromatography/mass spectrometry (GC/MS) was developed for the analysis of chelators and chelator fragments. Ion chromatography was utilized for the analysis of low molecular weight organic acids, e.g., oxalate, formate, acetate. Ion-pair chromatography was also developed for the analysis of chelators and chelator fragments. Liquid chromatography/mass spectrometry was utilized for the qualitative analysis of low molecular weight acids.

Tank waste samples were analyzed using the developed techniques. For samples with high concentrations of complexants (e.g. Tanks SY-101 and SY-103), approximately 70-90% of the measured organic carbon could be accounted for through speciation of the organics. The major water-soluble components were EDTA and oxalate. Speciation of the organic components in tank wastes has been an extremely important factor in helping to solve unresolved safety questions.

### INTRODUCTION

Large quantities of EDTA and HEDTA (approximately 240 and 1500 tons, respectively) have been used in defense-related activities at the Hanford site in southeastern Washington State (1) These chelators are now part of the complex mixed wastes found in large storage tanks at Hanford. Mixed waste is defined as waste containing both hazardous chemicals and radionuclides. The chelators form water-soluble complexes with most heavy metals, thereby enhancing the migration of heavy metals in soils. For example, studies at Oak Ridge National

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Laboratory demonstrated that EDTA caused the low-level migration of  $^{60}\text{Co}$  from intermediate-level liquid waste disposal pits and trenches (2). Another study at the Maxey Flats commercial low level waste disposal site revealed that Pu-EDTA and  $^{60}\text{Co}$ -EDTA migrated (3). In addition, after approximately 50 years of storage under radiolysis and favorable conditions for chemical degradation, other chelator fragments may have formed with equivalent or more complexing capability than the starting materials. Recent studies with simulated wastes indicate that chelator degradation at higher temperatures, is, in fact, quite rapid (4,5). As a result, the presence of chelators is an important consideration when handling and storing mixed wastes.

The Hanford Site has 177 high-level waste storage tanks. Of these, 25 tanks are being watched closely because of the possibility that flammable gas mixtures will be produced from the mixed waste contained in the storage tanks. One tank in particular, Tank 241-SY-101 (Tank SY-101), has exhibited episodic releases of flammable gas mixtures since its final filling in the early 1980s. A dominant source of hydrogen gas in the flammable gas tanks is from the C-H and N-H bonds in the chelators and chelator fragments. Studies of simulated waste mixtures (SWM) have indicated that chelator concentration influences gas generation and retention. It was postulated that the chelators form hydrophobic surfaces on solids in the SWM. These hydrophobic surfaces are more conducive to bubble attachment, which causes solids to float and eventually crust to form (6). Knowledge of chelator types and concentration is important for understanding crust formation and gas release.

Analytical techniques have been developed for the analysis of chelators, chelator fragments, organic acids, and phosphate-related components in tank wastes. Several techniques, including gas chromatography/mass spectrometry (GC/MS) and liquid chromatography (LC), have been utilized to analyze chelators. Derivatization GC/MS techniques that have been applied to the analysis of chelators (e.g. EDTA and NTA) include 1) reaction with boron trifluoride ( $\text{BF}_3$ )/methanol to form the methyl esters (7) and 2) reaction with propanol/HCl to form the propyl ester (8). Other analytical techniques exist for determining chelators and chelator-type compounds, among them, ion-pair chromatography (IPC) for separation and ultraviolet (UV) absorption of the copper(II) complex for detection. Another technique used reversed-phase chromatography with amperometric detection (9-12). Researchers have developed methods using reversed phase chromatography and have also examined several chelators, including both EDTA and HEDTA, by thermospray liquid chromatography/mass spectrometry (13). The base peak for most cases in that study was either  $(\text{M}+\text{H})^+$  or  $(\text{M}+\text{H}+18)^+$ , indicative of ammonium adduction. Electrospray mass spectrometry has also been utilized to examine chelators such as EDTA, HEDTA, and NTA in the negative ion mode (14). The base peak in most cases was  $(\text{M}-\text{H})^-$ . Historically, LMW organic acids, such as oxalic and glycolic acid, in tank waste samples were analyzed using non-suppressed ion chromatography (IC) with UV detection (15). However, high concentrations of nitrate and nitrite often interfered with quantitation, and UV detection exhibited poor sensitivity for low molecular weight (LMW) organic acids. Thermospray liquid chromatography-mass spectrometry (LC/MS) has also been used for qualitative determination of LMW organic acids and chelator fragments with moderate success (16). One advantage of using LC/MS over GC/MS is that derivatization is not required in LC/MS, and non-volatile inorganic species do not have to be removed as long as they are soluble in the mobile phase. However, oxalic acid could not be detected by LC/MS. Therefore, a simple but robust IC technique was developed for the analysis of LMW organic acids. This method required minimum sample preparation and was found to be effective at identification and quantification of these acids.

This paper represents a summary of the methods development and examples of results from the analysis of water-soluble organic components in tank waste. Waste samples from Tank SY-101, SY-103, and others have been analyzed using the developed techniques. The major components identified in samples from both Tanks SY-101 and SY-103 were oxalate and EDTA. The total organic carbon (TOC) was measured for the samples. Through organic speciation, 70-90% of the organic carbon was accounted for. Speciation of the organic components in tank wastes has been an extremely important factor in helping to solve unresolved safety questions. In addition, speciation of the organics in the complexant tank wastes showed that through chemical and radiolytic degradation, the organics were progressing to less energetic materials.

## **RESULTS AND DISCUSSION**

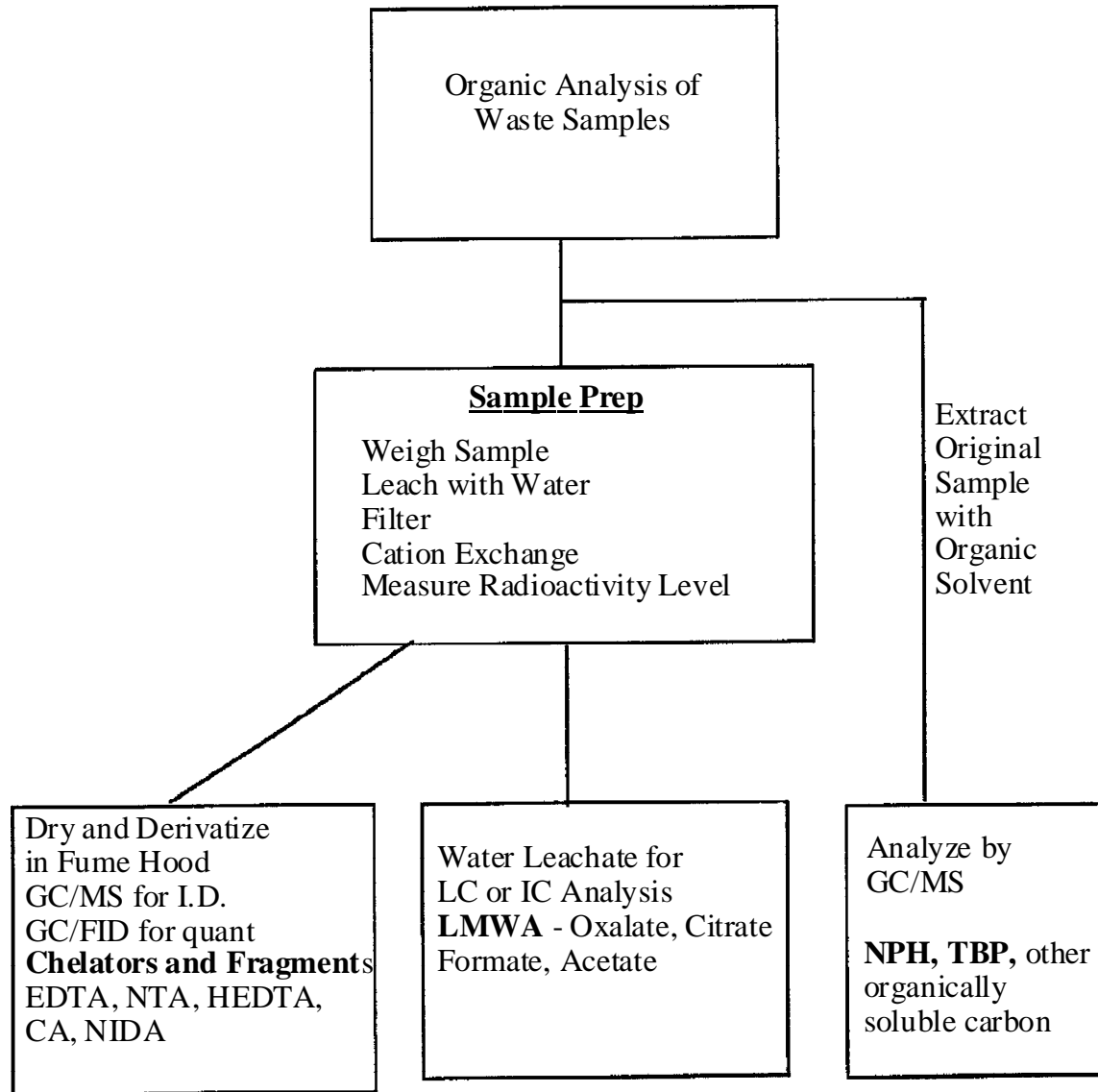
Figure 1 is a schematic illustrating the sample preparation procedure and analysis scheme developed for tank wastes. Briefly, for solids, the sample is leached with water overnight and eluted through the cation exchange column to reduce the radioactivity level; the sample preparation procedure occurs in the hot cell facility. For aqueous samples, an aliquot is applied directly to the cation exchange column. The column is eluted with NaOH to remove any organic carbon and combined with the water solution. The sample is then measured for radioactivity and then removed from the hot cell. An aliquot of the water solution is then dried in the fume hood for derivatization. Another aliquot is prepared for analysis of the low-molecular weight organic acids using liquid chromatography or ion chromatography. To determine the organically-soluble carbon, an aliquot of the starting waste is extracted with methylene chloride or chloroform and analyzed using GC/MS.

Table I shows the results of TOC measurements of waste samples from Tank SY-101 before and after elution through cation exchange resin. The results represent a portion of the total sample analyzed for TOC in the bulk sample. The results clearly indicate no addition or reduction of organic components occurs with elution through the cation exchange resin. In addition, the use of the hydrogen form significantly reduces the amount of organic carbon.

Table II lists the results from  $^{137}\text{Cs}$ ,  $^{90}\text{Sr}$ , and gross alpha analyses in samples from Tank SY-103, a tank waste similar in composition to Tank SY-101, before and after using cation exchange. The convective layer (C) is the upper-most layer, and the nonconvective layer (NC) refers to the lower layer samples. The results of radiochemical removal from samples indicate a manifold decrease in radioactivity, primarily noted in  $^{137}\text{Cs}$ . The radioactivity level for  $^{137}\text{Cs}$  was reduced by a factor of approximately 221 while  $^{90}\text{Sr}$  was reduced by a factor of 10-15. Complexation of  $^{90}\text{Sr}$  to waste chelators may represent a competitive process with the ion-exchange, limiting the removal of  $^{90}\text{Sr}$ . Current research is exploring this area.

**Table I.** Total Organic Measurements of Waste Sample from Tank SY-101

<u>Sample</u>	TOC( $\mu\text{g/mL}$ )	
	<u>Trial #1</u>	<u>Trial #2</u>
Tank Sample SY-101	2100	1995
After Separation Through Sodium Form of Resin	2200	2170
After Separation Through Hydrogen Form of Resin	470	490
Blank of Hydrogen Form	9.5	8
Blank of Sodium Form	<0.5	<0.5



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**Figure 1.** Schematic of Sample Preparation and Analysis of Tank Wastes

The analysis of the organic components in radioactive tank wastes is related to an accurate accounting of the various organic compounds in the waste versus the values obtained from TOC analysis. This provides a check on the various quantitation methods that are used to determine the compounds found in the waste. If TOC measurements are far higher than the total carbon represented in the GC, IC, or GC/MS quantitation, then additional analyses are warranted to determine the identity of any additional organic components. The results clearly indicate that elution through cation exchange as part of the sample preparation did not significantly affect the amount of organic carbon identified. Developing this procedure was extremely important in increasing the amount of TOC accounted for by speciation. However, the TOC of the sample should be measured before and after elution through the cation exchange resin to confirm the TOC is not altered. In other words, the cation exchange elution should neither introduce nor remove any organic carbon.

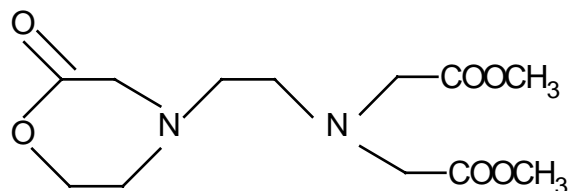
**Table II.** Results of  $^{137}\text{Cs}$ ,  $^{90}\text{Sr}$ , and Gross Alpha Analyses from Tank SY-103 Sample Before and After Elution Through Cation Exchange for Radioactivity Reduction

Sample	Isotope	Before( $\mu\text{Ci/g}$ )	After( $\mu\text{Ci/g}$ )
Convective	$^{137}\text{Cs}$	273	1.23
	$^{90}\text{Sr}$	6.92	0.55
	gross alpha	0.007	0.0000061
Nonconvective	$^{137}\text{Cs}$	260.80	0.29
	$^{90}\text{Sr}$	4.75	0.033
	gross alpha	0.002	0.00000143

Removing the principal fission products by ion exchange allows the sample to be removed from the shielded laboratory for work in a standard fume hood. The samples in their ion-exchanged form are sufficiently stripped of their fission products that the analyst can manipulate the samples without risk of exposure to excessive radioactivity. In the derivatization steps used in this laboratory to determine chelators such as EDTA, the sample size, sample dryness, and sample dispersion in the reaction vessel are found to be critical for obtaining a good conversion to the methyl esters. It is not possible to manipulate the samples in the hot cell to obtain these conditions.

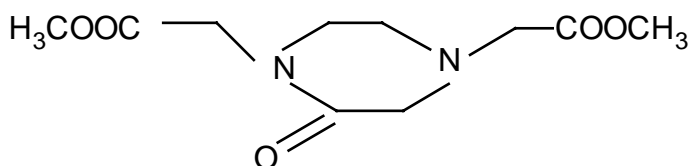
### Chelators and Chelator Fragments

In the reaction of chelators with  $\text{BF}_3/\text{methanol}$ , methylation occurs at the carboxylic acid sites. The mass spectrum of methylated-EDTA shows the parent ion is at  $m/z$  348. The base peak at  $m/z$  349 ( $M + H$ ) was observed in the chemical ionization mass spectrum. However, methylation does not occur at hydroxy sites in the reaction of  $\text{BF}_3/\text{methanol}$ . The mass spectrum of methylated HEDTA shows a parent ion at  $m/z$  288. The identification of  $m/z$  288 for methylated HEDTA was initially surprising because the expected molecular weight of methylated HEDTA ( $\text{Me}_3\text{-HEDTA}$ ) should be 320. Analysis of the  $m/z$  288 species using GC/Fourier transform infrared (FTIR) revealed the presence of a strong lactone absorbance. Consequently, the methylated lactone structure was derived and shown below.



The hydroxyethyl group of HEDTA resists methylation by  $\text{BF}_3/\text{methanol}$  and, instead, forms a cyclic, or intramolecular lactone with one of the neighboring acetate ligands. The parent ion was

confirmed with positive ion chemical ionization MS. Similarly, the mass spectrum of ethylenediaminetriacetic acid (ED3A, MW 234), derivatized with  $\text{BF}_3$ /methanol, shows the parent ion at  $m/z$  244, indicating formation of a lactam with the following structure.



Ethylenediaminediacetic acid (EDDA) was predicted to be a major product of chelator degradation (25). Both symmetrical ethylenediaminediacetic acid (s-EDDA) and unsymmetrical ethylenediaminediacetic acid (u-EDDA), were derivatized with  $\text{BF}_3$ /methanol to form the methyl esters; however, the reaction of s-EDDA with  $\text{BF}_3$ /methanol is not reproducible. This may be due, at least in part, to the irreversible formation of boron trifluoride complexes with this isomer.

### Waste Samples

Samples from Tank SY-101 and other tanks were analyzed for organic constituents. The major components identified as methyl esters include butanedioic acid (succinic acid), citric acid, NTA, EDTA, ED3A, and HEDTA. Figure 2 is a typical GC chromatogram of the derivatized tank waste from U-106. For Tank SY-101, the chelators and chelator fragments make up approximately 20-50% of the TOC, depending on the sample. The remaining TOC was thought to be LMW acids such as oxalic, glycolic, and formic acid, which may be the precursors or end products for hydrogen production in the waste tanks. This has been confirmed with subsequent IC analysis.

### Organic Acids

Analysis of organic acids in a complex matrix (slurries and sludge) containing excess amounts of nitrates, nitrites and other transition metal salts is difficult by conventional techniques. Separation using HPLC followed by UV-Vis detection is not practical because the target analytes do not contain a chromophore.

Analytes including, citric, succinic, glycolic and formic acid could be separated and quantitated by non-suppressed IC with UV detection technique. However, in the presence of nitrate and nitrite these LMW organic acids could not be quantitated by non-suppressed IC. Diluting the simulated waste sample was not an effective solution for reducing the interference from nitrate and nitrite, because dilution further reduced already low response of LMW acids. Alternatively, we found that IC using a gradient elution profile and suppressed conductivity detection was an effective method of analysis for quantifying organic acids in the presence of nitrates and nitrites and other impurities. All target acids, except glycolic, succinic, and acetic acid, were analyzed using the AS-11 column. Glycolic acid was found to co-elute with acetic acid on the AS-11 column, therefore, an ion-exclusion chromatography (IEC) with the AS-6 column was used to quantify glycolic and acetic acid. A continuing calibration standard of 4  $\mu\text{g/g}$  was run prior to each series of samples.

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No interferences from any inorganic anions were observed. Furthermore, the response of the LMW organic acid was significantly improved under IC conditions as opposed to HPLC conditions for identical concentrations. It is unlikely that glycolic and acetic acid can be quantified by other means, such as GC/MS analysis in this matrix. The samples contain such minor amounts of these materials that the preparation/handling steps associated with derivatization to make them amenable to GC analysis will give the samples ample opportunity to lose the extremely volatile methyl-esters of these acids. Succinate anion was also quantified using AS-6 column. Although succinate could be effectively analyzed by the AS-11 column, the AS-6 column was used for procedural convenience. Concentrations were determined using a linear calibration curve. Quantification based on high dilution is not ideal, but appears to be permissible, as the plots of standard concentration versus response exhibit linear behavior down to 100 ng/g for the key analytes. These analytes include acetate/glycolate, formate, oxalate, and citrate in our samples. The retention time for acetate and succinate anions separated and analyzed by the AS-6 column were  $15.37 \pm 0.20$  min and  $16.35 \pm 0.20$  min, respectively. The IonPac ICE-AS6 column uses an ion exclusion mechanism which allow retention and separation of weakly ionized acids based on the differences in pKa's. Therefore, strong inorganic acids, including nitric and nitrous acids are not retained by the stationary phase and elute in the void volume of the column.

Actual waste samples were successfully analyzed for LMW organic acids using IC with an AS-11 column. A typical IC chromatogram of a tank waste sample is shown in Figure 3. The only questionable separation at this point is the discrimination of acetate from glycolate, both of which are apparently feasible components in actual tank waste materials. To address this question, we will use AS-6 column which employs a separate chromatographic mechanism based on ion exclusion to distinguish these relatively similar acids.



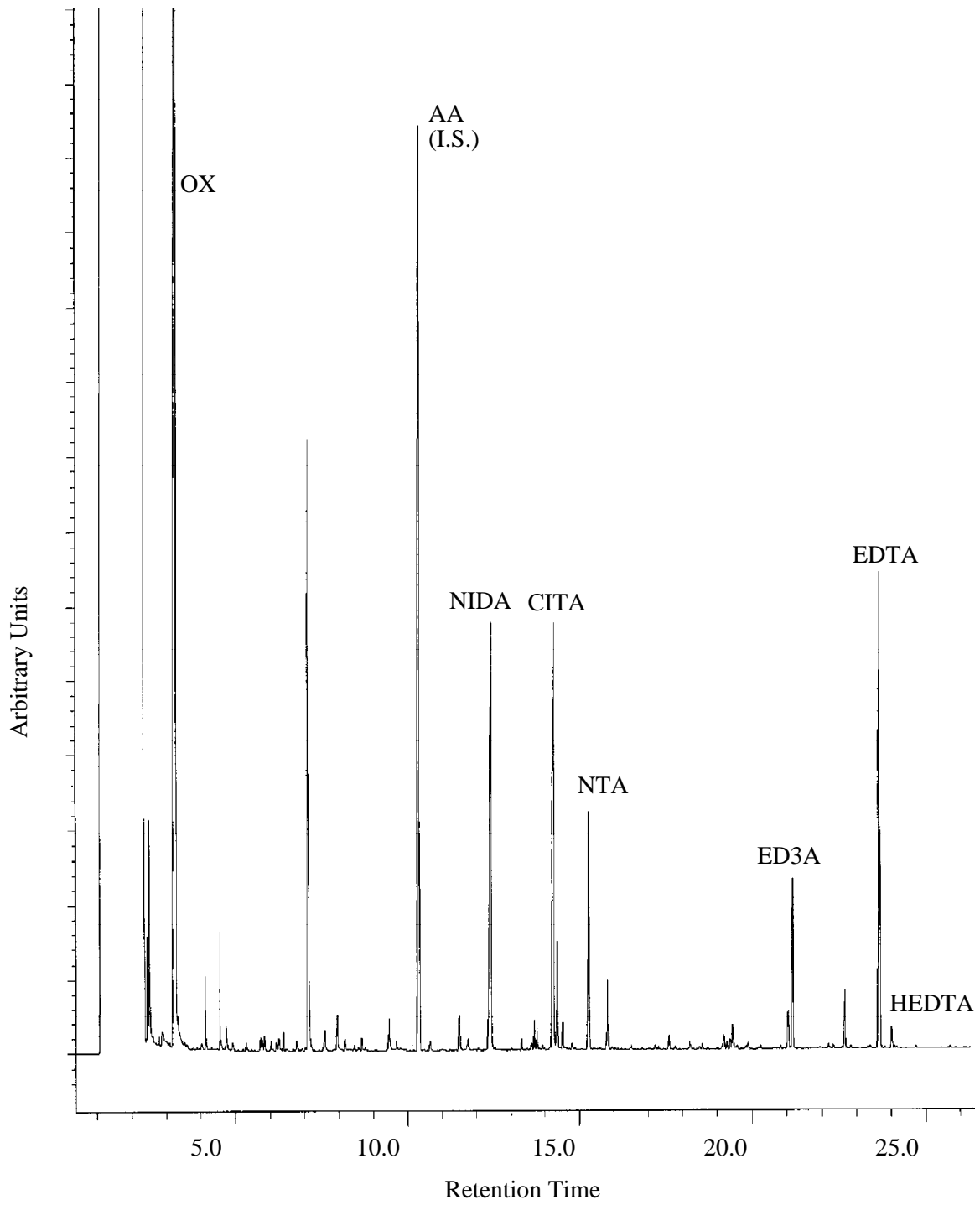


Figure 2. GC Chromatography of U-106 Sample

Table III lists the concentration of chelators, chelator fragments, low-molecular-weight acids, and amount of TOC accounted for in samples from Tank SY-101. For most tank samples, with a few exceptions, 70-90% of the organic carbon could be speciated with the utilization of the developed analytical techniques.

**Table III.** Total Organic Carbon (TOC) Accounted for by Chelators, Chelator Fragments, and Low Molecular Weight Organic Acids, in Tank 101-SY Segment Samples (mg C/g sample)

			Low Molecular	% TOC
<u>Sample</u>	<u>Segment #</u>	<u>Chelators<sup>(a)</sup></u>	<u>Weight Acids<sup>(b)</sup></u>	<u>Accounted For</u>
R4258/C	4	4.7(44%) <sup>(c)</sup>	3.3(30%)	87
R4259/C	6	3.3(33%)	4.5(44%)	77
R4260/C	9	4.8(46%)	4.4(41%)	91
R4261/C	11	6.4(52%)	2.5(23%)	81
R4262/NC	16	2.2(20%)	5.8(53%)	73
R4263/NC	17	3.6(32%)	6.8(61%)	93

(a) Includes chelators, chelator fragments, nitrosated chelator material, and several carboxylic acids.

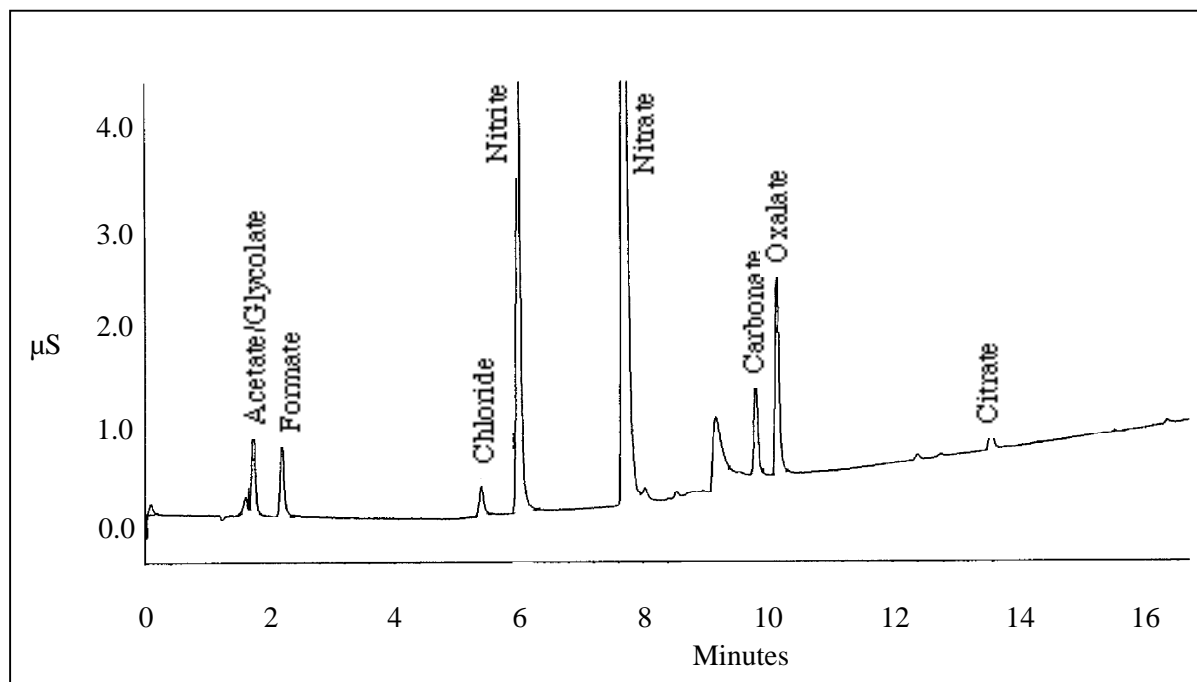
(b) Low molecular weight acids include acetic, formic, glycolic, and oxalic.

(c) Numbers in parentheses are percent of TOC accounted for by analyte category.

## CONCLUSIONS

The analysis of tank waste is a very complex analytical problem. Each tank sample presents unique concerns. In addition, nearly every tank sample has different organic components. For example, the major constituents in samples from Tanks 101-SY and 103-SY were complexants and low molecular weight organic acids. The major components in the floating organic layer in Tank C-103 were normal paraffin hydrocarbons, tributyl phosphate (TBP), and dibutyl butyl phosphonate. A sample from another organic waste tank, C-204, was found to contain primarily TBP. Samples associated with Tank C-106 that were obtained during washing and centrifuging experiments appeared to contain a waxy or oily substance. Derivatizing the sample with diazomethane revealed a large quantity of bis-(2-ethylhexyl)phosphate (17). Each tank sample was unique and required analytical methods development to identify and quantify organic species.

The single most important step in the sample preparation procedure is removing the principal fission products by cation exchange which allows the sample to be removed from the shielded laboratory for work in a standard fume hood. The samples in their ion-exchanged form are sufficiently stripped of their fission products that the analyst can manipulate the samples without risk of exposure to excessive radioactivity. The result of introducing this step into the sample preparation procedure was dramatically increasing the %TOC accounted for through speciation.



**Figure 3.** IC Chromatogram of LMW Acids in Tank Waste from Tank AN-107

The reaction of the waste sample with  $\text{BF}_3$ /methanol was very useful in identifying and quantitating major components; however, artifacts of the derivatization procedure were produced and identified. The major components included citric acid, NTA, HEDTA, EDTA, and ED3A. It is inferred from the data that IDA is also present in the waste samples. The identity of the most concentrated components was verified with high resolution MS measurements. The chelators and chelator fragments constitute only 20-50% of the TOC; it has been shown that the remaining components are low-molecular-weight acids such as oxalic, glycolic, and formic acid.

Analysis and quantitation of low-molecular-mass organic acid anions, in presence of nitrate, nitrites, and transition metal elements, at high pH values ( $>13$ ) can be carried out effectively by using ion-exchange chromatography techniques. Thus, extensive sample preparation, such as one needed for analysis by GC/MS (e.g.,  $\text{BF}_3$ /methanol derivatization) can be avoided. Additionally, the IC technique exhibited a significant improvement in analysis, separation and quantification over non-suppressed IC with UV detection and GC/MS techniques. The information gathered using IC will assist in determining the mechanism of chemical transformation of organic acids in presence of gamma radiation. Further, accurate determination of organic species will assist in predicting energetics in Hanford tanks. The results show the IC technique can be used for the analysis of LMW organic acid anions at high pH values ( $>13$ ), in presence of nitrate, nitrite, and other impurities such as those found in effluent from explosive and pesticide processing.

Organic speciation of components in tank wastes has been an extremely important factor in helping to solve unresolved safety questions. In addition, speciation of the organics in the complexant tank wastes showed that through chemical and radiolytic degradation, the organics were progressing to less energetic materials. This result helped provide evidence for closure of Defense Nuclear Facilities Safety Board Recommendation 93-5.

## EXPERIMENTAL

The experimental conditions for radioactivity reduction, the analysis of chelators and chelator fragments, and organic acids are discussed in the following sections.

### Radioactivity Reduction

Tank waste materials are generally very basic; the pH is usually greater than 12. For samples that we have encountered, it is not necessary to add base to the samples to ensure that carboxylate moieties remain soluble in the matrix. However, for samples that display a pH less than 10, adding sodium hydroxide can ensure the analytes remain in solution.

We converted cation exchange resin (AG 50W-X8, Biorad) from the hydrogen form to the sodium form with 6 N NaOH. The caustic was added in portions to a water slurry of the resin until the slurry remained basic (pH 8-9). The resin was allowed to equilibrate for an hour to ensure complete conversion to the sodium form; then it was filtered and rinsed with deionized water to remove excess sodium hydroxide.

The resin was loaded in plastic disposable columns (Econo-Pac, Biorad) using a bed volume of 18 mL of resin. The columns were used immediately upon loading, without allowing the resin an opportunity to dry. Blanks were run by passing 15 mL of 6 N NaOH through the column, followed by washing with 15 mL of deionized water. The blank solution was submitted for TOC analysis.

We prepared radioactive storage tank waste samples by dissolving 3-5 grams of the waste in 20 mL of water and stirring overnight. The pH was checked and adjusted if necessary. Insoluble solids were removed by passing through a 0.45  $\mu$ M filter (Acrodisc, Gelman). A measured aliquot was removed for TOC and radiochemical analysis.

The samples were passed through two pre-loaded columns arranged in series. The columns were rinsed by passing a column volume of 1 N NaOH (19 mL) to collect sample hold-up, and the eluents were combined. Samples of the eluent were taken for TOC and radiochemical analysis. All of the sample preparation is performed in the hot cell facility. For highly radioactive wastes, e.g. 3-11 R/h, a hot cell facility must be used. This room is composed of thick walls ( $\approx 1.3$  m) equipped with a sample entry port, viewing windows (lead glass and oil-filled), and remote manipulators, which are operated by a highly-trained specialist. When a radioactive sample is remotely handled in the hot cell, the procedure is time consuming, difficult, and requires specialized, deft artistry to complete the tasks. Sample turnaround is much lower when using the hot cell facilities. Wastes with a low-to-moderate total radioactivity level,  $\leq 1$  R/h, may be prepared and analyzed outside the hot cell in a radiation hood or glove box. The actual cutoff levels that differentiate lab bench work, glove box work, and hot cell work is usually based upon local practice or the judgment of the resident health physicist.

### Radiochemical Analysis

The samples were assayed for fission products ( $^{90}\text{Sr}$ ,  $^{137}\text{Cs}$ ) and for actinide content. Gamma energy analysis for  $^{137}\text{Cs}$  was done on a high-purity Ge detector (80% efficiency) with efficiency calibrated geometries. Alpha measurements were determined by pipetting aliquots onto stainless steel planchettes, drying over a flame, and counted using a standard alpha proportional counter.

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We determined  $^{90}\text{Sr}$  by separating Sr and using liquid scintillation counting (LSC) and counted the ingrowth of  $^{90}\text{Y}$  by Cherenkov counting. Samples and comparative standards were spiked with identical aliquots of  $^{85}\text{Sr}$  and loaded onto SrSpec<sup>®</sup> columns (EICHROM Industries) with 8 M  $\text{HNO}_3$ . They were rinsed free of  $^{90}\text{Y}$  and other fission products with 8 M  $\text{HNO}_3$ , and the purified  $^{90}\text{Sr}$  was eluted with water. The chemical yield for Sr was calculated based on a gamma assay of the  $^{85}\text{Sr}$  activity in each sample as compared to observed  $^{85}\text{Sr}$  activity in identical geometries. The samples were then counted without delay by LSC (Quantulus, Wallac Oy). The samples were counted in water using the Cherenkov radiation emitted as an effect from  $^{90}\text{Y}$  decay. The Cherenkov emission efficiency of  $^{85}\text{Sr}$  was calculated from the comparator standards containing only  $^{85}\text{Sr}$ . The  $^{90}\text{Sr}$  Cherenkov efficiency was determined from  $^{90}\text{Sr}$  freshly purified from the  $^{90}\text{Y}$  daughter, and  $^{90}\text{Y}$  Cherenkov efficiency was determined by counting known activities of  $^{90}\text{SrY}$  at equilibrium. The  $^{90}\text{Sr}$  activity was then calculated from several counts of the samples over a suitable ingrowth period. Activity at secular equilibrium was calculated by computational software. In all radiochemical assays, background efficiency calibrations and system controls were done to ensure that the data were valid.

### Total Organic Carbon Determination

Samples, blanks, standards, and spiked samples were prepared and analyzed using a UIC Coulometrics 5300 Carbon System with a coulometry detector. Acidification with sulfuric acid (4N) allows determination of total inorganic carbon; introduction of potassium persulfate and a silver nitrate catalyst followed by heating the sample to 600°C permits oxidation of most organic carbon species. The system is purged with purified oxygen to pass the  $\text{CO}_2$  to the coulometric cell. The entire analysis system is committed to the hot-cell environment with only the read-out being outside of the shielded facility. Samples, blanks, and standards were done in duplicate. A spiked sample is prepared by adding a known amount of standard glucose to a random sample. Recoveries were generally 90-95% of the spiked material. The hot persulfate oxidation to determine TOC and total carbon has been shown to be valid for samples containing high concentrations of sodium nitrite, sodium nitrate, and sodium hydroxide typical of the radioactive waste matrices encountered.

### Chelators and Chelator Fragments

Approximately 2 g of the solids from the tank sample were stirred overnight with 20 mL of deionized water in a hot cell facility. The solution was then filtered to remove insoluble solids. Most of the radioactivity associated with the sample was removed by cation exchange by allowing the sample to percolate through a bed of AG50W-X8 resin (Biorad), 20-50 mesh, prepared in the sodium form as discussed above. Aqueous samples were eluted directly through the cation exchange columns.

Measured aliquots of the water-soluble portion of the sample, representing about 0.25 g of the original waste sample, were taken to dryness in reactivials (VWR Scientific) at ca. 75°C using a gentle stream of dry nitrogen. Two milliliters of a 12%  $\text{BF}_3$ /methanol (Aldrich) was added, and the sample was heated to 100°C for 1 h. The solution was cooled, and 2 mL of chloroform were added. The entire solution was then quenched in a vial containing 8 mL of 0.4 M  $\text{KH}_2\text{PO}_4$  adjusted to pH 9.5. To ensure that the resulting solution maintained a pH between 7 and 8, pH paper was used. The vial was vortexed, and the aqueous and chloroform layers were allowed to separate. The chloroform layer, containing the derivatized organics was retained, and the

aqueous layer was discarded. At this point, essentially all of the radioactivity remained with the aqueous layer. The chloroform solution was monitored for radioactivity and then removed for subsequent GC/electron impact MS analysis. The derivatized waste sample was also analyzed using positive ion chemical ionization MS to confirm parent ion assignment.

### **Instrumentation**

A fused silica column (DB-5, 30 m X 0.25 mm i.d., 0.25- $\mu$ m film thickness, (J & W Scientific) was used in the splitless mode. The oven temperature was typically programmed in the following manner: 50°C for 1 min, 8°C/min to 300°C, and hold at 300°C for 5 min. The mass spectrometer was tuned daily with perfluorotributylamine (PFTBA). In these studies, the mass spectrometer was scanned from 50-500 amu and operated in the electron impact mode (70 eV). The source temperature was 200°C, the injector port temperature was 250°C, and the interfaces were also at 250°C.

Chemical ionization was carried out with both methane and isobutane in both positive ion and negative ion chemical ionization modes. The temperature of the source for positive ion chemical ionization MS was 200°C and 120°C for negative ion chemical ionization. The MS was scanned from 100-600 amu in the negative ion mode and 70-500 in the positive ion mode.

Accurate mass measurements were performed on a JEOL SX-102/SX-102 double-focusing MS equipped with a Unix data system. The instrument was tuned to a resolution of 5000 (10% valley definition). Data were acquired by scanning over the mass range of 50-500 at a rate of 3 sec per mass decade. Instrument tuning and real-time mass measurements were performed by leaking perfluorokerosene into the electron impact ion source from the septum inlet reservoir. Computer-assisted accurate mass assignments and subsequent elemental compositions were made on data obtained from averaging four consecutive scans over the gas chromatographic elution profile of the analyte. The instrument was equipped with an HP 5980 GC. The GC was fitted with 30 m X 0.25 mm i.d. DB-5 capillary column (J & W Scientific, Folsom, CA). The GC oven temperature was held at 50°C for 2 min., then programmed at 5°C/min to 250°C.

### **Organic Acids**

Organic acid stock solutions were prepared fresh daily by dissolving 25-50 mg of free acids or sodium salts of the free acids in 25 mL of deionized water. All standards solutions were made from commercially obtained reagent grade chemicals without further purification. Initially, standard solutions of glyoxalic acid, glycolic acid, oxalic acid, sodium citrate, sodium acetate, succinic acid, butyric acid and formic acid were prepared.

Analyses of LMW organic acid anions, including formic, glycolic, citric and oxalic acids were carried out using a Dionex model IC unit (Dionex, Sunnyvale, CA, USA) equipped with a Dionex Model CD20 conductivity detector. Most analyses were carried out using a Dionex IonPac AS-11 column. We used a Dionex IonPac ICE AS-6 column for glycolic acid quantification, since glycolic acid co-eluted with acetic acid on the AS-11 column. The standard concentrations bracketed the estimated concentrations of the samples.

The mobile phase contained a gradient of deionized water and a weak solution of sodium hydroxide for the AS-11 column. Two solutions, 5 mM and a 100 mM NaOH, were prepared from 18.5 M NaOH stock solution (15). The water used to prepare the mobile phase and run the

gradient was stirred under vacuum for over 12 h, and then sparged with helium to avoid interference from dissolved carbon dioxide. The column was allowed to equilibrate at initial conditions for at least 7 min before each run. The mobile phase for the AS-6 column was made up of 0.4 mM heptafluorobutyric acid in deionized water. We used 5 mM tetrabutylammonium hydroxide as a suppression eluent.

Radioactive samples were analyzed within a laboratory fabricated chromatography enclosure, which was located in a radiation fume hood. The enclosure was equipped with an AS-11 column, an ASRS-I Suppressor, and a conductivity cell. Samples were injected through a Rheodyne 9126 (Cotati, CA, USA) manual injection valve. The HPLC pump, the suppresser, and detector electronics were located outside the radiation hood. This arrangement allowed for simple and rapid switching between radioactive and non-radioactive analyses without concern for radioactive contamination of the key system components. The chromatographic conditions used for the analysis of radioactive and non-radioactive samples were identical.

Samples collected from Hanford tank wastes are typical example of highly-aged, relatively organic-rich, Hanford tank waste matrices. The cleanup procedure, performed within hot cell facilities at Hanford, reduced the amount of fission products present in the sample. The cleanup procedure utilized was discussed under the radioactivity reduction section. The treatment within the hot cell also results in a ten-fold dilution (w/w) of the sample into a dilute caustic matrix not significantly different from the matrix of the original sample. An additional 500-fold dilution was performed to dilute the major inorganic ions (nitrite and nitrate) to levels that would not overload the capacity of the analytical column. Previous experience has demonstrated that ion exchange sites within the IC column apparently do not quickly recover from an overload of these inorganic species, which results in a non-uniform elution of the weakly retained analytes (e.g. acetate, formate). This phenomenon is evident to the analyst by virtue of poorly resolved peaks, and decreased column efficiency for the monovalent carboxylates. We have found that diluting nitrate to a concentration that delivers 10-20  $\mu\text{S}$  response eliminates this problem.

## **FOOTNOTES**

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