

Pacific Northwest National Laboratory

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Organic Tanks Safety Program

Organic Analysis Progress Report FY 1997

Technical Task Leader: J. A. Campbell

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under Contract DE-AC06-76RLO 1830**

**Pacific Northwest National Laboratory
Richland, Washington 99352**

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Summary

This report describes the work performed during FY 1997 by Pacific Northwest National Laboratory in optimizing analysis techniques for identifying organic components in Hanford waste tank samples. The work was conducted for the Flammable Gas and Organic Tanks Waste Safety Programs. The major focus during FY 1997 was the analysis of actual tank wastes.

The methods developed during this task are illustrated by their application to samples listed below.

U-107 ⁽¹⁾	U-105 c136 seg7 (U-105 s)	AW-101 c139 seg21 (AW-101)
U-102 c144 seg6 (U-102)	AN-107	S-102
BY-105 c108 seg1 (BY-105 l)	BY-104 c117 (BY-104)	C-105 c76 seg1 (C-105 l)
A-102 Auger (A-102)	U-106 c148 seg2 (U-106 s)	U-106 c148 seg2 (U-106 l)
U-105 grab (U-105 grab)		

c = number, seg = segment number, l= liquid, s= solid

The samples from U-107 and AN-107 were grab samples; core and segment numbers do not apply. Samples C-105 c76 seg1, BY-105 c108 seg1, U-106 c148 seg2, and U-105 grab were liquid samples, and the rest were primarily solids. The methodology has been extended to the analysis of samples from Tank S-102 for Flammable Gas Generation Studies and analysis of simulated wastes to support Organic Waste Aging studies. The results reported here are from the most recent organic analyses and require further validation/verification. Table S.1 lists the samples received by Pacific Northwest National Laboratory (PNNL) for analyses, the jar/vial numbers, and associated laboratory identification numbers from the chain of custody (See also Appendix B).

Table S.1. Samples Shipped to PNNL with I.D. Numbers

<u>Tank</u>	<u>Jar/Vial #</u>	<u>Core</u>	<u>Seg</u>	<u>Sample I.D.</u>
BY-105	8394	108	1	S96M000118
BY-104	8410	116	2A	S96m000127
BY-106	6402	65	13	S96M000142
C-105	6744	76	1	S96M000122
A-102	7215	Auger		S96M000143
U-102	10042	144	6	S96M000155
U-106	10053	148	2	S96M000123
U-106	10063	148	2	S96M000145
AW-101	10213	139	21	S96M000146
U-108	9454	141	4	S96M000147
U-105	9477	136	7	S96M000148
U-105	7475	Grab		S96M000160

(1) The 241-prefix, common to all of the waste tanks mentioned in this report, has been omitted.

Samples from Tanks S-102, AN-107, U-107, U-105, U-106, U-108, A-102, BY-104, BY-105, BY-106, and U-106 were analyzed for organic constituents. Samples were analyzed using derivatization gas chromatography/flame ionization detection (GC/FID) for chelators, ion chromatography (IC) for low-molecular-weight acids, and ion-pair chromatography (IPC) for chelators. The major components identified include low-molecular-weight acids (e.g., oxalic acid), chelators (e.g., EDTA), and chelator fragments. The concentrations of analytes in the archived samples are summarized in Table S.2. Table S.3 summarizes the data obtained from received samples. Detailed validity checks, including results of duplicate analyses and internal standard recoveries, are discussed in Section 2.0.

Table S.2. Summary of Data from Analyses of Archived Samples. Concentrations are listed as mg C/g sample.

Components	Tank		
	AN-107	U-107	S-102
Ox	4.7	0.2	1.2
G/A	3.2	1.0	0.5
For	1.4	0.7	0.4
SA	0.02	0.02	0.2
NIDA	1.25	0.29	nd
CA	2.26	0.22	0.21
NTA	0.15	0.04	nd
EDTA	0.89	nd	nd
HEDTA	0.20	nd	nd
TOC	13.8	2.4	2.2

Ox - oxalate

G/A - glycolate/acetate

For - formate

SA - succinic acid

NIDA - N-nitrosoiminodiacetic acid

CA - citric acid

NTA - nitrilotriacetic acid

EDTA - ethylenediaminetetraacetic acid

HEDTA - N-(2-hydroxyethyl)ethylenediaminetriacetic acid

TOC - total organic carbon, experimentally determined

nd - not detected, detection limits vary with analytical technique

Table S.3. Summary of Data from Analyses of Received Samples. Concentrations are listed in mg C/g sample.

Components	Tank					
	U-108 (s)	BY-106	AW-101	U-105(s)	U-105	U-102
Ox	1.40	0.08	5.80	2.40	grab 0.31	2.18
G/A	0.10	nd	nd	1.60	2.12	1.12
For	0.10	nd	0.10	0.90	0.91	0.72
SA	nd	nd	0.02	0.02	nd	nd
NIDA	nd	nd	nd	1.40	1.53	nd
CA	0.11	nd	0.07	1.01	0.90	0.43
NTA	0.03	nd	nd	0.22	0.23	0.13
ED3A	nd	nd	nd	0.61	0.62	0.13
EDTA	nd	nd	nd	1.03	0.86	0.24
HEDTA	nd	nd	nd	2.42	0.63	nd

Table S.3. (continued)

Components	Tank					
	BY-105 (l)	U-106 (l)	U-106 (s)	A-102 Auger	BY-104	C-105 (l)
Ox	0.04	0.30	3.92	6.91	6.42	nd
G/A	0.50	4.31	2.23	0.21	nd	nd
For	0.10	2.03	0.71	0.21	nd	nd
SA	0.02	0.04	0.41	0.02	0.04	0.04
NIDA	nd	2.54	1.42	nd	0.02	nd
CA	nd	2.52	1.32	0.04	nd	nd
NTA	nd	0.40	0.53	nd	nd	nd
ED3A	nd	1.37	0.30	nd	nd	nd
EDTA	nd	2.16	1.23	nd	nd	nd
HEDTA	nd	5.02	1.43	nd	nd	nd

Ox - oxalate

G/A - glycolate/acetate

For - formate

SA - succinic acid

NIDA - N-nitrosoiminodiacetic acid

CA - citric acid

nd- not detected

NTA - nitrilotriacetic acid

EDTA - ethylenediaminetetraacetic acid

HEDTA - N-(2-hydroxyethyl)ethylenediaminetriacetic acid

The values used for oxalate in Table S.3 were obtained using GC/FID due to the large dilution factors required for IC analysis. The concentrations of formate and glycolate/acetate were obtained using IC.

For most of the tank waste samples, 80% to 95% of the total organic carbon (TOC) present after elution through the cation exchange column for radioactivity reduction was accounted for by speciation. The samples with the lowest accountability contained the lower TOC values. The TOC values measured before and after cation exchange were not significantly different except for two samples, BY-104 and U-105. The differences for these two samples were 37% and 45%, respectively. These results clearly indicate that a significant amount of organic carbon adsorbed on the cation exchange resin. The reason for this phenomenon, at this time, is not apparent. However, further studies are underway to understand this observation. In addition, for several samples, an early eluting peak in the ion chromatograms was incorrectly assigned as acetate/glycolate, giving an artificially high concentration. After further review and spiking of the samples with acetate, it was determined that this component was probably fluoride.

The results of analyses for the Gas Generation Studies were obtained for SY-103. Samples of 1) heated and 2) heated and irradiated material were analyzed using derivatization GC/MS, ion chromatography, and ion-pair chromatography. Results of analyses of 1) heated and 2) heated and irradiated samples from Tank S-102 are also included in this report.

In support of the Organic Waste Aging Studies, the effect of oxygen on the degradation of organics in simulated wastes was studied. Preliminary results indicate the destruction pathways for HEDTA and EDTA in the presence of oxygen were different than in the presence of argon. Similarly, the destruction pathways for thermal conditions vs. radiolytic conditions were different in oxygen and argon atmospheres.

The concentration of several organics, including EDTA, citrate, glycolate, and NTA were determined in 0.1 M NaOH and 2.0 M NaOH at 40°C and 50°C to support Solubility Studies (Scott Barney, Numetec). The solubilities of the organic salts are lower than those measured in simpler systems. This can be explained by the higher sodium concentrations and the higher sodium hydroxide concentrations in these complex mixtures. The complex waste solutions have sodium ion concentrations 3.4 to 7.0 molar higher than previous solution matrices. This causes a significant lowering of the solubilities of the organic sodium salts due to the common ion effect of sodium.

The methods associated with IC, IPC, cation exchange for radioactivity reduction, and derivatization GC/FID were documented and submitted to the Project Hanford Management Contractor (PHMC) for approval and comments. In addition, an internal assessment for Hanford Analytical Services Assurance Requirements Document (HASQARD) (DOE-RL 1997) compliance was performed.

Several manuscripts have been submitted for publication during FY 1997. A draft of the manuscript entitled "Analysis and Quantification of Organic Acids in Simulated and Actual Hanford Tank Wastes" by A.K. Sharma, S.A. Clauss, G.M. Mong, K.L. Wahl, and J.A. Campbell is included in Appendix A. This manuscript has been accepted for publication in the Journal of Chromatography.

Several techniques have been evaluated for directly analyzing chelator and chelator fragments in tank wastes: matrix-assisted laser desorption/ionization time of flight mass spectrometry and liquid chromatography with ultraviolet detection using copper complexation. Although not directly funded by the Tanks Safety Program, the success of these technologies has implications for both the Flammable Gas and Organic Tanks Safety Programs.

Reference

U.S. Department of Energy, Richland Operations (DOE-RL). 1997. *Hanford Analytical Services Quality Assurance Requirements Document*, DOE-RL-96-68, Rev. 1, Richland, Washington.

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Glossary

CA	citric acid
CE	capillary electrophoresis
CI	chemical ionization
ED3A	ethylenediaminetriacetic acid
EDTA	ethylenediaminetetraacetic acid
GC/FID	gas chromatography/flame ionization detection
GC/MS	gas chromatography/mass spectrometry
HASQARD	Hanford Analytical Services Quality Assurance Requirements Document
HEDTA	N-(2-hydroxyethyl)ethylenediaminetriacetic acid
HP	Hewlett-Packard
HPLC	high performance liquid chromatography
IC	ion chromatography
IDA	iminodiacetic acid
LMWA	low-molecular-weight acid
MS	mass spectrometry
MSD	mass selective detector
NED3A	n-nitrosoethylenediaminetriacetic acid
NIDA	nitrosoiminodiacetic acid
NTA	nitrilotriacetic acid
NPH	normal paraffin hydrocarbon
PHMC	Project Hanford Management Contractor
PFK	perfluorokerosene
PFTBA	perfluorotributylamine
PNNL	Pacific Northwest National Laboratory
SA	succinic acid
S-EDDA	symmetrical ethylenediaminediacetic acid
TIC	total inorganic carbon
TOC	total organic carbon
U-EDDA	unsymmetrical ethylenediaminediacetic acid
UV	ultraviolet

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1.0 Introduction

The Organic Analysis and Methods Development Task is being conducted by Pacific Northwest National Laboratory (PNNL) as part of the Organic Tank Waste Safety Project. The objective of the task is to apply developed analytical methods to identify and/or quantify the amount of particular organic species in tank wastes. In addition, this task provides analytical support for the Gas Generation Studies Task, Waste Aging, and Solubility Studies (Numetec).

Approximately 50 waste samples were analyzed during FY 1997, including samples and duplicates. These samples were analyzed using three separate analytical techniques: derivatization gas chromatography/flame ionization detection (GC/FID), ion-pair chromatography (IPC), and ion chromatography (IC). This sample load represents a significant increase in the number of samples analyzed from previous years. Tanks for which samples were analyzed in FY 1993-1997 are listed below.

<u>Fiscal Year</u>	<u>Samples Analyzed</u>
1993	SY-101 ⁽¹⁾
1994	C-103, SY-101
1995	C-102, C-103, BY-108, SY-103
1996	C-204, C-106, S-102
1997	S-102, AN-107, U-107, U-105, U-106, C-105, BY-104, BY-105, AW-101, BY- 110, U-108, A-102

An additional 50 waste samples were also analyzed in support of Gas Generation and Waste Aging. The results of these analyses have clearly shown that degradation of the organics has occurred. The results have been an integral part of resolving the safety issue.

This report presents the results from analyses of tank waste samples archived at Pacific Northwest National Laboratory (PNNL) and received from the Project Hanford Management Contractor (PHMC), which included samples associated with both the Flammable Gas and Organic Tank Waste Safety Programs. The data are discussed in Section 2.0. In addition, the results of analytical support for analyzing 1) simulated wastes for Waste Aging, 2) tank waste samples for Gas Generation, and 3) simulated wastes associated with solubility studies discussed in Sections 3.0, 4.0, and 5.0, respectively. The latter part of FY 1997 was devoted to documenting the analytical procedures, including derivatization gas chromatography/mass spectrometry (GC/MS) and GC/FID for quantitation, ion-pair chromatography (IPC), IC, and the cation exchange procedure for reducing the radioactivity of samples.

The documentation of analytical procedures is included here and discussed in Section 6.0 and Section 7.0 discusses other analytical procedures. The references are listed in Section 8.0 and future plans are discussed in Section 9.0. Appendix A is a preprint of a manuscript accepted for publication. Appendix B contains the cc mail messages and chain-of-custody forms for the samples received for analyses. Appendix C contains the test plan for analysis of tank waste samples.

(1) The 241-prefix, common to all waste tanks discussed in this report, has been omitted.

Preliminary data are given from an evaluation of alternative methods to analyze chelator and chelator fragments directly, requiring no derivatization before analysis. The method optimization was not directly funded by the Organics Tanks Safety Program; however, the results have important implications for the entire Tank Waste Safety Program.

Additional tank samples need to be analyzed to determine the ruggedness of the analytical methods being used to analyze waste. Although efforts to date have been extremely successful in determining organics present in tank waste, minor adjustments of analytical methods will most likely be required to account for inevitable changes in the sample matrix. Therefore, continuous efforts to improve the robustness of organic-analysis techniques are warranted.

2.0 Results of Tank Waste Analysis

The following portion of the report discusses the results of analyses from samples archived at PNNL and those received during FY 1997. This section provides the preliminary results from IC for low-molecular weight acids (LMWAs), IPC for analyzing chelators and chelator fragments, and GC/MS for analyzing chelators, degradation products, and extractable organic carbon. The preparation and analysis scheme is illustrated in Figure 2.1.

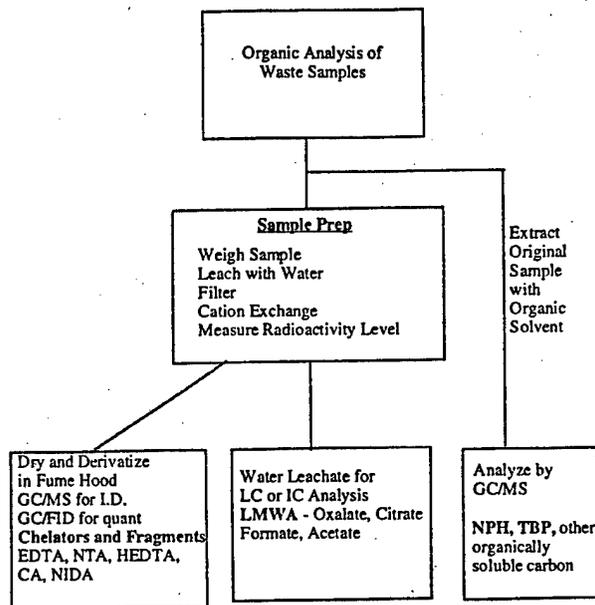


Figure 2.1. Schematic of Sample Preparation and Analyzers

2.1 Archived Samples at PNNL

Five tank waste samples from three different tanks, S-102, U-107, and AN-107, were analyzed for organic content. The S-102 sample was the same one used for Gas Generation Studies. The results from the analyses of LMWAs using IC are shown in Table 2.1. The results are provided in terms of mg analyte per gram sample as received (wet basis) in addition to mg carbon per gram sample as received. Acetate and glycolate co-elute under the conditions used for this analysis and are therefore reported together. Acetate and glycolate could be chromatographically separated using another column, but were not analyzed under these conditions. Figure 2.2 illustrates a typical chromatogram for a waste sample.

Table 2.1. Data of Ion Chromatography Analyses (mg C/g sample) Obtained from Five-Point Calibration Data on Samples from Tanks S-102, U-107, and AN-107

Tank Sample	Acetate/Glycolate	Formate	Oxalate	Citrate
S-102	0.5	0.4	1.2	nd
U-107	1.0	0.7	0.2	0.2
U-107 dup	0.9	0.6	0.1	0.2
AN-107	2.8	1.0	2.9	1.6
AN-107 dup	3.2	1.4	4.7	1.7

nd = not detected: limit of detection is approximately 5 ppm; accounting for dilution limit of detection is approximately 150 ppm

dup = instrumental analysis of second sample, samples were split post cation exchange elution

Table 2.2 lists the results of analyses for chelators and chelator fragments using derivatization GC/FID. The results are presented in terms of mg analyte/g sample as received. Adipic acid was added as an internal standard after elution through the cation exchange resin and prior to GC/FID analysis. The percent recovery yield of this standard for all samples is greater than 89%. A typical GC chromatogram is shown in Figure 2.3. The major components are identified. The component at a retention time of 8.0 min is a contaminant of the derivatization process.

In most cases, the analyte can only be efficiently detected by one of the analysis methods used. However, oxalate and citrate can be quantitated either by derivatization GC/FID or IC. Comparison of the oxalate concentrations shows relatively good agreement.

Table 2.3 compares the concentration of oxalate determined by derivatization GC/FID and IC. Table 2.4 lists the measured total organic carbon (TOC), organic carbon determined by speciation of the LMWA, chelators, total of LMWA and chelators, and the percent of the measured TOC accounted for by speciation. In most cases, 86-100% of the TOC was accounted for by speciation. The one exception is the U-107 duplicate, where only 56% of the TOC was accounted for.

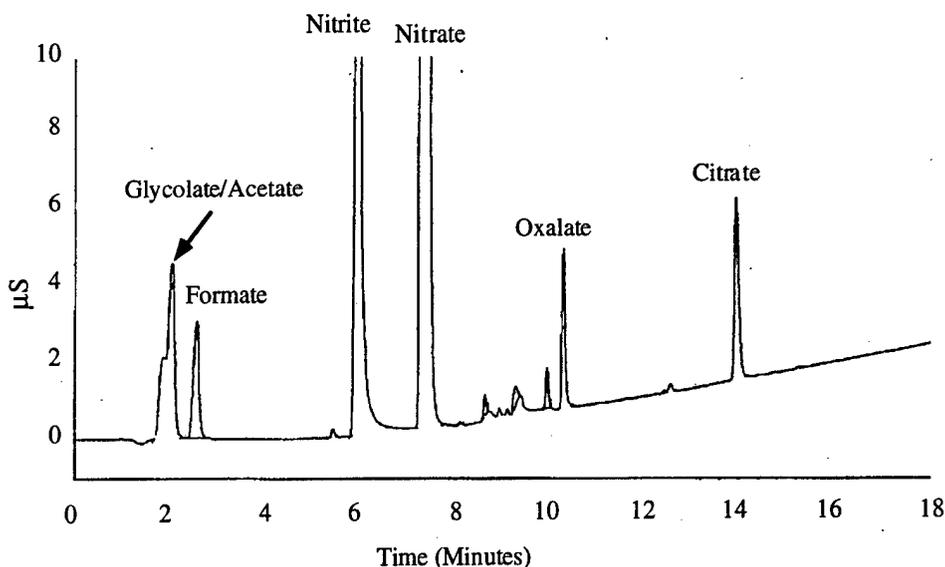


Figure 2.2. IC Chromatogram of AN-107 Sample

Table 2.2. Derivatization GC/FID Results (mg C/g of sample as received) of PNNL-Archived Samples and S-102 Sample Used for Gas Generation and Recovery Yield of the Internal Standard

Tank Sample	SA	NIDA	CA	NTA	EDTA	ED3A	HEDTA	AA Yield ^(a)
AN-107	0.02	1.20	1.95	0.15	0.89	1.08	0.18	91.56
AN-107 dup	0.02	1.25	2.26	0.12	0.75	1.33	0.20	94.95
S-102	0.17	nd	0.21	nd	nd	nd	nd	98.22
U-107	0.02	0.22	0.10	0.04	nd	0.03	nd	91.72
U-107 dup	0.02	0.29	0.22	0.04	nd	nd	nd	89.50

SA succinic acid
 NIDA N-nitrosoiminodiacetic acid
 CA citric acid
 NTA nitrilotriacetic acid
 EDTA ethylenediaminetetraacetic acid
 ED3A ethylenediaminetriacetic acid
 HEDTA N-(2-hydroxyethyl)ethylenediaminetriacetic acid

(a) Recovery yield for internal standard in % yield, adipic acid (AA)

nd = not detected: detection limits approximately 20 ppm, including dilution factors detection limit is approximately 150 ppm

dup = not actual sample duplicate, split after elution through cation exchange resin

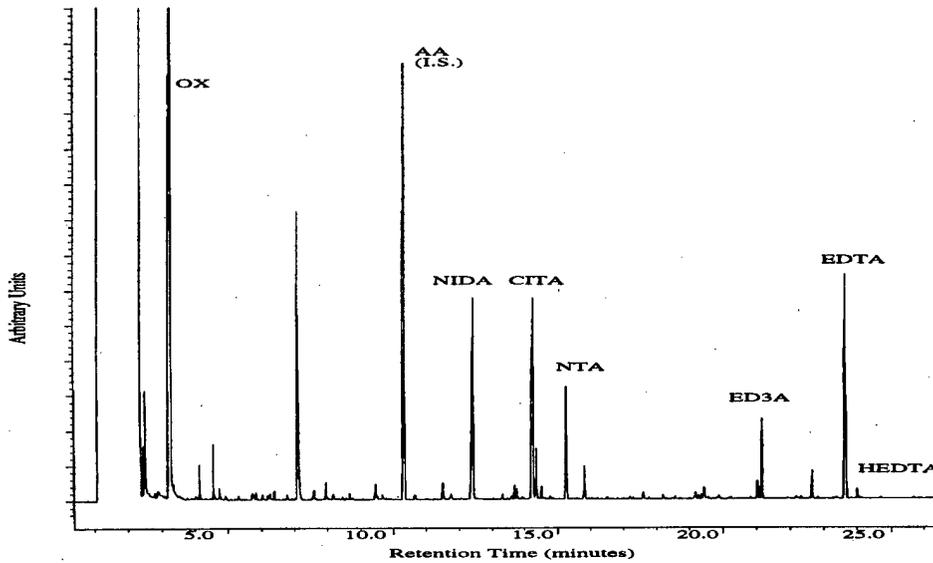


Figure 2.3. GC Chromatogram of U-106 Sample

Table 2.3. Comparison of Oxalate Concentrations

<u>Tank Sample</u>	<u>Oxalate Carbon by BF₃</u> (mg/g)	<u>Oxalate Carbon by IC^(a)</u> (mg/g)
AN-107 1	2.49	2.9
AN-107 1 dup	2.74	
AN-107 2	2.84	4.7
AN-107 2 dup	2.98	
S-102	2.58	1.2
U-107 1	0.17	0.2
U-107 1 dup	0.32	
U-107 2	0.12	0.2
U-107 2 dup	0.12	

Samples 1 and 2 are not sample duplicates. The sample is divided after elution through the cation exchange resin.

The agreement between the IC and derivatization GC/FID results is fairly good. One of the major disadvantages of IC is the dilution factor required because of the high nitrate and nitrite concentrations. This results in a higher degree of variability than is desired. One of the problems associated with derivatization GC/FID is that the recovery is related to the dryness of the sample. The derivatization process is highly affected by the dryness of the sample. In other words, if the sample is wet, one would expect the recovery to be much less than with a truly dry sample.

Table 2.4. Total Organic Carbon Accountability

<u>Tank Sample</u>	<u>TOC^(a)</u>	<u>LMWA^(b)</u>	<u>Chelators</u>	<u>Total</u>	<u>% Accounted^(c)</u>
AN-107	13.8	8.3	3.5	11.8	86
AN-107dup	14.7	11.0	3.7	14.7	100
S-102	2.2	2.10	0.17	2.3	100
U-107	4.4	2.1	0.28	2.4	56
U-107 dup	2.8	2.1	0.31	2.4	86

(a) total organic carbon as determined experimentally (mg C/g sample)

(b) mg C/g as determined by speciation

(c) total accounted for by speciation/TOC

2.2. Samples Received from PHMC

The samples analyzed in FY 1997 and their designations are listed below.

BY-106 c65 seg 13 (BY-106)	BY-104 c116 seg 2A (BY-104),	A-102 Auger (A-102)
AW-101 c139 (AW-101)	U-106 c148 seg 2 (U-106 s)	U-105 c136 seg 7 (U-105)
U-108 c141 seg 4 (U-108)	U-102 c144 seg 6 (U-102)	C-105 c76 seg 1 (C-105)
BY-105 c108 seg 1 (BY-105)	U-106 c148 seg 2 (U-106 l)	U-105 grab (U-105 grab)

The letter c is the core number and seg is the segment designation. Samples C-105, BY-105, U-106, and U-105 grab were liquid samples; the rest of the samples were solids. A list of jar numbers and sample identification numbers is shown in Table 2.5. A copy of the chain of custody and original sample list from Dan Reynolds are included in Appendix B. The samples were analyzed according to the test plan included in Appendix C.

Table 2.5. Samples Shipped to PNNL Including I.D. Numbers

<u>Tank</u>	<u>Jar/Vial #</u>	<u>Core</u>	<u>Seg</u>	<u>Sample I.D.</u>
BY-105	8394	108	1	S96M000118
BY-104	8410	116	2A	S96m000127
BY-106	6402	65	13	S96M000142
C-105	6744	76	1	S96M000122
A-102	7215	Auger		S96M000143
U-102	10042	144	6	S96M000155
U-106	10053	148	2	S96M000123
U-106	10063	148	2	S96M000145
AW-101	10213	139	21	S96M000146
U-108	9454	141	4	S96M000147
U-105	9477	136	7	S96M000148
U-105	7475	Grab		S96M000160

Table 2.6 lists the measurements of TOC both before and after cation exchange for radioactivity reduction. The results represent the average of two determinations. A negative percent difference indicates the loss of organic carbon, and a positive difference indicates an introduction of organic carbon. Typical percent differences in TOC measurements are in the range of 10-20% (Campbell et al. 1996). The results clearly indicate that for two samples, Tanks BY-104 and U-105, a significant portion of the organic carbon is adsorbed onto the cation exchange column. Further studies are underway to understand this phenomenon. Table 2.7 shows the average of duplicate analyses using IC of the tank samples received by PNNL in FY 1997.

Table 2.6. Measurement of TOC Before and After Cation Exchange (mg C/g sample)

<u>Sample</u>	<u>TOC Before</u>	<u>TOC After</u>	<u>% Difference</u>
BY-106	0.19	0.22	+12
BY-104	10.4	6.6	-37
A-102 Auger	8.9	8.0	-4
AW-101	7.8	6.7	-16
U-106 s	22.0	18.9	-14
U-105	21.1	11.5	-45
U-108	3.4	3.8	+11
U-102	5.1	*	
C-105	3.5	3.1	-10
BY-105 1	1.7	1.3	-2.3
U-106 1	28.2	22.8	-17
U-105 (grab)	12.5	10.5	-16

* not reported due to experimental problem

Table 2.7. Ion Chromatography Results from Received Samples (mg C/g Sample)

<u>Sample ID</u>	<u>Acetate/Glycolate</u>	<u>Formate</u>	<u>Oxalate</u>	<u>Citrate</u>
U-105 grab	2.1	0.9	nd	0.30
U-106 l	4.3	2.0	0.2	2.5
C-105	nd	nd	nd	nd
BY-105 l	0.5	0.1	nd	nd
BY-104	nd	nd	4.2	nd
AW-101	nd	0.10	2.3	nd
BY-106	nd	nd	nd	nd
U-108	0.10	0.1	0.5	nd
A-102	0.4	0.2	4.2	nd
U-106 (s)	2.2	0.7	2.0	1.0
U-105 (s)	1.6	0.9	1.7	1.0
U-102	1.1	0.7	1.6	0.4

Table 2.8 shows the results obtained using IPC in mg C/g sample as received. It should be noted that s-EDDA cannot be analyzed by the presently used method of derivatization GC/FID, but can be analyzed using ion-pair chromatography. Figure 2.4 is a chromatogram of actual waste. The unlabelled peaks are either contaminants or excess Cu present in the mobile phase.

Table 2.8. Ion-Pair Chromatography Results (mg C/g Sample as Received) for EDTA, s-EDDA, and NTA

<u>Tank Sample</u>	<u>EDTA</u>	<u>s-EDDA</u>	<u>NTA</u>
U-105	5.2	0.34	1.05
U-105 dup	5.0	0.31	1.04
U-106 s	10.6	0.68	2.17
U-106 dup	8.77	0.38	1.59
U-106 l	4.16	0.22	0.50
U-106 dup	3.96	0.21	0.51
U-108	1.92	nd	nd
U-108 dup	1.71	nd	nd
A-102 Auger	nd	nd	nd
A-102 Auger dup	nd	nd	nd
BY-106	nd	nd	nd
BY-105 dup	nd	nd	nd
BY-104	nd	nd	nd
BY-104 dup	nd	nd	nd
BY-105	nd	nd	nd
BY-105 dup	nd	nd	nd
U-105 grab	3.17	0.25	nd
U-105 grab dup	3.20	0.26	nd

nd = not detected, limit of detection with dilution factor is approximately 150 ppm

Table 2.9 shows the results of GC/FID analyses of the received samples. Table 2.10 lists the results of analyses of the drainable liquids from U-106, AW-101, U-108, and A-102. Table 2.11 is a summary of the results from the analyses of received samples. The sum of the concentration for LMWA and chelators is also listed. In addition, the total of organic carbon speciated as LMWA and chelators is also shown. The TOC has been experimentally determined. In most cases, the TOC accountability is 80-100%.

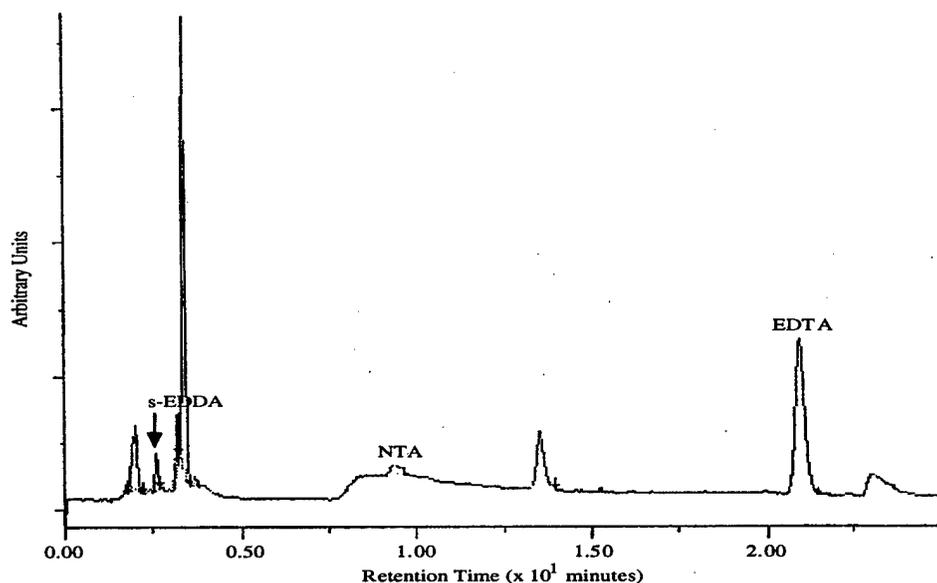


Figure 2.4. Ion Pair Chromatogram of U-106 Sample

Table 2.9. Results of Derivatization GC/FID Analyses of Tank Waste Samples. Concentrations are expressed in mg C/g sample.

Sample Name	OX	SA	NIDA	CA	NTA	ED3A	EDTA	HEDTA	% yield AA
U-108 (s)	1.40	nd	nd	0.11	0.03	nd	nd	nd	97
BY-106	0.08	nd	113						
AW-101	5.80	0.02	nd	0.07	nd	nd	nd	nd	122
U-105 (s)	2.40	0.02	1.40	0.80	0.22	0.61	1.03	2.42	100
U-105 grab	0.31	0.02	1.53	0.90	0.23	0.62	0.86	0.63	116
U-102	2.18	nd	nd	0.43	0.13	0.13	0.24	nd	94
BY-105 (l)	0.04	0.02	nd	nd	nd	nd	nd	nd	100
U-106 (l)	0.30	0.02	2.54	2.53	0.40	1.37	2.16	5.02	114
U-106 (s)	3.92	0.04	1.42	1.33	0.53	0.30	1.23	1.43	114
A-102 Auger	6.91	0.22	nd	0.04	nd	nd	nd	nd	101
BY-104	6.42	0.04	0.02	nd	nd	nd	nd	nd	96
C-105	nd	0.40	nd	nd	nd	nd	nd	nd	96

OX oxalic acid
 SA succinic acid
 AA adipic acid-internal standard
 NIDA nitrosoiminodiacetic acid
 CA citric acid
 NTA nitrilotriacetic acid
 ED3A ethylenediaminetriacetic acid
 EDTA ethylenediaminetetraacetic acid
 HEDTA N-(2-hydroxyethyl)ethylenediaminetriacetic acid
 nd not detected

Table 2.10. Results of Analyses of Centrifuged Liquids (mg C/g sample)

GC file No.	Sample Name	OX	SA	NIDA	CA	NTA	ED3A	EDTA	HEDTA	SUM	% yield
											AA
619-J	U-106-1 CL	0.11	0.02	1.14	0.24	0.19	0.46	0.06	2.06	4.17	97
619-K	U-106-2 CL	0.11	0.02	1.05	0.22	0.19	0.42	0.04	1.78	3.72	91
619-L	AW-101-1 CL	0.40	0.04	nd	0.15	0.02	nd	nd	nd	0.21	106
619-M	AW-101-2 CL	0.39	0.04	nd	0.17	0.02	nd	nd	nd	0.23	112
619-N	U-108-1 CL	0.09	0.02	0.48	0.07	0.04	0.09	nd	nd	0.70	88
619-P	U-108-2 CL	0.09	0.03	0.63	0.18	0.06	0.16	0.05	nd	1.11	100
619-Q	A-102-1 CL	0.21	0.05	0.08	0.09	0.01	nd	nd	nd	0.23	111
619-R	A-102-2 CL	0.24	0.06	0.08	0.11	0.01	nd	nd	nd	0.26	97

Table 2.11. Summary of Data from Analysis of Tank Waste Sample and Amount of TOC (mg C/g sample) Accounted for by Speciation

	LMWA	Chelators	TOC	Total
U-105 grab	4.2	3.8	10.5	8.0
U-106 (s)	8.1	5.8	17.9	13.9
C-105	bdl	0.04	bdl	0.04
BY-105	0.6	0.02	1.2	0.6
BY-104	6.4	0.06	6.6	6.4
AW-101	5.8	0.17	6.7	5.9
BY-106	0.1	bdl	0.20	0.1
U-108	1.6	0.11	3.3	1.7
A-102 Auger	7.3	0.06	8.0	7.4
U-106 (l)	9.0	12.0	22.9	21.0
U-105 (s)	5.9	5.3	11.5	11.2
U-102	4.4	0.4	5.1	4.8

Qualitative data for the organically-soluble carbon in samples AN-107, U-107, U-105 c136, C-105 c76, U-106 c148, and U-102 c144 are given below:

AN-107	Negligible organic extractables
U-107	Negligible organic extractables
U-105 c136	Traces of normal paraffin hydrocarbon (NPH)-type hydrocarbons, Unknown Material with ions 204, 220.
C-105 c76	Significant tributyl phosphate, butyl dioctylphosphate
U106 c148	Traces hydrocarbon, Unknown material with ions 204, 220
U102 c144	Unknown material with ions 204, 220.

A "significant" amount generally means that >250,000 height counts were observed from a 1-microliter injection of concentrated extractant (200-microliter total) obtained from 1.0 to 1.5 grams of actual tank wastes. The materials were diluted with aqueous media and partitioned with methylene chloride; the extractables were further dried and concentrated to 200 microliters for analysis. Quantitation and possible further characterization are to be done as soon as possible. Samples were generally done in duplicate.

We suspect that the 204, 220 ions (modest amounts per sample, not in every sample) might be a plasticizer from flexible tubings used for blow-down during sample preparation. This substance is

not evenly distributed in all samples, however. Samples U-105 and U-106 contain only a trace of NPH-related materials.

The amount of TBP in C-105 is significant enough to warrant quantification and further examination. Tank C-105 has not afforded evidence of chelators or LMWA materials. The presence of butyl dioctylphosphate (BOOP) in this sample suggests that there might also be D2EHP in this sample; further derivatization with diazomethane is contemplated.

Table 2.12 lists the amount of drainable liquids obtained by centrifuging approximately 10 g of the solid sample. Table 2.13 lists the percent solids for several of the samples. This is obtained by heating a weighed-sample to approximately 110°C for approximately 6 hours.. All of the weight loss is presumed to be attributable to the loss of water.

Table 2.12. Volume of Liquid Obtained Using Centrifugation

<u>Sample I.D.</u>	<u>Volume (mL)</u>
U-105 grab	0.5
BY-105	1.0
A-102 Auger	5.0
U-105	3.0
U-106	1.5
AW-101	1.5

Table 2.13 Percent Solids

<u>Sample I.D.</u>	<u>% Solids</u>
U-105 grab	72.07
U-105 grab dup	72.18
BY-105	66.32
BY-105 dup	66.96

3.0 Gas Generation Studies

Waste samples have been analyzed for the Flammable Gas Generation Task. A composite sample (Bryan et al. 1996) from the convective layer of Tank SY-103 was heated to 60, 75, 90, 105, and 120°C for 800 hours. Those samples were analyzed and reported (Campbell et al. 1996).

The samples were then subjected to gamma radiation and heat at the five temperatures above and submitted for analysis. The analytical results for the original SY-103 sample are shown in Table 3.1 (Campbell et al. 1996) for comparison. Tables 3.2 and 3.3 are the results from IC and ion-pair chromatography, respectively. Samples were heated to 200° and 450° C and the results are included. The results at 450° C indicate the destruction of the organic constituents. Table 3.4 lists the results of derivatization GC/FID analysis of the heated and irradiated samples.

Table 3.1. Summary of Analyses of Samples from Tanks SY-101 and SY-103 (mg C/g Sample)

Analyte	SY-101 Convective	SY-103 Convective	SY-101 Nonconvective	SY-103 Nonconvective
NIDA	1.04	0.20	0.82	0.16
NTA	0.33	0.14	0.22	0.16
CA	0.32	0.42	0.31	0.56
ED3A	0.30	0.25	0.28	0.16
EDTA	2.23	0.55	0.80	0.65
HEDTA	nd	0.03	nd	nd
SA	0.07	0.02	0.05	0.02
Oxalate	1.9	nd	5.7	6.0
Glycolate	0.48	tbd	nd	tbd
Formate	1.4	1.2	0.62	0.9
Acetate	0.81	0.6	nd	0.7
NPH ^(a)	800		20	
OH		28600 ^(b)		15000 ^(c)

(a) ppm
 (b) µg/mL
 (c) µg/g
 nd not detected

Table 3.2 IC Results (mg C/g sample) of Gas Generation Studies on Heated and Irradiated Samples from Tank SY-103

Sample	Acetate/Glycolate	Formate	Oxalate	Citrate
33°	1.42	1.84	nd	nd
60°	1.73	2.13	1.08	nd
60 Dup	1.50	1.81	nd	nd
75°	1.64	2.05	1.37	0.86
75° Dup	1.46	2.28	0.62	nd
90°	1.56	2.07	nd	nd
105°	1.27	2.07	nd	nd
120°	1.10	2.43	0.45	nd
Heated to 200°	1.81	2.58	1.83	nd
Heated to 450°	nd	nd	nd	nd

Table 3.3 Ion-Pair Chromatography ($\mu\text{g C/g}$ sample) Results Heated and Irradiated of Tank SY-103 Sample

<u>Sample</u>	<u>EDTA</u>	<u>s-EDDA</u>	<u>u-EDDA</u>	<u>ED3A</u>	<u>NTA</u>
33°	40	26.6	37.4	37.6	258
60°	404	26.0	27.1	12.3	236
60°Dup	467	9.00	37.5	18.8	289
60° Dup-1	727	nd	68.4	nd	73.5
75°	353	8.50	26.6	29.2	187
75° Dup	570	29.0	32.2	27.9	273
90°	470	13.6	nd	nd	267
105°	462	22.3	16.8	13.8	264
120°	342	nd	19.9	24.0	194
200°	492	nd	nd	nd	357
450°	nd	nd	nd	nd	44.0

Table 3.4. Results of GC/FID Analyses ($\mu\text{g C/g}$ sample as received) of Tank SY-103 (Heated and Irradiated) Sample for Gas Generation Studies

<u>Sample</u>	<u>Oxalic</u>	<u>Succinic</u>	<u>% Adipic yield</u>	<u>NIDA</u>	<u>Citric</u>	<u>NTA</u>	<u>ED3A*</u>	<u>EDTA</u>	<u>Total $\mu\text{g/g}$ carbon</u>
33°C	113	15	98	469	409	100	134	133	1374
Dup	119	19	104	514	504	108	184	144	1592
60°C	131	20	111	573	394	116	197	175	1605
Dup	547	17	96	339	279	111	115	97	1504
60°C	664	28	100	323	376	118	161	155	1796
Dup	135	22	105	553	299	114	143	117	1382
75°C	188	8	92	372	287	101	145	116	1217
Dup	117	16	98	505	443	119	156	145	1502
75°C	291	13	99	473	384	117	97	144	1519
Dup	210	10	99	420	359	115	179	144	1436
90°C	161	nd	99	484	433	130	148	159	1515
105°C	112	16	97	450	191	110	126	89	1093
Dup	121	19	104	494	199	109	166	119	1227
120°C	96	32	92	216	25	82	110	73	633
Dup	96	34	101	209	33	94	99	105	670

Table 3.5 lists the results of analyses from the original or untreated Tank S-102 samples (Campbell et al. 1996.). Table 3.6 lists the IC results of the heated samples, and Table 3.7 lists the results of the heated and irradiated samples from Tank S-102, respectively. The only component detected by GC/FID was oxalate. Table 3.8 lists the GC/FID results of the heated samples, and Table 3.9 shows the results of GC/FID analyses of the heated and irradiated samples. The designations A and B refer to independent sample duplicates.

Table 3.5. Concentrations ($\mu\text{g C/g}$ sample) of Analytes in Original S-102 Sample

<u>Analyte</u>	<u>Concentration</u>
EDTA	<10
ED3A	<10
citric acid	160
palmitic acid	80
NTA	10
oxalic acid	2300
succinic acid	20
sulfur	450
stearic acid	50
N-butylbenzenesulfonamide	140

Table 3.6. Results of IC Analyses of the Heated Samples from Tank S-102

<u>Sample ID</u>	<u>Oxalate Organic Carbon (mg/mL)</u>	<u>Glycolic Acid Organic Carbon (mg/mL)</u>	<u>Total Organic Carbon (mg/mL)</u>
60° A	1.772	0.3682	2.1401
80° A	1.345	0.2384	1.5834
100° A	4.424	0.3464	4.7704
100°	1.306	0.2599	1.5662
120° A	4.508	0.4298	4.9382
120°	1.313	0.3145	1.6276

The designations A and B refer to independent sample duplicates.

Table 3.7. Results of IC Analyses of Heated and Irradiated Samples from Tank S-102. Concentrations are mg C/g sample.

<u>Sample ID</u>	<u>Oxalate</u>	<u>Glycolic Acid</u>	<u>Total</u>
60° A	2.055	0.3911	2.4459
60° B	2.399	0.3262	2.7253
60° B dup	2.094	0.4122	2.5063
80° A	2.578	0.3898	2.9679
80° B	2.825	0.4924	3.3178
80° B dup	2.437	0.3345	2.7719
100° A	1.578	0.4374	2.0157
100° B	2.040	0.4083	2.4485
120° A	1.476	0.5107	1.9865
120° B	1.999	0.5633	2.5620

The designations A and B refer to independent sample duplicates.

Table 3.8. Results of GC/FID Analyses of Heated Samples from Tank S-102

<u>Sample Number</u>	<u>Int. Std Adip</u>	<u>Ox quant (mg c/g sample)</u>
60° A	1140322	2.68
60° A dup	1123976	2.57
60° B	1118380	2.48
60° B dup	1219508	2.62
80° A	1057412	1.68
80° A dup	1069844	1.60
80° B	1201640	3.29
80° B dup	1108796	3.18
100° A	1200344	6.44
100° A dup	115938	5.86
100° B	1138573	1.81
100° B dup	1040006	1.68
120° A	1129604	5.95
120° A dup	1165824	6.37
120° B	1044206	1.67
120° B dup	1055063	1.57

The A and B designations refer to independent sample duplicates. The term dup refers to duplicate analysis.

The following discussion is related to the original SY-103 concentrations and the heated-irradiated sample. No comparisons are available for the heated and the heated-irradiated samples. When the heated samples were analyzed, the methods for analysis were not yet optimized. In comparing the results of the concentrations of the original tank sample vs. the heated-irradiated sample, several trends are observed. For example, the concentration of acetate/glycolate appears to be increasing as the temperature was increased for these samples (Figure 3.1). The first data point at 20°C represents the concentration in the original tank sample. The same trend is observed with formate. In contrast, the concentration of EDTA appears to be decreasing. A similar trend is observed for citric acid (Figure 3.2). The concentration of oxalate, however, remains fairly constant (Figure 3.3). These observations are consistent with the results observed by Camaioni (1998). In aging experiments (heated-irradiated), similar trends were observed. The radiation dose in the two experiments, gas generation and aging, were not equivalent. The dose rate was higher in the aging experiments. As a result, the relative amount of decrease or increase was slightly higher in the aging experiments. In other words, the trends were more defined in the aging experiments.

Table 3.9. Results of GC/FID Analyses of Heated and Irradiated Samples from Tank S-102

<u>Sample ID</u>	<u>Int. Std. Adipic (Peak Area)</u>	<u>Oxalate (mg C/g)</u>
60° A	912741	2.20
60° A dup	1256181	2.32
60° B	897670	2.41
60° B dup	1271370	3.15
60° B -1	923111	2.49
60° B-1 dup	1234121	3.21
80° A	885343	2.90
80° A dup	1231829	3.48
80° A-1	1309350	3.77
80° A-1 dup	1258659	3.94
80° B	863443	3.06
80° B dup	1271007	3.82
80° B-1	1325146	4.48
80° B-1 dup	1278767	3.89
100°A	903003	1.52
100° A dup	1269368	2.48
100° A-1	1338170	2.34
100° B	918968	2.99
100° B dup	1226563	2.88
100° B -1	1328740	3.01
100° B-1 dup	1346355	3.11
120° A	901211	1.50
120° A dup	1227551	2.03
120° A-1	1334472	1.91
120° A-1 dup	1359707	2.06
120° B	952774	2.15
120° B dup	1141699	2.53
120° B-1	1357543	3.11
120° B-1 dup	1342385	3.04

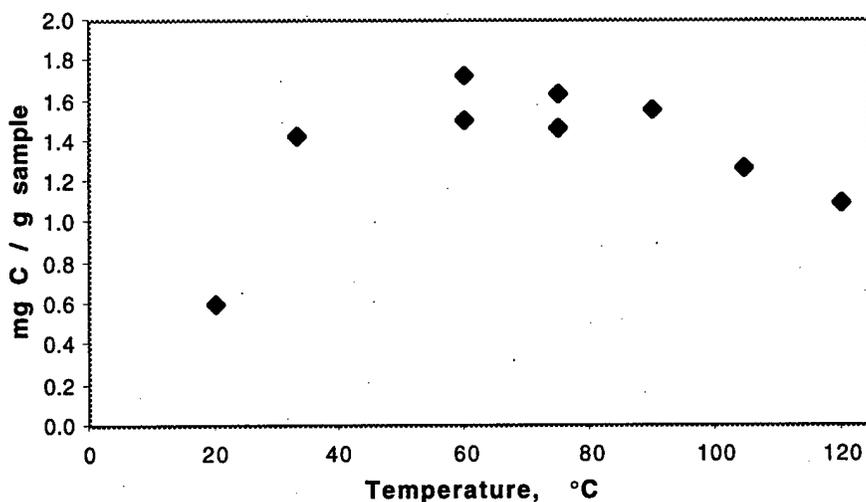


Figure 3.1. Results of IC Analyses for Acetate/Glycolate of Heated-Irradiated SY-103 Samples

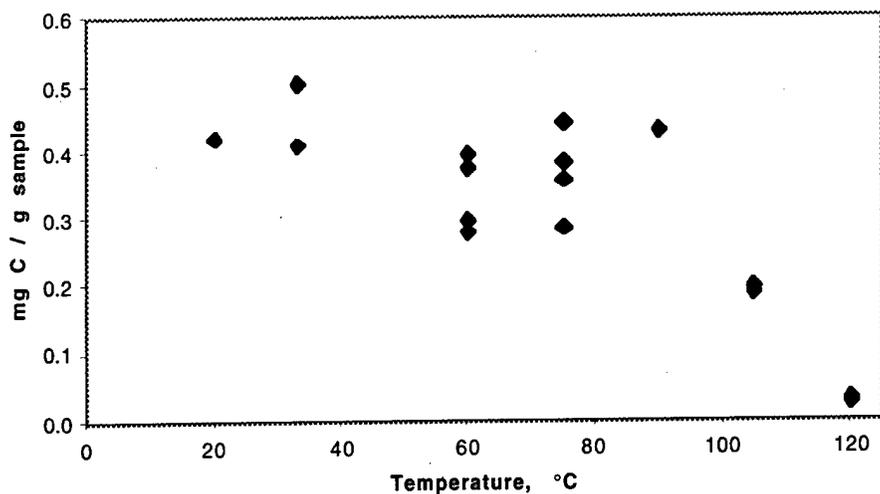


Figure 3.2. GC/FID Results for Citric Acid

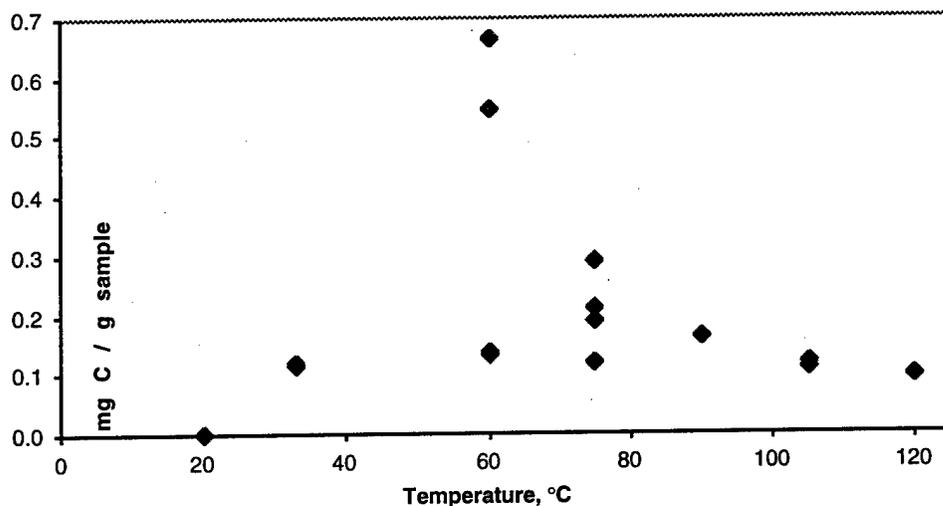


Figure 3.3. Results for Oxalic Acid by GC/FID

It should be noted that the gas generation results (Bryan et al. 1997, King et al. 1997) show that more gas was generated for the SY-103 samples than the S-102 samples. This observation is supported by the analysis of the heated-irradiated samples. The oxalate concentration and relative percentage of TOC made up of oxalate are higher in S-102 than in SY-103. The fraction of TOC consisting of C-H and N-H containing chelates and chelate fragments is higher in SY-103 than S-102, leading to a higher observed hydrogen generation rate in SY-103.

The major constituent detected in S-102 samples was oxalate. There was no difference in the

oxalate concentrations in the heated samples and the heated-irradiated samples (Figures 3.4-3.5). This is also true for glycolic acid (Figures 3.6-3.7). As a result of these observations, it is recommended that before organic speciation of heated and heated and irradiated samples for gas generation, the TOC and oxalate concentrations should be determined. This would eliminate analyses that provide no additional information regarding gas generation.

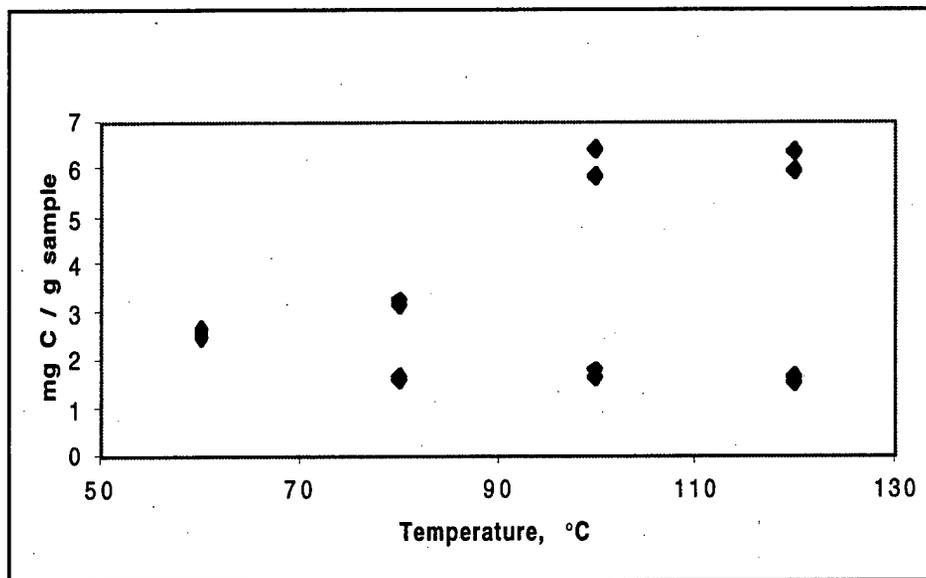


Figure 3.4. Results of GC/FID Analyses for Oxalate in Heated Samples from S-102

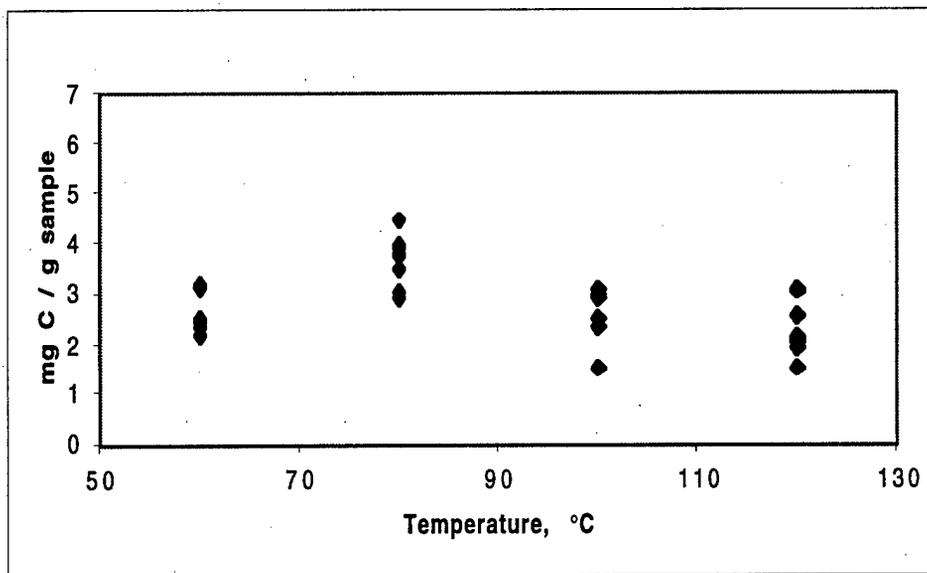


Figure 3.5. Results of GC/FID Analyses of Oxalate in Heated-Irradiated Samples of S-102

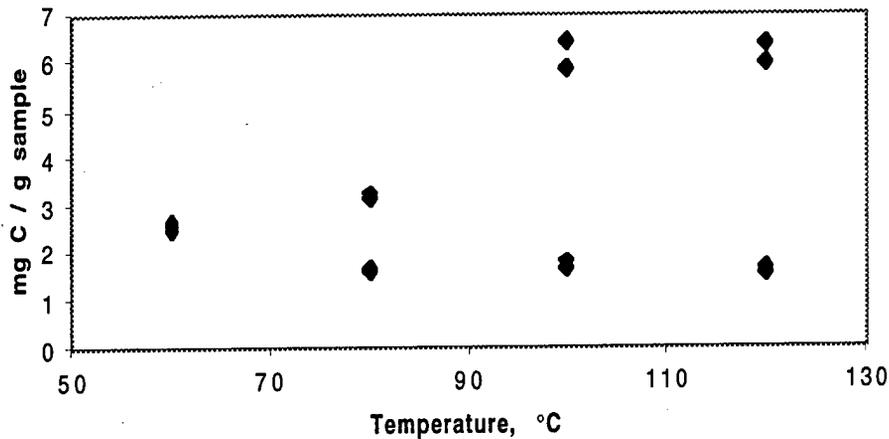


Figure 3.6. Results of IC Analyses for Glycolate in Heated Samples of S-102

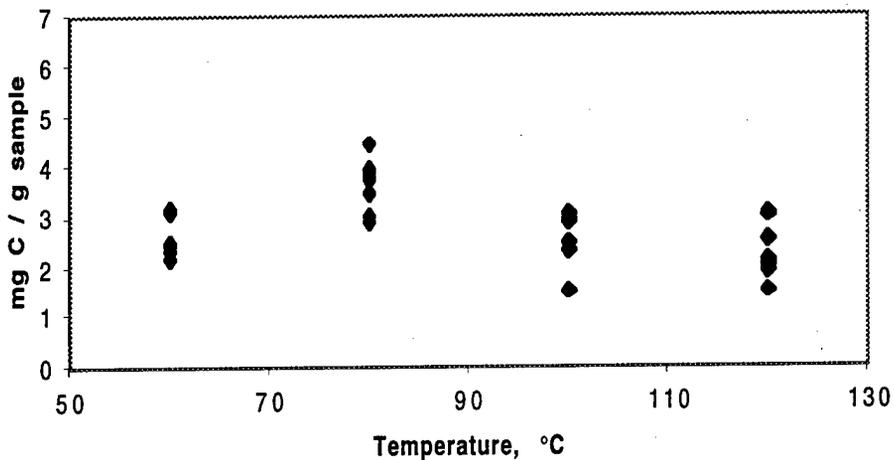


Figure 3.7. Results of IC Analyses for Glycolate in Heated-Irradiated Samples of S-102

Preliminary organic analysis of AW-101 waste (solids) indicates less than 30% is composed of oxalate. We have shown that corresponding liquid will have less oxalate present. As a result of these analyses, it is also recommended that heated and heated-irradiated samples of AW-101 liquid be analyzed for the organic constituent analysis and the relationship of the organic constituents to gas generation. Preliminary oxalate and TOC determinations indicate these samples may provide an insight into gas generation. In addition, if sufficient sample is available, the heated samples related to SY-103 should be reanalyzed.

4.0 Analysis of Organic Acids and Chelators in Tank Waste Simulants for Waste Aging Studies

The focus of the FY 1997 tank aging study was to try to decouple the thermal effects from radiolysis using simulated wastes. Several samples were run at elevated temperatures for varied lengths of time without gamma irradiation. Additionally, samples were also run in radiolytic conditions at lower and higher temperatures than those expected in the tank. We are still gathering the data using IC to characterize LMWA and IPC for analyzing chelators (EDTA and HEDTA). During the course of analysis, some questions were raised that Fe (III) may be interfering with EDTA analysis. It was believed that Fe (III) may compete with Cu (II) to complex with EDTA during sample preparation {Cu (II) being one of the ion-pair reagent} and may lead to lower values of EDTA concentration than the actual amount present. To address this question, we prepared four solutions of EDTA in the equimolar presence of Fe (III) at pH 4.00 {no Fe (III), 1 mM EDTA}, pH 11.00 {1 mM EDTA, 1 mM Fe (III)}, pH 13.02 {1 mM EDTA, 1 mM Fe (III)}, pH 7.69 {1 mM EDTA, 1 mM Fe (III)}. We found from this study that the Fe (III) falls out (as hydrated iron oxide) of the solution when the pH is raised to 13.00. We were able to recover over 95% of EDTA by using Cu as the complexing agent in the presence of Fe (III) in solution with pH 13.02. Therefore, the presence of iron in the simulated waste would not interfere with EDTA and HEDTA quantification because the pH of the simulated waste is 13.27.

The effect of the presence and absence of O₂ was also studied during the FY 1997 waste aging study. We have analyzed the samples that were irradiated in an argon atmosphere. We are currently interpreting the data collected from the analysis of LMWA and the chelators. It appears that the destruction pathway in the presence of argon (absence of O₂) is significantly different for EDTA and HEDTA. Similarly, the destruction pathway in thermal conditions vs radiolytic conditions does not appear to be the same. Approximately 30 samples have been analyzed.

The data obtained in this task have been reported in the Waste Aging Studies 1997 report (Camaioni et al. 1997).

5.0 Organic Solubilities in a Complex Tank Waste Simulant

The results discussed here were in support of the Solubility Studies (Scott Barney, Numetec) and reported by Barney (Barney 1997). Most of the organic solubility measurement data for this project have been obtained using a simplified waste simulant consisting of an aqueous solution of sodium nitrate, nitrite, and hydroxide in equilibrium with a single solid organic salt (and sometimes with crystalline sodium nitrate). Actual waste mixtures are, of course, more complex and contain other sodium salts, metal hydrous oxides, mixtures of organic salts, and other components. To determine the effects of these additional components on the solubilities of four important organic salts, two complex mixtures were prepared containing 17 components known to exist in the wastes. These components are given in Table 5.1. Most of the components are present in excess of their solubilities, so that the actual concentrations were less than those shown. Only sodium nitrite and sodium hydroxide were unsaturated. Several of the metal nitrates reacted with sodium hydroxide to produce a hydrous oxide precipitate that simulates the presence of sludge waste. Nickel and calcium were likely complexed with the high concentrations of EDTA or NTA present. The solubilities of sodium EDTA, citrate, glycolate, and NTA were measured at about 0.3 and 6.0 M NaOH in these mixtures. In addition, equilibrium concentrations of nitrate and nitrite were determined in this complex matrix.

Table 5.1. Components of Simulated Complex Waste Mixtures

Saturated Components	Final Molarity if Totally Dissolved
Na ₄ EDTA	0.4
Na ₃ Citrate	0.4
NaGlycolate	2.5
Na ₃ NTA	0.6
NaNO ₃	3
Na ₂ CO ₃	0.3
Na ₂ SO ₄	0.05
Na ₃ PO ₄	0.1
Al(NO ₃) ₃	nd
Fe(NO ₃) ₃	nd
Cr(NO ₃) ₃	nd
Bi(NO ₃) ₃	nd
Ca(NO ₃) ₂	nd
Ni(NO ₃) ₂	nd
ZrO(NO ₃) ₂	nd
Unsaturated Components	
NaNO ₂	1.0
NaOH	0.1 and 2.0

nd - not determined

The equilibrium concentrations of dissolved components in the aqueous phase are shown in Table 5.2. The solubilities of the organic salts are lower than those measured in simpler systems. This can be explained by the higher sodium concentrations and the higher sodium hydroxide concentrations in these complex mixtures. The complex waste solutions have sodium ion concentrations 3.4 to 7.0 molar higher than previous solution matrices. This causes a significant lowering of the solubilities of the organic sodium salts due to the common ion effect of sodium.

Table 5.2. Equilibrium Concentrations (Molarity) of Complex Waste Mixture Components

Component	40 °C		50 °C	
	0.1 M NaOH	2.0 M NaOH	0.1 M NaOH	2.0 M NaOH
Na ₄ EDTA	0.52	0.36	0.54	0.38
Na ₃ Citrate	0.19	0.15	0.17	0.15
NaGlycolate	2.26	2.53	1.97	2.34
Na ₃ NTA	0.32	0.08	0.33	0.06
NaNO ₃	3.03	3.47	2.53	3.20
NaNO ₂	3.03	3.08	2.58	2.91
NaOH	0.30	6.10	0.26	5.72

6.0 DRAFT OF DOCUMENTED PROCEDURES

The procedures discussed in this section are draft procedures applied to sample analyses prior to the HASQARD assessment and review by the client quality engineer and project manager.

6.1 Mixed Hazardous Waste Samples by Derivatization GC or GC-MS: Determination of Chelators and Their Degradation Products in Tank Wastes

1.0 Scope And Application

- 1.1 This method describes the analysis of chelators and their degradation products in mixed hazardous waste samples by derivatization gas chromatography-mass spectrometry (GC-MS) (Grant et al. 1995) or by GC-FID. Examples of chelators and their degradation products that can be analyzed by this method include but are not limited to ethylenediaminetetraacetic acid (EDTA), N-(2-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA), ethylenediaminetriacetic acid (ED3A), nitriloacetic acid (NTA), citric acid, oxalic acid, and succinic acid.
- 1.2 The method is applicable to wastes with radioactivity levels ranging from none to high. Ordinarily, samples are pre-treated in a hot-cell facility to reduce radioactivity levels to those that can be manually handled in a contamination area fume hood. This method is only applicable to use by experienced technical personnel under the supervision of qualified scientists.

2.0 Summary of Method

The waste samples are ordinarily subjected to ion exchange to reduce radioactivity levels (See method "Activity Reduction via Cation Exchange for Carboxylate Analysis"), and known aliquots are taken to complete dryness. Presumably, the only organic species applicable to this method will be water soluble carbon compounds (carboxylates). The extract is derivatized with BF_3 /methanol (MeOH) to form methyl esters of carboxylic acids. The derivatized extract is monitored for radioactivity and then analyzed by GC using Flame Ionization Detection (GC-FID); GC-MS, using electron impact mode; or GC-MS using chemical ionization, which may be useful to confirm identifications. In current use, most waste components (Citric acid, NTA, EDTA, HEDTA) are so well defined that confirmation amounts to GC retention time/FID analysis; confirmation may be required in certain instances by GC/MS.

3.0 Interferences

- 3.1 This derivatization procedure will methylate carboxylic acids, but substituent groups in certain organic analytes do not afford full derivatization. Quantitative data for HEDTA, for example, should be interpreted with caution because the HEDTA response apparently represents the lactone form and not the free hydroxy species. This effect is currently under investigation. Most carboxylates and chelators do not suffer from these irregularities and afford apparent quantitative results, if carefully quenched and extracted from the media.
- 3.2 Iminodiacetic acid (IDA), ethylenediaminetriacetic acid (ED3A), and other species containing secondary amines afford appreciable secondary derivatization in waste matrices containing nitrites. These materials may produce, as an unavoidable artifact

of the method, N-nitroso compounds such as N-nitrosoiminodiacetic acid (NIDA) or N-nitroso ED3A. These materials in the final analyte are likely byproducts from the analytical conditions, and should probably be reported as the parent molecules IDA and ED3A.

- 3.3 This procedure is not reproducible for the derivatization of the symmetrical ethylenediaminediacetic acid.
- 3.4 The product methyl ester of iminodiacetic acid (IDA) easily decomposes if the extraction solution has a pH < 7. A similar fate apparently exists for the lactone of methylated HEDTA. Both of these species must be quantitated with carefully controlled, slightly basic (pH 7.5) conditions. Multiple samples should be considered if quantitative data for IDA- or HEDTA-related analytes are to be determined. The quenching solution utilized is pH 9 to 9.5 and used in a titrating amount *versus* BF₃ • methanol so that the final extraction medium is at pH 7 to 7.5.

4.0 Safety

Gloves and protective clothing should be worn to protect against unnecessary exposure to organic solvents and contaminants. When handling radioactive samples, all applicable radiochemical handling procedures and health physics monitoring practices should be followed.

Boron trifluoride reagents and the hydrofluoric acid hydrolysis product from its use are toxic and cause irreversible injury to tissue and bone. Gloves are necessary when using these reagents. Calcium gluconate gels are often prescribed as relief for skin exposures from these materials; ordinarily the affected area is quickly washed with water, and calcium gluconate gel is applied for 30 minutes to the area contacted by hydrofluoric acid. Often there are no immediate symptoms from contact with these materials.

5.0 Apparatus And Equipment

- 5.1 Gas chromatograph/Mass Spectrometer: Hewlett Packard 5988A gas chromatograph/mass spectrometer (or equivalent) with electron impact (EI) and chemical ionization (CI) capabilities.
- 5.2 Gas Chromatograph: Hewlett Packard 5980 (or equivalent) must be capable of splitless injection. Flame ionization detector (Hewlett Packard Co.) equipped with helium make-up gas, hydrogen generator, and high purity compressed air source.
 - 5.2.1 Fused silica capillary column: DB-5, 30m x 0.25 mm i.d., 0.25 mm phase thickness (or equivalent column)
- 5.3 Vortex mixer to stir solutions
- 5.4 Reactival heating block
- 5.5 Reactivals (Pierce Chemical Co. or equivalent)
- 5.6 pH meter with pH probe covering the pH range of at least 2 to 12

- 5.7 Disposable 40 mL shell vials, teflon-lined closures., 7-mL shell vials, teflon-lined closures, GC autosample vials, 2-mL volume.
- 5.8 Calibrated Eppendorf pipettes; 1 mL, 100 microliter.
- 5.9 Balance for sample weighing from mg to g capacity

6.0 Reagents

- 6.1 Reagent Water: deionized water polished with an organic removal cartridge to meet ASTM 1193 Type II water standard for low organic content.
- 6.2 Boron Trifluoride/methanol: 12% w/v for sample derivatization (Aldrich Chemical Co. or equivalent)
- 6.3 Standards: EDTA, HEDTA, NTA, ED3A, IDA, NIDA, citric acid, succinic acid, and oxalic acid.
- 6.4 Hydrochloric Acid: reagent grade, 12M.
- 6.5 Preparation of Calibration Standards: A stock solution is prepared containing a known amount (~5 mg/mL) in 0.1 M NaOH of the chelators that are expected in the sample, e.g., succinic acid, IDA, NIDA, citric acid, NTA, EDTA, and HEDTA. Concentrations of chelators in the standard solution should be greater than the expected concentrations in the sample solutions. A known aliquot (1 to 3 mL) of standard solution is placed in a 5-mL reactivial, blown to dryness, and derivatized simultaneously with the sample as described in Section 8.1.
- 6.6 Perfluorotributylamine (PFTBA): for MS calibration and instrument performance assessment
- 6.7 Chloroform: reagent grade
- 6.8 Buffer solution of 0.4 M K_2HPO_4 , which has been pH adjusted to 9.0-9.5 with NaOH.
- 6.9 NaOH for pH adjustment; reagent grade, solutions of 6M are convenient.
- 6.10 pH Standards: commercial pH 4, 7, 10 standards; pH paper, 0-14 range; EM ColorpHast (E. Merck) or equivalent.
- 6.11 Helium: 99.9% or better, for GC carrier gas.
- 6.12 Compressed Air: breathing air quality.
- 6.13 Methane and isobutane for CI reagent gases.
- 6.14 Nitrogen: for blow down procedure for solvent evaporation.

- 6.15 Na_2SO_4 : anhydrous: for sample drying
- 6.16 Adipic acid (CAS 124-04-9), derivative yield tracer, Aldrich Chemical Co, 99%.
- 6.17 Ethanol, reagent grade (denatured); free from non-volatile denaturants.

7.0 Sample Collection, Preservation, and Handling

Sample collection, preservation, and handling should be addressed in the planning process.

Of paramount importance to the assay of tank wastes is the record of any substantial volume addition or dilution of the native material taken from the tank. Each operation that adds liquid volume to the retrieved material must be taken into account in the final assay calculation of chelator content as it relates to the tank material. Most of the dilution to the sample will occur in ion exchange treatment (see method "Activity Reduction via Cation Exchange for Carboxylate Analysis").

8.0 Procedure

8.1 Sample Preparation

- 8.1.1 A known aliquot of aqueous sample derived from tank waste (2 to 5 mL) is placed in a 5-mL reactival. The pH of the solution is adjusted to approximately neutral (pH 7) by addition of microliter amounts of 12 M HCl (testing droplets with pH paper). A known aliquot of adipic acid (ca. 200 micrograms) in ethanol solution is added, and the entire sample is evaporated to dryness with a steady stream of dry nitrogen at a temperature not greater than 70°C . To achieve complete dryness, it may be necessary to manipulate the sample, i.e., the vial may be tilted to spread out thickened salts onto the vial wall. None of the target carboxylates are volatile under these conditions; this drying procedure may take 48 hours.
- 8.1.2 After the sample is completely dry, approximately 2 mL of a 12% (w/v) solution of BF_3 in methanol is added to the reactival, and the sample is heated to 100°C for 1 hour.
- 8.1.3 The sample is cooled, and then 2 mL of chloroform is added.
- 8.1.4 The solution is transferred to a test tube containing 15 mL of 0.4 M K_2HPO_4 that had been adjusted to pH 9.0 to 9.5 with NaOH. The goal is to provide an amount of phosphate buffer that will titrate the acid formed from hydrolysis of BF_3 . The analyst can verify the amount of buffer to use by titration of the BF_3 reagent *versus* the buffer beforehand, checking the results with pH paper.
- 8.1.5 The sample is vortexed, and the aqueous and chloroform layers are allowed to separate.
- 8.1.6 The aqueous layer is decanted from the top and discarded (it must be monitored for radioactivity before disposal). The bottom chloroform layer

(~2 mL) contains the derivatized organics for analysis.

- 8.1.7 The volume of the solution should be recorded through the remainder of the sample preparation steps. Quantification is based on the assumption that the chelators are now contained in the 2-mL chloroform layer. Any extra dilutions, concentrations, or filtering that affect this final volume must be taken into account when performing quantitative calculations.
- 8.1.8 About 100 mg to 200 mg of anhydrous Na_2SO_4 is added to collect entrained water. The dried solution should be transferred to a clean microvial, such as that used for GC autosampling.
- 8.1.9 At this point, the chloroform layer should have less than 1% of the radioactivity of the original sample. Dried chloroform will have negligible residual radioactivity from even the most radioactive samples; if there is significant activity in the samples, the samples still contain entrained water and should be re-dried with sodium sulfate. The activity contained in the samples is verified with cognizant radiological control personnel; the sample can then be removed from the protected area and analyzed by GC-FID or GC/MS methods. Positive ion chemical ionization MS may be used to confirm parent ion assignment.

8.2 GC-FID Analysis

- 8.2.1 Though all FID system parameters differ, depending on manufacturer and individual effects for optimum sensitivity, the following gas flows were found to be optimum for an HP FID system on an HP 5890 series II GC.

Hydrogen:	Inlet pressure 20 psi; 70 mL/min at the detector exit.
Air:	Inlet pressure 35 psi; 600 mL/min at the detector exit
He make-up gas:	30 mL/ min
Detector temperature:	260 ° C.

Injector port temperature: 250°C

Splitless injection

Temperature program:

Initial temperature: 50°C, hold for 1 min

Program: 50°C to 300°C at 8°C/min

Final temperature: 300°C, hold for 5 min

Column: DB-5, 30m x 0.25 mm i.d., 0.25 mm phase thickness (or equivalent column)

Head pressure: 15 psi; held constant throughout the run; carrier gas velocity at 50°C ca. 35 cm/sec.

8.3 GC-MS analysis

8.3.1 Chromatographic conditions

Injector port temperature: 250°C

Splitless injection

Temperature program:

Initial temperature: 50°C, hold for 1 min
Program: 50°C to 300°C at 8°C/min
Final temperature: 300°C, hold for 5 min

Column: DB-5, 30m x 0.25 mm i.d., 0.25 mm phase thickness (or equivalent column)

Head pressure: 15 psi; held constant throughout the run; carrier gas velocity at 50°C ca. 35 cm/sec.

8.3.2 Mass Spectrometric Conditions

Interface temperature	250 °C
Ion source temperature	200 °C
Electron Impact (EI)	
Scan range	50-500 amu
Electron energy	70 eV
Chemical Ionization (CI)	
Reaction gas	isobutane
Scan range	70-500 amu, positive ion mode

8.3.3 Calibration and Tuning: Perfluorotributylamine (PFTBA) is used to tune and calibrate the MS before unknown analysis. All calibration results and instrument parameters should be documented.

8.3.4 Once calibration and system performance have been completed and documented, response curves can be generated with standard solutions. A series of dilutions of the derivatized (follow Section 8.1) standard solution are made with chloroform. If concentration ranges of the chelators present in the sample solutions are unknown, at least the following dilutions of the stock solution should be made (assuming the stock solution concentration is 2-5 mg/mL): 1:1, 1:5, 1:10, 1:25, 1:50 and 1:100.

8.3.5 One mL of each of the standard dilutions should be injected onto the GC column, preferably by autosampler. If manual injections must be made, the use of an internal standard, added at the final sample volume, must be made. Naphthalene d-8 has been successfully used in this capacity; however, the method has been employed as an external standard method. Data collection is started as described in instrument manuals. If an autosampler is available, then a batch run can be set up as described in manuals.

8.3.6 A response curve is prepared for each analyte in the standard solution by plotting the area of the GC peak vs mg methylated chelator injected.

8.3.7 One mL of unknown sample is injected onto the GC column for GC-MS analysis. Data collection is started as described in instrument manuals. If an autosampler is available, then a batch run can be set up as described in the manuals.

8.3.8 Final results are calculated based on sample size and all sample dilutions and other sample manipulations performed. The response curve is used to obtain

quantitative information.

9.0 Quality Control

- 9.1 Because of the variability in mixed waste samples, modifications to the sample preparation and/or derivatization procedure may be necessary. Modifications to this method should be supported by appropriate QC methods and should meet the objectives of the project. Standards and samples are ordinarily run in duplicate or triplicate. With most analytes, there is excellent ($\pm 5\%$) agreement with duplicates of standard materials; duplicate samples, when properly dried should agree within $\pm 10\%$ for EDTA, NTA, and Citric acid (if these are present in the sample). Again, those materials capable of cycling into lactones or lactams (HEDTA, ED3A) have not given reproducibility within the above limits; the chemistry of the work-up is suspected to unavoidably influence these analytes. For duplicated analyses, the largest value observed for HEDTA and/or ED3A is likely to be closest to the actual amount; due to the apparent ready hydrolysis of these lactone or lactam analytes.

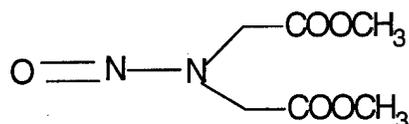
For each analysis, the yield of added adipic acid must be taken into account as a measure of the derivatization efficiency of each sample. A known quantity of adipic acid is added before derivatization, and the yield of this material is calculated after the derivatization procedure. If there is a problem with the $\text{BF}_3 \cdot \text{Methanol}$ reagent, or the sample is not entirely dry, or there are matrix interferences with the conversion of all the materials to methyl esters, the yield of dimethyl adipate can be very useful to gauge whether the derivatization reaction was successful or not. Yields of adipic acid ester less than 80% are very suspect and have been found to be associated with samples that have not undergone complete reaction with the derivatizing reagent.

No formal studies of accuracy or precision in a tank matrix have been attempted with this method.

10.0 Method Performance

- 10.1 A waste sample representing a composite of several segments of actual waste obtained by core drilling a waste from a double-shell storage tank was analyzed by this method. This material was highly radioactive, with a high concentration of nitrate and nitrite, a hydroxide ion concentration of 2 M, and a total organic carbon (TOC) content of 1.5-2.1%. Results indicate the presence of EDTA, HEDTA, ED3A, NTA, citric acid, and succinic acid (Figure 1.). Table 6.1 identifies the peaks in Figure 1 and gives their molecular structures as determined by high resolution MS. Figure 2 gives the mass spectra of several of the peaks in Figure 1. The concentrations of the major components from the analysis of samples from a tank waste (Tank 101-SY at Hanford)) are shown in Table 6.1.

The other minor components have been tentatively identified as chelator fragments or carboxylic acids. One component, whose structure is shown below, is thought to have formed either as a result of an interaction between the organics and the high nitrate and nitrite content in the waste tank or as an artifact of the derivatization process.



The chelators and chelator fragments constitute only 20 to 30% of the TOC.

- 10.2 Recoveries of the target organic compounds associated with Tank 101-SY wastes were determined by addition of standard amounts of these materials comparable to that contained in the intermediate waste extract from ion exchange processes. Analytes chosen for the study were succinic acid, nitrilotriacetic acid (NTA), citric acid, ethylenediamine tetraacetic acid (EDTA), and hydroxyethyl-ethylenediamine triacetic acid (HEDTA). These materials were added to the waste matrix in 0.5-0.8 mg/g matrix solution. In addition, a deuterated analogue of EDTA (with the deuteriums located in non-exchangeable positions on the N,N' bridge) was added (0.5 mg/g matrix solution) as a direct probe of derivatization efficiency.

The spiked samples were thoroughly dried under a gentle stream of nitrogen at 70°C. An additional unspiked sample of each representative matrix was run for comparison purposes as a basis to calculate the recovery of the added spiked materials.

The samples were derivatized in the normal fashion using boron trifluoride-methanol complex to methylate the acids and quenching the reaction with pH 9 phosphate buffer. HEDTA methyl ester was found to be exceptionally sensitive to the pH of the final solution; in cases where the quenching solution was allowed to become acidic (pH 6), the amount of HEDTA methyl ester in the extracts was observed to fall dramatically.

Each sample was extracted with a known volume of chloroform and quantitated by GC-MS *versus* an internal standard (naphthalene-dg). Each sample was quantitated twice, with the average of the two runs being determined. The recovery was determined by subtracting the calculated amount of the target materials in the unspiked samples from that found in the spiked samples. Typical recoveries were found to be essentially quantitative, within experimental error (see following list).

Succinic Acid	101%
Citric Acid	108%
NTA	111%
EDTA	117%
d ₄ -EDTA	85%
HEDTA	27%

The value obtained for d₄-EDTA may be low because of bias introduced in experiments to determine the relative response factors (RRF) for each analyte. It is possible that the RRF determined for d₄-EDTA was artificially high, resulting in an apparent depressed recovery amount for this analyte. To establish that d₄-EDTA does not suffer deuterium exchange under the rather rigorous conditions of the experiment, a sample of d₄-EDTA was derivatized in a matrix that did not contain EDTA. No diminution of signal or creation of ordinary EDTA were observed in the mass spectrum of this simulant.

The recovery of HEDTA (above) is typical for this analyte. Previous reports have indicated that only 30% of the HEDTA converts to a lactone form amenable to analysis by GC (Strachan 1986).

- 10.3 Problems with BF_3/MeOH derivatization: HEDTA forms a lactone on derivatization with BF_3/MeOH . Because only 30% of the HEDTA forms a lactone and the remaining 70% contains an unreacted hydroxyethyl group that does not migrate on a GC column, the response factor of methylated HEDTA is 30% less on a molar basis than that of EDTA or NTA. ED3A forms a lactam. The reaction of symmetrical ethylenediaminediacetic acid (s-EDDA) is not reproducible. Compounds similar to IDA and ED3A with free amine hydrogens will tend to form nitroso compounds under these conditions with BF_3 (Lewis acid) or when derivatized under basic conditions with dimethyl sulfate. Thermospray LC-MS studies under basic conditions have indicated that IDA is the component present in the waste samples.

11.0 Calculations

Calculations are based upon standards prepared, derivatized, and recovered in the same dilution scheme as actual samples. The amount of each chelator component per GC sample is directly read from the calibration curves generated per analyte.

For each analysis, the yield of added adipic acid must be taken into account as a measure of the derivatization efficiency of each sample. A known quantity of adipic acid is added before derivatization, and the yield of this material is calculated after the derivatization procedure. If there is a problem with the BF_3 -Methanol reagent, or the sample is not entirely dry, or there are matrix interferences with the conversion of all the materials to methyl esters, the yield of dimethyl adipate can be very useful to gauge whether the derivatization reaction was successful or not. Yields of adipic acid ester less than 80% are very suspect and have been found to be associated with samples that have not undergone complete reaction with the derivatizing reagent.

Most GC samples are representative of an aliquot of actual tank material that has been subjected to ion-exchange cleanup in a hot-cell facility. The overall calculation must take into account the volume of the aliquot used for derivatization, the volume of the aliquot containing the total sample, and any sub-sampling losses that may have taken place during hot-cell processing (such as removal of a portion of the sample for TOC analysis). When each of these factors is included in the calculation, an estimate of each chelator concentration per gram of tank material can be made.

To compare TOC data with chelator concentration; each chelator result must be multiplied by a factor representative of the carbon content (%) of each species before derivatization. Thus, citric acid, as derivatized, must be multiplied by 0.375 ($\text{C}_6/\text{C}_6\text{H}_8\text{O}_7$) to attempt a mass balance *versus* the carbon values obtained from TOC experiments.

12.0 Accuracy And Precision

With most analytes, there is excellent ($\pm 5\%$) agreement with duplicates of standard materials; duplicate samples, when properly dried, should agree within $\pm 10\%$ for EDTA, NTA, and citric acid (if these are present in the sample). Again, those materials capable of cycling into lactones or lactams (HEDTA, ED3A) have not given reproducibility within the above limits; the chemistry of the work-up is suspected to unavoidably influence these analytes. For duplicated analyses, the largest value

observed for HEDTA and/or ED3A is likely to be closest to the actual amount due to the apparent ready hydrolysis of these lactone or lactam analytes.

No formal studies of accuracy or precision in tank matrix have been attempted with this method.

13.0 References

Grant, K. E., R. B. Lucke, J. A. Campbell, L. J. Sears, and A. P. Toste. 1994. "Determination of Chelators and their Degradation Products in Mixed Hazardous Wastes by Derivatization GC/MS." Submitted to *Anal. Chem.*

Strachan, D. M., R. O. Lokken, R. D. Scheele, and A. P. Toste. 1986. *Complex Concentrate Pretreatment: F.Y. 1986 Progress Report*. PNL Technical Report, PNL-7687, Pacific Northwest Laboratory, Richland, Washington.

6.2 Method for the Analysis and Quantification of Organic Acids in Simulated Hanford Tank Waste and Hanford Tank Waste by Ion Chromatography (IC)

1.0 Scope And Application

- 1.1. Quantification of short chain acids and inorganic anions in a single run is an important application for the biotech, chemical, and power industry. The ion chromatography (IC) method can be used to detect and analyze low molecular weight (LMW) organic acids in simulated tank waste and actual tank waste from a single sample injection in one gradient run using hydroxide eluent systems. This method can potentially be applied in the analysis of effluents containing nitrates and nitrites such as those collected from pesticides and explosives processing plants. The analytes that can be determined by this method is listed below in Table 1:

Table 1: CAS Registry Number of the Analytes Analyzed by IC

<u>Analyte</u>	<u>CAS registry number</u>
Acetic acid	64-19-7
Formic acid	64-18-6
Oxalic acid	144-62-7
Citric acid	77-92-9
Glyoxalic acid	298-12-4
Glycolic acid	79-14-1
Maleic acid	(Z)-[110-16-7]
Malic acid	6915-15-7
Malonic acid	141-82-2

In addition to the above mentioned organic acid anions, inorganic anions including, nitrate, nitrite, sulfate and phosphate can also be quantified by this method.

- 1.2 This method shall be used by a cognizant scientist or technician under the close supervision of a qualified analyst. If radioactive samples are to be analyzed, the analyst should have completed all the training requirements for handling the radioactive samples. A current radiological work permit (RWP) should be signed and followed by the analyst before handling the radioactive samples.

2.0 Key Words

Ion Chromatography (IC): Chromatographic separation technique based upon the retention of anions or cations upon a fixed stationary phase from a mobile phase.

Hydroxide Eluent System: A mobile phase containing very dilute (0.5 mM to 5 mM) sodium hydroxide solution.

IonPac® AS-11 Column: An anion exchange column specifically designed to resolve a large number of inorganic anions and organic acid anions from a single sample injection in one gradient run using hydroxide eluent system.

IonPac AG11 Guard Column: A guard column placed prior to the analytical column to prevent sample contaminants from eluting onto the analytical column.

Anion Self Regenerating Suppressor (ASRS): A unit device for providing continuous autosuppression of conductivity arising from the electrolysis of the eluent.

CD20 Conductivity detector: Detector used for detecting ionic species by constantly measuring the conductivity of the eluent solution.

Anion Trap Column (ATC): A column used for minimizing the baseline shift caused by increasing the anionic contaminant level in the eluent as the ionic concentration of the eluent is increased over the course of gradient analysis.

GP40 Gradient Pump: The pumps used for moving the eluent through the column, ASRS and the detector and for creating a gradient of the eluents.

Simulant waste material (SWM): A preparation used to study Hanford tank waste chemistry. The SWM contains most of the constituents found in Hanford tanks with the exception of the radionuclides.

Low Molecular Weight (LMW) acids: Short chain fatty acids.

3.0 Introduction

Historically, LMW organic acids, such as oxalic and glycolic acid, in tank waste samples were analyzed using HPLC with UV detection. However, high concentrations of nitrate and nitrite often interfered with quantitation while UV detection exhibited poor sensitivity for LMW organic acids. Thermospray liquid chromatography-mass spectrometer (LC/MS) has also been used for qualitative determination of LMW organic acids and chelator fragments with moderate success. 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.

The IC method developed by our research group was used to detect and analyze LMW organic acids in simulated tank waste and actual tank waste. The results from our investigation show that IC can be effectively used to identify and quantify LMW organic acids in the presence of high nitrate and nitrite concentrations found in Hanford tank waste samples.

4.0 Method Summary

- 4.1 A Dionex® IC unit equipped with a model CD20 conductivity detector, a model GP40 gradient pump, and an ASRS unit was used for the analysis of LMW organic acid anions in simulated waste. Radioactive samples were analyzed within an in-house fabricated chromatography enclosure, which was located in a radiation fume hood. The enclosure was equipped with an AS-11 column, an ASRS-I suppresser, and a conductivity cell. A switching valve was used to switch the flow of the eluent phase from the non-radioactive compartment to the radioactive compartment. Thus, the same GP40 pump was used for pumping the fluids through radioactive as well as non-radioactive chambers; however, since the radioactive chamber was upstream from the GP40 pump, there is no risk of it getting contaminated.
- 4.2 An aliquot of the sample is loaded, after appropriate dilution, in the sample loop of the injector. The injection is made by a pneumatically controlled injection port using nitrogen gas. The IC unit is controlled using a computer that is used to make the injection, to control the gradient pump, and to store the data as a chromatogram. Each run has a 7-minute equilibration time before injection.
- 4.3 Identification as well as quantification is made by injecting freshly prepared organic acid anion standards and comparing the retention times with that of the sample chromatogram. The concentration is determined by using a calibration curve.

5.0 Prerequisites

- 5.1 This procedure is written such that a cognizant scientist will be able to follow the method and perform LMW organic acid anion analysis using IC. Technical staff implementing this procedure should have general training in instrumental analysis.
- 5.2 It is also required that the analyst understand the principles of analytical chemistry and general chemistry. Staff must be trained, and the training documented, before they can apply this method. Unless noted otherwise, all steps of this procedure are performed by the analyst. Additional training for radiological worker (RW-II) and radiological hood operation training must be completed by the user before handling radioactive samples.

6.0 Interferences

- 6.1 While using the AS-11 column for the analysis of SMW material, it was observed that the glycolate anion interfered with the acetate anion. However, this interference can be readily resolved by using the AS-6 column, which is capable of analyzing glycolate in the presence of acetate. The eluent and the conditions for analysis by the AS-6 column are different than that for the AS-11 column.

7.0 Safety

- 7.1 Tank waste samples are classified as mixed hazardous waste and may be radioactive as well as corrosive. These samples should be handled with precaution. Always wear gloves and safety glasses while handling corrosive samples. Instructions provided in the RWP must be followed at all times. A proper radiological worker permit must be obtained before starting any radiological work. Simulated waste samples are not radioactive; however, they are corrosive due to the presence of large quantities of sodium hydroxide, sodium nitrate, and sodium nitrite. Therefore, protective gloves and safety glasses must be worn while handling simulated waste material.
- 7.2 Since the eluent for the mobile phase is made from sodium hydroxide solution, all precautions for handling corrosive material should be observed for preparing the mobile phase.
- 7.3 The ASRS should never be allowed to run without fluids running through it or it may get destroyed permanently if allowed to run without eluent going through it. Always check for bubbles (indication of H₂ gas) in outlet from the ASRS while operating the unit.

8.0 Apparatus and Materials

To minimize corrosion of the chromatograph as well as prevent metals from contaminating the eluants, all components of the IC in contact with the eluant solution as it travels from the reservoir to detector cell are made from polymeric and other non-metallic materials. A Dionex ion chromatography unit (DX 500) consists of following components:

- Pressurized Eluant Containers
- Eluant Pump
- Injection Valve and AS40 Auto Sampler
- Separator Column
- ASRS
- Conductivity Detector
- Computer

- 8.1. **Pressurized Eluant Containers:** Eluants are stored above the IC in bottles. Either glass or plastic bottles may be used. To keep the eluant pump primed and prevent gas bubbles from forming inside the eluant, an inert gas (preferably Helium) is continuously bubbled through the eluant. Degassing is critical when using hydroxide eluant as it may absorb CO₂ from air, which may result in a baseline drift due to large carbonate and bicarbonate peaks.
- 8.2. **Eluant Pump:** The GP40 gradient pump is an integral part of a Dionex DX 500 chromatography system. It is a microprocessor based, dual piston, variable-speed, gradient delivery system designed to blend and pump mixtures of up to four different mobile phases at precisely controlled flow rates. The pump can deliver the selected mobile phase composition isocratically or as a multistep linear or curved gradient. A Digital Signal Processor (DSP) provides high-speed control of pump flow and pressure. The pump can be controlled locally, using the front panel or from a remote host computer. The pump has two basic modes of control, Direct control and Method control, which enables it to operate with or without reference to time-based events.
- 8.3. **Injection Valve and AS40 Auto Sampler:** The injection valve is a Rheodyne valve operated by two air solenoid valves. A regulated source of air or N₂ pressure is used to provide 80-120 psi of pressure required to operate the solenoid valve. The AS40 Automated Sampler is an automatic sampler capable of delivering 0.2 mL to 5.0 mL of sample to the sample loop. It can hold between 66 and 88 vials, depending upon the size of the vials used (either 0.5 mL or 5 mL). All injections of the simulated waste were made using an AS40 auto sampler while the radioactive samples were injected manually in a radiological fumehood
- 8.4. **Separator Column:** Although most analysis can be carried out using an AS-11 column, separation is needed when glycolic acid and acetic acid are present in the sample. An AS-6 column was found most suitable for this type of separation. An AS-11 column system consists first of an ATC column, followed by an AG-11 guard column, and finally an AS-11 column. The ATC column is not used with the AS-6 column, which is an ion exclusion column.
- 8.5. **ASRS:** The anion self regenerating suppression system generates high-capacity suppression while adding minimum dead volume to the analytical system. The ASRS requires a constant water feed through the regenerant chambers to achieve suppression. Water is delivered to the suppresser regenerant chambers via autosuppression recycle mode. The autosuppression recycle mode uses the neutralized conductivity cell effluents as the source of water. As the eluent passes through the ASRS, it is neutralized to form its weakly ionized form. After passing through the conductivity cell, the effluent is redirected to the regenerant inlet on the ASRS, thus supplying it with the source of water containing minute amounts of diluted analytes. The amount of water flowing through the regenerant is therefore limited to the eluant flow rate. Due to this limitation, the autosuppression recycle mode cannot be used with eluents containing organic solvents.
- 8.6. **Conductivity Detector:** The CD20 is the conductivity detector used for detecting and quantifying ionic analytes in IC. It is especially useful for those analytes that lack UV chromophores and cannot be determined with adequate sensitivity by UV absorbance. This includes a wide variety of both organic and inorganic molecules, cations as well as anions. The major organic analytes are carboxylic, sulfonic, and phosphonic acids, and primary, secondary, and tertiary amines. Conductivity detection with eluant suppression provides good sensitivity.
- 8.7. **Computer:** The Dionex DX 500 ion chromatography unit is controlled by a remote host computer with a DX LAN interface installed and peaknet software installed on the host computer. The computer is used to run the unit and collect and analyze the data.

9.0 Reagents And Consumable Materials

The eluants used were aqueous solutions of sodium hydroxide and water. Helium was used for degassing the solution and N₂ was used for pneumatic control.

10.0 Sample Preservation And Handling

Samples of SWM were received in stainless steel bombs. These samples were diluted 3.85 times (130 mL in 500 mL of water) and stored in the refrigerator. The samples were further diluted 250 fold before injecting on the IC. Diluted samples of Hanford tank waste were received from the hot cell facilities. These were further diluted about 100 to 1000 fold before injecting upon the column in the radiological fumehood. Radioactive samples should be transferred under close supervision of a qualified RPT.

11.0 Calibration and Standardization

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. 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 ppb for the key analytes. A 4-point calibration curve was generated by analyzing a set of 1:100 (0.01-0.02 mg/mL), 1:250 (nd4 - nd8 mg/mL), 1:500 (nd2 - nd4 3 mg/mL) and 1:1000 (nd1-nd2 mg/mL) dilutions of the stock solution of the standards. This procedure of linear regression generates a linear equation of the form

$$Y = MX + C$$

where Y =	Area count or response
X =	Concentration (in µg/mL)
C =	Y intercept or offset
M =	Slope

Initially, standard solutions of glyoxalic acid, glycolic acid, oxalic acid, sodium citrate, sodium acetate, succinic acid, butyric acid, and formic acid were prepared. However, glyoxalic acid and butyric acid were not detected in the samples, and these two acid standards were not used.

12.0 Procedure

12.1 Analysis by Ion Chromatography

A Dionex model IC unit (Dionex Corp., Sunnyvale, California, USA) equipped with a Dionex, Model CD20 conductivity detector was used to analyze LMW organic acid anions, including formic, glycolic, citric, and oxalic acids. A Dionex AS-11 column was used for most analyses. We used a Dionex AS-6 column to quantify glycolic acid since glycolic acid co-eluted with acetic acid on the AS-11 column. The AS-11 chromatographic conditions are listed in Table 2.

Table 2. AS-11 Conditions

Guard Column:	Dionex AG11
Analytical Column:	Dionex AS11
Anion Suppressor:	ASRS-I, 4 mm
Flow:	2.0 mL/min
Sample Volume:	25 µL
Column Temperature:	Ambient
Detection:	Conductivity

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. The water used to prepare the mobile phase and run the gradient was stirred under vacuum for over 12 hours and then sparged with helium to avoid interference from dissolved carbon dioxide. Gradient conditions used for AS-11 column separation are shown in Table 3. The column was allowed to equilibrate at initial conditions for at least 7 minutes before each run.

Table 3: Mobile Phase Gradient

<u>Time (minutes)</u>	<u>% Water</u>	<u>5 mM NaOH</u>	<u>100 mM NaOH</u>
0.0	90	10	0
2.9	90	10	0
6.4	0	100	0
18.4	0	65	35

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 eluant. Further details for AS-6 column conditions are listed in Table 4.

Table 4: AS-6 Column Conditions:

Guard Column:	None
Analytical Column:	Dionex ICE-IonPac AS6 (9 x 250 mm)
Flow:	1.0 mL/min.
Sample Volume:	25 µL
Mobile Phase:	0.4 mM heptafluorobutyric acid
Detection:	Conductivity
Suppresser:	AMMS-ICE
Suppression Eluant:	5 mM tetrabutylammonium hydroxide
Suppression Eluant Flow:	3 mL/min.
Column Temperature:	Ambient

12.2 Chromatography Conditions for Hanford Tank Waste Samples:

Radioactive samples were analyzed within an in-house 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, California, 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 to analyze radioactive and non-radioactive samples were identical (see Tables 2 and 3).

12.3 Rad/Non-Rad Ion Chromatography Simplified Protocol

The two IC systems are separate, isolated boxes with the electrical and plumbing for each on different streams. As much as possible, the connections for each system that the operator has to make have been simplified to the interchange of wires and switching of pump flow to the desired box. Follow the following steps to make a switch between rad and non-rad IC:

- 12.3.1 Turn off the CD20 detector using the front panel on-off button. Open up the CD20 detector front face, choose between the two detector cables labeled "RAD" or "COLD," and plug each into their proper sockets. (The two red and one black wires can be disconnected by pressing the ends of the clear plastic connector. The eight-pin connector with all the different small wires is disconnected by pressing on the left side of the button and pulling out.)
- 12.3.2 Open up the LC20 column enclosure and find the ASRS connector cable. Choose either the "RAD" connector (labeled) or use the short connector (cold) to the ASRS in the LC20 box.
- 12.3.3 Select a stream flow for the pump with the Rheodyne selector valve to the left of the pump. It is labeled "HOT" or "COLD" on the block it is anchored to. Move the lever to the desired position. Leave it there during the duration of the work.
- 12.3.4 Turn on the pump and verify that there is flow to the desired system.
- 12.3.5 Turn on the CD20 and verify that when the ASRS is ON, bubbles are coming out of the waste line.
- 12.4 Procedure for radioactive sample analysis: Make sure that there is pump flow to the "RAD" system.
 - 12.4.1 Use the "RADRUN" method on the PeakNet software. The method has no signal for "INJECT," "RELAY," or "TTL."
 - 12.4.2 The TTL logic cannot support the AS40 autosampler being "on" while using the rad system. Turn it off and unplug it. Leaving it on will not allow the signal to be sensed from the Rheodyne valve in the Rad fumehood.
 - 12.4.3 Turn the manual Rheodyne valve to LOAD; inject only about 200 μ L via Rheodyne syringe.
 - 12.4.4 Rotating the valve to "INJECT" starts the run clocks on the CD20, GP40, and PeakNet software. Leave the valve on and inject through the run.
 - 12.4.5 The method is stopped and clocks and pumps reset to initial conditions by turning the Rheodyne valve to "LOAD."
- 12.5 Procedure for non-radioactive sample analysis: The methods for analyzing non-radioactive samples were named "carboxyl.met" and "AS-6.met" for the AS11 and the AS6 column, respectively. Turn AS40 auto sampler on and set-up the desired method. The Rheodyne valve that directs the flows should be turned to the cold side.

13.0 Method Performance

Table 5 lists results from the analysis of irradiated and unirradiated simulant using IC. As shown in Table 5, all target analytes were successfully analyzed using IC without any inorganic interferences. Significant quantities of formic, oxalic, glycolic, and citric acid were determined along with small amounts of acetic and succinic acid. For example, the detected levels of oxalic acid concentration were as high as 8.5 mg/g (1.5 MGy dose rate). The highest concentration observed for acetic acid was

0.55 mg/g, and succinic acid concentration was nd2 mg/g (1.5 MGy dose rate).

Table 5: Concentration (in mg/g) of Reactants and Products in g-Irradiated Tank Waste Simulant

<u>Dose (MGy)</u>	<u>Formic Acid</u>	<u>Oxalic Acid</u>	<u>Glycolic Acid</u>	<u>Citric Acid</u>	<u>Acetic Acid</u>	<u>Succinic Acid</u>
0 (control)	nd	nd	8.34±0.03	15.4±0.1	0.19±0.2	nd
0.30	0.8±0.1	1.7±0.1	7.54±0.11	14.9±0.1	0.35±0.1	1.0 ¥ 10 ⁻⁴
0.50	1.7±0.2	2.8±0.2	6.77±0.02	13.8±0.1	0.42±0.1	2.9 ¥ 10 ⁻⁴
1.00	2.5±0.1	3.5±0.2	5.91±0.01	12.6	0.48±0.1	10.9 ¥ 10 ⁻⁴
1.50	4.5±0.2	8.5±0.2	5.30±0.01	11.4±0.1	0.55±0.01	17.8 ¥ 10 ⁻⁴

Analysis of Hanford Tank Waste: Several actual waste samples were successfully analyzed for LMW organic acids using IC by the AS-11 column. Figure 1 illustrates the elution scheme of LMW organic acids in a sample from Hanford Tank AN-107. The concentrations of these acids were determined by an external standard method and are listed in Table 6.

Table 6: Concentration (in mg/g) of LMW Organic Acids in Hanford Tank Waste

<u>Tank I. D.</u>	<u>Acetic/Glycolic Acid</u>	<u>Formic Acid</u>	<u>Oxalic Acid</u>	<u>Citric Acid</u>
S-102	1.2	1.7	4.4	0.0
U-107	2.3±0.1	2.5±0.3	0.6±0.1	0.5±0.1
AN-107	7.6±0.5	4.5±0.5	14.2±3.3	4.4±0.2

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, the AS-6 column will be used, which employs a separate chromatographic mechanism based on ion exclusion to distinguish these relatively similar acids.

6.3 Method for the Analysis of Radioactive Tank Waste Samples Using Ion-Pair Chromatography

1.0 Scope and Application

- 1.1 This method is applicable for the determination of chelators and chelator fragments in tank waste and simulated tank waste. Aliquots of tank samples are analyzed using ion-pair chromatography (IPC) coupled with an ultraviolet absorbance detector. Detection is achieved by forming the copper complex of the analytes. The analytes are identified by matching the sample retention time with that of standards. The common analytes that may be determined by this method are shown in Table 1.

Table 1. Common Analytes and their CAS Registry Numbers

<u>Analytes</u>	<u>Abbreviation</u>	<u>CAS Registry Number*</u>
Ethylenediaminetetraacetic acid	EDTA	60-00-4
2-(Hydroxyethyl)diaminetriacetic acid	HEDTA	150-39-0
Nitrilotriacetic acid	NTA	139-13-9
Ethylenediaminetriacetic acid	ED3A	xxx
Symmetrical-ethylenediamindiacetic acid	s-EDDA	5657-17-0
Unsymmetrical-ethylenediamindiacetic acid	u-EDDA	xxx

*CAS numbers for the free acids are given.

- 1.2 This method shall be used only by experienced technicians under the close supervision of a qualified analyst. Training qualifications of the technicians must be documented. It should be noted that tank waste samples are not typical analytical samples. They are highly radioactive, highly basic, and separate phases may be present.

2.0 Summary Of Method

- 2.1 Samples are received from the 325 hot cell facility where they have undergone treatment to remove a large portion of the radionuclides (see procedure AOAM-03).
- 2.2 An aliquot of sample is neutralized, doped with copper sulfate, and brought to known volume. This sample is transferred to an autosampler vial. Sometimes filtering or settling is required before analysis.
- 2.3 The samples are run on a high performance liquid chromatograph (HPLC) using IPC. The sample results are compared to those of standards.

3.0 Interferences

- 3.1 Known peaks that are not related to chelators that could interfere with this procedure include unbound copper and nitrite and nitrate ions. Typically these do not adversely affect the results. The NTA peak sometimes rides in the copper peak, which tails excessively. This has not been a problem in quantitating the NTA. The nitrite ion elutes between the NTA and EDTA peaks. The nitrate ion elutes later than the EDTA. The column should be replaced if baseline resolution between the EDTA and nitrate is not achieved.

- 3.2 Some of the earlier eluting peaks may coelute on columns that have degraded. These include ED3A, s-EDDA, and HEDTA. There is a current effort to find a column that is less likely to lose its selectivity for these compounds. The gradient conditions listed in Section 8.2 gives a better separation of these compounds than do the isocratic conditions.

4.0 Safety

- 4.1 The samples can be expected to be radioactive. Read, understand, and follow the guidelines set forth in the current Radiological Work Permit.
- 4.2 The samples can also be expected to be caustic. Proper precautions should be observed when handling caustic samples.
- 4.3 There is high pressure associated with the HPLC; however, the volumes are so small that this is generally not a concern. The main concern with the HPLC is that a leak could lead to radioactive contamination. Because of this, the HPLC is double contained within a contamination area.

5.0 Apparatus and Equipment

- 5.1 Waters High Performance Liquid Chromatograph, or equivalent: This consists of two model 510 pumps, a WISP™ autosampler, an HPLC column, and a UV absorbance detector. A computer equipped with HPLC controlling and integrating software manages this system.
- 5.2 Column: Adsorbosphere C-8; 250 mm x 4.6 mm, 5µm particle size, or equivalent.
- 5.3 Disposable 20-mL shell vials, Teflon-lined closures, WISP autosample vials, 4-mL volume.
- 5.4 pH strips, 0-14 range.
- 5.5 Balances: to 0.1 mg for standards, to 0.1 g for HPLC reagents.
- 5.6 pH meter with pH probe covering the pH range of at least 2 to 12.
- 5.7 Gelman Acrodisc® LC13 PVDF filter or equivalent; 5-mL Hamilton Gastight syringe with Luer tip, or equivalent

6.0 Reagents and Consumable Materials

- 6.1 HPLC reagents: MilliQ™ Water, or equivalent, filtered to 0.45 µm (after dissolving buffers); dodecyltrimethylammonium bromide; potassium dihydrogen phosphate; sodium hydroxide, 6 M.
- 6.2 Reagents for sample preparation: phosphoric acid, 2 N; copper sulfate, 0.5 M.
- 6.3 Standards.

7.0 Sample Collection, Preservation, and Storage

- 7.1 Collection is not part of the scope of this method.
- 7.2 Preservation: No special precautions are taken for sample preservation.

7.3 Storage: Samples are stored at room temperature out of direct bright light. Radiological storage guidelines dictate where storage is allowed.

8.0 Ion-Pair Chromatography Conditions

8.1 Isocratic Conditions:

Flow: 2.0 mL/min.

Sample Volume: 20 μ L

Detection: UV, 280 nm, as Copper complex

Mobile phase: nd2M dodecyltrimethylammonium bromide, and 0.05 M potassium dihydrogen phosphate, pH 6.5.

8.2 Gradient Conditions:

Flow: 2.0 mL/min.

Sample Volume: 20 μ L

Detection: UV, 280 nm, as Copper complex

Mobile phase: Component A: nd2M dodecyltrimethylammonium bromide, and 0.05 M potassium dihydrogen phosphate, pH 6.5.

Component B: nd2M dodecyltrimethylammonium bromide, and 0.05 M potassium dihydrogen phosphate, pH 5.5.

<u>Gradient</u>	<u>Time (%A)</u>	<u>Time (%B)</u>
0.0	0	100
5.0	0	100
10	100	0
25	100	0

9.0 Calibration And Standardization

9.1 Preparation of Calibration Standards: The linearity of this method was determined. Table 2 lists the masses and concentrations of each analyte used in this test. Additionally, a serial dilution was made of the first six standards.

9.2 Calibration Curves: A serial dilution containing all of the first six analytes listed in Table 2 was prepared. The dilutions were in the following ratios: 2:5, 1:5, 1:10, and 1:25. Calibration curves for these analytes were prepared from chromatographs of these standards.

9.3 The following calibration curves were developed on MS Excel.

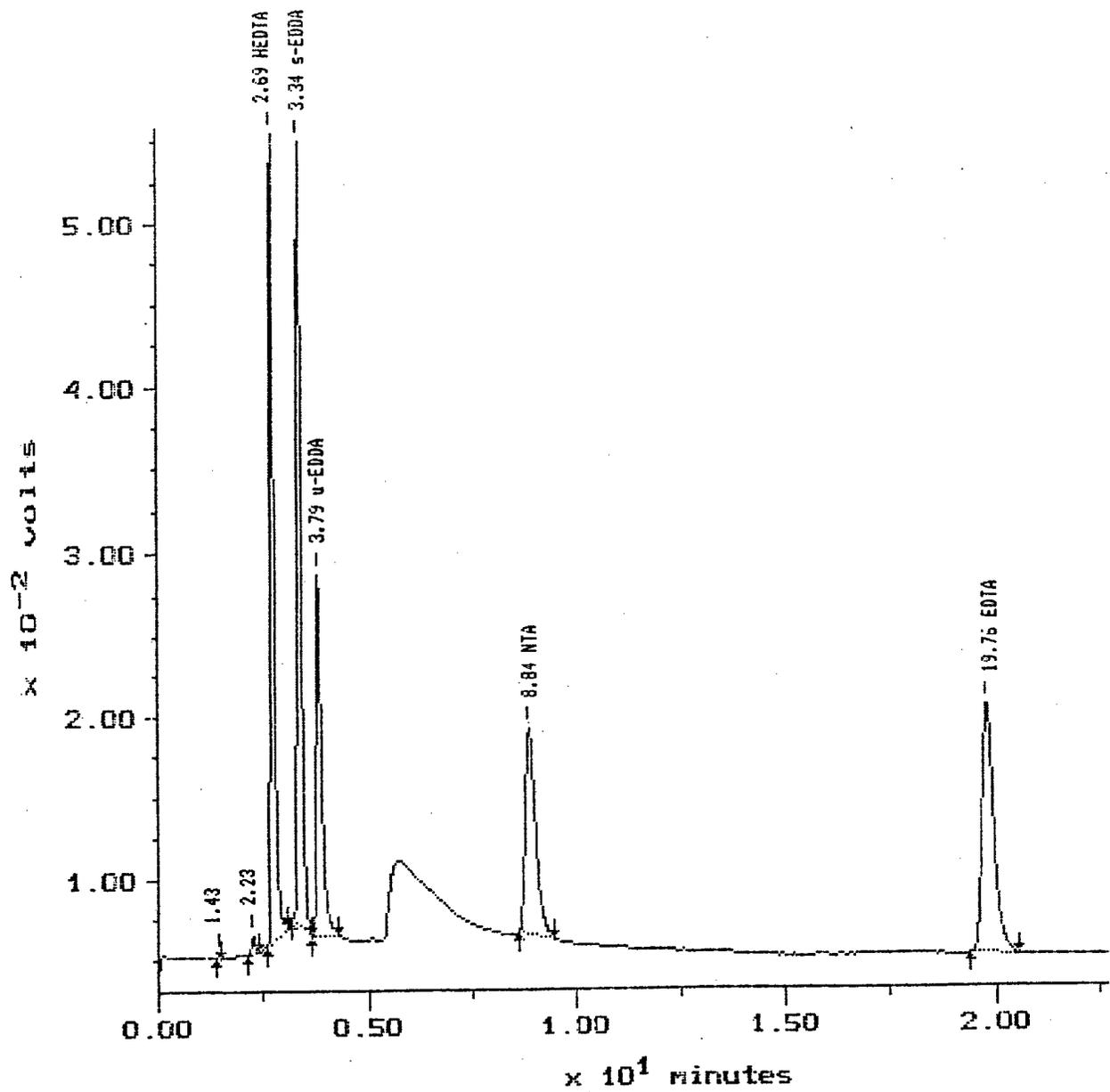


Figure 1. Chromatogram Generated from Gradient Conditions

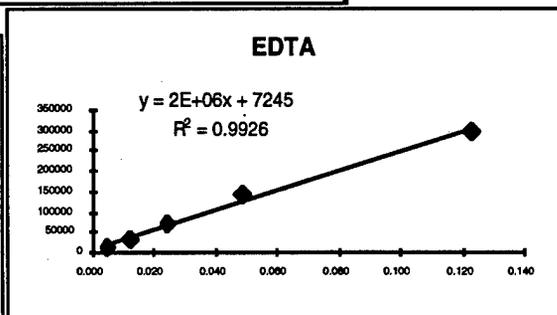
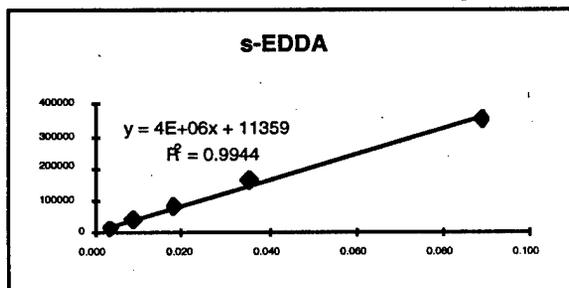
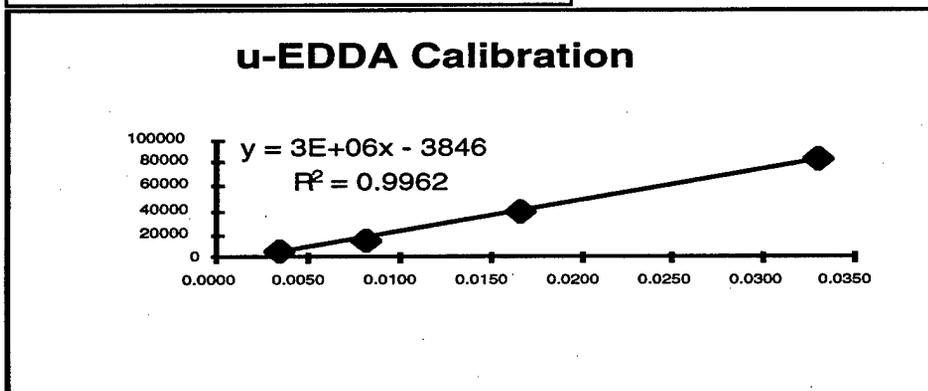
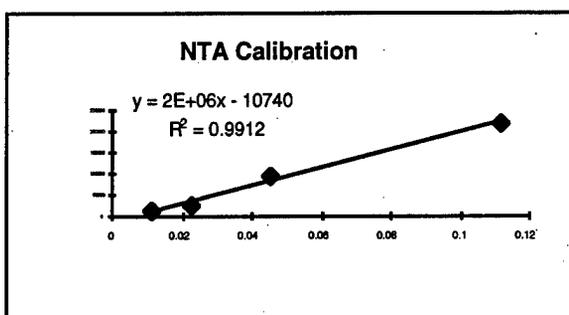
Table 2. The Masses and Concentrations of Each Analyte Used in Preparing Calibration Standards

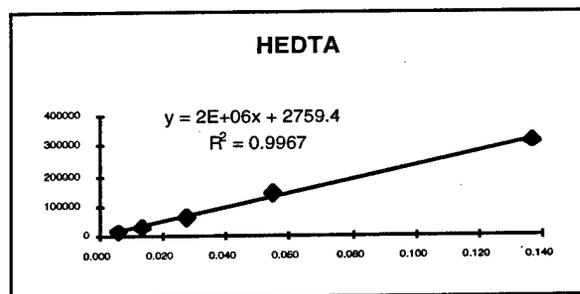
Chelator	Mass (mg)	Stock Conc. (mg/mL)	Final Conc. (mg/mL)	Retention Time
NA ₃ NTA	28	1.12	0.112	8.8
u-EDDA	20.6	0.82	0.082	3.8
s-EDDA	22.3	0.89	0.089	3.3
NA ₄ EDTA	30.7	1.23	0.123	19.8
IDA*	26.6	1.06	0.106	3.1†
NA ₃ HEDTA	34.1	1.36	0.136	2.7
NIDA**(in 5 mL)	4.5	0.9	0.09	9.1†
ED3A(in 5 mL)	5.4	1.08	0.108	2.4

* Iminodiacetic Acid

** N-nitroso-iminodiacetic acid

† Poor response.





- 9.4 Having established that the response curves of each analyte are linear, the concentrations of samples are usually determined by normal external standard calculations.
- 9.5 Detection Limits: Detection limits were determined by examination of the 1:25 dilution chromatograph.

10.0 Quality Control

To check the performance of this procedure, duplicate samples are prepared. The results of these should not vary by more than 20%. Further standards are prepared at two concentration levels. The results of each sample are calculated versus both these standards. The results of these should not vary by more than 20%. The final reported result is the average of the result calculated from the two standards.

If there is the possibility of matrix interference, and none has ever been observed, at least one sample should be processed by standard addition, as well as the normal external standard procedure. These results should not vary by more than 10%.

10.1. Documentation

10.1.1. One of the objectives of the test consists of maintaining records to document the quality of data that are generated. Data quality shall be defined by the Organic Safety Program Quality Assurance Program (MCS-027B, Revision 2). Method qualification documentation will be maintained as quality records for this procedure. Ongoing data quality checks are compared with established performance criteria to determine if the results of analysis meet the performance characteristics of the method.

10.1.2 Refer to the QA Plan (MCS-027B, Revision 2) for data review and exception reporting requirements.

10.2. Records

10.2.1. Data packages for each tank waste analysis may include the following items if required by the client:

- Calibration data
- Continuing calibration analysis data
- Sample analysis data

- Blank sample and system blank (if applicable) data
- Replicate sample analysis data
- Summary report
- Excel Table for inclusion in final report.

The entire data packet shall be checked by the Analyst for completion and accuracy. Upon completion of this first level of review, the Analyst shall obtain review of the data by an independent technical reviewer.

10.2.2. All raw and processed data, associated reports, and methods shall be archived on optical storage media on a monthly basis.

10.2.3. Project files shall contain all method qualification information.

10.3. Calibration

10.3.1. This method requires user calibration (Category 2 Measuring & Test Equipment [M&TE]) of the analytical system. Documentation of calibration shall include the following:

- Record the calibration results with the corresponding data.
- Identify the standards used with the corresponding data.
- Maintain supporting documentation that identifies the accuracy of the standards and the traceability of the standards to nationally recognized standards (National Institute of Standards and Technology or equivalent) or accepted values of natural physical constants. If nationally recognized standards are not used, the acceptability of the standards used shall be documented.
- Documentation must also include the calibrator's name and the date the calibration was performed.

10.4. Sample Analysis - The minimum QC requirements are to monitor the external calibration-standard peak area by the analysis of continuing calibration standards, the analysis of reagent blanks, and replicate analysis of selective samples.

10.4.1. Analysis of Reagent/System Blanks (ICB or CCB) - Before processing any samples, the Analyst must demonstrate, through the analysis of a blank, that the level of interference, carry-over, or contamination within the retention time window of interest is less than the EQL.

At a minimum, the CCB shall be analyzed following the CCV and after every 15 samples and blanks or every 12 hours, whichever is more frequent in a sample analysis sequence.

The ICB shall be run following the ICV in a calibration sequence.

10.4.2. Continuing Calibration Verification - A CCV shall be analyzed before

the analysis of each sample set. If samples are to be run over 24 h, a CCV should be interspersed at a minimum of 12-h intervals, or after each set of 15 samples and blanks during the course of the analysis, whichever is more frequent. The response for an analyte shall fall within $> 25\%$ D, relative to the average response factor derived in the initial calibration. If the response for any analyte differs by more than the 25 %D window, a second CCV shall be analyzed. If the analyte responses for a second CCV fall within the 25 %D window, continue to analyze the samples. If the analysis of a second CCV fails to produce analyte results that meet the 25 %D criteria, a new calibration curve must be generated before analyzing any new samples. Samples analyzed before the failed CCVs must also be reanalyzed. The cause of the failed CCV should be determined if possible and noted on the sample sequence log sheet. A new CCV shall be prepared and analyzed before analysis of the sample set. This CCV shall also be evaluated according to the 25 %D criterion.

10.4.3. A chart of continuing calibration checks shall be generated as per the Quality Assurance Plan for the Pacific Northwest National Laboratory Organic Safety Program Quality Assurance Program (MCS-027B, Revision 2) to monitor instrument and method performance.

10.4.4. Duplicate Sample Analysis - A duplicate analysis shall be performed on one tank waste per sample set if sufficient sample is available. The results from the original and replicate analyses of a sample must be less than 20 %RPD for all analytes present at concentrations greater than the EQL.

If a replicate analysis of a sample fails the 20% RPD criterion, the cause of the failure shall be evaluated, corrected if possible, and the replicate sample shall be reanalyzed. If the replicate reanalysis passes the 20% RPD criterion, the replicate reanalysis shall be accepted and the impact of the corrective action shall be evaluated for samples already analyzed within the analytical batch to determine if re-analysis is required. The data package for the sample set shall contain a narrative documenting details of the replicate reanalysis. If the second replicate reanalysis fails to produce results meeting the 20% RPD criterion, corrective action shall be taken and the entire sample set shall be reanalyzed. The results from both the first and second analyses shall be recorded in the analytical documentation file. The results from the second analyses shall be reported and flagged as appropriate.

11.0 Procedure

11.1 Sample Preparation:

- Place 1 mL of sample into a shell vial. The vial is marked to indicate the 10-mL level.
- Phosphoric acid, 2 N, is added to bring the pH to neutral. Usually 2 mL is required.
- Add 50 μL of 0.5 M CuSO_4 with swirling.
- Dilute the sample to 10 mL with water.
- If there is visible cloudiness, filter the sample through an Acrodisc LC13 into a autosampler vial. As an alternative, the sample can be allowed to settle.

11.2 Ion-Pair Chromatography

Refer to instrument operating manual for operation of the chromatograph.

12.0 Calculations

- 12.1 Area counts are determined by the computer. Before performing calculations, the baselines are examined manually for accuracy.
- 12.2 Calculations are based on the following equation:

$$\text{Conc.} = \frac{\text{Area Sample} \times \text{Conc. Standard}}{\text{Area Standard}}$$

- 12.3 Final concentrations are calculated based on the procedure dilutions and original sample weights as reported by the hot cell staff.

13.0 Accuracy and Precision

- 13.1 I have to look some of this up or do some of these experiments. I did them a long time ago and they should be repeated.

14.0 Records

- 14.1 Records of all analyses shall be kept in the analyst's files. Documentation of method deviation or any unusual events shall be noted in the project LRB.

6.4 Method for the Reduction of Radioactive Components Using Cation Exchange

1.0 Scope and Application

- 1.1 This method describes an approach to reduce the amount of fission products from mixed waste materials so that analyses for organic acids and chelators may be conveniently done. Examples of chelators and their degradation products that can be analyzed by this method include, but are not limited to, ethylenediaminetetraacetic acid (EDTA), N-(2-hydroxyethyl) ethylenediaminetriacetic acid (HEDTA), ethylenediaminetriacetic acid (ED3A), nitriloacetic acid (NTA), citric acid, oxalic acid, succinic acid, acetic acid, glycolic acid, and formic acid. The method relies on exchange of metals in the waste matrix for sodium without appreciable holdup of anionic species (as organic carboxylates).
- 1.2 Ordinarily, samples undergo this pre-treatment in a hot-cell facility to reduce radioactivity levels so that they may be manually handled in a contamination area fume hood. This method is only applicable for use by experienced technical personnel under the supervision of qualified scientists.

2.0 Summary Of Method

The waste samples are subjected to ion exchange to reduce radioactivity levels using Dowex 50W-X8 ion exchange resin (Bio-Rad), which has been exchanged to the sodium form before use. The only organic species applicable to this method will be water soluble carbon compounds (carboxylates). Other organic materials present in tank wastes, which lack solubility in water, will be held in the resin layer and effectively removed from the sample during ion exchange.

3.0 Interferences

- 3.1 To obtain a quantitative yield of carboxylates through the anion exchange media, the liquid media must support the analytes in solution throughout the exchange procedure. Since many of the chelators (e.g., EDTA) are virtually insoluble in weakly acidic or neutral conditions, the column and resin must be kept at least pH 12.
- 3.2 There has been ample study done of the sorption of non-ionic organics upon cation exchange resins of the styrene-divinylbenzene type. This hold-up potential may limit the usefulness of this method for the analysis of alcohols, sugars, and like materials suspected to be in specific matrices. Since these materials appear to undergo chromatographic distribution on the resin, it may be possible to elute non-ionics from ion exchange resins; the present procedure has been designed for removal of fission product cations from carboxylates, and no development has been made toward clean-up of non-ionic carbon compounds.
- 3.3 Water insoluble organics will adsorb onto the ion exchange media. These are best analyzed for in a separate solvent extraction procedure, before ion-exchange or with an additional aliquot of sample. Example materials of this type that are commonly found associated with radioactive waste processes include tributylphosphate and intermediate length hydrocarbons such as tridecane.

4.0 Safety

- 4.1 This procedure is intended for use within a hot-cell facility. Most samples of radioactive tank waste materials are so highly radioactive (thousands of $\mu\text{Ci/g}$) that direct handling is precluded. Any sample leaving the hot-cell environment needs careful monitoring by radiation control personnel to determine the extent of exposure inherent to the sample as well as any external contaminations that may be present on the packaging.
- 4.2 When subsequently handling radioactive samples, all applicable radiochemical handling procedures and health physics monitoring practices should be followed.

5.0 Apparatus and Equipment

- 5.1 Beakers, assorted sizes to 2-L volume
- 5.2 Mechanical stirrer, overhead model, speed control, teflon paddle
- 5.3 Buchner funnel; qualitative, fast filter paper to fit (Whatman 4 or equivalent); filter flask, 2 L
- 5.4 Plastic column supports: Econo-Pac (BioRad 732-1010); Poly-Prep (BioRad 731-1550) chromatography columns; stopcocks with luer connections (BioRad 732-8102) or equivalent
- 5.5 Glass stir rods
- 5.6 pH meter with pH probe covering the pH range of at least 2 to 12
- 5.7 0.45 μm in-line syringe filter (Gelman Acrodisc hydrophilic PVDF, Cellulose Acetate, or equivalent)

6.0 Reagents

- 6.1 Reagent water: deionized water polished with an organic removal cartridge to meet ASTM 1193 Type II water standard for low organic content.
- 6.2 Dowex AG 50W-X8 resins, prepurified, hydrogen form. Two mesh sizes are used: 20-50 and 100-200.
- 6.3 Sodium hydroxide, 97% pellets (Aldrich 22,146-5, or equivalent)
- 6.4 pH standards: commercial pH 4, 7, 10 standards; pH paper, 0-14 range; EM ColorpHast (E. Merck) or equivalent.

7.0 Sample Collection, Preservation, and Handling

Sample collection, preservation, and handling should be addressed in the planning process.

Of paramount importance to the assay of tank wastes is the record of any substantial volume addition or dilution of the native material taken from the tank. Each operation that adds liquid volume to the retrieved material must be taken into account in the final assay calculation of chelator content as it relates to the tank material. Most of the dilution to the sample will occur during ion

exchange treatment. Total organic carbon (TOC) measurements are typically taken of aliquots from the liquid before, during, and after ion-exchange to determine the amount of organic carbon subjected to loss in the procedure. The volume (or weight) removed at each step must be taken into account in the final assay of speciated organics per gram of original waste materials.

8.0 Procedure

- 8.1 Dowex 50W-X8 resins (Bio -Rad) in two mesh sizes are employed: 20:50 mesh and 100:200 mesh. A 500-gram bottle of the commercial hydrogen form resin (in either of the mesh grades used) is placed in a 1-L beaker. Deionized water is added to slurry the resin. The mix is stirred with a mechanical stirrer, stir rod, and stir paddle (NOTE: magnetic stir bars tend to break up the resin beads, and should not be used).
- 8.2 Sodium hydroxide (6 N) is added as a thin stream (ca. 50 mL) over several minutes. The resin tends to darken as the neutralization reaction takes place.
- 8.3 Sodium exchange is accomplished when the mixture will maintain pH >11 for 10 minutes. Use of 0-14 pH paper is convenient to monitor the exchange. Excess sodium hydroxide should not be employed; the goal is to add only enough caustic to exchange H^+ for Na^+ on the resin bead.
- 8.4 The resin is allowed to stir for 1 hour at pH >11. The dark aqueous layer is filtered out, and the resin is washed with an equivalent amount of DI water and used immediately. When placed in storage, the resin may be stable indefinitely; however, resin that has been stored for more than a month should be washed with an additional dilute solution of NaOH to ensure that the surface is still equilibrated with sodium.
- 8.5 The flow rate from Econo-Pak or Poly-Prep (Bio - Rad) disposable plastic columns is the principal limiting factor for contact time of the sample and the ion exchange resin. Two methods have been employed to increase the contact time of the sample with the resin bed:
 - 8.5.1 A disposable plastic stopcock (Bio -Rad) is placed on the end of the column after a full bed of 20-50 mesh resin has been placed in the column, and the drip rate set to about 1 drop per 3-5 seconds.
 - 8.5.2 A bed of 100-200 mesh sodium form 50W-X8 is placed in the bottom of either the Econo-Pak (ca. 2-3 mL depth) or Poly Prep column (ca. 1-mL depth), the excess water is allowed to drip away, and the larger 20-50 mesh resin is carefully decanted into the column on top of the smaller resin bed. The smaller particles limit the flow rate through the column, and the increased surface area of the smaller resin beads increases the exchange of sodium to the sample.
- 8.6 The best columns do not have voids, air bubbles, or channels in the resin bed. The best way to ensure that the columns remain properly packed is to place caps on the top and bottom of the column bed after packing with resin. The columns are delivered to the hot-cell in this condition.
 - 8.6.1 Columns with visible channeling can be remedied by careful stirring with a thin glass rod or by rapping the column against a hard surface to alleviate entrained air.

NOTE: The following procedural steps are to be performed in the shielded hot-cell facility by qualified hot-cell technicians. Additional steps to de-water or solvent extract a particular sample may precede the ion exchange procedure.

- 8.7 An appropriate quantity of tank waste material (0.5 gram for Poly-Prep columns, up to 3 grams for Econo -Pak columns) is transferred into a tared vessel. If the sample is solid, it is diluted with at least 2 mL DI water/gram of sample. The pH is checked with wide range (0-14) pH paper.
 - 8.7.1 If the pH is not strongly alkaline, up to 2 mL 6 N NaOH is added to the sample.
- 8.8 The samples are covered and stirred overnight to allow dissolution of precipitated oxalates and other slightly soluble carboxylates that might be in the sample.
- 8.9 The samples are removed from stirring, filtered with a 0.45- μ m in-line syringe filter (Gelman Acrodisc hydrophilic PVDF, Cellulose Acetate, or equivalent), and the filter medium rinsed with 1 mL water.
 - 8.9.1 The sample volume and mass may be recorded at this point, and a sample removed for TOC analysis (combined PNL-ALO-380 and modified PNL-ALO-381 techniques). It is imperative to know the quantity (mass and volume) removed at this point to allow calculation of the TOC amount/gram waste and to account for the amount removed from the total sample at this point.
- 8.10 Two ion exchange columns per sample are treated with one column volume of 1 N NaOH, allowing enough liquid to drain from the column without allowing the resin bed to dry out.
- 8.11 The columns are arranged in series, so that the effluent from the top column drains into the bottom column. The sample filtrate is applied to the top column. After all of the sample has passed through both columns, a rinse of two column volumes (40 mL if two Econo Pak columns are used, 18 mL if Poly -Prep columns are used) of 1 N NaOH is allowed to drip through the column beds as a rinse. At this point, it is assumed that the entire sample has been in contact with the ion exchange media for a sufficient time to allow exchange and that the sample is entirely washed from the ion exchange column.
 - 8.11.1 The sample volume and mass may be recorded at this point, and a sample removed for TOC analysis (combined PNL-ALO-380 and modified PNL-ALO-381 techniques). It is imperative to know the quantity (mass and volume) removed at this point to allow calculation of the TOC amount/gram waste and to account for the amount removed from the total sample at this point.
 - 8.11.2 Calculation can be made between the TOC measured before ion exchange and after ion exchange to determine if there is significant hold-up of the soluble carbon upon the ion exchange resin. Typical yields have been >90% of the carbon present before ion exchange has been found in the column effluent.

- 8.12 The effluent is weighed and the volume estimated. The samples are monitored for contamination and activity by radiation control technicians; they are properly labeled and packaged and delivered for chemical speciation analysis. Typical analytical procedures amenable for these solutions include Ion Chromatography (see Method for Analysis and Quantification of Organic Acids in Simulated Hanford Tank Waste and Hanford Tank Waste by Ion Chromatography), Derivatization GC/GC-MS (See Derivatization of Chelators and their Degradation Products in Mixed Hazardous Waste Samples by Derivatization GC or GC-MS) and Ion Pair Liquid Chromatography (Chelators and their Degradation Products in Mixed Hazardous Waste Samples by Ion -Pair HPLC).
- 8.13 All records of weights, dilutions, and sampling weights for TOC amounts are delivered with the samples from the hot-cell facility.

9.0 Quality Control

- 9.1 Studies have been done^{2,4} that demonstrate that the Na⁺ form of the resin does not contribute to the carbon load or TOC content of the sample. Several lots of AG50W- X8 resin were converted to the Na⁺ form, thoroughly washed with water, and TOC values obtained on elution of a blank sample. These values were <1 µg C/g eluent; which is far less than the significant carbon load from an actual sample, which are typically 10000 µg C/g sample. Additional studies with EDTA and HEDTA spikes indicated that the recovery of these chelators from a spiked blank matrix were on the order of 90% to 95% of the original chelator added to the spike.⁴
- 9.2 No formal studies of accuracy or precision for recovery of spikes in tank matrix have been attempted with this method.

10.0 Method Performance

- 10.1 A waste sample representing an actual waste obtained by core drilling a waste from a double-shell storage tank was analyzed by this method. This material was highly radioactive, with a high concentration of nitrate and nitrite, a hydroxide ion concentration of 2 M and a total organic carbon (TOC) content of 0.94%. Calculation of the TOC remaining after the ion exchange procedure showed a value of 0.85%.⁴ The difference of 0.09% is not considered to be significant in light of the reproducibility of values using the TOC methods (modified PNL ALO 381 and PNL ALO 380 methods). However, it is of note that invariably the values of TOC obtained after ion exchange are lower than those values calculated from TOC results on the native sample.
- 10.2 For actual waste samples recovered from Tank 241-SY-103, the fission products were reduced dramatically by the procedure.^{2,4} These values are tabulated in Table 1.

Table 1. Tabulated Values of Fission Products from Waste Samples from Tank 241-SY-103

<u>Tank layer</u>	<u>Nuclide</u>	<u>Activity Reduction Factor</u>
Non-convective	¹³⁷ Cs	900
Non-convective	⁹⁰ Sr	150
Non-convective	gross alpha	1,400
Convective	¹³⁷ Cs	220
Convective	⁹⁰ Sr	13
Convective	gross alpha	1200

The apparent difference of ⁹⁰Sr removal may reflect the degree of chelation of Sr within the sample. These effects have been documented in studies of Sr-EDTA complexes with electrospray ionization mass spectrometry (ESI-MS)⁵. In general, those samples that contain a larger amount of strongly chelating compounds (such as EDTA and HEDTA) will exhibit more carry-through of fission products (by very gross Geiger counter assay) than those samples that do not contain chelators.

11.0 Calculations

11.1 Calculations are done at the end of the exchange process to determine the total dilution factor introduced to the sample by performing the cation exchange procedure. The following assumptions are made:

1. All chelator carbon is solubilized in the dissolution process
2. No significant hold-up of solubilized carbon is apparent in the syringe filter
3. No significant hold-up of solubilized carbon is apparent in the resin bed, so long as a full column volume of rinse media (1 N NaOH) is used.

The calculation is made according to dilutions and sample diversion to TOC analyses after the initial weighing of the sample:

{Weight Sample/Final eluent weight} - {fraction used for TOC} =
concentration of sample in final eluent product.

The most convenient intermediate calculation for the loss of sample to TOC is determined by

{Total weight at time of sample before TOC sampling event} =
 Fraction of sample remaining after
 Total weight at time of sample before TOC sampling event
 TOC sample event.

12.0 Accuracy and Precision

No formal studies of accuracy or precision in the tank matrix have been attempted with this method.

13.0 References

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7.0 Analytical Techniques

This section discusses in general terms the analytical techniques utilized for sample analysis. Included in this section are discussions of total organic carbon measurements and accurate mass measurements. These discussions are not included under the section 6.0 entitled "Draft Procedures".

7.1 Ion Chromatography for Low-Molecular-Weight Acids

7.1.1 Standard Organic Acid Preparation

Organic acid standards were freshly prepared by dissolving 25-50 mg of free acids or sodium salts of the acids in 25 mL of deionized water. All standard solutions were prepared from commercially obtained reagent-grade chemicals without further purification.

Initially, we prepared standard solutions of glyoxalic acid, glycolic acid, oxalic acid, sodium citrate, sodium acetate, succinic acid, butyric acid, and formic acid. However, we did not detect glyoxalic acid and butyric acid in the samples; therefore, these two acid standards were not used. An IC unit (Dionex Corp., Sunnyvale, California, USA) equipped with a conductivity detector (Dionex, model CD20) was used to analyze LMWA organic acid anions, including formic, glycolic, citric, and oxalic acids. An AS-11 column (Dionex) was used for most analyses. We used an AS-6 column (Dionex) for glycolic acid quantification since glycolic acid co-eluted with acetic acid on the AS-11 column. Concentrations were determined using a linear calibration curve. Quantification based on high dilution is not ideal except for reducing radioactivity levels, but appears to be permissible, as the plots of standard concentration versus response exhibit linear behavior down to 100 ppb for the key analytes acetate/glycolate, formate, oxalate, and citrate in our samples. For example, Figure 7.1 shows a linear plot of formate response and formate concentration. The standard concentrations bracketed the theoretical concentrations of the samples. The IC conditions for use with the AS-11 column are listed below.

Guard column: Dionex AG11
Analytical Column: Dionex AS11
Anion Suppressor: SRS
Flow: 2.0 mL/min
Sample Volume: 25 μ L
Detection: Conductivity
Mobile Phase: Gradient

7.1.2 Mobile Phase Preparation

The mobile phase was comprised of a gradient of water and a weak solution of sodium hydroxide for the AS 11 column. Two solutions, 5 mM and 100 mM NaOH, were prepared from 18.5 M NaOH stock solution. The water used to make the solution and run the gradient was stirred under vacuum for over 12 hours and then sparged with helium to avoid interference from dissolved carbon dioxide. The gradient conditions used for the AS-11 column are shown in Table 7.1. The column is allowed to equilibrate with 0.5 mM NaOH for at least 7 minutes after each run.

Table 7.1. Mobile Phase Gradient

<u>Time (minutes)</u>	<u>% Water</u>	<u>5 mM NaOH</u>	<u>100 mM NaOH</u>
0.0	90	10	0
2.9	90	10	0
6.4	0	100	0
18.4	0	65	35

The mobile phase for the AS-6 column was made up of 0.4 mM pentafluorobutyric acid in water. We used 5 mM tetrabutylammonium hydroxide as a suppression eluant. Further details for

the AS-6 column conditions are listed below.

Guard column:	None
Analytical Column:	Dionex ICE-IonPac AS6 (9x250 mm)
Flow:	1.0 mL/min.
Sample Volume:	25 μ L
Mobile Phase:	0.4 mM pentafluorobutyric acid
Detection:	Conductivity
Suppresser:	AMMS-ICE
Suppression eluant:	5 mM tetrabutylammonium hydroxide
Suppression eluant flow:	3 mL/min.

Earlier attempts to analyze LMW organic acids included high-performance liquid chromatography (HPLC) with ultraviolet (UV) detection. For identification and quantification of acetic, formic, and glycolic acid, an ion exclusion column (Waters Inc.) was used with 0.01 N H₂SO₄ as the mobile phase. However, due to high nitrate and nitrite concentration, quantification of citrate, succinate, and glycolate in a simulated waste sample was difficult. Oxalic acid was quantified by HPLC using a Dionex AG4A guard column and Dionex AS4A analytical column, with 75% of 1.7 mM NaHCO₃ and 25% 1.8 mM Na₂CO₃ as the isocratic mobile phase. A variable wavelength UV detector was used with the wavelength fixed at 210 nm.

Chromatography Conditions for Real Waste Samples: The IC of real-waste samples, which were found to have low levels of radioactivity, was accomplished using an isolated chromatography enclosure equipped with a Rheodyne 9126 manual injection valve, AS-11 column (DIONEX), and isolated conductivity cell. The major advantage of this system is that it allows for quick switching from use with radioactive samples to ordinary analysis without concern for radioactive contamination of the key components used in ordinary analysis. The separation employed allows for rapid screening of mono-, di-, and tri-valent carboxylic acids in a ramped sodium hydroxide elution (see Table 7.1): 0.5 mM NaOH for 3 minutes, ramping to 5 mM NaOH over the next 3.5 min (total time = 6.5 minutes), then ramping to 37.5 mM NaOH over the next 12 minutes (total time = 18.5 minutes). With this system, good separation can be obtained for the organic acids (formate, oxalate, citrate) from other potential interfering inorganic anions (fluoride, chloride, nitrite, nitrate, sulfate, and phosphate).

Preparation of Real Tank Waste Samples: Real waste samples were successfully analyzed using IC. Hanford Tank AN-107 is an example of a highly aged relatively organic-rich Hanford tank waste matrix. The sample tank material was dissolved in water and subjected to cation exchange, using Dowex AG50W-X8 cation exchange resin in columns to reduce the amount of fission products in the sample for subsequent carboxylate and chelator analysis (Campbell et al. 1997). This treatment also results in a 10X dilution (g/g) of the sample into a dilute caustic matrix not drastically different from the matrix of the original sample. To do IC, an additional 500X dilution was used to dilute the major inorganic ions (nitrite and nitrate) to levels that would not overload the separating power of the column. 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 overlapping and poorly resolved peaks for the mono-valent carboxylates. We have found that diluting nitrate to a concentration that delivers 10-20 microsiemens response eliminates this problem.

7.2 Ion-Pair Chromatography for Chelators and Chelator Fragments

The instrumentation used to optimize separation and identification of the chelator fragments in a standard mixture and in simulated waste samples included a Hewlett Packard Series 1050 Isocratic HPLC pump, a Unicam 4225 UV detector, and an HP 3396 Series II integrator for data collection. The analytical column was a Brownlee RP 18, 25 cm x 4.6 mm, spheri-5 monofunctional 5 μ C18 with equivalent guard column. The mobile phase consisted of 0.02 M dodecyltrimethylammonium bromide as the ion-pairing agent and 0.05 M potassium dihydrogen phosphate to buffer the system. The pH was brought up to 5.5 using 6 N NaOH. Samples were prepared by weighing 50 mg in 25 mL of solution and pipetting 1 mL of the latter into

a 10-mL volumetric flask. A 50- μ L quantity of 0.5 M CuSO_4 was added to complex with the analytes, thus making them visible to the detector. The solution was then diluted to the mark, and 20 μ L was injected into the HPLC for ion-pair chromatographic analysis.

Chromatographic analysis of the waste samples was carried out on a Waters Liquid Chromatographic system that included a Waters HPLC Pump Model 510, a Waters 484 Tunable Absorbance Detector, a Waters Millipore System Interface Module, and a Waters 712 WISP autosampler. Data were processed using an NEC APCIV Advanced Personal Computer Power Mate 1 with an AMDEC Video-310A monitor and a Panasonic KX-P1180 multimode printer.

The analytes in the wastes were separated using an Adsorbosphere C-8 analytical column (25 cm x 4.6 mm, particle size 5 μ m) with an Adsorbosphere C-8 cartridge guard column. The flow rate was 1.5 mL/min, and the sample volume injected was 20 μ L. The analytes were detected as the copper complex by means of a UV detector at 280 nm. The mobile phase consisted of nd2 MM dodecyltrimethylammonium bromide as the ion-pairing agent and 0.05 M potassium dihydrogen phosphate to buffer the solution to pH 6.5.

Sigma provided EDTA in the form of the tetrasodium salt: hydrate and HEDTA in the form of the trisodium salt (the salts of these chelators were used because of the low solubility of EDTA and HEDTA in water). Aldrich provided IDA and NTA (nitriloacetic acid), D. Meisel of Argonne National Laboratory provided S-EDDA and U-EDDA, and the ED3A used was synthesized here at PNNL. We placed 50 mg of each chelator in a 25-mL volumetric flask and added Milli-Q water to the mark. We pipetted 1 mL of this solution into a 10-mL volumetric flask and added 50 μ L of 0.5 M CuSO_4 . The solution was then swirled and diluted to volume with water. The final concentration of the chelator was 0.200 mg/mL. These standards were then analyzed as the copper complex by ion-pair chromatography.

Two actual waste samples, SB-2 and 6800-2, taken from the native convective layer in Tank SY-103, were also analyzed. The convective layer is a transparent brine that floats on top of the nonconvective layer, a granular gray-colored sludge. The waste samples were passed through a Bio-Rad Analytical Grade Cation Exchange Column containing 7 mL of Dowex resin (50W-X8, 50-100 mesh, sodium form) in a remote-handling hot cell, which removed almost all of the radioactivity caused by primary fission products in the waste before being transferred to the instrument for analysis. The cation exchange process reduces the radioactivity levels by as much as 1000-fold without removing or introducing any organic carbon and has been described in detail by J. A. Campbell et al. Sample SB-2 was heated to 60°C for about 2 weeks. It was diluted by a factor of 25 using several steps of water and water with 1 N NaOH in the process of going through the cation exchange column. Sample 6800-2 was not heated. It was diluted by a factor of 8.7, again from repeated washings of water as well as water and 1 N NaOH through the column. The original samples had a density of 1.4 g/mL. Twenty μ L of the diluted samples were injected directly and analyzed as the copper complex by ion-pair chromatography.

A quantitative analysis of EDTA in the waste samples was performed using a standard solution of EDTA, 0.204 mg/mL, prepared as described previously.

Calibration curves showing the linear response of several of the chelator standards were obtained using ion-pair chromatography with a pH gradient. The mobile phase used for this work consisted of 1) component A - nd2 M dodecyltrimethylammonium bromide and 0.05 M potassium dihydrogen phosphate, pH 6.5 and 2) component B - nd2 M dodecyltrimethylammonium bromide and 0.05 M potassium dihydrogen phosphate, pH 5.5.

7.3 Derivatization GC/MS for Chelators and Degradation Products

The derivatization of the chelator standards, the procedure for analysis of waste samples, and instrumental conditions will be discussed.

7.3.1 BF_3 /Methanol Methylation of Chelator Standards

Approximately 1 mL of a 12% w/v solution BF_3 /methanol (Aldrich) was added to about 5 mg of the chelator in a reaction vial, and the mixture was vortexed and heated for varying lengths of time (1 to 2 h) at 100°C , depending on the chelator being derivatized. One mL of chloroform was added to the cooled reaction mixture and vortexed. A buffer solution (0.4 M KH_2PO_4) was made, and the pH was adjusted to 9.5 using sodium hydroxide. When this buffer solution was added to the contents of the vial, the solution was separated into two layers, and an aliquot was removed from the chloroform layer for GC/MS analysis. Parent ion assignment was confirmed by using positive ion chemical ionization MS.

7.3.2 Analysis of Waste Samples

The waste samples represented several segments of actual waste obtained by core sampling the waste in Tank 101-SY. This material was highly radioactive and contained high molar concentrations of nitrate and nitrite; the OH^- concentration was at least 2 M. The TOC for these samples was 1.1-1.4%.

For highly radioactive wastes, e.g., 3-11 R/h, a hot cell facility must be used. This room is composed of thick walls (≈ 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, ≤ 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 are usually based upon local practice or the judgment of the resident health physicist.

Approximately 2 g of the solids from the composite 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. The resin must not be used in the usual H^+ form since the chelator analytes tend to precipitate from solution as insoluble free acids when the matrix is exposed to the acid form of the resin. The sodium form of the cation exchange resin is conveniently prepared by stirring the resin with sufficient 6 N NaOH until the solution remains basic to pH paper. The resin is then washed with deionized water. After elution through the cation exchange resin, the net reduction of fission products (chiefly ^{137}Cs and ^{90}Sr) was sufficient (2-3 mR/h per sample) that the sample could be removed from the hot cell environment and safely worked within a protected hood.

Measured aliquots 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% 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 KH_2PO_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.

Total Organic Carbon Measurements

Total organic carbon was determined using the hot persulfate oxidation method (Baldwin et al. 1994). This procedure uses the wet oxidation/extraction method of hot acidic silver-catalyzed persulfate oxidation, followed by measurement of CO_2 by coulometry detector. All carbon species, as liquids, acid-soluble sludges, or acid-soluble solids, are oxidized to CO_2 by the silver-ion-catalyzed persulfate reaction.

7.3.3 Instrumentation

GC/MS Conditions

A fused silica column (DB-5, 30 m X 0.25 mm i.d., 0.25- μ 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

Accurate mass measurements used to verify the identity of unknown components by providing elemental composition were performed on a JEOL SX-102/SX-102 double-focusing MS. 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 a 30 m \times 0.25 mm i.d. DB-5 capillary column (J & W Scientific, Folsom, California). The GC oven temperature was held at 50°C for 2 min., then programmed at 5°C/min to 250°C.

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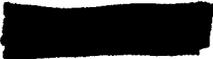
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9.0 Future Plans

The objective of the organic analysis task is to apply organic analytical methods to identify and/or quantify the specific organic species in actual tank wastes for both the Organic Tanks Safety Program and the Flammable Gas Safety Program. As analytical problems, such as different waste types, interferences, etc., arise, methods will be modified to produce the needed results. Initial efforts in FY 1998 will focus on documentation and more rigorous development of the ion-pair LC method for quantitative determination of chelator fragments to avoid costly and problematic derivatization GC/FID and GC/MS currently employed. In addition, efforts to interface this LC method to MS for verification of component identification will be pursued.

Present plans for FY 1998 include stopping the Actual Waste Analysis Task in the Flammable Gas Project and continuing the Advanced Tank Waste Analysis Task in the Organic Tanks Safety Project. Analytical capabilities will be used to support other PNNL Flammable Gas Tasks, such as Gas Generation Studies (Sam Bryan, Task Leader) and Gas Bubble Retention Studies (Phil Gauglitz, Task Leader) as needed. In addition, analytical support will be provided for the Waste Aging Studies (Don Camaioni, Task Leader). Considerable effort during FY 1998 will be devoted to HASQARD compliance and procedural documentation. In addition, efforts will be undertaken to understand the loss of organic carbon in the cation exchange sample preparation procedure for samples from Tanks BY-104 and U-105.

Appendix A 

**Analysis and Quantification of Organic Acids in
Simulated Hanford Tank Waste and Hanford Tank
Waste**

SECRET

Analysis and Quantification of Organic Acids in Simulated Hanford Tank Waste and Hanford Tank Waste

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Abstract:

Simulated Hanford tank waste samples were analyzed for organic acids before and after g-irradiation. Ion-exchange chromatography (IC) was used for the analysis for low-molecular-weight (LMW) organic acids and proved to be an improvement over the previously used high performance liquid chromatography-ultraviolet detection (HPLC-UV) method. Known quantities of sodium salts of ethylenediaminetetra acetic acid (EDTA), N-(2-hydroxyethyl)ethylenediaminetetraacetic acid (HEDTA), citric acid, and glycolic acid were added to the tank waste simulants before exposure. The breakdown products of gamma-irradiated simulated tank waste samples included formic, succinic, and oxalic acids. These acids were identified and quantified using IC without any interference from nitrates, nitrites, or any other inorganic anions in the simulated waste. However, when HPLC-UV was used, nitrates and nitrites were found to interfere with the quantification of LMW organic acids. Ion chromatography techniques were also used on actual Hanford tank waste to quantify and analyze LMW organic acids. These efforts will assist in understanding Hanford tank waste chemistry and improving the carbon balance of tank waste samples.

Introduction:

The U. S. Department of Energy has 177 single and double shelled tanks at the Hanford site in south-central Washington state that contain mixed hazardous waste. A mixed hazardous waste is defined as a waste containing both hazardous chemicals and radionuclides. In addition, these tanks contain large quantities (150-250 tons) of chelators including ethylenediaminetetra acetic acid (EDTA) and N-(2-hydroxyethyl)ethylenediaminetetraacetic acid (HEDTA) (1). The chelators form water-soluble complexes with cations, including radionuclides and heavy metals, thus enhancing their migration in soils (2, 3). Furthermore, after over 40 years of storage under radiolytic conditions, chelator degradation fragments may have been produced that may also form cation complexes. Therefore, the knowledge of chelator degradation mechanisms and their breakdown products is essential for the safe handling and storage of tank waste. Efforts are underway to study the effects of radiolysis on these chelators and their breakdown products by exposing simulated waste to radiolytic conditions for varying lengths of time. Simulant waste material (SWM) is a preparation used to study Hanford tank waste chemistry. The SWM contains most of the constituents found in Hanford tanks with the exception of the radionuclides. This material can be studied without the hindrance associated with highly radioactive samples. Previous experiments with SWM have indicated that low molecular weight (LMW) organic acids, including formic and oxalic acids, are formed when HEDTA and EDTA, in an inorganic matrix, are exposed to radiolysis. However, organic quantification is difficult in the complex tank waste matrices due to interference from inorganic components.

The usual method for LMW organic acid analysis is capillary gas chromatography (GC) with or without mass spectrometry after solvent extraction and derivatization (4, 5). The derivatization techniques used are (a) formation of methyl esters using BF_3 /methanol or diazomethane, (b) formation of trimethylsilyl esters using trimethylsilyl reagents and, (c) formation of butyl esters using HCl/butanol. Another routine method for analyzing LMW organic acids is high performance liquid chromatography (HPLC). Organic acids have been analyzed using normal phase silica separation, but more frequently they have been separated underivatized (6, 7) or as their phenacyl derivatives (8). A cation-exchange column for HPLC separation with a dilute acid as mobile phase and UV detection at 210 nm has also been used for LMW organic acid analysis (9). However, UV detection is not specific as several organic and inorganic species absorb at 210 nm. Other methods of organic acid analysis include plasmaspray liquid chromatography (10,11) and ion-exclusion partition chromatography (12).

Historically, LMW organic acids, such as oxalic and glycolic acid, in tank waste samples were analyzed using HPLC with UV detection (13). However, high concentrations of nitrate and nitrite often interfered with quantitation. Poor sensitivity for LMW organic acids was exhibited by UV detection. A thermospray liquid chromatography-mass spectrometer (LC/MS) has also been used for qualitative determination of LMW organic acids and chelator fragments with moderate success (4). 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 (4). However, oxalic acid could not be detected by LC/MS. Therefore, a simple but robust IC technique was developed to analyze LMW organic acids. This method required minimum sample preparation and was found to be effective for identifying and quantitating these acids (14).

The IC method developed by our research group was used to detect and analyze LMW organic acids in simulated tank waste and actual tank waste. The components identified and quantified in actual Hanford tank waste include formic, oxalic, and citric acid. The results of these analyses are reported here. This method can potentially be applied to analyze effluents containing nitrates and nitrites such as those collected from pesticides and explosives processing plants. The results from our investigation show that IC can be effectively used to identify and quantify LMW organic acids in the presence of high nitrate and nitrite concentrations found in Hanford tank waste samples and also in effluents from pesticide and explosive processing plants.

Experimental Methods:

Standard Organic Acid Preparation:

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. However, glyoxalic acid and butyric acid were not detected in the samples, and these two acid standards were not used.

Analysis by Ion Chromatography:

Analyses of LMW organic acid anions, including formic, glycolic, citric and oxalic acids, were carried out using a Dionex model IC unit (Dionex Corp., Sunnyvale, California, USA) equipped with a Dionex, Model CD20 conductivity detector. A Dionex AS-11 column was used for most analyses. We used a Dionex 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 AS-11 chromatographic conditions are listed in Table 1.

Table 1: AS-11 Conditions

Guard column	Dionex AG11
Analytical Column	Dionex AS11
Anion Suppressor	ASRS-I, 4 mm
Flow	2.0 mL/min
Sample Volume	25 μ L
Column Temperature	Ambient
Detection	Conductivity

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. The water used to prepare the mobile phase and run the gradient was stirred under vacuum for over 12 hours and then sparged with helium to avoid interference from dissolved

carbon dioxide. Gradient conditions used for AS-11 column separation are shown in Table 2. The column was allowed to equilibrate at initial conditions for at least 7 minutes before each run.

Table 2: Mobile Phase Gradient

<u>Time (minutes)</u>	<u>% Water</u>	<u>5 mM NaOH</u>	<u>100 mM NaOH</u>
0.0	90	10	0
2.9	90	10	0
6.4	0	100	0
18.4	0	65	35

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 eluant. Further details for AS-6 column conditions are listed in Table 3.

Table 3: AS-6 Column Conditions:

Guard column:	None
Analytical Column:	Dionex ICE-IonPac AS6 (9x250 mm)
Flow:	1.0 mL/min.
Sample Volume:	25 µL
Mobile phase:	0.4 mM heptafluorobutyric acid
Detection:	Conductivity
Suppresser:	AMMS-ICE
Suppression eluant:	5 mM tetrabutylammonium hydroxide
Suppression eluant flow	3 mL/min.
Column Temperature	Ambient

Chromatography Conditions for Hanford Tank Waste Samples:

Radioactive samples were analyzed a chromatography enclosure that was fabricated inhouse. It 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, California, 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 (see Tables 1 and 2).

Simulated Tank Waste Preparation

About 130 mL of simulant slurry were prepared by mixing a variety of inorganic salts with sodium hydroxide and deionized water. The specific chemical composition of the simulant is summarized in Table 4 (15).

Table 4: Composition of Simulated Tank Waste

<u>Species</u>	<u>mg/g</u>	<u>Species</u>	<u>mg/g</u>	<u>Species</u>	<u>mg/g</u>
HEDTA ⁻³	16.9	Al ⁺³	1.493	Ca ⁺²	0.080
EDTA ⁻⁴	3.1	F ⁻	1.281	Mn ⁺²	0.068
Citrate ⁻³	17.3	Pb ⁺²	1.066	Cr ⁺³	0.044
Glycolate ⁻	11.3	PO ₄ ⁻³	0.507	Cl ⁻	nd4
NO ₃ ⁻	109	SO ₄ ⁻²	0.506	Pd ⁺²	nd3
Na ⁺	107	Bi ⁺²	0.419	Rh ⁺³	nd3
OH ⁻	39.3	Ce ⁺³	0.377	Ru ⁺⁴	nd3
NO ₂ ⁻	37.9	Ni ⁺²	0.099	H ₂ O	640
Fe ⁺³	2.61				

The simulant samples were exposed to various doses of gamma irradiation for 1-2 weeks in a sealed stainless steel bomb reactor. The bomb reactor was recovered after irradiation. Four aging tests were run, one each at 0.3, 0.5, 1.0, and 1.5 MGy at 70°C. The average temperature within the tanks has been estimated to be above 65°C; therefore, these experiments were conducted at 70°C. After irradiation, the contents of the vessel were quantitatively transferred to a 500-mL volumetric flask and diluted to volume with water. The resulting solution was further diluted 250-fold and analyzed using IC for organic acids. In addition, a non-irradiated control simulant was mixed and then analyzed.

Preparation of Hanford Tank Waste Samples:

Actual Hanford tank waste samples were successfully analyzed using IC. Samples collected from Hanford Tank AN-107 are typical examples 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 in the sample (16). A hot cell is a room built with thick walls (~1.3 m), equipped with a sample entry port, viewing windows made from leaded glass and filled with oil, and remote manipulators (5). A hot cell must be used to handle highly radioactive wastes (~3-11 R/h) safely. All samples are prepared in the hot cell using remotely controlled mechanical arms. The cleanup procedure used Poly prep, 40 mm × 8 mm, disposable fritted columns packed with AG50W-X8 cation exchange resin, sodium form (Bio-Rad, Hercules, California). The treatment within the hot cell also results in a 10-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 mono-valent carboxylates. We have found that diluting nitrate to a concentration that delivers 10-20 microsiemens response eliminates this problem.

Analysis by anion exchange and acid exclusion method:

The chromatographic conditions used for anion exchange and acid exclusion chromatography are listed in Tables 5 and 6. Anion exchange chromatography was used primarily to determine the oxalic acid content of the samples. This separation was carried out in a basic mobile phase.

Table 5: Anion Exchange Chromatographic Conditions

Column:	Dionex Ion Pac A54A (250 mm x 4.0 mm)
Guard Column:	Dionex Ion Pac AG4A (50 mm x 4.0 mm)
Mobile Phase:	1.3 mM NaHCO ₃ and 1.4 mM Na ₂ CO ₃
Flow:	2 mL/min
Detection:	UV, 210 nm
Sample Volume:	10 µL
Column Temperature	Ambient

Ion exclusion chromatography was used to determine a variety of organic acids. With this technique, formic acid, acetic acid, and glycolic acid, among others, were determined. The target analytes were quantitated using the external standard method. Analyte peaks were confirmed by co-injection of the sample and standard. Acid-exclusion chromatographic conditions are listed in Table 6.

Table 6: Acid-Exclusion Chromatographic Conditions

Guard column:	Waters IC-PAK, Guard-PAK
Analytical Column:	Waters IC-PAK, 7.8 x 300 mm
Flow:	0.6 mL/min
Sample Volume:	20 µL
Detection:	UV, 210 nm.
Mobile phase:	0.01 N H ₂ SO ₄
Column Temperature	Ambient

Attempts to analyze LMW organic acids included acid-exclusion chromatography with UV detection. The conditions are listed in Table 6. However, nitrate and nitrite were highly concentrated, making it difficult to quantify citrate, succinate, and glycolate in waste samples. Oxalate could not be analyzed on the Waters IC-PAK column because it co-eluted with the nitrate. However, oxalic acid was successfully quantified using an anion exchange system with a UV detector set at 210 nm and Dionex Ion Pac A54A column. The instrument conditions are listed in Table 5. This method was abandoned in favor of the much more sensitive procedure outlined in Tables 1 and 2.

Results and Discussion:

Analysis of organic acids in a complex matrix (slurries and sludges) containing excess amounts of nitrates, nitrites, and other transition metal salts is difficult by conventional techniques. Separation using LC followed by UV-vis detection is not practical because the target analytes do not contain a chromophore. Initial attempts to analyze and quantify the organic acids in simulated tank waste by liquid chromatography with UV detection met with several problems. For example, two methods were required to analyze oxalic, acetic, formic, citric, succinic, and glycolic acid because oxalic acid could not be analyzed by the same method that was used for the remaining acids. Furthermore, high concentrations of nitrate and nitrite made it difficult to quantify citrate, succinate, and glycolate. Figure 1(a) shows an LC chromatogram of a standard mixture of LMW organic acids, while Figure 1(b) is a chromatogram of a simulated waste under identical conditions.

Insert Figure 1(a) here

Insert Figure 1(b) here

As seen in Figure 1(a), citric, succinic, glycolic, and formic acid could be separated and quantitated by the LC technique. However, in the presence of nitrate and nitrite, these LMW organic acids could not be quantitated by LC {see Figure 1(b)}. Diluting the simulated waste sample was not an effective solution for reducing the interference from nitrate and nitrite because dilution further reduced the 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 transition metal impurities. All target acids, except glycolic, succinic, and acetic acid, were analyzed using the AS-11 column. Glycolic acid was found to co-elute along with acetic acid on the AS-11 column; therefore, an AS-6 column was used to quantify glycolic and acetic acid. It is unlikely that these two LMW acids can be quantified by other means, such as GC/MS analysis. 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 the 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 ppb for the key analytes. These analytes include acetate/glycolate, formate, oxalate, and citrate in our samples. For example, Figure 2 shows a linear plot of formate response versus formate concentration. The retention time for each organic acid separated and analyzed by the AS-11 column is listed in Table 7.

Insert Figure 2 here

Table 7: Retention Time of Carboxylic Acid Anion using the AS-11 Column.

<u>Organic Acid Anion</u>	<u>Retention Time (minutes)</u>
Formate (HCOO ⁻)	2.56 (± 0.20)
Oxalate	10.31 (± 0.20)
Citrate	13.94 (± 0.20)

An IC chromatogram of a 4-ppm standard solution illustrates the elution scheme using the AS-11 column in Figure 3(a). Figure 3(b) is a chromatogram of a simulated waste under identical conditions.

Insert Figure 3(a) here

Insert Figure 3(b) here

As shown in Figure 3(b), no interference from any inorganic anions was observed. Furthermore, the response of the LMW organic acid was significantly improved under IC conditions as opposed to HPLC conditions for identical concentration. The retention time of carboxylic acid anions separated and analyzed by the AS-6 column is listed in Table 8. A chromatogram of a 4-ppm standard solution in Figure 4(a) illustrates the elution scheme of these acid anions on the AS-6 column, while Figure 4(b) shows the analysis of a simulated waste sample by the AS-6 column.

Table 8: Retention Time of Carboxylic Acid Anion using the AS-6 Column

<u>Organic Acid Anion</u>	<u>Retention Time (minutes)</u>
Glycolate	9.59 (± 0.20)
Acetate	15.37 (± 0.20)
Succinate	16.35 (± 0.20)

Insert Figure 4(a) here

Insert Figure 4(b) here

As shown in Table 4, citric acid and glycolic acid were added to the slurry before irradiation. Therefore, the concentration of these acids in the control sample should be non-zero. Table 9 lists results from analyzing irradiated and unirradiated simulant using IC. As shown in Table 9, all target analytes were successfully analyzed using IC without any inorganic interferences. Significant quantities of formic, oxalic, glycolic, and citric acid were determined along with small amounts of

acetic and succinic acid. For example, the detected levels of oxalic acid concentration were as high as 8.5 mg/g (1.5 MGy dose rate). The highest concentration observed for acetic acid was 0.55 mg/g, and succinic acid concentration was nd mg/g (1.5 MGy dose rate).

Table 9: Concentration (in mg/g) of reactants and products in g-irradiated tank waste simulant.

Dose (MGy)	Formic Acid	Oxalic Acid	Glycolic Acid	Citric Acid	Acetic Acid	Succinic Acid
0 (control)	nd	nd	8.34±0.03	15.4±0.1	0.19±0.2	nd
0.30	0.8±0.1	1.7±0.1	7.54±0.11	14.9±0.1	0.35±0.1	1.0 ¥ 10 ⁻⁴
0.50	1.7±0.2	2.8±0.2	6.77±0.02	13.8±0.1	0.42±0.1	2.9 ¥ 10 ⁻⁴
1.00	2.5±0.1	3.5±0.2	5.91±0.01	12.6	0.48±0.1	10.9 ¥ 10 ⁻⁴
1.50	4.5±0.2	8.5±0.2	5.30±0.01	11.4±0.1	0.55±0.01	17.8 ¥ 10 ⁻⁴

Analysis of Hanford Tank Waste: Several actual waste samples were successfully analyzed for LMW organic acids using IC by the AS-11 column. Figure 5 illustrates the elution scheme of LMW organic acids in a sample from Hanford Tank AN-107. The concentration of these acids was determined by an external standard method and are listed in Table 10.

Table 10: Concentration (in mg/g) of low-molecular weight organic acids in Hanford tank waste.

Tank I. D.	Acetic/Glycolic Acid	Formic Acid	Oxalic Acid	Citric Acid
S-102	1.2	1.7	4.4	0.0
U-107	2.3±0.1	2.5±0.3	0.6±0.1	0.5±0.1
AN-107	7.6±0.5	4.5±0.5	14.2±3.3	4.4±0.2

Insert Figure 5 here

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 the AS-6 column, which employs a separate chromatographic mechanism based on ion exclusion to distinguish these relatively similar acids.

Conclusion:

Analysis and quantitation of LMW organic acids in the presence of nitrate, nitrites, and transition metal elements can be carried out effectively by using ion chromatography techniques. Thus, extensive sample preparation, such as one needed for analysis by GC/MS (BF₃/methanol derivatization) can be avoided. Additionally, the IC technique was found to show a significant improvement in analysis, separation, and quantification over LC-UV and GC/MS techniques. The information gathered using IC will assist in determining the mechanism of chemical transformation of organic acids in the presence of gamma radiation. Further, accurate determination of organic species will assist in predicting energetics in Hanford tanks. This study shows that the IC technique can be used to analyze LMW organic acids in effluent from explosive and pesticide processing.

Acknowledgment:

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Figure Captions

Figure 1(a): LC Chromatogram of LMW organic acid standards (no simulant present) with UV Detection

Figure 1(b): LC Chromatogram of LMW organic acids (in simulated waste) with UV Detection

Figure 2: Variation in Concentration Vs. Response for Formic Acid on AS-11 Column

Figure 3(a): IC Chromatogram of 4-ppm LMW organic acids standards (in absence of simulated waste) with conductivity detection using AS-11 Column

Figure 3(b): IC Chromatogram of LMW acids in simulated waste (after 1-MGy exposure) with conductivity detection using AS-11 Column

Figure 4(a): IC Chromatogram of 4-ppm LMW organic acids standards (in absence of simulated waste) with conductivity detection using AS-6 Column

Figure 4(b): IC Chromatogram of LMW acids in simulated waste (after 1-MGy exposure) with conductivity detection using AS-6 Column

Figure 5: IC Chromatogram of LMW acids in Hanford Tank Waste (Tank I. D., AN-107) with conductivity detection using AS-11 column

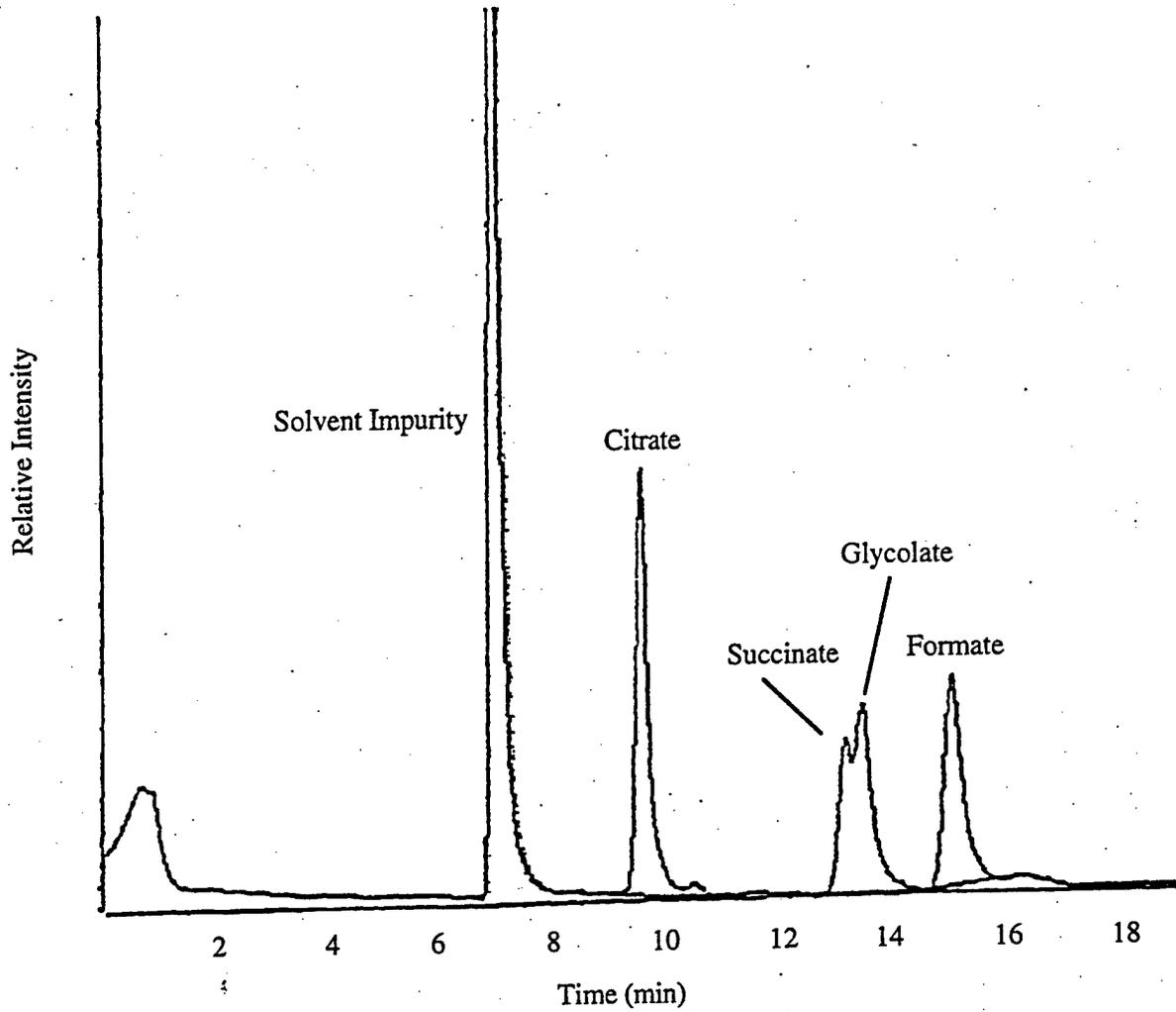


Fig (a)

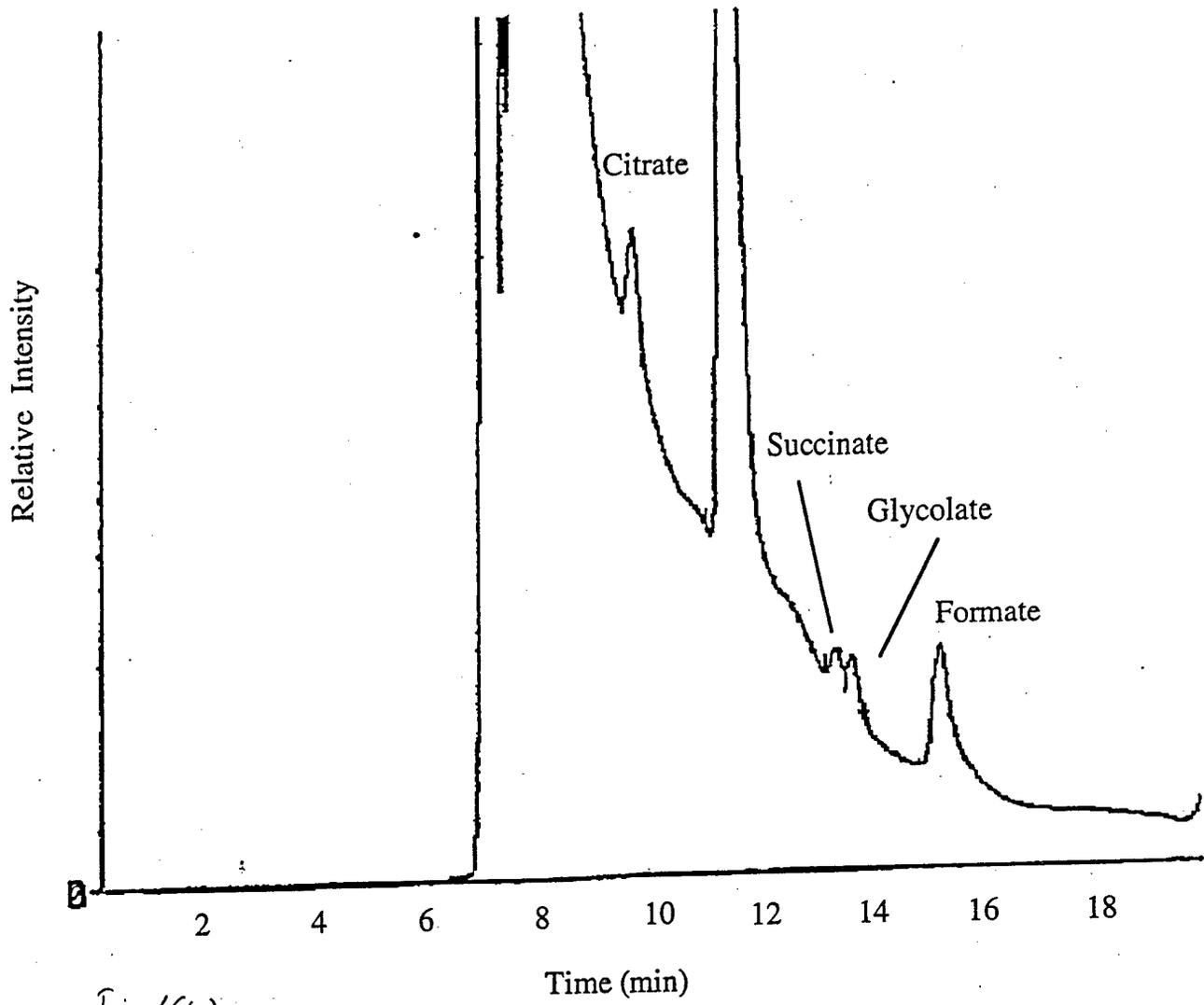


Fig (6)

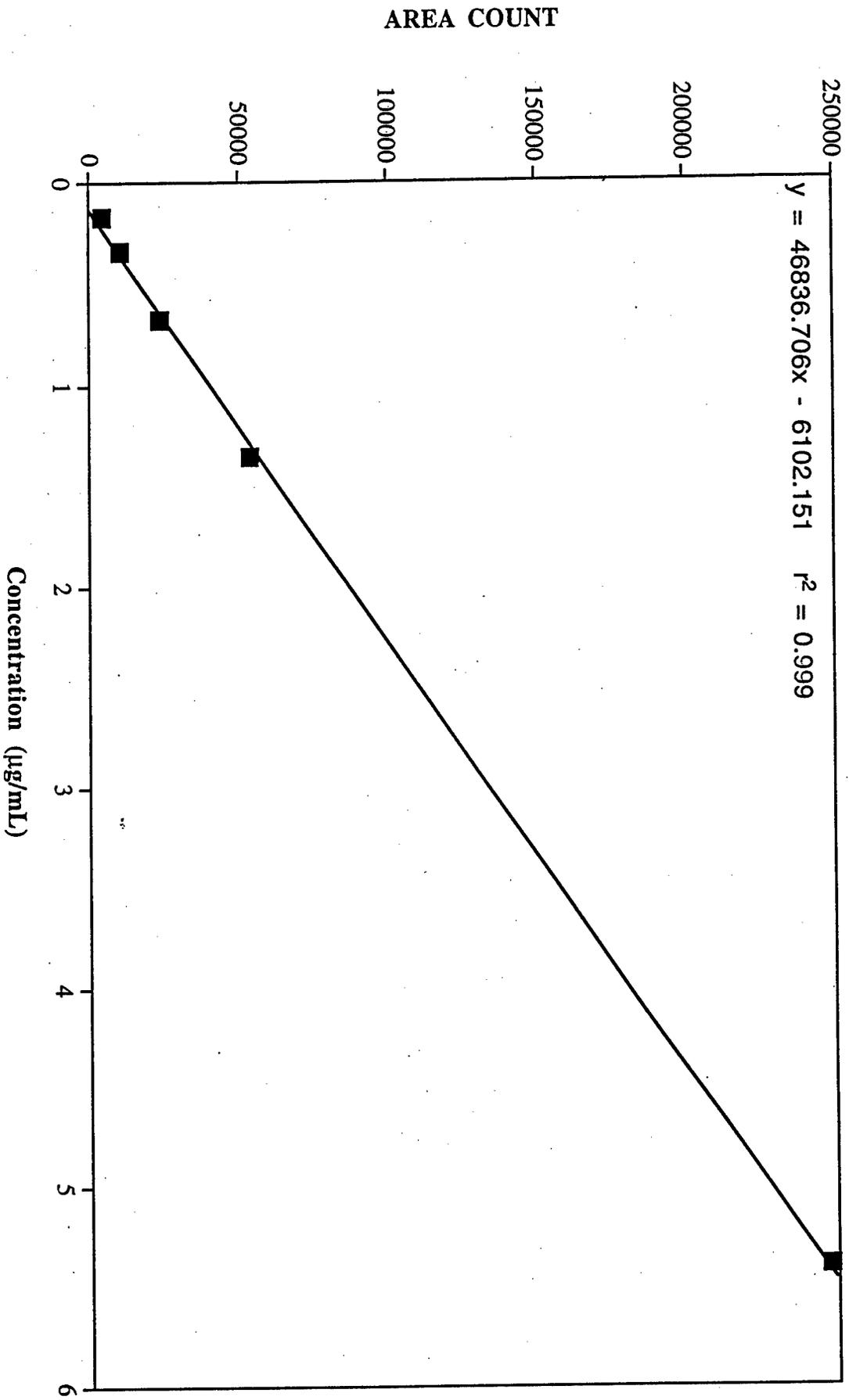


Figure 3: Variation in Concentration vs. Response for formic acid on AS-11 column.

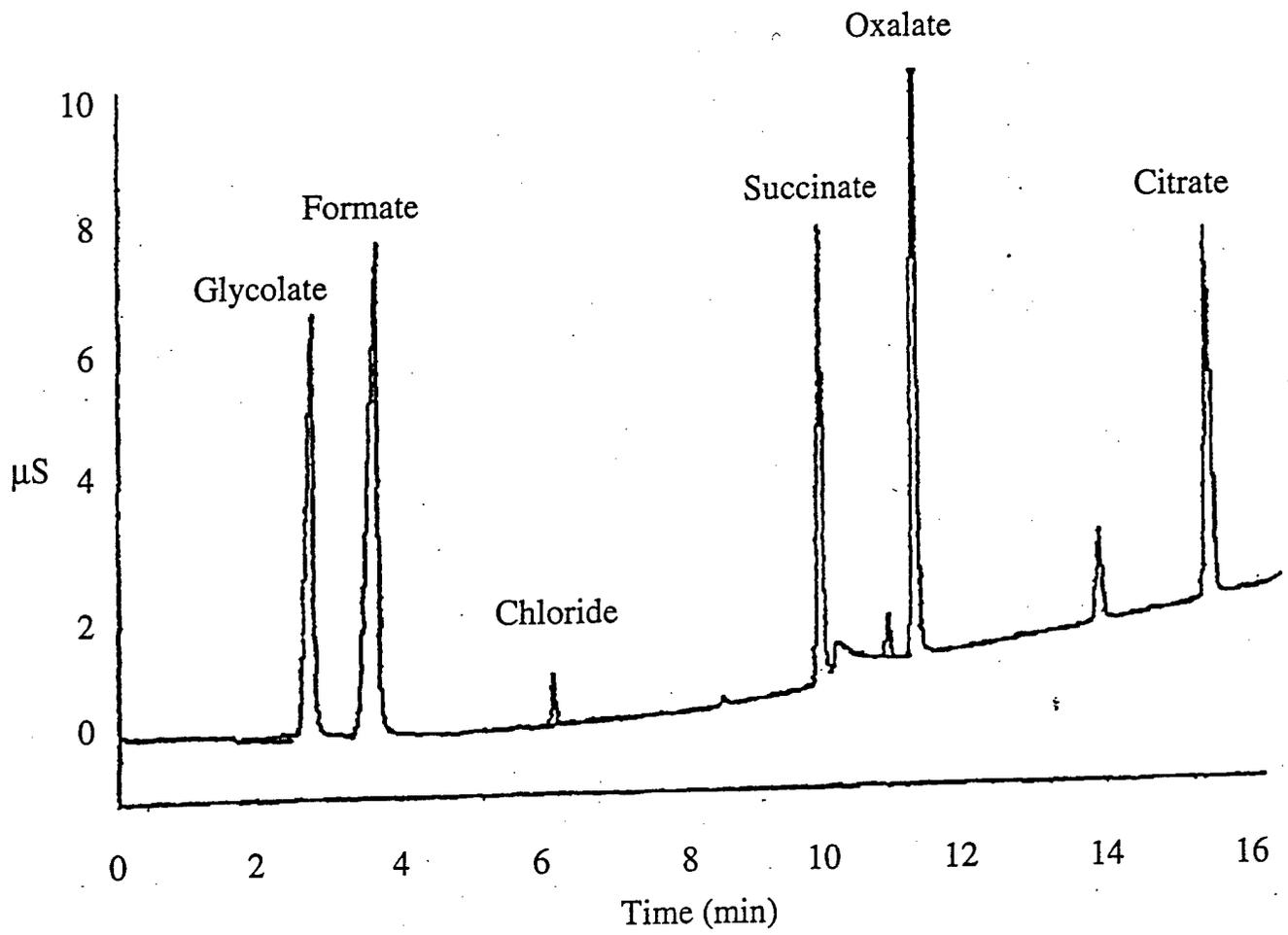
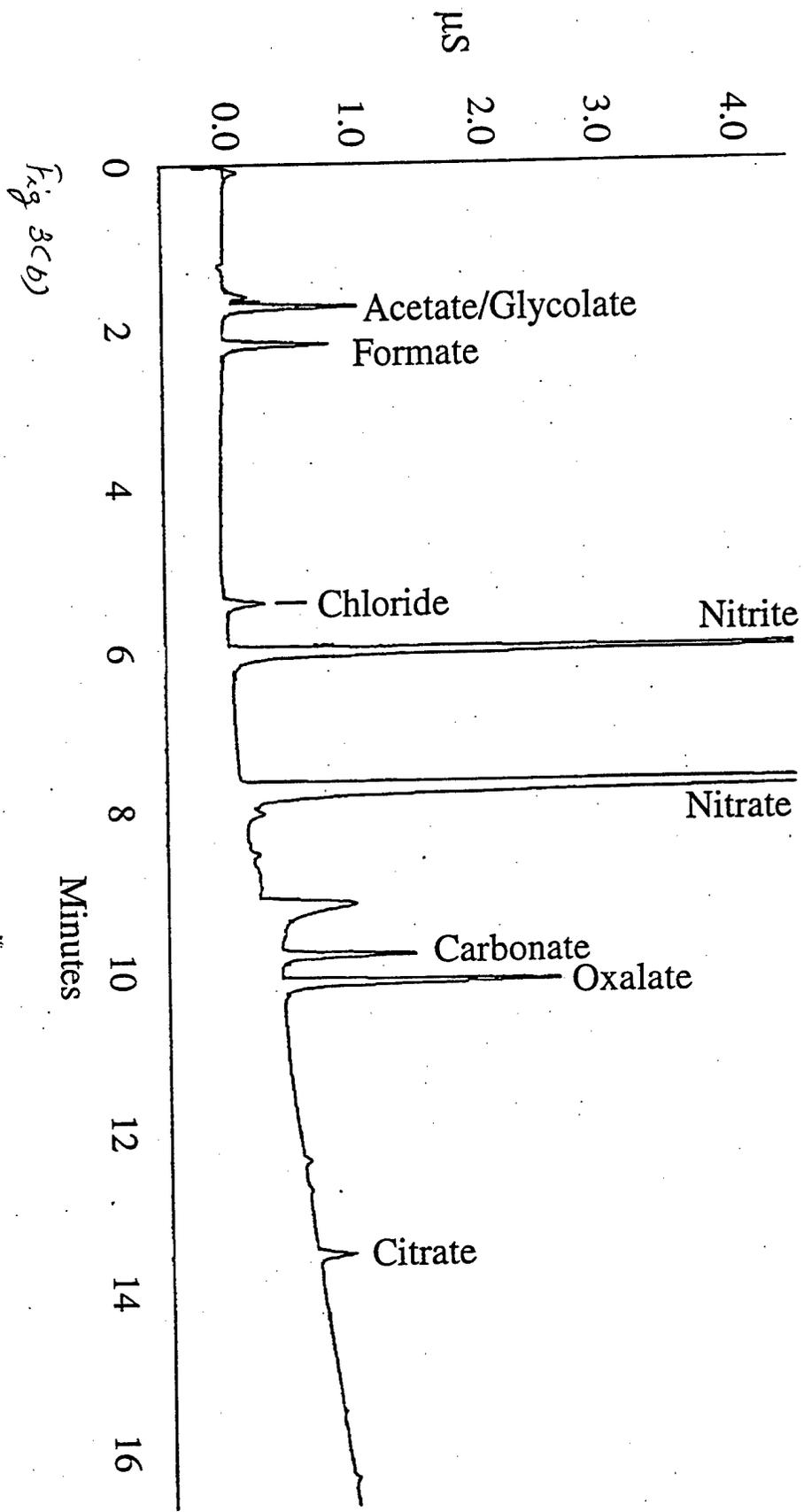


Fig 3(a)



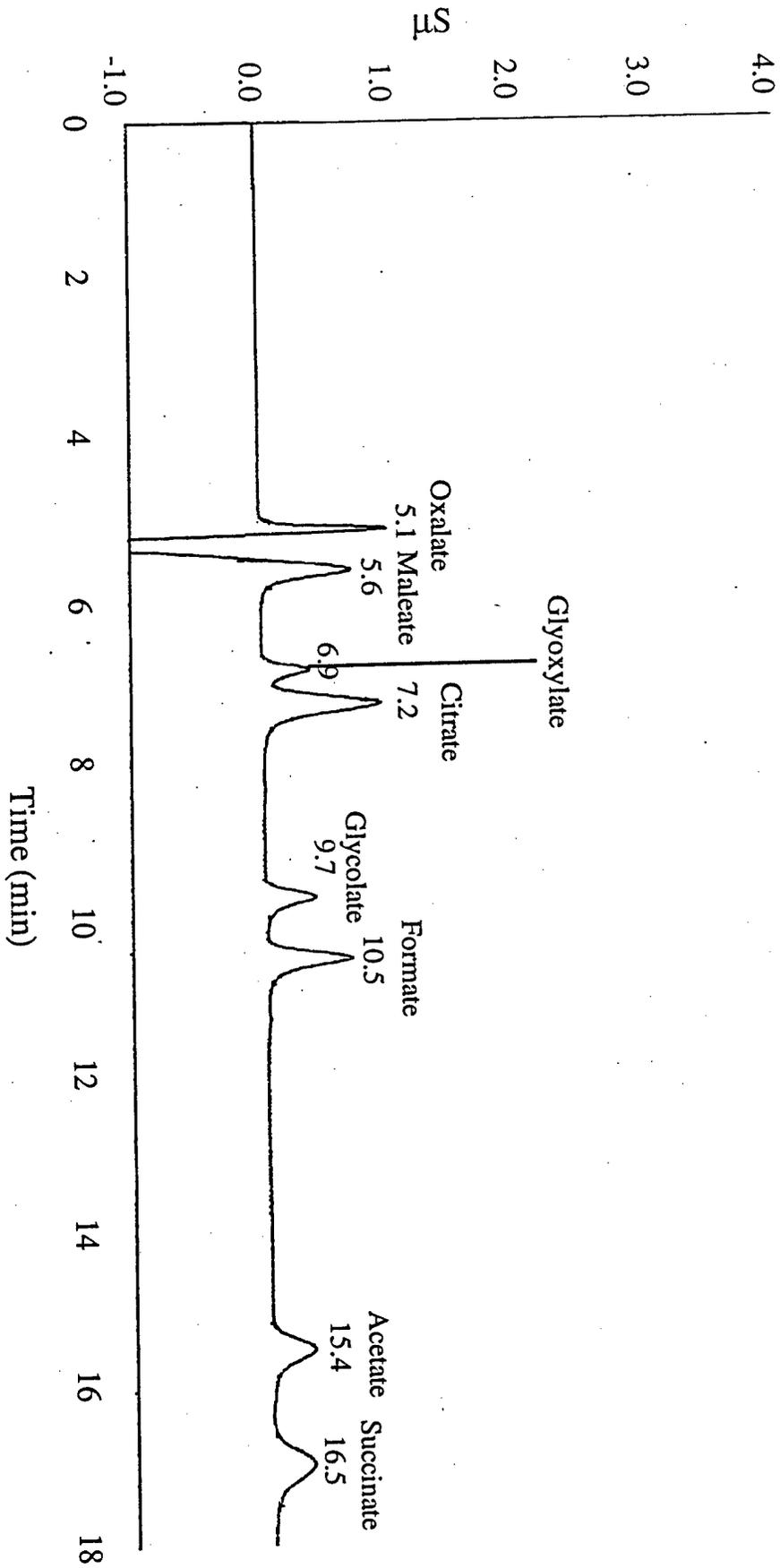


Fig 4(a)

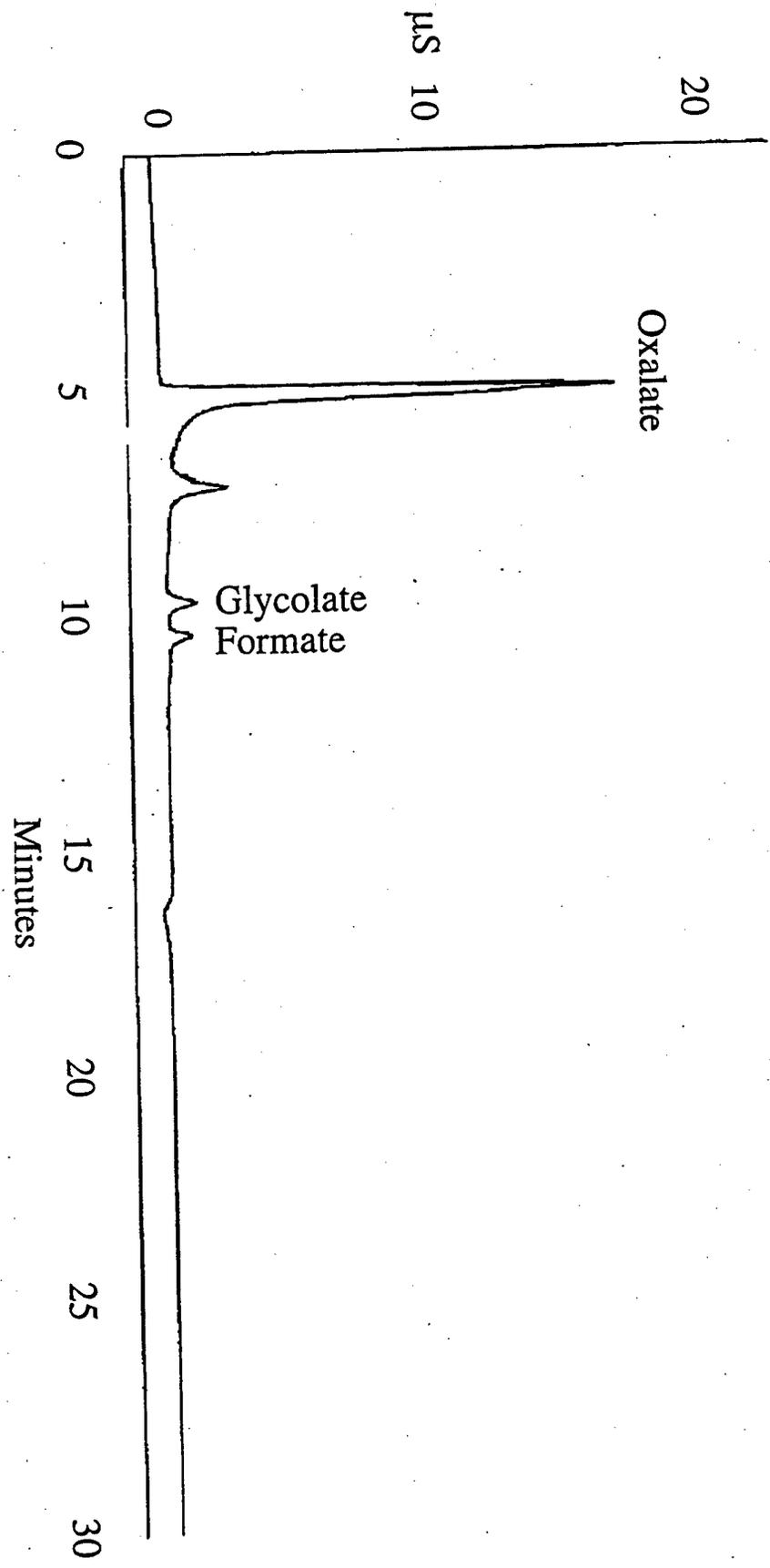


Fig 4(b)

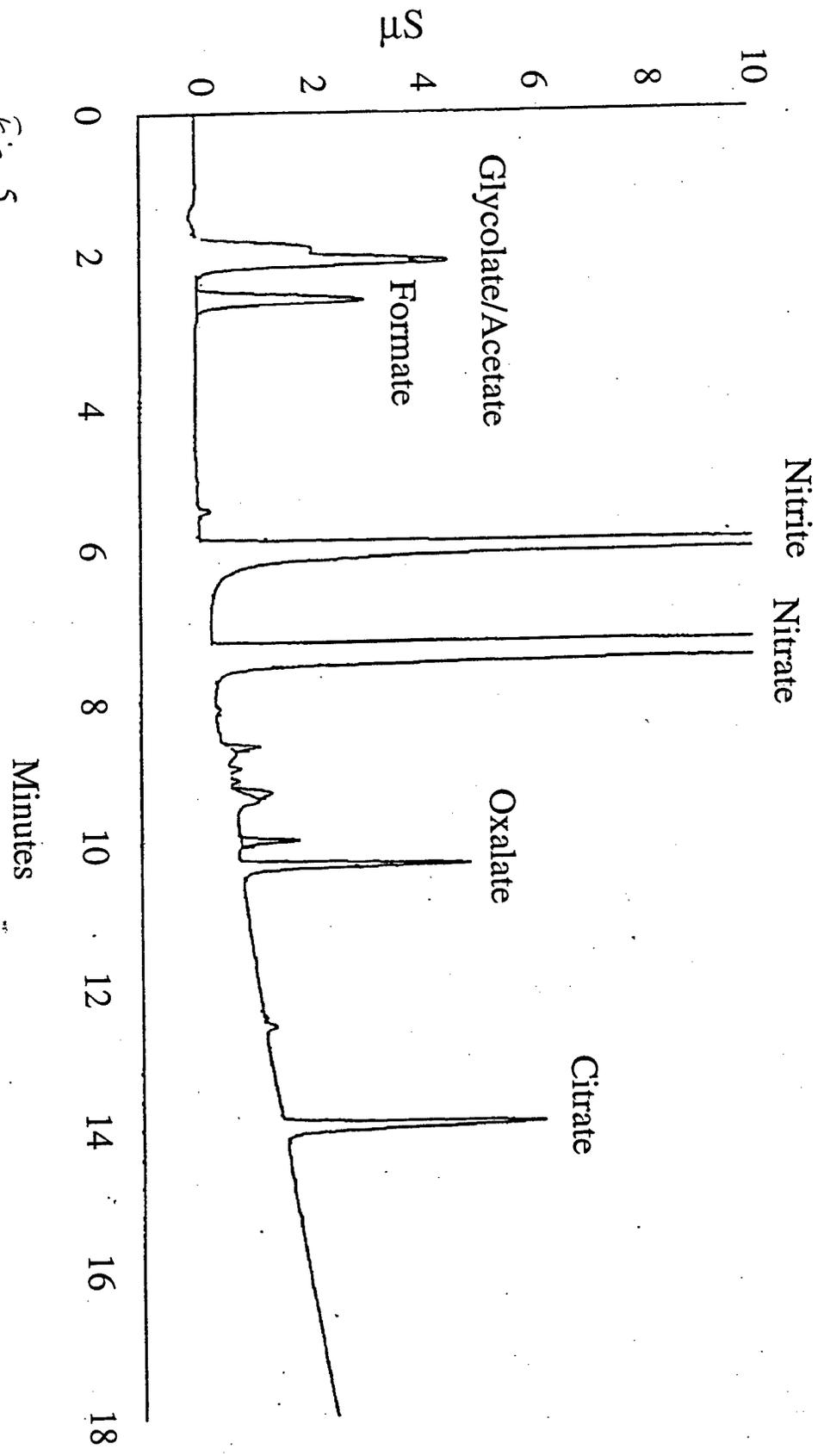


Fig 5

Appendix B

cc:mail Messages and Chain-of-Custody Form

From: Lockheed Martin Hanford Corp.
 Phone: 373-3115 R2-11
 Date: November 6, 1996
 Subject: SAMPLES TO SHIP TO PNNL FOR ORGANIC SPECIATION

To: K. M. Hall *[Signature]* R2-12

cc: H. Babad S7-14
 J. A. Campbell P8-08
 D. A. Dodd T6-50
 R. T. Hallen P8-38
 N. W. Kirch *[Signature]* R2-11
 J. G. Kristofzski R2-12
 J. E. Meacham S7-14
 DAR File/LB

Reference: WHC-SD-WM-TP-378, "Test Plan for Samples from Hanford Waste Tanks 241-BY-103, BY-103, BY-105, BY-106, BY-108, BY-110, TY-103, U-105, U-107, U-108, and U-109, Revision 0, dated 1995.

The Organic-Nitrate Safety Program is basing resolution of the safety issue on the fact that organics have degraded in the waste. To assist in this resolution, actual waste are to be analyzed for the various organic species present in the waste (Reference). This test plan is currently being revised to address additional tanks. The speciation of organics is performed at Pacific Northwest National Laboratories.

The following 2 tables show the samples that need to be shipped to Battelle Pacific Northwest National Laboratories. PNNL has stated that they would prefer about 20 grams of sample but less would be acceptable. Table 1 shows those wastes identified. Included is a 222-S archive jar or vial number when known.

Table 1
Samples to Ship from 222-S to PNNL

Tank	Jar/Vial #	Core	Segment	Sub	Sample #	Comments
BY-105	8394	108	1	Drn Lq	S95T003327	High DSC
BY-104	8410	116	2A		S95T003526	TOC 2.8%
BY-106	6402	65	13	Sludge	S95T000338	TOC 2% DSC 667 to 1365
C-105	6744	76	1		S95T000514	TOC 3.2%, DSC 452
A-102	7215	Aug				TOC 1.5%
U-102	10042	144	6	UH	S96T002783	
U-106	10053	148	2	UH	S96T001046	
U-106	10063	148	2	Drn Lq	S96T003050	
AW-101	10213	139	21	UH	S96T003583	DSC 1000
U-107	9272	134	5A		S96T001068	TOC 9520 ug/g
U-108	9454	141	4	UH	S96T002253	DSC up to 609
U-105	9477	136	7	UH	S96T001711	
U-105	7475	Grab				High TOC

Westinghouse Hanford Company

CHAIN OF CUSTODY/SAMPLE ANALYSIS REQUEST

C.O.C. No.

Page 1 of 1
MSIN FAX 372-1070

Collector: 222-S Laboratory
 Contact/Requestor: Marty L Martin/Larry L Fritts
 Telephone No.: 373-3261
 Purchase Order/Charge Code: H2003
 SAF No.: 222-S Hotcell 11A
 Sample Origin: n/a
 Logbook No.: n/a
 Ice Chest No.: n/a
 Method of Shipment: n/a
 Bill of Lading/Air Bill No.:
 Offsite Property No.:

Sample No.	Lab ID	Date	Time	No./Type Container	Sample, Analyte	Preservative
BY106 C65	S96H000142	SO		1/20 mL	Organic Speciation	none
BY104 C116	S96H000127	SO		1/20 mL	Organic Speciation	none
A102 Auger	S96H000143	SO		1/20 mL	Organic Speciation	none
AV101 C139	S96H000146	SO		1/20 mL	Organic Speciation	none
U106 C148	S96H000145	SO		1/20 mL	Organic Speciation	none
U105 C136	S96H000148	SO		1/20 mL	Organic Speciation	none
U108 C141	S96H000147	SO		1/20 mL	Organic Speciation	none
U102 C144	S96H000155	SO		1/20 mL	Organic Speciation	none

Protocol: n/a
 Data Turnaround: n/a
 POSSIBLE SAMPLE HAZARDS/REMARKS (List all known wastes):
 MSDS: Yes No
 SPECIAL INSTRUCTIONS:
 ship c/o Clark Carlson.

Relinquished By	Print	Sign	Date/Time	Received By	Print	Sign	Date/Time	Matrix*
Relinquished By	R. AKITA	A Akita	1-29-97/1400	Received By	MARTY L MARTIN	[Signature]	1-29-97/1400	S = Soil DS = Drum Solids SE = Sediment DL = Drum Liquids SO = Solid T = Tissue SL = Sludge WI = Wipe W = Water L = Liquid O = Oil V = Vegetation A = Air X = Other
Relinquished By	MARTY L MARTIN	[Signature]	1-30-97/1315	Received By	ED L COOPER	ED L Cooper	1-30-97/1315	
Relinquished By	ED L COOPER	[Signature]	1-30-97/2230	Received By	[Signature]	[Signature]	1/30/97 2:29	

FINAL SAMPLE DISPOSITION:
 Disposal Method (e.g., Return to customer, per lab procedure, used in process):
 Disposed by:
 All samples containing hazardous materials shall be picked up by requestor and returned to parent container or site of origin.
 DISTRIBUTION: White - Remain with Samples Color - Customer

Westinghouse Hanford Company

CHAIN OF CUSTODY/SAMPLE ANALYSIS REQUEST

C.O.C. No.

Page 1 of 1

Collector: 222-S Laboratory SAF No. Telephone No. 373-3261 MSIN 16-06 FAX 372-1870
 Contact/Requestor: Marty L Martin/Larry L Fritts Purchase Order/Charge Code M2003
 Sample Origin: 222-S Hotcell 11A Logbook No. n/a Ice Chest No. n/a Temp. n/a
 Project Title: Organic Safety Issue (Shipment to PNNL) Method of Shipment: Bill of Lading/Air Bill No.
 Shipped to (Lab): PNNL Data Turnaround: n/a Offsite Property No.

Sample No.	Lab ID	Date	Time	No./Type Container	Sample Analysis	Preservative
C105 C76	S96M000122	L		1/20 mL	Organic Speciation	none
BY105 C108	S96M000118	L		1/20 mL	Organic Speciation	none 842
U106 C140	S96M000123	L		1/20 mL	Organic Speciation	none 12/17
U105 6LAG	S96M000160	L		1/20 mL	Organic Speciation	none 1

POSSIBLE SAMPLE HAZARDS/REMARKS (List all known wastes) MSDS Yes No Hold Time

SPECIAL INSTRUCTIONS: Ship c/o Clark Carlson.

Relinquished By	Print	Sign	Date/Time	Received By	Print	Sign	Date/Time
Relinquished By	R. AKITA	R. Akita	1-29-97/1400	Received By	MARTY L MARTIN	[Signature]	1-29-97/1450
Relinquished By	MARTY L MARTIN	[Signature]	1-30-97/1315	Received By	ED L COOPER	ED L COOPER	1-30-97/1315
Relinquished By	ED L COOPER	[Signature]	1-30-97/2291	Received By	[Signature]	[Signature]	1/30/97/2:29

FINAL SAMPLE DISPOSITION: 1

Disposal Method (e.g., Return to customer, per lab procedure, used in process) Disposed By

Matrix*
 S = Soil DS = Drum Solid
 SE = Sediment DL = Drum Liquid
 SO = Solid T = Tissue
 SL = Sludge WI = Wipe
 W = Water L = Liquid
 O = Oil V = Vegetation
 A = Air X = Other

All samples containing hazardous materials shall be picked up by requestor and returned to parent container or site of origin.
 DISTRIBUTION: White - Remain with Samples Color - Customer

Appendix C

Test Plan

ORGANIC TANKS SAFETY PROGRAM

TEST PLAN FOR THE SPECIATION OF ORGANICS
IN ACTUAL TANK WASTES TO SUPPORT VERIFICATION
OF SOLUBILITY AND AGING ASSUMPTIONS

C. D. Carlson
J. A. Campbell
Pacific Northwest National Laboratory

H. Babad
Westinghouse Hanford Company

February 27, 1997

Prepared For
the U. S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest National Laboratory
Richland, Washington 99352

1.0 INTRODUCTION

This test plan will detail the efforts to determine the organic species present Hanford Tank which are currently on or could potentially be placed onto the Organic Tanks Watchlist. Since the report on the deflagration of a waste tank in Krishtym, USSR (Fisher 1990), the presence of organics in nitrate bearing wastes became a significant safety issue at the Hanford Site. Using information from the Krishtym deflagration, a set of 26 experiments using various combinations of sodium acetate with sodium nitrate/sodium nitrite and diluents were performed to determine the reactivity of these mixtures. Sodium acetate was used as the organic species because it provided the highest energy content per unit of organic carbon of the organic complexant thought to be present in the tanks, providing a margin of safety. From these results, the safety criteria was determined to be 10% by weight organics as sodium acetate on a dry weight basis (3% TOC on a dry weight basis) (Babad and Turner 1993).

The nature and quantity of organic compounds in high-level waste has an impact on a variety of TWRS programs. Such waste may contain complexants added during strontium removal in B-Plant in the 1960's; solvents and their degradation products from Uranium metal recovery (dates) Purex and Redox process fuel reprocessing and/or small quantities of a variety of surface active agents used for corrosion protection (hot water and steam boiler plants) and equipment and facility decontamination. Organic complexants are associated with both the generation of flammable gasses in the waste and the potential for initiated nitrate-nitrite-organic fuel propagation reactions in the waste. Complexants also interfere with the separation of wastes, during pretreatment, into HLW and LLW fractions required for disposal. The presence of organic solvents, extractants and their water insoluble degradation products are associated with the "solvent fire" safety issues and will effect the solids-liquid separation operations associated with waste pretreatment. At present, little is known about the concentration or effects of surfactants on either interim safe storage of the waste or retrieval and pretreatment. The effects of organics on either interim safe storage or disposal are highly species and concentration specific, necessitating a flexible cost effective program of organic speciation. Such a program has been developed by PNNL scientists in collaboration with WHC chemists.

In order to provide a more reasonable value for the reactive nature of the organics containing wastes present in the tanks, the identity of those organics must first be determined. From the tank fill data (Agnew et al, 1995), the amounts and types of organics which were added to the tanks can be estimated to a close approximation, but due to thermal and radiolytic degradation of the wastes (Camaioni et al. 1995) the nature of the organic carbon currently present in the tanks will be significantly different. The determination of the nature of the organics present in the tanks has been studied under the Flammable Gas Program for several

years (Campbell et al. 1995) and the current work will build on this knowledge to provide a better understanding of the organic species present in the tanks.

Organic speciation is a complex analytical process that aims at identifying the specific organic chemicals in a variety of diverse and heterogeneous waste mixture and where possible quantifying the concentrations of the major species in that waste. Speciation requires initial decontamination of the waste to allow chemists to perform complex analyses of the mixtures in low and non-radiation facilities. Identification and quantitation of the organic waste constituents can then be carried out by a variety of methods that are described below.

2.0 METHODOLOGY

Table 1. General Available Methodology

<u>Analytical Technique</u>	<u>Analytes</u>	<u>Constituent Type</u>	<u>Method Focus and Quantification</u>
Derivatization Gas Chromatography/Mass Spectrometry	Chelators Chelator Fragments	Complexants Aging Products [EDTA, NTA, IDA, ED3A, HEDTA, succinic, citric acids and their salts]	Poly-functional Carboxylic Acids (Species identification and (Qualitative) analysis)
Derivatization Gas Chromatography with Flame Ionization Detection	Chelators Chelator Fragments	Complexants Aging Products [EDTA, NTA, IDA, ED3A, HEDTA, succinic, citric acids and their salts]	Poly functional Carboxylic Acids (Quantitative) Analysis)
Liquid Chromatography and/ or Ion Chromatography	Chelators Chelator Fragments	Low Molecular Weight Acids	Oxalate, formate, acetate, glycolate (Quantitative) Analysis)
High Resolution Mass Spectrometry	Solvents Extractants Chelators Chelator Fragments	All Organic Species Capable of being volatilized	Qualitative Identification of unknowns
Spectroscopy -Infrared -Raman -UV-Visible	Solvents Extractants Chelators Chelator Fragments	Functional Groups in all organic species	Quantitative or Qualitative analysis depending on standard availability
Nuclear Magnetic Resonance -Proton -Phosphorous-31 -Carbon-13	Solvents Extractants Chelators Chelator Fragments	Functional groups and structural environments in all organic species	Quantitative or Qualitative analysis depending on standard availability

Table 2. Species Specific Methodology

<u>Specific Analyte</u>	<u>Analytical Technique</u>	<u>Degree of Quantification</u> [Note 1]	<u>Method Complexity</u>
EDTA	Derivatization GC/MS	Species Identification	sample must be dried prior to derivatization, low sample size to reagent ratio, complex
	Derivatization GC	Quantitation	
HEDTA	Derivatization GC/MS	Species Identification	sample must be dried prior to derivatization, low sample size to reagent ratio, complex
	Derivatization GC	Quantitation	
NTA	Derivatization GC/MS	Species Identification	sample must be dried prior to derivatization, low sample size to reagent ratio, complex
	Derivatization GC	Quantitation	
IDA	Derivatization GC/MS	Species Identification	sample must be dried prior to derivatization, low sample size to reagent ratio, complex
	Derivatization GC	Quantitation	
ED3A	Derivatization GC/MS	Species Identification	sample must be dried prior to derivatization, low sample size to reagent ratio, complex
	Derivatization GC	Quantitation	
Succinic Acid	Derivatization GC/MS	Species Identification	sample must be dried prior to derivatization, low sample size to reagent ratio, complex
	Derivatization GC	Quantitation	
Citric Acid	Derivatization GC/MS	Species Identification	sample must be dried prior to derivatization, low sample size to reagent ratio, complex
	Derivatization GC	Quantitation	
Oxalate	Ion Chromatography or Liquid Chromatography	Quantitation	sample analyzed directly, not as complex as derivatization

Acetate	Ion Chromatography or Liquid Chromatography	Quantitation	sample analyzed directly, not as complex as derivatization
Glycolate	Ion Chromatography or Liquid Chromatography	Quantitation	sample analyzed directly, not as complex as derivatization
Formate	Ion Chromatography or Liquid Chromatography	Quantitation	sample analyzed directly, not as complex as derivatization
TPB	GC/MS		extract analyzed directly
NPH	GC/MS		extract analyzed directly
Aging Products (Water Insoluble)	GC/MS		extract analyzed directly
	NMR		limited by radioactivity and concentration
	IR/Raman		quantitation possible for known matrix
	UV-Visible		quantitation but non-selective

phosphates
(D2EHP)

derivatization and
analysis by GC/MS

Note 1. Typical limits of detection by GC/MS or GC/FID are 50-100 ppm.

3.0 SAMPLE SELECTION

Since funding and time is limited for the completion of this project, the tank samples to be used will be that remaining from other sampling programs, such as the Characterization Program. This will limit the number of samples which will be available for the speciation. However, from the list of currently available samples, representative tank samples can be collected for most of the safety issues.

A number of issues and characteristics regarding organic species in the tanks drive the Hanford Site Characterization Program. From these issues and the availability of samples, an initial set of tanks have been identified as potential samples for organic speciation. Table 2.1 shows the samples and the sample availability.

Table 2.1 Samples for Organic Speciation.

Tank ID	Safety Issue	Sampling Information	Sample Availability
C-103	Organic Watch List Floating Organic Layer	2 push cores	
U-107	Organic Watch List High Organic Salt Content	2 grab samples	< 100 g
BY-110	Ferrocyanide Tank	6 rotary cores	
AW-101	Flammable Gas Tank	2 push cores 3 auger samples	available from 1996 cores
C-106	High Heat Tank	1 push core	unknown
AZ-101	Aging Waste Tank	2 push cores 5 grab samples	only diluted liquid (1:10)
BY-106			solid
BY-104			solid
S-104	Representative REDOX sludge waste	3 push cores	170 g
U-105			grab sample

In addition to this list, samples from tanks A-102, U-108, U-104, U-102, C-105, BY-105, and U-106 are available. These samples have been identified as having potentially large quantities of organic as listed in the Hanford Defined Wastes (Agnew 1996). The following samples have been received in the first shipment and include BY-106, BY-104, A-102, AW-101, U-106, U-105, U-108, U-102, C-105 (liquid), BY-105 (liquid), U-106 (liquid), and U-105 (grab sample, liquid).

4.0 SAMPLE PREPARATION AND ANALYSIS

After receiving samples in the 325-hot cell facility, the sample must be decontaminated to allow analysis to be carried out by PNNL professional staff, in what essentially low or non-radiation zones. Variation of two methods for decontamination are used, depending on the nature of the organic species being investigated. The decontamination procedures involve either leaching of the solid waste samples with water and passing leachate containing the water soluble organics through a cation exchange resin to reduce the levels of radioactivity. Prior to elution through the cation exchange column, the sample will be visually inspected to determine whether it is primarily solid or liquid. If the sample consists of liquid, the sample preparation will proceed. If the sample is solid, drainable liquid will be obtained if possible by centrifugation. A portion of the remaining solid will be analyzed for % moisture. Sufficient water is used to assure the dissolution of even low solubility aging products such as sodium oxalate. Values for total organic carbon are obtained at various steps in the procedure to ensure that organic carbon is neither removed or introduced during decontamination. Total organic carbon analysis is done by either by either silver catalyzed persulfate oxidation or the furnace fusion method [or both, depending on the nature of the organic species expected].

Alternatively for samples believed to contain entrained or separable solvents and extractants or their water insoluble reaction products, the sample is extracted with a low boiling solvent (e.g., hexane or methylene chloride) to remove solvent miscible components from the waste samples, and the organic solutions washed with appropriate leachate (e.g., sodium carbonate and EDTA) to remove radionuclides from water insoluble waste such as NPH/TBP or waste organic oils. If needed, the low boiling solvent can be stripped, and the residual organics can be speciated as described below. In addition, the solid and liquid samples will be extracted. A portion of the sample will be extracted with an organic solvent and analyzed using GC/MS to determine any organically-soluble carbon such as TBP and NPH.

An aliquot of the aqueous solution will be removed and evaporated to dryness. After drying, the resulting material will be derivatized (Campbell et al. 1994) and analyzed by GC/MS to identify chelators and chelator fragments. The organic components will be quantified using GC/flame ionization detection (FID).

Another aliquot of the solution will be analyzed by LC of IC with conductivity detection for low molecular weight acids (Campbell et al. 1994, 1995). The aqueous sample will also be analyzed by ion-pair chromatography LC for chelators and chelator fragments.

5.0 DATA

The data obtained will be the concentration of the organic components in the convective and nonconvective layer samples (depending on availability). In the description of the results, the method used for analysis will be identified along with the quantity of the species present. In addition, any special handling and problems associated with eh analysis will be described in full. The list of analytical techniques to be used can be seen in Section 2.0.

6.0 TEST PROCEDURE

Testing will be conducted at PNNL under the following technical procedures (Campbell et al. 1994):

- LC and IC for the analysis of low-molecular-weight acids
- Ion pair chromatography for analysis of chelators
- Derivatization GC/MS for the qualitative analysis of chelators and chelator fragments
- GC/FID for quantitative analysis of chelators and chelator fragments
- GC/MS for the analysis of organically-soluble carbon

7.0 SAFETY

The following Safe Operating Procedures govern work performed at 325A HLRF and contain applicable hazard assessment and training requirements:

- 325-A-1, 325A HLRF - Use of the 30/5 Ton Crane
- 325-A-4, Transfer Mechanism Operation
- 325-A-8, Waste Removal from "A", "B", and "C" Cells
- 325-A-12, 325A HLRF - Assembling, Using, and Disassembling the Port Adaptor
- 325-A-21, Liquid Waste Disposal
- GEN-325-SPM-1, 325 Building Sample Packaging and Movement
- GEN-325-WM-1, Waste Management Routing, Storage, and Disposal of Hazardous, Low-level Radioactive, or Radioactive Mixed Waste
- GEN-325-GB-1, Use of Glove Box Enclosures for Radiological Operations
- GEN-325-FH-1, Use of Laboratory Fume Hoods for Radiological Operations

The following Safe Operating Procedures will govern the work performed in the 329 building:

- AOAM-329-LC1, Analysis of Organics in Potentially Radiologically Contaminated Samples by Liquid Chromatography and Mass Spectrometry
- RAD-329-FH1, Use of Laboratory Fume Hoods for Radiological Operations for 329
- AOAM-329-SP1, Sample Preparation for the Analysis of Extractable Organic Compounds from Radioactive Samples
- AOAM-329-MS2, Routine GC/MS Instrumentation for Analysis of Potentially Radiologically Contaminated Samples

8.0 Quality Assurance

Work performed using this test plan will meet Impact Level II requirements as described in PNL-MA-70. All Data generated in the 325A HLRF will be recorded on test instructions or directly in a laboratory record book. The completed test instructions will be entered into the appropriate laboratory record book at a later time.

9.0 CHANGE CONTROL

Changes affecting the objectives of the testing identified in this test plan shall be reviewed and approved by PNNL Tank Waste Safety Management. The significance of the changes will be determined by the PNNL project manager or his designated alternate. Major changes will be documented by issuing a revision to this test plan. Minor changes will be made by marking issued copies of the current version of this plan. All minor changes shall be signed and dated by the cognizant engineer/scientist (J. A. Campbell).

10.0 REFERENCES

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