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Flammable Gas Safety Program

Analytical Methods Development: FY 1993 Progress Report

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MASTER

Abstract

Six samples of core segments from Tank 101-SY, obtained during the window E core sampling, have been analyzed for organic constituents. Four of the samples were from the upper region, or convective layer, of the tank and two were from the lower, nonconvective layer.

The samples were analyzed for chelators, chelator fragments, and several carboxylic acids by derivatization gas chromatography/mass spectrometry (GC/MS). The major components detected were ethylenediaminetetraacetic acid (EDTA), nitroso-iminodiacetic acid (NIDA), nitrilotriacetic acid (NTA), citric acid (CA), succinic acid (SA), and ethylenediaminetriacetic acid (ED3A). The chelator of highest concentration was EDTA in all six samples analyzed.

Liquid chromatography (LC) was used to quantitate low molecular weight acids (LMWA) including oxalic, formic, glycolic, and acetic acids, which are present in the waste as acid salts. From 23 to 61% of the total organic carbon (TOC) in the samples analyzed was accounted for by these acids. Oxalate constituted approximately 40% of the TOC in the nonconvective layer samples. Oxalate was found to be approximately 3 to 4 times higher in concentration in the nonconvective layer than in the convective layer.

During FY 1993, LC methods for analyzing LWMA, and two chelators N-(2-hydroxyethyl) ethylenediaminetriacetic acid and EDTA, were transferred to personnel in the Analytical Chemistry Laboratory and the 222-S laboratory.

Executive Summary

This report describes the status of developing analytical methods to account for the organic constituents in Hanford waste tanks, with particular emphasis on those tanks that have been assigned to the Flammable Gas Watch List. The methods that have been developed are illustrated by their application to samples obtained from Tank 241-SY-101 (101-SY). The analytical data are to serve as an example of the status of methods development. The marked improvement in ability to account for organic carbon in 101-SY samples, documented in this report, is a result of significant improvement in techniques for isolating constituents relatively free from radioactive contamination and for improvements in derivatization methodology. Additional constituents have been accounted for with the use of a new high resolution mass spectrometer.

Six samples of core segments from Tank 101-SY, obtained during the window E core sampling, have been analyzed for organic constituents. Four of the samples were from the upper region, or convective layer, of the tank and two were from the lower, nonconvective layer.

Values for total organic carbon (TOC) ranged from 1.0 to 1.4%; this range is consistent with TOC data obtained from other sub-samples of core segment composites. Among the samples analyzed, the bottom of the nonconvective layer has the highest TOC value. The combined techniques of derivatization gas chromatography/mass spectrometry (GC/MS) and liquid chromatography (LC) have accounted for approximately 71 to 93% of the TOC depending on the sample. Table I summarizes the data for low molecular weight acids (LMWA), chelators, and chelator fragments. These component types constitute the majority of the carbon accounted for.

Chelators, chelator fragments, and several carboxylic acids have been quantitated in the core segment samples using derivatization GC/MS. The major components detected were ethylenediaminetetraacetic acid (EDTA), nitroso-iminodiacetic acid (NIDA), nitrilotriacetic acid (NTA), citric acid (CA), succinic acid (SA), and ethylenediaminetriacetic acid (ED3A). The chelator of highest concentration was EDTA in all six samples analyzed. The amount of organic carbon accounted for by derivatization GC/MS varies from 20 to 52% of the TOC depending on the sample. Preliminary results indicate the chelators and chelator fragments constitute more of the organic carbon in the convective than the nonconvective layer.

The reproducibility of derivatization GC/MS results, based on duplicate analyses, is estimated to be approximately 10%. In addition, sub-sample variation is estimated to be 14-20%, depending on the component. Recoveries based on results from spiked simulated wastes are estimated to be approximately 50-60%. The analytical results were not corrected for recoveries. The variability from sample to sample is both a function of sample heterogeneity and analytical irreproducibility.

Liquid chromatography has been used to quantitate LMWA (oxalic, formic, glycolic, and acetic acids, which are present in the waste as acid salts). Approximately 23 to 61% of the TOC is accounted for by these acids. Oxalic acid constitutes approximately 40% of the TOC in the nonconvective layer samples. The reproducibility for the LC determination of oxalic acid is approximately 5%. The concentration of oxalate in the nonconvective layer is approximately 3 to 4

times higher than the convective layer. The nonconvective layer sample from the lowest layer analyzed has the highest percentage of water-soluble organic carbon in the form of LMWA.

Previous work with 101-SY composite samples has identified normal paraffin hydrocarbons (NPH) as components of the water-insoluble portion of the 101-SY TOC. The NPH fraction was isolated by extracting the sample with methylene chloride. Analysis of the methylene chloride extracts by GC/MS indicated that this material accounts for an additional 2 to 3% of the TOC of the samples. It is expected that this will also hold true for the current six samples, which are presently undergoing NPH analysis.

The elemental compositions of 25 components in the derivatization GC/MS total ion chromatogram have been determined using high resolution mass spectrometry (HRMS). Several nitroso compounds have been unambiguously identified. However, the nitroso compounds may be formed during the derivatization procedure; they have not yet been found by methods that do not involve acidic conditions of derivatization or separation. Thermospray LC/mass spectrometry (LC/MS) has been used to identify many of the small organic acids, including citric, acetic, formic, and glycolic. Several components in both the LC and LC/MS chromatograms are unidentified.

Nitroso compounds have been identified by GC/MS after derivatization of the waste extracts with boron trifluoride. The reaction of iminodiacetic acid (IDA) spiked in a dried, simulated waste sample containing nitrate, nitrite, and hydroxide with boron trifluoride/methanol produces NIDA as the major product. These results demonstrate that IDA, if present in the original waste, is probably a precursor for the production of NIDA during the boron trifluoride/ methanol derivatization. Under derivatization conditions, NIDA is stable. A probable precursor for two other nitroso compounds found in the derivatization product is ED3A. The question remains whether nitroso compounds are present in the original waste. Procedures for direct analysis of the waste samples for nitroso compounds by LC/MS under basic conditions that do not involve derivatization will be applied in the near future.

Transferring analytical methods is an important aspect of this project. An LC method for LMWA and an LC method for analyzing N-(2-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA) and EDTA have been transferred to personnel in the Analytical Chemistry Laboratory (ACL) and the laboratory at 222-S during FY 1993. These methods are presently being used by ACL personnel to analyze tank waste samples before grout treatment. Techniques involving derivatization GC/MS and LC for analyzing chelators, chelator fragments, and LMWA will be transferred to ACL personnel in FY 1994. Further discussions with Steve Metcalf, Westinghouse Hanford Company (WHC), are scheduled for additional methods transfer to the laboratory at 222-S.

A procedure has been adopted and implemented to fully document methods development transfer. The method will be developed and transferred to designated personnel. A cover statement will be signed by both the transferor and the receiver. The test plan will then be developed, completed, and signed by the test plan author and technical group leader. The entire package, which includes the transferred method, cover statement, and test plan, will be forwarded to the appropriate WHC project manager.

Table S.1. Carbon Accounted for by Chelators, Chelator Fragments, and Low Molecular Weight Acids in Tank 101-SY Window E Core Segment Samples (mg C/g sample)

<u>Sample^(a)</u>	<u>Segment #</u>	<u>Chelators^(b)</u>	<u>Low Molecular Weight Acids^(c)</u>	<u>%TOC Accounted For</u>
R4258/C	4	4.7 (44%) ^(d)	3.3 (30%)	74
R4259/C	6	3.3 (33%)	4.5 (44%)	77
R4260/C	9	4.8 (46%)	4.4 (41%)	87
R4261/C	11	6.4 (52%)	2.5 (23%)	75
R4262/NC	16	2.2 (20%)	5.8 (53%)	73
R4263/NC	17	3.6 (32%)	6.8 (61%)	93

(a) Sample R4264, a nonconvective layer sample, was lost during preparation; the analysis is in progress.

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

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

(d) Parentheses give percent of TOC accounted for by analyte category.

C Convective layer

NC Nonconvective layer

Glossary

ACL	Analytical Chemistry Laboratory
BSA	N-bis(trimethylsilyl)acetamine
BSTFA	bis(trimethylsilyl)trifluoroacetamide
CA	citric acid
ECD	electron capture detection
ED3A	ethylenediaminetriacetic acid
EDTA	ethylenediaminetetraacetic acid
FID	flame ionization detection
FTIR	fourier transform infrared
GC/MS	gas chromatography/mass spectrometry
HEDTA	N-(2-hydroxyethyl)ethylenediaminetriacetic acid
HPLC	high performance liquid chromatography
HRMS	high resolution mass spectrometry
IDA	iminodiacetic acid
LC	liquid chromatography
LC/MS	liquid chromatography/mass spectrometry
LMWA	low molecular weight acids
NED3A	n-nitrosoethylenediaminetriacetic acid
NIDA	nitroso-iminodiacetic acid
NTA	nitrilotriacetic acid
NPH	normal paraffin hydrocarbons
PEG	polyethylene glycol
PFK	perfluorokerosene
PFTBA	perfluorotributylamine
s-EDDA	symmetrical ethylenediaminediacetic acid
SA	succinic acid
SIM	selected ion monitoring
SWM	simulated waste material
TCE	2,2,2-trichloroethanol
TFAA	trifluoroacetic anhydride
TMCS	trimethylchlorosilane
TMS	trimethylsilyl
TOC	total organic carbon
u-EDDA	unsymmetrical ethylenediaminediacetic acid
UV	ultraviolet

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1.0 Introduction

The objectives of this task are to develop and document extraction and analysis methods for organics in waste tanks and to extend these methods to the analysis of actual core samples to support proposed mechanisms for gas production. This report documents progress at Pacific Northwest Laboratory^(a) during FY 1993 on methods development, the analysis of Tank 241-SY-101 (101-SY) waste, total organic carbon (TOC) accounted for, and transfer of documented, developed analytical methods to personnel in the Analytical Chemistry Laboratory (ACL) and the 222-S Laboratory. This report is intended as an annual report of progress, not a completed work.

The literature has been searched for references applicable to analytical methods for organics in mixed hazardous wastes (Clauss and Bean, 1993a; Clauss and Bean 1993b). The results of the search indicate that few analytical methods for organic analysis of mixed hazardous wastes have been reported in the literature. High performance liquid chromatography (HPLC), derivatization gas chromatography/mass spectrometry (GC/MS), and liquid chromatography/mass spectrometry (LC/MS) are the major analytical techniques that have been developed in these studies for analyzing chelators and chelator fragments. Ion chromatography/MS, derivatization GC/MS, and HPLC are also being developed to identify other degradation products, such as oxalate and glycolate.

In FY 1992, the primary emphasis was the quantitation of chelators and chelator fragments. The sample preparation and derivatization was performed entirely in the hot cell facilities. Parameters that were critical to reproducible results, such as temperature control and dryness of the sample, could not be rigidly controlled. In addition, a relatively large sample size (≈ 2 g) was derivatized. The component of highest concentration in most of the samples was n-nitrosoiminodiacetic acid (NIDA) as determined by GC/MS. The concentration of individual chelators was approximately the same from sample to sample. During that period, the elemental compositions of many of the components in the derivatization GC/MS total ion chromatogram were unknown. The structures of some of the major components were determined by mass spectral interpretation of electron impact and chemical ionization spectra.

The TOC accountability was quite poor at the end of FY 1992, in part due to a major emphasis on the analysis of chelators and chelator fragments. For most samples analyzed by derivatization GC/MS, the amount of water-soluble organic carbon accounted for was 10 to 20%.

At the beginning of FY 1993, liquid chromatography (LC) methods were in the process of being developed for analyzing low molecular weight acids including oxalic, acetic, formic, and glycolic acids. Anion exchange chromatography for analyzing oxalate under basic conditions was begun, and anion exclusion liquid chromatography for analyzing formic, acetic, glycolic, and glyoxylic acids was initiated. In addition, chromatographic conditions (acidic mobile phases) for use with thermospray LC/MS to identify low molecular weight acids (LMWA) were investigated. None of these analytical methods under development were at a stage where technology transfer was feasible.

(a) Pacific Northwest Laboratory is operated for the U. S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO 1830.

This report describes the progress made in FY 1993 in developing more effective procedures for separating and preparing samples, for isolating and derivatizing components, and for identifying components. These improvements have substantially increased the proportion of organic carbon accounted for by the analyzed organic compounds, from about 10 to 20% to 73 to 93%. In addition, several methods developed during this work either have been transferred or are in the process of being transferred to other laboratories for routine applications.

2.0 Summary of Results

At the beginning of FY 1993, a set of eight core segment composite samples of Tank 101-SY from the window E sampling period were being analyzed for chelators, chelator fragments, and carboxylic acids. Four samples were from the convective layer, and four were from the nonconvective layer. Throughout FY 1993, the composite samples were used to refine the analytical methods. The use of simulated wastes was not as beneficial as real wastes for methods development; many of the properties of real waste are not duplicated in simulated wastes. Subsamples were used to determine the best sample size to reagent ratio in derivatization GC/MS and to evaluate procedures for removing a major portion of the radioactivity (without loss of organic carbon) to enable the derivatization to be performed in the fume hood. Subsamples were also used to perfect LC methods for LMWA. After the analytical procedures were in a final stage of development, additional subsamples of the composite samples were requested from the hot-cell facilities to perform analyses with the refined methods. Unfortunately, the segment composite samples were found to have been inadvertently discarded during a hot-cell cleanup. Additional samples from window E core sampling were requested from Westinghouse Hanford Company (WHC) archived samples. These core segments have been analyzed using the improved analytical methods, and the results are here reported.

A new sample preparation procedure has been developed that resulted in a better accounting for the organic carbon. A 5-g aliquot of tank waste is stirred overnight with 10 mL of water. The filtered aqueous solution is then passed through a bed of cation exchange resin and rinsed with 10 mL of water. All of the above is performed in the hot cell, and the resulting solution is sufficiently low in activity to allow removal to a fume hood. An aliquot is concentrated to dryness under a stream of nitrogen. The dry material is derivatized with boron trifluoride/methanol, and the derivatized material, in chloroform, contains less than 5% of the original radioactivity. It can then be analyzed by GC/MS for derivatized components.

Removing most of the radioactivity with cation exchange without loss of organic carbon material permitted derivatization in a fume hood. Using a fume hood for sample preparation made it much easier to control the temperature of the reaction and the dryness of the sample; both of these parameters are critical for the derivatization procedures. The fume hood permitted use of a much smaller sample size for derivatization. This improvement in the method allows the ratio of reagent to sample to be high enough to maximize the recoveries and minimize the matrix effect. The results not only gave much higher concentrations of derivatized components in the samples, but produced analyses that revealed sharp differences in component concentrations with depth in the waste tank.

Tables 2.1 through 2.3 contain the TOC data, concentration of chelators by derivatization GC/MS, and LC results for oxalate, glycolic, acetic, and formic acids, respectively. In the convective layer of the current samples, the chelators comprise approximately 33 to 52% of the TOC. The LMWA constitute approximately 23 to 44% of the TOC. In the nonconvective layer samples, chelators account for 20 to 32% of the TOC. The LMWA represent 53 to 61% of the TOC in the nonconvective layer. The major components of the derivatizable organics include ethylenediaminetetraacetic acid (EDTA) and NIDA. The major constituents of the LMWA portion

are oxalate and formic acid. The concentration of oxalate is about 3 to 4 times higher in the nonconvective layer than the convective layer.

The reproducibility of the results from derivatization GC/MS is estimated to be approximately 10% from duplicate manual injections of the same sample. Sub-sample variation is estimated to be approximately 14-20%, depending on the compound. Recoveries, based on simulated wastes, is estimated to be 50-60%. However, the simulated wastes may not be similar to the actual wastes. It is estimated that the recoveries may be higher with the actual tank waste samples. The analytical results were not corrected for recoveries. The reproducibility for the LC measurement of oxalic acid is estimated to be 5%. The determination of the other small acids is estimated to be approximately 10%, due to baseline drift. Recovery of oxalic acid from spikes in simulated waste was over 90%. The variability from sample to sample is a combination of sample heterogeneity and analytical irreproducibility.

Many unknown components were not identified in the derivatization GC/MS total ion chromatogram. The high resolution mass spectrometer was used to provide elemental compositions of 25 major components. Several nitroso compounds were identified in the derivatized water-soluble fraction of the samples. Some NPH was identified in methylene chloride extracts of the waste samples.

Thermospray LC/MS was used to identify low molecular weight acids in actual waste samples. A separation technique was developed using acidic conditions; components identified from the analysis of actual tank waste samples included NIDA, citric acid, acetic, formic, and glycolic acids. Oxalic acid could not be determined by thermospray LC/MS because the second carboxyl group does not protonate under the separation conditions used and thus cannot be detected. However, oxalic acid could be detected using plasmaspay (similar to thermospray but with corona discharge for additional ionization) LC/MS. Other LC/MS techniques explored during FY 1993 included both plasmaspay and electrospray. Both of these techniques have thus far only been used with standards and have not been used to analyze actual waste samples.

Nitroso compounds have been identified by analyzing waste samples using the following methods: derivatization with boron trifluoride and subsequent GC/MS analysis, LC/MS with an acidic mobile phase, and LC with an acidic mobile phase. Acid conditions favor the formation of N-nitroso compounds from amine-type groups in the presence of nitrite. The reaction of iminodiacetic acid (IDA) spiked in a dried, simulated waste sample containing nitrate, nitrite, and hydroxide with boron trifluoride/methanol produces NIDA as the major product. These results demonstrate that IDA can be a precursor for the production of NIDA. Other experiments indicate that NIDA is stable under derivatization conditions. In the same vein, a probable precursor for another nitroso compound, n-nitrosoethylenediamine triacetic acid (NED3A), is ethylenediaminetriacetic acid (ED3A). Boron trifluoride is a Lewis acid. Even with the highly basic waste sample, the derivatization conditions promote the formation of the nitroso compounds. Components like IDA and ED3A, both secondary amines, may react with the nitrite and nitrite under derivatization conditions to form these compounds. At this time, NIDA has not been identified in waste samples by direct analysis, that is, by isolating and detecting the underivatized material. A direct analysis procedure, using thermospray LC/MS with a mobile phase of pH 10.5, is in progress.

Several analytical techniques developed by our group have been successfully transferred to personnel in the Analytical Chemistry Laboratory (ACL) and the 222-S Laboratory in FY 1993. Some LC methods for EDTA, hydroxyethylenediaminetetraacetic acid (HEDTA), and for LMWA have been used by personnel in the ACL to analyze waste samples before grout treatment. In addition, a procedure for transferring the developed techniques has been established. Other techniques are scheduled to be transferred during FY 1994.

Table 2.1. Preliminary TOC Data (mg C/g sample) for Tank 101-SY Window E Core Segment Samples

<u>Sample</u>	<u>Segment #</u>	<u>TOC^(a)</u>
R4258/C	4	11.0 (1.4) ^(b)
R4259/C	6	10.1 (6.4)
R4260/C	9	10.6 (6.9)
R4261/C	11	10.9 (7.0)
R4262/NC	16	11.4 (7.0)
R4263/NC	17	11.0 (12.0)
R4264/NC ^(c)	22R	14.1 (10.8)

(a) Based on the average of duplicate analyses.

(b) Relative percent difference in parenthesis.

(c) Sample analysis in progress.

C Convective layer

NC Nonconvective layer

Table 2.2. Results of Derivatization^(a) GC/MS Analyses on Tank 101-SY Window E Core Segment Samples Concentration of Major Components (mg C/g Sample)

<u>Sample #</u>	<u>NIDA</u>	<u>NTA</u>	<u>CA</u>	<u>ED3A^(b)</u>	<u>EDTA</u>	<u>HEDTA^(c)</u>	<u>SA</u>	<u>TOC Accounted For^(d)</u>	<u>% TOC Accounted For</u>
R4258/C	1.30	0.40	0.44	0.19	2.00	-	0.07	4.8	44
R4259/C	.88	0.32	0.22	0.18	1.30	-	0.05	3.3	33
R4260/C	1.00	0.30	0.38	.050	1.70	-	0.08	5.0	46
R4261/C	0.97	0.29	0.23	0.34	3.90	-	0.08	6.4	52
R4262/NC	0.24	0.06	0.14	0.32	0.81	-	0.02	2.2	20
R4263/NC	1.40	0.37	0.47	0.24	0.79	-	0.08	3.5	32
R4264/NC ^(e)									

(a) Derivatization performed in fume hood

(b) Assuming response similar to EDTa

(c) HEDTA was found in window E composite samples, but not in the segment subsamples

(d) Total includes minor components not included in this summary table

(e) Sample analysis in progress

C Convective layer

NC Nonconvective layer

NIDA mitrilotriacetic acid

NTA nitrilotriacetic acid

CA citric acid

ED3A ethylenediaminetriacetic acid

EDTA ethylenediaminetetraacetic acid

HEDTA N-(2-hydroxyethyl) ethylenediaminetriacetic acid

SA succinic acid

Table 2.3. LC Results for Oxalate, Formic, Glycolic, and Acetic Acids (mg C/g Sample) for 101-SY Window E Core Segment Samples

<u>Sample</u>	<u>Oxalic</u>	<u>Glycolic</u>	<u>Acetic</u>	<u>Formic</u>	<u>Total</u>	<u>% TOC Accounted For</u>
R4258/C	1.7	0.6		1.1	3.3	30
R4259/C	2.0	0.43	0.81	1.4	4.5	44
R4260/C	1.8	0.6		1.9	4.4	41
R4261/C	1.6			1.0	2.5	23
R4262/NC	5.0			0.87	5.8	53
R4263/NC	6.4			0.37	6.8	61
R4264/NC ^(a)						

(a) Sample analysis in progress.

C Convective layer

NC Nonconvective layer

3.0 Discussion of Methods

3.1 Derivatization GC/MS

3.1.1 Analysis of Waste by BF_3 /Methanol Derivatization - GC/MS

A total ion chromatogram for the boron trifluoride/methanol-derivatized waste sample is shown in Figure 3.1.1. Figures 3.1.2 (a through f) are the mass spectra of the components 1 to 6 in Figure 3.1.1. Appendix B lists all of the window C and E samples that have been or are being analyzed. The major components identified as methyl esters in both derivatization procedures (fume hood and hot cell) include succinic acid, citric acid, NIDA, NTA, ED3A, and EDTA. The GC/MS results obtained from the samples derivatized in the hot cell show that in most cases NIDA had the highest concentration, and the percent of water-soluble organic carbon accounted for by the chelators and chelator fragments amounted to approximately 10 to 20%. When the derivatization was performed in the fume hood, the TOC accounted for by chelators was 20 to 52%. The improved analysis has shown that EDTA is the chelator in the greatest abundance for all samples analyzed. The highest percentage of TOC as chelators was found in the bottom of the convective layer. A comparison of the GC/MS results of samples derivatized in the hood vs. hot cell indicate the concentration of EDTA was underestimated when the derivatization was performed in the hot cell facility.

The reproducibility of the results from derivatization GC/MS is estimated to be approximately 10% from duplicate manual injections of the same sample. Different sub-samples were analyzed to determine the sub-sample variation. This is estimated to be approximately 16% for EDTA, 14% for NIDA, 20% for NTA and ED3A. Recoveries, based on simulated wastes, is estimated to be 50-60%. However, the simulated wastes may not be similar to the actual wastes. During the drying process and derivatization, simulated waste samples appear to behave very differently. It is estimated that the recoveries may be higher with the actual tank waste samples. The analytical results were not corrected for recoveries. The use of deuterated standards should provide a better indication of reproducibility and recovery. The variation from sample to sample may be both a function of sample heterogeneity and analytical irreproducibility.

The GC/MS results obtained from samples derivatized in the fume hood are more reproducible than those from derivatization in the hot cell. The parameters that are critical to the success of the derivatization reaction (temperature and dryness of the sample) could not be rigidly controlled in the hot cell. The use of cation exchange to remove the radioactivity made it possible to reduce the radioactivity level and remove the samples from the hot cell. In addition, the sample size derivatized in the hot cell was approximately 2 g. The sample size derivatized in the fume hood was approximately 150 to 200 mg. The reason for the low recoveries obtained from derivatization in the hot cell was probably due to the sample size/reagent ratio. The matrix effect for these samples is very high; with a high sample size/reagent ratio, most of the reagent was consumed and, as a result, the reaction was incomplete. With the sample size/reagent ratio lower, the reaction is more complete, and the concentrations of the chelators are much higher. Also, with these types of samples, it is mandatory to run the derivatization reaction with fresh BF_3 /methanol to ensure a complete reaction.

Peak 1	NIDA
Peak 2	CA
Peak 3	NTA
Peak 4	ED3A
Peak 5	EDTA
Peak 6	HEDTA

Figure 3.1.1. Total Ion Chromatogram of Derivatized Core Composite Sample

Methyl ester of NIDA

* Confirmed by high resolution mass spectrometry

39205113.7 & 8B/W

(a) Peak #1

Figure 3.1.2. Mass Spectrum

Methyl ester of citric acid

MW = 234

(b) Peak #2

39205113.9 & 10B\

Figure 3.1.2. (contd)

Methyl ester of NTA

MW = 233

(c) Peak #3

Figure 3.1.2. (contd)

39205113.11 & 12B/W

Methyl ester lactone of ED3A

(d) Peak #4

Figure 3.1.2. (contd)

39205113.13 & 14B\A

Methyl ester of EDTA

MW = 348

39205113.15 & 16B/

(e) Peak #5

Figure 3.1.2. (contd)

Methyl ester lactone of HEDTA

MW = 288

(f) Peak #6

Figure 3.1.2. (contd)

39205113.17 & 18B/W

3.1.2 Detailed Investigations of BF_3 /methanol Derivatization of Chelators

In the reaction of chelators with BF_3 /methanol, methylation occurs at the carboxylic acid sites, but not at the hydroxy sites. The mass spectrum of the methyl ester of HEDTA shows a parent ion at m/z 288, which indicates formation of a lactone with molecular weight (MW) = 288 and the following structure. The mass spectrum is shown in Figure 3.1.3. The parent ion was confirmed with positive ion chemical ionization mass spectrometry.

The identification of m/z 288 for methylated HEDTA was initially surprising because the expected molecular weight of methylated HEDTA (Me_3 -HEDTA) should be 320. Analysis of the m/z 288 species using GC/Fourier transform infrared (FTIR) spectroscopy revealed the presence of a strong lactone absorbance. Consequently, the methylated lactone structure was derived. The hydroxyethyl group of HEDTA resists methylation by boron trifluoride/methanol and, instead, forms a cyclic, or intramolecular lactone, with one of the neighboring acetate ligands.

The sensitivity or response factor of methylated HEDTA was substantially lower than that of EDTA or NTA, 30% less on a molar basis. This discrepancy was resolved when the methylated HEDTA was analyzed by direct probe/MS. The MW 288 lactone accounted for approximately 30% of the species detected. Trimethylated HEDTA with an unreacted, or free, hydroxyethyl group accounted for the remaining 70% of the HEDTA. It is speculated that the species is simply too polar to migrate through the GC columns.

To test whether the trimethylated HEDTA was sorbed onto the GC column, two experiments were performed. First, HEDTA was silylated, and the product was analyzed by MS and GC/MS. A single species, the tetratrimethylsilyl ether of HEDTA, chromatographed nicely as a single GC peak. As a second test, methylated HEDTA was silylated using the silylating reagents N -bis(trimethylsilyl)acetamine (BSA) and trimethylchlorosilane (TMCS). The reaction product was then analyzed using MS and GC/MS. Two species were identified as two distinct GC peaks: first, the MW 288 lactone and, second, the mixed derivative of HEDTA, the trimethyl ester, mono(trimethylsilyl)ether of HEDTA. This confirmed that the underivatized hydroxyethyl group of HEDTA rendered any such derivative too polar to migrate through the GC column. The results of these recovery investigations are shown in Figure 3.1.4. Such chemical complexities are often encountered when analyzing chelating agents or their degradation products.

Similarly, the mass spectrum of ED3A, MW 234, derivatized with BF_3 /methanol, shows the parent ion at m/z 244 (Figure 3.1.5), indicating formation of a lactam with the following structure.

Both symmetrical ethylenediaminediacetic acid (s-EDDA) and unsymmetrical ethylenediaminediacetic acid (u-EDDA), structures shown below, were derivatized with boron trifluoride/methanol to form the methyl esters. However, the yield from the reaction of s-EDDA with boron trifluoride/methanol is not reproducible. This may be due, at least in part, to the irreversible formation of boron trifluoride complexes with this isomer.

s-EDDA

u-EDDA

The proposed structures for the corresponding lactams are shown below.

u

s

The corresponding electron impact mass spectra are shown in Figures 3.1.6. The base peak for derivatized u-EDDA is m/z 113. The base peak for derivatized s-EDDA is m/z 85 with fragment ions m/z 143 and 102. Accurate mass measurements indicate that m/z 143 is derived from loss of CHO, presumably from the lactam ring.

39205113.17

Figure 3.1.3. Mass Spectrum of Methylate HEDTA (Intramolecular Lactone from Reaction with Boron Trifluoride/Methanol)

Figure 3.1.4. Source of the MW 288 Chelator Fragment (HEDTA)

Figure 3.1.5. Mass Spectrum of Derivatized ED3A

(a) Unsymmetrical

(b) Symmetrical

Figure 3.1.6. Mass Spectra of EDDA

3.1.3 Diazomethane Methylation

Chelators react slowly with diazomethane in this procedure, which takes place at ambient temperatures; in some cases, several hours are needed to complete the reaction. Diazomethane derivatization also produces more side products, which results in a more complex chromatogram. A total ion chromatogram of diazomethane-derivatized iminodiacetic acid (IDA) is shown in Figure 3.1.7(a). Excess diazomethane often yields multiple methylated products. For example, the mass spectrum of IDA (Figure 3.1.7(b)), when derivatized with excess diazomethane, shows a peak at m/z 175. The simple methyl ester would be expected to have a molecular weight of 161. This indicates that the N is being methylated as well as the two carboxylic acid groups. The structure of the actual derivative formed is

with molecular ion m/z 175. Similar multiply-methylated products have been observed in the reaction of diazomethane with dansyl derivatives of amino acids (Campbell et al. 1990).

When ED3A was derivatized using this method, the product was identified as an intramolecular lactam with the following structure.

Similarly, HEDTA gave an intramolecular lactone with the following structure.

(a) Total Ion Chromatogram

Figure 3.1.7. IDA Derivatized with Diazomethane

(b) Mass Spectrum of Peak #2

Figure 3.1.7. (contd)

3.1.4 Bis(trimethylsilyl)trifluoroacetamide Silylation

Silylation takes place at each of the carboxylic acid groups and at any hydroxy groups of the chelator. Trimethylsilyl (TMS) derivatives tend to hydrolyze, so analysis should be performed as soon as possible. In the case of chelators, interpretation of the mass spectrum can be rendered difficult by extensive fragmentation and low intensity of the parent ion. The mass spectrum of bis(trimethylsilyl)trifluoroacetamide (BSTFA)-derivatized HEDTA is shown in Figure 3.1.8. The spectrum shows the weak parent ion at m/z 566.

Figure 3.1.8. Mass Spectrum of HEDTA Derivatized with BSTFA

3.1.5 Butanol/HCl Butyl Esterification

This method gave good results with few, if any, side products. A slightly higher flame ionization detection (FID) response was obtained with the butyl ester formed by reaction with butanol/HCl compared to the methyl esters formed by reaction with either diazomethane or BF_3 /methanol. Heating times required for product formation varied from chelator to chelator. Figure 3.1.9 shows the mass spectrum of the butyl ester of EDTA. A weak parent ion is observed at m/z 516. This was confirmed using positive ion chemical ionization mass spectrometry. The structure of the butyl ester of EDTA is shown below.

The reaction of s-EDDA and u-EDDA with butanol/HCl appears to be very reproducible with the formation of the corresponding lactams.

Figure 3.1.9. Mass Spectrum of Butyl Ester of EDTA

3.1.6 Chloroethanol/HCl Chloroethyl Esterification

This method was developed with the goal of producing a product whose enhanced electronegativity would lend itself to analysis using electron capture detection (ECD) and negative chemical ionization mass spectrometry. Both these detection techniques hold out the promise of enhanced detection sensitivity.

Several chelators including HEDTA, EDTA, and IDA were derivatized to form the chloroethyl esters. All three chelators gave mass spectra showing fairly intense parent ions. The main drawback is the large number of chloroether and chloroester side products produced in substantial amounts by S_N2 side reactions among the reagent molecules and the chloroethyl esters formed. These side reactions increase with time and give rise to a very complex total ion chromatogram. However, the mass spectrum showing the parent ion and its important fragments can be successfully extracted in each case. Figure 3.1.10 shows the mass spectrum of the chloroethyl ester of HEDTA, which indicates formation of a lactone with MW = 384. The structure of the parent ion at m/z 384 is shown below.

The large peak at m/z 270 is due to the following structure.

These derivatized compounds were also examined using GC/ECD and negative ion chemical ionization MS with isobutane as the reagent gas. Figure 3.1.11 (a) is a chromatogram of the chloroethyl ester derivative of HEDTA detected by an electron capture detector. Figure 3.1.11 (b) is a negative ion mass spectrum of the chloroethyl ester of HEDTA. The parent ion is m/z 384 and m/z 419 is $(M+Cl)^-$. The peak m/z 312 is the result of cleavage in the lactone. Accurate mass measurements revealed the composition to be $C_{11}H_{18}O_6N_2Cl_2$. The phenomenon of Cl^- addition in negative ion chemical ionization has been observed by other researchers (Stemmler and Hites 1985).

Figure 3.1.10. Mass Spectrum of HEDTA Derivatized with Chloroethanol/HCl

(a) Chromatogram of GC/ECD

(b) Negative Ion Mass Spectrum

Figure 3.1.11. Chloroethyl Ester of HEDTA

3.1.7 Assessment of Derivatization Techniques for Analysis of Wastes

Derivatization with diazomethane, BSTFA, butanol/HCl, chloroethanol/HCl, and BF₃/methanol has been shown to be applicable for the analysis of organic complexing agents and their degradation products. Each of the techniques has disadvantages. For example, the reaction of chelators with boron trifluoride/methanol was not reproducible in the case of s-EDDA. The reaction with BSTFA produced components with very weak parent ions detected by mass spectrometry. The reaction with diazomethane required lengthy reaction times and produced multiple-methylated products. The reaction with chloroethanol/HCl produced large amounts of side products. All of the derivatization procedures resulted in the formation of intramolecular lactones and lactams for specific components.

The reaction of the waste sample with boron trifluoride/methanol was very useful in identifying major components. The major components included citric acid, NTA, HEDTA, EDTA, succinic acid, NIDA, and ED3A. The improvements in the sample preparation procedure provided more reproducible data. The most significant improvement came when the derivatization was performed in the fume hood rather than the hot cell.

3.2 Liquid Chromatography-Determination of Low Molecular Weight Acids

3.2.1 Anion Exchange and Anion Exclusion Separation

Anion-exchange chromatographic separation was used primarily to determine the oxalate content of the samples. This chromatography is carried out in a basic mobile phase. The separation of oxalic acid as sodium oxalate from all the other constituents in the samples was quite good as seen in Figure 3.2.1.

Ion-exclusion chromatographic separation was used to determine a variety of organic acids. With this technique, formic acid, acetic acid, and glycolic acid, among others, were determined. Figure 3.2.2 shows a typical chromatogram developed from ion exclusion chromatography. Quantitation was performed by external standard. Confirmation of peak identity was done by coinjection of standards.

Not all of the peaks in the ion-exclusion chromatography could be identified. Figure 3.2.3 shows the separation of a tartaric acid spike from a sample component. Figure 3.2.3 also shows the coelution of a formic acid spike with formic acid in the sample. The compounds that were identified in the samples with confidence by ion exclusion chromatography were glycolic acid, formic acid, and acetic acid.

The concentration of oxalate was the highest of the four analytes determined by LC in most of the samples (see Table 2.3). The concentration of formic acid was higher than oxalate in only one sample. In addition, the concentration of oxalate was highest in the bottom of the nonconvective layer. Oxalate constituted approximately 50% of the total of the four LMWA analytes in the convective layer and approximately 80 to 90% in the nonconvective layers.

The estimate of reproducibility for the LC determination of oxalate is approximately 5%. Estimation of reproducibility for the LC determination of the other LWMA is estimated to be 10%, due to baseline drift. Recovery of oxalic acid from spiked simulated waste was 91%. Recoveries for the other LMWA is estimated to be lower than that of oxalic acid. The variation of sample to sample is both a function of sample heterogeneity and analytical irreproducibility.

39310055.20

Figure 3.2.1. LC Chromatogram of Oxalate Determination

39310055.22

Figure 3.2.2. Typical Chromatogram from Ion Exclusion Chromatography for Determination of Glycolic, Formic, and Acetic Acids

Figure 3.2.3. LC Chromatogram Indicating Unidentified Components in Anion Exclusion Chromatogram

3.2.2 Separations with an Organic Acid Analysis Column

An LC method for analyzing small molecular weight acids has been developed to supplement the ion chromatographic effort. A Bio-Rad HPLC Organic Acid analysis column, Aminex Ion Exclusion HPX-87H 300 X 7.8 mm with compatible guard column, was used. The temperature of the column was maintained at 60°C with 0.1N H₂SO₄ as the mobile phase. The flow rate was 0.8 mL/min. Detection was accomplished with a UV detector at 210 nm. A standard mixture containing oxalic acid, citric acid, tartaric acid, gluconic acid, glyoxylic acid, glycolic acid, formic acid, and acetic acid was analyzed. In addition, a simulated waste sample from earlier studies by S.A. Bryan (Bryan et al. 1992) was spiked with the mixture of acids and analyzed with this procedure. The pH of the simulated waste sample was adjusted to pH 2.0 before analysis. Preliminary results indicate this method provides good separation and chromatography. Retention times for several of the components are oxalic acid-6.4 min, citric acid- 7.7 min, glyoxylic acid- 9.3, glycolic acid- 11.9 min, formic acid- 13.6 min, and acetic acid- 14.8 min.

Samples from D. Meisel, at Argonne National Laboratory, were also analyzed using this technique. The control sample contained citrate, HEDTA, EDTA, nitrate, and nitrite. The irradiated sample contained the same starting materials, but had undergone irradiation. After heating the irradiated sample, Meisel and coworkers found that approximately ten times as much hydrogen was produced as the heated, non-irradiated sample. A chromatogram of solution C (control) is shown in Figure 3.2.4. Also included in Figure 3.2.4 is a chromatogram of an actual waste sample. A chromatogram of solution I (irradiated) is shown in Figure 3.2.4. The components detected and identified, based on retention time only, in the irradiated sample include citric acid, glycolic acid, formic acid, glyoxylic acid, and acetic acid (tentative). The concentrations of glyoxylic acid, glycolic acid, and gluconic acid (tentative) are somewhat higher in the irradiated sample. The chromatogram of the sample with irradiation and heating is shown in Figure 3.2.4. The retention times of 8 to 12 min indicates the appearance and disappearance of components.

The primary difference between the simulated samples and the actual waste samples is the presence of NIDA in the real waste.

(a) Composite Sample

(c) Meisel's Irradiated Sample

(b) Meisel's Control Sample

(d) Meisel's Irradiated and Heated Sample

Figure 3.2.4. Anion Exchange Chromatogram

3.3 Extraction of Waste to Isolate Solvent-Soluble Base-Neutral and Acid Fractions

Figure 3.3.1 is a total ion chromatogram of the methylene chloride extract of the base-neutral fraction, and Figure 3.3.2 is a total ion chromatogram of the methylene chloride extract of the acid fraction. These fractions were produced by extraction of the basic waste from window E core composites (see Appendix A) with methylene chloride to remove base-neutrals, followed by pH adjustment to 3 and methylene chloride extraction of acids.

The peaks indicated are NPH (C_{12} through C_{15}) and are present in both the base-neutral and acid fractions. Typically, one would expect the acid fraction to contain little NPH; however, due to low extraction efficiency, NPH exists in both fractions. Stromatt also found NPH present in the samples from Tank 101-SY, window E (Jones et al. 1992). The other peaks, particularly in the acid fraction, are compounds formed by addition reactions across the double bond in cyclohexene, used as an inhibitor in methylene chloride (Campbell et al. 1987). The mass spectra of these components indicate a base peak at m/z 81.

39310055.1

Figure 3.3.1. Total Ion Chromatogram of the Methylene Chloride Extract of Base-Neutral Fraction

39310055.2

Figure 3.3.2. Total Ion Chromatogram of the Methylene Chloride Extract of Acid Fraction

3.4 High Resolution Mass Spectrometry: Accurate Mass Measurement

Figure 3.4.1 is a high resolution mass spectrometry (HRMS) total ion chromatogram. Table 3.4.1 lists the structures determined by . Figure 3.4.2 is an example of the type of data obtained by HRMS. The major fragment loss in many of these components is 59 which is a loss of COOCH_3 . The best fit for the structure of m/z 246 is $\text{C}_9\text{H}_{16}\text{O}_5\text{N}_3$. The next fragment ion is the result of HNO loss from m/z 246 to m/z 215. The structure of m/z 215 is $\text{C}_9\text{H}_{15}\text{O}_4\text{N}_2$. High resolution mass spectrometry is not only useful for determining the empirical formula of the parent compound, but also for determining the structures of fragment ions.

This represents the first example of an actual waste sample analyzed by HRMS. The previous accurate mass measurement of NIDA was determined on a sample of NIDA produced by the reaction of HEDTA and nitric acid. Other nitroso compounds as well as NIDA were identified by HRMS. These are nitroso compounds possibly related to ED3A.

Figure 3.4.1. Total Ion Chromatogram of Derivatized Sample from HMRS
SC Denotes Solvent Contaminant and S Denotes Spike Component

[Elemental Composition]

Data : J62393-03

Sample: 101SY-1196

Inlet : Reserv.

RT : 25.18 min

Elements : C 10/0, H 20/0, O 10/1, N 4/0

Mass Tolerance : 80ppm, 5mmu if m/z < 62, 60mmu if m/z > 750

Unsaturation (U.S.) : -0.5 - 10.0

Date : 23-Jun-93 16:33

Note : BF3 derivative

Ion Mode : EI+

Scan#: 1164

Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition
246.1110	5.3	+53.7 / +13.2	3.5	C 10 H 16 O 6 N
		-43.0 / -10.6	3.0	C 10 H 18 O 5 N 2
		+8.1 / +2.0	3.5	C 9 H 16 O 5 N 3
		+70.0 / +17.2	-0.5	C 5 H 16 O 8 N 3
		+59.1 / +14.6	4.0	C 8 H 14 O 5 N 4
215.1034	29.4	+53.4 / +11.5	3.5	C 10 H 15 O 5
		-57.3 / -12.3	3.0	C 10 H 17 O 4 N
		+1.2 / +0.3	3.5	C 9 H 15 O 4 N 2
		+72.1 / +15.5	-0.5	C 5 H 15 O 7 N 2
		+59.7 / +12.8	4.0	C 8 H 13 O 4 N 3
175.0843	11.5	-51.0 / -11.0	3.5	C 8 H 15 O 3 N 4
		+19.9 / +4.3	-0.5	C 4 H 15 O 6 N 4
		-72.9 / -12.8	1.5	C 8 H 15 O 4
		-1.0 / -0.2	2.0	C 7 H 13 O 4 N
		-16.4 / -2.9	6.5	C 10 H 11 O N 2
174.0803	100.0	+70.8 / +12.4	2.5	C 6 H 11 O 4 N 2
		+55.5 / +9.7	7.0	C 9 H 9 O N 3
		-65.2 / -11.4	2.0	C 6 H 13 O 3 N 3
		+6.6 / +1.2	2.5	C 5 H 11 O 3 N 4
		-51.1 / -8.9	2.0	C 8 H 14 O 4
145.9834	21.8	+21.2 / +3.7	2.5	C 7 H 12 O 4 N
		+5.8 / +1.0	7.0	C 10 H 10 O N 2
		+78.0 / +13.6	7.5	C 9 H 8 O N 3
		-43.3 / -7.5	2.5	C 6 H 12 O 3 N 3
		+28.9 / +5.0	3.0	C 5 H 10 O 3 N 4
116.0712	5.8	-11.9 / -1.7	4.0	C 4 H 2 O 6
		-30.3 / -4.4	8.5	C 7 O 3 N
		+74.2 / +10.8	4.5	C 3 O 6 N
		-2.7 / -0.4	4.5	C 2 O 5 N 3
		+0.1 / +0.0	1.5	C 5 H 10 O 2 N
		+11.7 / +1.4	2.0	C 3 H 8 O N 4

Figure 3.4.2. Example of High Resolution Data

Table 3.4.1. Molecular Structures Determined by High Resolution Mass Spectrometry

<u>Compound #</u>	<u>Molecular Formula</u>	<u>Structure</u>	
1	$C_2H_2O_4$	HOOC—COOH	Oxalic Acid
2	$C_3H_4O_4$	HOOC—CH ₂ —COOH	
3	$C_4H_6O_4$	HOOC—CH ₂ —CH ₂ —COOH	Succinic Acid
4	$C_5H_8O_4$	$ \begin{array}{c} \text{HOOC—CH}_2\text{—CH—COOH} \\ \\ \text{CH}_3 \end{array} $	
5	$C_5H_9O_4N$	$ \begin{array}{c} \text{CH}_2\text{—COOH} \\ \diagup \\ \text{H}_3\text{C—N} \\ \diagdown \\ \text{CH}_2\text{—COOH} \end{array} $	
6	Unknown	Interference peaks, low intensity	
7	$C_5H_8O_4$	HOOC—CH ₂ —CH ₂ —CH ₂ —COOH	
8	Unknown	Interference peaks, low intensity	
9	$C_6H_{12}O_4$	HOOC (CH ₂) ₄ COOH	

Table 3.4.1. (contd)

Compound #	Molecular Formula	Structure
1 0	$C_4H_7O_4N$	$ \begin{array}{c} \text{CH}_2\text{---COOH} \\ \diagup \\ \text{HN} \\ \diagdown \\ \text{CH}_2\text{---COOH} \end{array} $ <p>IDA</p>
1 1	Unknown	Interfering peaks, low intensity
1 2	$C_4H_5O_5N_2$	$ \begin{array}{c} \text{CH}_2\text{---COOH} \\ \diagup \\ \text{O=N---N} \\ \diagdown \\ \text{CH}_2\text{---COOH} \end{array} $ <p>NIDA</p>
1 3	$C_6H_9O_7$	$ \begin{array}{c} \text{CH}_2\text{---COOH} \\ \\ \text{OH---CH}_2\text{---COOH} \\ \\ \text{CH}_2\text{---COOH} \end{array} $ <p>Citric Acid</p>
1 4	$C_6H_9O_6N$	$ \begin{array}{c} \text{HOOC---CH}_2\text{---N} \\ \diagup \quad \diagdown \\ \text{CH}_2\text{---COOH} \quad \text{CH}_2\text{---COOH} \end{array} $ <p>NTA</p>
1 5	$C_7H_{13}O_5N_3$	$ \begin{array}{c} \text{CH}_3\text{---N} \\ \\ \text{N} \\ \\ \text{O} \end{array} \begin{array}{c} \diagup \quad \diagdown \\ \text{CH}_2\text{---CH}_2\text{---N} \\ \diagup \quad \diagdown \\ \text{CH}_2\text{---COOH} \quad \text{CH}_2\text{---COOH} \end{array} $
1 6	$C_8H_{12}O_5N_2$	$ \begin{array}{c} \text{HOOC---CH}_2\text{---N} \\ \diagup \quad \diagdown \\ \text{CH}_2\text{---CH}_2\text{---N} \\ \diagup \quad \diagdown \\ \text{CH}_2\text{---COOH} \quad \text{CH}_2\text{---COOH} \end{array} $ <p style="text-align: center;"> $\text{O}=\text{C---CH}_2$ </p> <p> $\star \text{HOOC---CH}_2\text{---N} \begin{array}{c} \diagup \quad \diagdown \\ \text{CH}_2\text{---CH}_2\text{---N} \\ \diagup \quad \diagdown \\ \text{CH}_2\text{---COOH} \quad \text{CH}_2\text{---COOH} \end{array}$ </p>

39309032.3

Table 3.4.1. (contd)

Compound #	Molecular Formula	Structure
1 7	$C_8H_{13}O_7N_3$	
1 8	$C_{10}H_{16}O_8N_2$	
1 9	$C_{10}H_{16}O_6N_2$	
2 0	$C_7H_{11}O_6N$	

39309032.4

* Indicate components detected as intramolecular lactones or lactams

3.5 Thermospray LC/MS: Determination of Low Molecular Weight Acids

In this study, a method for analyzing small organic acids in mixed hazardous wastes was developed using thermospray LC/MS. The acids investigated were oxalic acid, citric acid, tartaric acid, gluconic acid, glyoxylic acid, glycolic acid, formic acid, and acetic acid. These acids, particularly glycolic acid, are difficult to analyze by other techniques, such as derivatization GC/MS. Analysis using HPLC/MS shows some advantages over GC analysis in that derivatization is not required, and the non-volatile inorganic species do not have to be removed as long as they are soluble in the mobile phase. A standard mixture of these acids was used to determine conditions suitable for maximum separation. Calibration curves were prepared to check for linearity of response.

A synthetic waste sample containing nitrate, nitrite, 2 M NaOH, EDTA, HEDTA, and citrate was spiked with the standard acids to determine the detection limits of the analytes. Synthetic waste samples were analyzed by both LC and thermospray LC/MS techniques. The ions observed in thermospray LC/MS differed somewhat, depending on whether the sample went through the column or was analyzed by direct injection. An actual waste sample from a waste storage tank, Tank 101-SY, was analyzed using thermospray LC/MS. Citric, glycolic, N-nitrosominodiacetic, and acetic acids were identified in the actual waste sample.

Several different mobile phases were investigated to see which would give the best separation of the acids. Among these were 0.01 M H_2SO_4 , 0.1 M $\text{HC}_2\text{H}_3\text{O}_2$, 0.01 M and 0.001 M HCl, and 0.1% H_3PO_4 . All showed substantial separation of the organic acids, but the retention times for tartaric acid and glyoxylic acid were similar to citric acid (eluted as a shoulder on the citric acid peak) and glyoxylic acid (eluted as shoulder on the gluconic peak), respectively, for the last three mobile phases listed above. This may not present much of a problem since neither tartaric acid nor gluconic acid are likely to be constituents of real waste. A mobile phase of 0.01N H_2SO_4 gave a good separation of all of the acids under the instrument conditions stated earlier. All of the acids can be detected except for hexanoic, a straight-chain monocarboxylic acid that is not very soluble in water. The aldehyde function on glyoxylic acid is labile, oxidizing readily to produce oxalic acid. If quantitation is desired, this standard should be made up daily. The very large peaks at the beginning of the chromatogram may be due to nitrates, etc. Bicarbonate is also present in the sample which could give rise to a carbonic acid peak.

3.5.1 Analysis of Waste Sample Using Thermospray LC/MS

A total ion thermospray LC/MS chromatogram of an actual waste sample is shown in Figure 3.5.1. Figures 3.5.2 are the total ion chromatogram, extracted ion plot of m/z 193 for citric acid, and m/z 98 for glycolic acid, respectively. In addition, a small contribution from acetic acid m/z 97 is visible at about 16 min.

The thermospray mass spectrum of NIDA is shown in Figure 3.5.3 (a). Figure 3.5.3 (b) is a mass spectrum of the peak at retention time 8.0 min in the total ion chromatogram, which closely resembles the spectrum of the NIDA standard. The component NIDA was also observed as a major component in the GC/MS total ion chromatogram of actual waste obtained by reacting the waste sample with boron trifluoride/methanol to produce the methyl esters. Further research is underway to determine whether NIDA is an artifact of the sample preparation and analysis under acidic conditions

or whether it exists as a component in the actual waste. Research is now focusing on identification of the other peaks in the waste sample, particularly the large peaks at 7 and 8 to 9 min. Other acid standards obtained through commercial sources or synthesis are being used for this purpose. Diglycolic acid has been tentatively identified as the peak ion 7.75 min. Some constituents are clearly co-eluting.

Figure 3.5.1. Total Ion Thermospray LC/MS Chromatogram of Composite Sample.

(a) Total Ion Chromatogram

(b) Extracted Ion Plot M/Z 193
for Citric Acid

(c) Extracted Ion Plot M/Z 97
for Glycolic Acid

(d) Extracted Ion Plot M/Z for
Acetic Acid

Figure 3.5.2. Thermospray LC/MS of Composite Sample

(a) NIDA

Figure 3.5.3. Mass Spectrum

39310055.8

(b) Component at 8.0 Minutes

Figure 3.5.3. (contd)

3.5.2 Detailed Investigation of Thermospray LC/MS Methods for Low Molecular Weight Acids

The mobile phase selected for thermospray LC/MS was 0.001N HCl because it is considerably more volatile than 0.01 H₂SO₄. A mobile phase of 0.001N HCl has been used with some success by Pacholec (Pacholec et al. 1986) in characterizing mixtures of organic acids by ion-exclusion partition chromatography-mass spectrometry. Water is flushed through the entire system at the end of each day to prevent damage to instrument components from the HCl.

All of the acids except oxalic acid gave results in positive ion thermospray with the filament either on or off. Oxalic acid has the lowest pK_a value of all the acids studied and cannot be determined by this method. However, oxalic acid is readily detectable by several other methods, including HPLC, plasmaspray MS (which is similar to thermospray except a plasma discharge is present to assist ionization), and GC/MS after derivatization with butanol/HCl.

The acids were studied by direct injection into the thermospray system (by-passing the column), and the results were compared to those obtained when the same acids passed through the column and then into the thermospray system. One interesting observation from this work is that several of the acids do not give the same ions in both procedures. A typical example is citric acid. Figure 3.5.4 shows the mass spectrum for citric acid on direct injection, and Figure 3.5.5 shows the mass spectrum of citric acid after passing through the column and into the thermospray system. On direct injection, (M + 18)⁺ is the largest peak while in the case of passage through the column, (M + 1)⁺ is present, but 131 is the largest peak, and neither (M + 18)⁺ nor (M + 1 + 18)⁺ are present.

The most common ions observed in both cases were M + 1 = (M+H)⁺ and M + 18 = (M+H₂O)⁺. Large background effects that may be the result of hydrated chloride species are a persistent problem if scanning were done at mass values much less than 80. An ion-suppression column for removal of chloride ions would make the detection of lower molecular weight-acids, such as formic acid, easier. Acetic acid is readily detectable due to m/z 97 which appears to be due to (M + H + 2H₂O)⁺.

Table 3.5.1 compares direct injection and through the column for several acids. From these results, it appears that differing degrees of protonation and hydration may occur within the column as opposed to simply within the mobile phase. More hydration occurs on direct injection for some of these acids. This phenomenon is probably due to chemistry with the column and is under further investigation.

Figure 3.5.4. Mass Spectrum of Citric Acid by Direct Injection LC/MS

Figure 3.5.5. Mass Spectrum of Citric Acid after Passing Through Analytical Column MS

Table 3.5.1. Ions Detected by Direct Injection vs. Through Analytical Column

<u>Acid</u>	<u>Direct Injection</u>	<u>Through Column</u>
Acetic Acid $\text{CH}_3\text{CO}_2\text{H}$ Mol. wt. 60.05		97 (M+1+36) 100% No other ions of any significance.
Citric Acid $\text{HO}_2\text{CCH}_2\text{C}(\text{OH})(\text{CO}_2\text{H})\text{-CH}_2\text{CO}_2\text{H}$ Mol. wt. 192.13	210 (M+18) 100% 193 (M+1) 73% 211 (M+1+18) 65% 165 33% 147 19% 194 (M+2) 5% 131 5% 149 6%	131 100% 149 33% 147 17% 193 (M+1) 2%
Gluconic Acid ^(a) $\text{HOCH}_2[\text{CH}(\text{OH})_4]\text{CO}_2\text{H}$ Mol. wt. 196.16	170 (M+1-18) 100% 197 (M+1) 50% 196 (M) 214 (M+18) 4% 117 90%	125 (M+1-72(4H ₂ O)) 100% 179 (M+1-18) 98% 99 24% 143 (M+1-54 (3H ₂ O)) 22% 197 (M+1) 12%
Glycolic Acid ^(b) $\text{HOCH}_2\text{CO}_2\text{H}$ Mol. wt. 76.05	95 (M+1+18) 100% 113 (M+1+36) 71% 94 (M+18) 26% 131 (M+1+54 (3H ₂ O)) 20% 153 15%	95 (M+1+18) 100% 113 (M+1+36) 12% 77 (M+1) 4% 153 2%
Glyoxylic Acid ^(c) OHCCO_2H Mol. wt. 74.04	122 100% 91 91% 121 62% 109 30% 179 16% 123 14% 104 12% 92 (M+18) 10% 95 16%	95 100% ^(d) 113 8% ^(d) 92 (M+18) 2%

Table 3.5.1. (contd)

Hexanoic Acid $\text{CH}_3(\text{CH}_2)_4\text{CO}_2\text{H}$ Mol. wt. 116.16	135 (M+1+18)	100%	135 (M+1+18)	100%
	153 (M+1+36)	58%	99 (M+1-18)	32%
	136 (M+2+18)	9%	117 (M+1)	22%
	233	7%	153 (M+1+36)	6%
	117 (M+1)	4%		
Tartaric Acid $\text{HO}_2\text{CCH}(\text{OH})\text{CH}(\text{OH})\text{CO}_2\text{H}$ Mol. wt. 150.09	169 (M+1+18)	100%	151 (M+1)	100%
	151 (M+1)	79%	91	38%
	168 (M+18)	55%	97 (M+1-54 (3H ₂ O))	

- (a) Scan was 75 to 300 to see if the 77 (M+1) was there.
- (b) (M+1) would not show since scan was 80 to 300.
- (c) (M+1) would not show since scan was 80 to 300 and the molecular weight is 74.
- (d) Since the 95 and 113 appear at a different retention time than that observed for glycolic acid, some conversion (disproportionation) may be occurring toward the end of the column or in the spray.

3.5.3 Assessment of Applicability of Thermospray LC/MS to Waste Samples

Thermospray LC/MS and HPLC procedures developed for analyzing small organic acids in mixed hazardous wastes, have proved successful in detecting the acids in both synthetic and actual waste samples. A separation of the acids was obtained and response was very good, even at low concentrations, except for hexanoic acid, which is not very soluble in water, and oxalic acid, which responds well in HPLC, but gives no response in positive-ion thermospray. Since a number of these acids, especially glycolic acid, have been difficult or impossible to separate by GC procedures, these methods show considerable promise.

3.6 Liquid Chromatography for EDTA and HEDTA

This method was applied to simulated tank waste samples. The LC method uses copper (II) cation added to the waste samples and an ion-pair reagent. The column used was a C-8 column; both HEDTA and EDTA were detected as the copper complexes at 280 nm. This method has been successfully transferred to the ACL and 222-S Laboratory personnel. The method is being used by ACL personnel to analyze waste samples prior to grout treatment.

3.6.1 Liquid Chromatography

The HEDTA and EDTA were easily separated with retention times of 2.7 and 16.5 minutes, respectively (Figure 3.6.1). No evidence of interfering peaks appeared in a simulated waste material (SWM) reference recipe preparation that had no added chelators. The calibration curve for EDTA was linear ($r=1.0$) over the range of 0.003 M to 0.03 M. This corresponds to undiluted simulated waste mixture concentrations of 0.08 M and 0.8 M. The concentration of EDTA in the SWM ranged from 0.085 M to 0.255 M. The calibration curve for HEDTA was linear ($r=0.99$) over the range of 0.009 M to 0.023 M. This corresponds to undiluted simulated waste mixture concentrations of 0.2 M and 0.57 M. The concentration of HEDTA in the SWM ranged from 0.175 M to 0.525 M.

The recovery of chelators spiked into the simulated waste reference recipe that had no added chelators ranged from 95.4% to 105% for EDTA and 99.7% to 105% for HEDTA. Recovery tests that were performed at concentrations of 0.1 M and 0.2 M for both chelators are shown in Table 3.6.1. The composition of the simulated waste formulation is shown in Table 3.6.2. Results of the analysis are listed in Table 3.6.3. In addition to the chelator concentration, Table 3.6.3 also gives the ratio of the assayed concentration to the expected concentration. Two batches were prepared of each variant, and the results were consistent from batch to batch, with the exception of the reference recipe for EDTA in day 41 after heating. This consistency indicated good precision of the method.

The HEDTA concentration appears unchanged in the reference recipe and high chelator variants. In the two low chelator variants, the HEDTA concentration appears greater in the supernatant layer. Unlike the HEDTA, the EDTA concentration appears to be stable in the low chelator variants. The EDTA concentration appears to have diminished in the reference recipe and the high chelator variants, especially the high AlO_2^- variant.

In none of the cases did a decrease in one chelator concentration result in an increase in the concentration of the other. It therefore appears that no interfering species were formed by decomposition of either chelator.

The method described here is similar to the method described by W. R. Grace and Company. However the Grace method placed the copper (II) cation in the mobile phase rather than in the sample. This required samples of pH less than 4.2 to avoid precipitation of $\text{Cu}(\text{OH})_2$. Because the samples were at pH 6.5, we could not use copper in the mobile phase without generating excessive back pressure in the chromatography equipment. The copper(II) complexes of these chelators are stable over a pH range of 4 to 10, so it was possible to add copper directly to the samples.

The HPLC and sample preparation methods described here can be used to analyze SWM for EDTA and HEDTA. In further studies, the separation of other chelators and simulated waste mixture degradation products will be carried out. Future studies will also apply the method to actual mixed waste samples from Hanford waste tanks.

39208046.3

Figure 3.6.1. LC Chromatogram Illustrating Separation of HEDTA and ETDA

Table 3.6.1. Recovery of EDTA and HEDTA from Simulated Waste Mixtures

<u>Recovery of 0.1M Chelator Spike</u>			<u>Recovery of 0.2M Chelator Spike</u>		
Result	HEDTA	EDTA	Result	HEDTA	EDTA
Run 1	101%	100%	Run 1	105%	102%
Run 2	99.7%	95.7	Run 2	101%	105%
Average	100%	97.9%	Average	103%	104%

Table 3.6.2. Composition of Simulated Waste Formulations^(a)

<u>Component</u>	<u>Reference Formulation</u>	<u>High AlO₂- High Chelator</u>	<u>Low AlO₂- Low Chelator</u>	<u>High AlO₂- Low Chelator</u>	<u>Low AlO₂- High Chelator</u>
NaAlO ₂	2.1	3.15	1.05	3.15	1.05
Na ₄ EDTA	0.17	0.255	0.085	0.085	0.255
Na ₃ HEDTA	0.35	0.525	0.175	0.175	0.525
NaCl	0.35	0.35	0.35	0.35	0.35
Na ₃ PO ₄	0.20	0.20	0.20	0.20	0.20
NaNO ₂	3.1	3.1	3.1	3.1	3.1
NaNO ₃	3.1	3.1	3.1	3.1	3.1
Na ₂ CO ₃	0.4	0.4	0.4	0.4	0.4
NaF	0.1	0.1	0.1	0.1	0.1
NaOH	2.9	2.9	2.9	2.9	2.9
Cr(NO ₃) ₃	1.5x10 ⁻³	1.5x10 ⁻³	1.5x10 ⁻³	1.5x10 ⁻³	1.5x10 ⁻³
Cu(NO ₃) ₂	2.1x10 ⁻⁴	2.1x10 ⁻⁴	2.1x10 ⁻⁴	2.1x10 ⁻⁴	2.1x10 ⁻⁴
Fe(NO ₃) ₃	2.0x10 ⁻³	2.0x10 ⁻³	2.0x10 ⁻³	2.0x10 ⁻³	2.0x10 ⁻³
Ni(NO ₃) ₂	3.1x10 ⁻³	3.1x10 ⁻³	3.1x10 ⁻³	3.1x10 ⁻³	3.1x10 ⁻³

(a) All concentrations in molar (M) units.

Table 3.6.3. Results of Analysis of Simulated Waste Mixtures

Day 16 of Heating

<u>Sample Type</u>	<u>Result HEDTA</u>	<u>Result EDTA</u>	<u>Ratio of Found To Expected for</u>	
			<u>HEDTA</u>	<u>EDTA</u>
Reference	0.54	0.12	1.53	0.70
Reference	0.43	0.11	1.22	0.67
High Al	0.55	0.15	1.06	0.57
High Chelator	0.56	0.13	1.07	0.51
Low Al	0.53	0.21	1.01	0.81
High Chelator	0.59	0.20	1.12	0.79
High Al	0.34	0.09	1.92	1.01
Low Chelator	0.33	0.08	1.89	0.98
Low Al	0.31	0.08	1.80	0.91
Low Chelator	0.36	0.09	2.04	1.05
Reference	0.39	0.10	1.11	0.60
Reference	0.35	0.06	0.99	0.34
High Al	0.44	0.08	0.83	0.30
High Chelator	0.48	0.08	0.91	0.32
Low Al	0.56	0.20	1.07	0.80
High Chelator	0.55	0.20	1.04	0.80
High Al	0.36	0.09	2.05	1.11
Low Chelator	0.35	0.08	1.98	0.95
Low Al	0.30	0.07	1.72	0.87
Low Chelator	0.31	0.08	1.76	0.93

3.6.2 LC/MS of Chelators

The LC/MS method that has been developed involves an RP 2 Lichrosorb column with ammonium acetate as the mobile phase and the thermospray interface. Separation of EDTA and HEDTA has been achieved. Mass spectra of Cu(EDTA) and Cu(HEDTA) have been obtained with thermospray LC/MS. It is apparent the spectra of EDTA and HEDTA are different, making the identification unambiguous. However, particle-beam LC/MS produced extensive fragmentation, making the identification of the chelators very difficult. The use of particle-beam LC/MS with chemical ionization shows promise. In addition, negative ion electrospray mass spectral data have been obtained on the chelators (uncomplexed), and the spectra show the $(M-H)^-$ as the base peak.

3.7 Electrospray-Determination of Low Molecular Weight Acids

Examples of mass spectra are shown in Figures 3.7.1 (a) and 3.7.1 (b). The primary ion observed in negative ion electrospray in most instances was $(M-H)^-$.

(a) HEIDA

Figure 3.7.1. Electrospray Mass Spectrum

(b) EDTA

Figure 3.7.1. (contd)

3.8 Plasmaspray LC/MS - Determination of Low Molecular Weight Acids

Plasmaspray LC/MS is corona-discharge assisted thermospray. A schematic is shown in Figure 3.8.1. Spectra were obtained using a VG 7070 high resolution mass spectrometer located at Montana State University in Bozeman, Montana. The mobile phase consisted of methanol/water (80/20) and 0.1 M ammonium hydroxide. The source temperature was 250°C. The spray parameters were electrode - 130 V, capillary temperature- 185°C, discharge current- 300 μ A, ion extraction - 120 V, and ion focus - 22 V.

Examples of mass spectra are illustrated in Figures 3.8.2 (a) and 3.8.2 (b). The primary ion observed in negative ion plasmaspray in most instances was (M-H)⁻.

39310055.17

Figure 3.8.1. Schematic of Plasmaspray

39310055.18

(a) Oxalic Acid

Figure 3.8.2. Plasmaspray Negative Ion Mass Spectrum

39310055.19

(b) Citric Acid

Figure 3.8.2. (contd)

3.9 Experimental Evidence for and Against the Presence of Nitroso Compounds in Waste

Nitroso compounds have been identified in the waste samples using derivatization GC/MS, LC/MS with an acidic mobile phase, and LC under acidic conditions. The mass spectrum of the derivatized, synthesized standard is identical to the mass spectrum observed in the GC/MS total ion chromatogram. The thermospray mass spectrum of the derivatized, synthesized standard is identical to the thermospray mass spectrum of the major component in the total ion chromatogram. However, in both of these instances, the separation or derivatization involves acidic conditions or reaction with a Lewis acid. In addition, the retention time of NIDA in the LC chromatogram (basic conditions) is identical to one of the unidentified peaks. This is illustrated in Figure 3.9.1. The ultraviolet (UV) spectrum of these two components is identical; the maximum absorbance is at approximately 240 nm.

A procedure is being developed to utilize thermospray LC/MS with NH_4CO_3 as the mobile phase ($\text{pH} \approx 10.5$). Preliminary results are very encouraging. The thermospray mass spectrum of NIDA obtained under strictly basic conditions is shown in Figure 3.9.2. An experiment was attempted to analyze a waste sample by thermospray LC/MS under basic conditions. Unfortunately, the column appears to have lost its separatory powers and everything eluted in the dead volume. No separation was obtained. This problem has now been corrected. The improved chromatography is illustrated in Figure 3.9.3 (a through d). Figures 3.9.3 (a) and 3.9.3 (b) are chromatograms of NIDA under the separation conditions. Figures 3.9.3 (c) and 3.9.3 (d) are chromatograms of simulated waste spiked with NIDA and detected at 210 and 240nm. However, the results of a selected ion monitoring (SIM) of m/z 180 and 136 are very interesting. The ratio of m/z 180 and 136 in simulated samples with NIDA spikes are practically identical with the ratio found in the actual waste. A simulated waste sample without NIDA shows a very different ratio of m/z 180 and 136. The spectra are shown in Figure 3.9.4 (a through c). The evidence does not totally indicate the presence of NIDA in waste Tank 101-SY, but the evidence does not prohibit its presence under basic conditions. The possibility does exist that the nitroso compounds are present in the real waste. Further studies are underway. Another promising procedure being investigated involves derivatization under basic conditions with a methylating reagent.

(a) Without Spiked NIDA

(b) With Spiked NIDA

Figure 3.9.1. LC Chromatogram of Composite Waste Sample

39310055.11

Figure 3.9.2. Thermospray Mass Spectrum of NIDA Obtained Under Basic Conditions

(a) Standard of NIDA
Detected at 210nm

(b) Standard of NIDA
Detected at 240nm

(c) SimulatedWaste Spiked
with NIDA at 210nm

(d) SimulatedWaste Spiked
with NIDA at 240nm

Figure 3.9.3. LC (Basic conditions) Chromatogram

(a) In Simulated Waste Spiked with NIDA

Figure 3.9.4. Selected Ion Monitoring of M/Z 180 and 136

39310C55.12

(b) In Simulated Waste with

Figure 3.9.4. (contd)

39310055.13

(c) In Waste Tank Sample

Figure 3.9.4. (contd)

4.0 Methods Development Transfer

A method has been accepted to fully document methods development transfer. The method will be developed and transferred to designated personnel. A cover statement will be signed by both the transferor and the receiver. The test plan will then be developed, completed, and signed by the test plan author and technical group leader. The entire package, which includes the transferred method, cover statement, and test plan, will then be forwarded to the appropriate WHC project manager.

Various methods have been transferred to personnel in the ACL and the laboratory at 222-S. The LC method for LMWA and the LC method for HEDTA and EDTA have been transferred to the personnel at the ACL and the laboratory at 222-S. These methods are being used by the ACL in the analysis of tank waste samples before grout treatment. The derivatization GC/MS methods and the LC/MS methods for chelators, chelator fragments, and LMWA will be transferred to the ACL during FY 1994. Further discussions are scheduled with Steve Metcalf, WHC, for additional transfer of methods.

5.0 Future Work

Future work will focus on determining whether NIDA exists in the tank waste. This work will apply thermospray LC/MS, under basic conditions, to the analysis of tank waste.

Additional efforts will focus on the use of deuterated standards as internal standards during the derivatization process. Standards such as deuterated succinic acid and EDTA will be evaluated for stability and reactivity with the matrix in tank waste samples.

Technology transfer will also be a major aspect of this program. Additional methods will be transferred to both ACL and 222-S laboratory personnel. Methods that are scheduled to be transferred to ACL and 222-S include derivatization GC/MS for chelators, chelator fragments, and carboxylic acids and LC/MS for the identification of LMWA. The developed techniques will also be transferred to the Organics Tanks Program.

During an experiment to increase the amount of water soluble organic carbon being leached into water, a sample of the convective layer was heated to approximately 60°C while being stirred with water. There was a significant amount of gas produced; a large enough volume of gas to blow the stopper off. A sample of the convective layer will be analyzed prior and after heating to monitor the disappearance of organic carbon analytes. The results may indicate the analytes responsible for the gas production.

6.0 References

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Appendix A

Experimental Procedures

Appendix A

Experimental Procedures

A.1 Derivatization Gas Chromatography/Mass Spectrometry (GC/MS)- Determination of Chelators and Chelator Fragments

Waste Sample Extraction/Derivatization

The waste sample represented a composite of several segments of actual waste obtained by core drilling the waste in Tank 241-SY-101. This material was highly radioactive, contained a high concentration of nitrate and nitrite, and the OH^- concentration was 2 M. The total organic carbon (TOC) was 1.5 to 2.1%.

Hot Cell Derivatization Procedure

Approximately 2 g of the solids from the composite sample were stirred overnight with 20 mL of doubly-distilled water. The solution was filtered, and the aqueous solution was evaporated down to dryness in Reactivials (VWR Scientific) using nitrogen blowdown techniques. This involves heating the sample while blowing a steady stream of nitrogen over the sample. Approximately 2 mL of 14% BF_3 /methanol (Aldrich) was added, and the sample was then heated to 100° C for 1 h. The solution was cooled, and 1 mL of chloroform was added. The entire solution was then poured into a test tube containing 2 mL of 0.1 M KH_2PO_4 adjusted to pH 7.0. The Reactivial was rinsed with 1 mL of chloroform, and this was also added to the test tube. The test tube 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, approximately 90 to 95% of the radioactivity remains with either the aqueous layer or undissolved solid material. The chloroform solution was monitored for radioactivity and then removed from the hot cell for subsequent gas chromatography(GC)/electron impact mass spectrometry(MS) analysis. The derivatized waste sample was also analyzed using positive ion chemical ionization mass spectrometry to confirm parent ion assignment.

The above procedure was all done in the hot cell facilities. The hot cell facilities are used for the preparation, e.g., sample dissolution, dilution, and solvent extraction, and occasionally, the analysis of nuclear wastes. For highly radioactive wastes, e.g., 3 to 11 R/h, the hot cell 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 processed in the hot cell, the procedure is both time consuming and tricky. These procedures cannot be performed by just anyone, anywhere, in any laboratory, when highly radioactive samples are involved. Special training is required. Sample turnaround is much lower when using the hot-cell facilities. Wastes with low-to-moderate specific or total radioactivity, ≤ 1 R/h, may be prepared and analyzed outside the hot cell in a radiation hood or

glove box. The actual cutoff levels which differentiate lab bench work, glove-box work, and hot-cell work is usually based upon local practice or the judgement of the resident health physicist.

Hot Cell Extraction/Radiochemical Hood Derivatization

Approximately 5 g of waste was weighed out and stirred with 10 mL of doubly-distilled water overnight. The aqueous phase was filtered through a 0.45 μ m filter. The filtrate was then passed through a cation exchange column (10 g, AG50W-X8 resin), rinsed using an additional 10 mL of water to quantitatively remove the organic material from the resin. The resulting sample volume was 20 mL. After surveying the samples for radioactivity levels, the aqueous solution containing the organics was removed from the hot cell facilities.

Aliquots (2 mL) of the sample were transferred to teflon-sealed vials, evaporated to dryness using nitrogen blow down techniques, and derivatized with 2 mL of BF_3 /methanol. The sample was heated to 100°C for 1 h. The sample was then hydrolyzed with a KH_2PO_4 solution and extracted with chloroform as described previously. The chloroform extract was then analyzed by Gas Chromatograph/Mass Spectrometry (GC/MS).

In calculating the concentration of organic constituents, mechanical extraction loss experienced from the initial 10 mL extraction was estimated by determining the water present in the original samples, adding the 10 mL of water used for the extraction to that water, and then subtracting the volume of water recovered to determine the mechanical loss. Water content of samples was determined by measuring the percent solids. (Appendix D)

Aliquots were also measured for LC analysis. Dilutions of the original solutions were usually necessary due to the concentration levels.

Methylation using the reaction with diazomethane, silylation by bis(trimethylsilyl)trifluoroacetamide (BSTFA), butyl esterification with butanol/HCl, chloroethyl esterification with chloroethanol/HCl, and methylation with BF_3 /methanol were carried out on chelator standards obtained from Aldrich and independent sources. All mass spectral analyses were performed on a Hewlett Packard HP 5988A GC/MS system.

Other experimental conditions are described below:

BF_3 /methanol Methylation

Reaction of BF_3 /Methanol with chelator standards

Approximately 1 mL of a 10% w/v solution of boron trifluoride (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 5 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 consisting of 1 M KH_2PO_4 was made, and the pH was adjusted to 6.92 using sodium hydroxide. When this buffer solution was added to the contents of the vial, the solution separated into two layers and an aliquot was pipetted from the bottom layer, the chloroform layer, for GC/MS analysis. Parent ion assignment was confirmed by using positive ion chemical ionization mass spectrometry.

Methylation with Diazomethane

Preparation of diazomethane:

In brief, a mini Diazald apparatus (Aldrich) was used to generate the diazomethane. Ethanol (95%, 10 mL) was added to a solution of potassium hydroxide (5 g) in water (10 mL) in the reaction vessel. A solution of Diazald (5 g) in ether (45 mL) was added to the separatory funnel. The reaction vessel was then warmed to approximately 65°C with a water bath, and the Diazald solution was added over a period of about 30 min. The diazomethane solution was collected and then stored in a refrigerator. Precautions should be taken due to the explosive properties of diazomethane.

Reaction of diazomethane with chelator standards:

Approximately 5 mg of the chelator was dissolved in 5 mL of ether. Approximately 200 to 500 μ L of the diazomethane solution was added until the solution was slightly yellow. A small aliquot of this solution was analyzed using GC/MS. Approximately 500 μ L of additional diazomethane was added to the solution. Parent ion assignment was confirmed using positive ion chemical ionization MS.

Silylation with BSTFA

Procedures for making trimethylsilyl derivatives of amino acids using BSTFA have been reported (Knapp 1979, p. 270).

Reaction of BSTFA with chelator standards:

Approximately 1 mg of the chelator was combined with approximately 0.5 mL of BSTFA (Aldrich) in a reaction vial. The sealed vial was sonicated for 1 min and then heated for 30 min. at 70°C. The contents were then diluted with CH_2Cl_2 , and a 1 mL aliquot was analyzed using GC/MS. Parent ion assignment was confirmed by using positive ion chemical ionization MS.

Butyl Esterification with Butanol/HCl

Esterification of nitrilotriacetic acid (NTA) and certain other amino acids with n-butyl alcohol/HCl is described in reference Knapp (1979, p. 299).

Reaction of butanol/HCl with chelator standards:

About 0.5 to 1.0 mg of the chelator was placed in a 2 mL reaction vial. Approximately 1 mL of a solution made by mixing 20 mL of butanol with 5 mL of 3N HCl was added to the vial. The vial was sonicated and then heated at 70°C for 1 to 2 h. Hexane was added to the mixture in a separatory funnel, and the water was removed. A rotary evaporator was used to volatilize the solvents while the butyl ester remained. The butyl ester was analyzed using GC/MS. Parent ion assignment was confirmed using positive ion chemical ionization MS.

Chloroethyl Esterification with Chloroethanol/HCl

This method was suggested by work done by R.V. Smith and S.L. Tsai on the use of 2,2,2-trichloroethanol (TCE)/trifluoroacetic anhydride (TFAA) for derivatizing carboxylic acids for electron capture detection (Smith and Tsai 1971). The procedure was modified by substituting chloroethanol for trichloroethanol and HCl for TFAA to improve reactivity and decrease side-reactions as well as the molecular weight of the resulting derivative.

Reaction of chloroethanol/HCl with chelator standards:

Ten mg of the chelator was mixed with 1 mL of chloroethanol (Aldrich) and 1 drop of concentrated HCl in a 2 mL vial, and the sealed reaction mixture was heated for 4 h at 80°C. The resulting solution was evaporated to dryness with a stream of prepurified N₂ by means of a Pierce model 18780 Reacti-Vap Evaporating unit. The solid was dissolved in 1 mL of ethyl acetate, and 1 µL was injected for analysis using GC/MS. Parent ion assignment was confirmed by using positive ion chemical ionization MS.

Instrumentation

GC/MS Conditions

The instrument was equipped with a HP 5980 GC operated in the splitless mode. A fused silica column (DB-5, 30m X 0.25 mm i.d., 0.25 µm film thickness, J & W Scientific) was used. 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 to 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 mass spectrometer was scanned from 100 to 600 amu in the negative ion mode and 70 to 500 in the positive ion mode.

Accurate Mass Measurements

Accurate mass measurements were performed on a VG 70-EHF double-focusing mass spectrometer equipped with a VG 11-250 data system. The instrument was tuned to a resolution of 5000 (10% valley definition). Data were acquired by scanning the magnetic field exponentially down over the mass range of 230 to 90 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 a Varian Model 3700 gas chromatograph. The GC was fitted with 30 m X 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.

Gas Chromatography/Electron Capture Detection

A Hewlett-Packard 5890 GC equipped with a ^{63}Ni ECD was used for analyzing the chloroethyl esters. A fused silica (DB-5, 30 m X 0.25 mm i.d., 0.25 μm film thickness, J & W Scientific) column was used with the following temperature program: 50°C for 1 min, 50 to 300°C at 8°C/min, and 300°C, for 10 min. The detector interface temperature was 300°C and the injector port temperature was 280°C. The GC was operated in the splitless mode with a 1- μL injection volume.

A.2 Liquid Chromatography for Low Molecular Weight Acids

Apparatus

Anion exchange chromatography was performed with a model 510 solvent delivery pump, a model 712 WISP autosampler, and a model 484 variable wavelength UV absorption detector (Waters Associates, Milford, Massachusetts). The column was an Ion Pac A54A (250 mm x 4.0 mm) equipped with an Ion Pac AG4A guard column (50 mm x 4.0 mm) (Dionex, Sunnyvale, California). The chromatographic data were collected and processed by Maxima 820, v3.02, software (Dynamic Solutions, Ventura, California) on a model APC IV NEC computer (NEC, Foxborough, Massachusetts). The mobile phase was 1.3 mM NaHCO_3 and 1.4 mM NaCO_3 at a flow rate of 2 mL/min. Detection was accomplished at 210 nm. The sample volume injected for analysis was 10 μL .

Ion exclusion chromatography was performed on a model 1090 high performance liquid chromatograph (HPLC) equipped with a diode array detector, and a data collection system (Hewlett-Packard, Palo Alto, California). The column was an IC-PAK 50 μm , 300 x 7.8 mm, 7 μm , equipped with a guard column (Waters Associates). The mobile phase was 0.01 N H_2SO_4 at a flow rate of 0.6 mL/min. Detection was accomplished at 210 nm. The typical sample volume injection was 20 μL .

The cleanup procedure used Poly prep, 40 mm x 8 mm, disposable fritted columns packed with AG50W-X8 cation exchange resin, hydrogen form (Bio-Rad, Hercules, California). The cleanup procedure was performed within hot-cell facilities on the Hanford Reservation.

Reagents

Citric, formic, gluconic, glycolic, gluconic, oxalic, and tartaric acids were all purchased from Aldrich Chemical Company (Milwaukee, Wisconsin). Acetic acid was purchased from Baker. Sodium bicarbonate and sodium carbonate were purchased from Fisher Scientific. Sulfuric acid was from Baker. Water was purified with a Milli-Q water system (Millipore, Bedford, Massachusetts).

Sample Preparation

Aliquots of the samples were dried into 5-mL reaction vials for storage. Because of the alkalinity of the samples ($\text{pH} > 13$), the acids were in non-volatile salt forms, and therefore were not lost on drying. Water, 5 mL, was added to a dried sample, and the sample was sonicated for 1 h.

After sonication, a 2.5 mL aliquot, of sample was withdrawn. The other half, also 2.5 ml, was retained for different experiments. The aliquot was loaded onto water rinsed AG50W-X8 resin, 2 mL bed, in a Poly-prep column. The eluent was captured in a scintillation vial, and the resin was rinsed with 1 mL of additional water. The eluent was transferred to a secondary scintillation vial, and its radioactivity was measured. If the sample's radioactivity was below 1 to 2 mR, then it was removed from the hot cell. If it was above that level, it was run through fresh ion exchange resin, and its radioactivity was tested again.

With the radioactivity level diminished, the sample could be handled in fume hoods. The contents of the scintillation vial were transferred to a 5-mL volumetric flask and taken to the mark with water. Samples were then withdrawn from this volumetric flask for chromatographic analyses.

A.3 Analysis of Acid and Base-Neutral Solvent Extracts

Sample Preparation

A 2-g aliquot of a composite sample (pH 13) was mixed with 10 mL of methylene chloride and vortexed for three min. The solution was filtered and concentrated to approximately 100 μ L for GC/MS analysis. The pH of the original solution was then adjusted to 3 with the addition of HCl. The slurry was then mixed with 10 mL of methylene chloride and vortexed for 3 min. The solution was then filtered and concentrated to approximately 100 μ L for analysis using GC/MS.

Instrumentation

The extracts were analyzed using a JEOL SX 102/SX 102 double focusing tandem mass spectrometer in the electron impact mode and equipped with a JEOL UNIX data system. Instrument tuning and real-time mass measurements were performed by leaking perfluorokerosene (PFK) into the electron impact ion source from the septum inlet reservoir. The instrument was equipped with a Hewlett-Packard 5890 gas chromatograph. The GC was fitted with a 30 m X 0.25 mm i.d. DB-5 capillary column (J & W Scientific, Folsom, California). The GC oven temperature was held at 50°C for 1 min, then programmed at 8°C/min to 300°C.

A.4 High Resolution Mass Spectrometry-Accurate Mass Determination, Empirical Formula

Accurate mass measurements were performed on a JEOL SX 102/SX 102 double focusing tandem mass spectrometer equipped with a JEOL UNIX data system. The instrument was tuned to a resolution of 10,000 (10% valley definition). Data was acquired by scanning the magnetic field exponentially down over the mass range of 30 to 600 at a rate of second per mass decade. Instrument tuning and real-time mass measurements were performed by leaking PFK 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 a Hewlett-Packard 5890 gas chromatograph. The GC was fitted with a 30 m X 0.25 mm i.d. DB-5

capillary column. The GC oven temperature was held at 50°C for 2 min, then programmed at 5°C/min to 250°C.

A.5 Thermospray LC/MS of Low Molecular Weight Acids

Reagents

Gluconic acid, sulfuric, formic, acetic, phosphoric, and hydrochloric acid were obtained from Aldrich. Gluconic acid was in the form of the potassium salt. Formic acid and acetic acid were diluted from the concentrated acid reagents. Tartaric acid and hexanoic acid were obtained from Chem Services. The sulfuric acid, acetic acid, phosphoric acid, and hydrochloric acid used in preparing the mobile phases were diluted from the concentrated acid reagents. Milli-Q water was used for all dilutions. N-Nitroso-iminodiacetic acid was synthesized in the following manner.

Synthesis of N-Nitroso-iminodiacetic acid (NIDA)

The synthetic procedure was similar to that reported in the literature (Warren and Malec 1972). To a 500-mL, four-necked flask—equipped with an overhead stirrer, an addition funnel, and a thermometer—were added 26.6 g (20 mmoles) of iminodiacetic acid (Aldrich) and 200 mL of 1 M phosphoric acid. The contents of the flask were heated to 50°C, and a solution of 27.6 g (400 mmoles) of sodium nitrite in 60 mL of water was added dropwise. The reaction was then stirred for 1 min and extracted with 5 100-mL portions of diethyl ether. The ethereal extract was dried (MgSO₄) and concentrated to yield a yellowish white residue, which after recrystallization from ethyl acetate-hexane afforded 13 g of nitroso acid.

Instrument Conditions

Liquid Chromatography

A Bio-rad HPLC Organic Acids column, Aminex Ion Exclusion, HPX-87H, 300 X 7.8 mm, with compatible guard column was used. The mobile phase for this part of the work was 0.001 N HCl (isocratic). The LC oven temperature was 40°C, and the flow rate was 0.6 mL/min. A typical run time was 25 min. Standards of organic acids were analyzed using direct flow injection and after introduction onto the analytical column. A mixture of organic acids was also analyzed after separation by the analytical column.

Mass Spectrometry

The thermospray analyses were performed using the HP 5988A LC/MS in the isocratic mode. The ion source was 275°C, and the stem initial temperature was 100°C. Typical values for the tip and the vapor were 230°C and 272°C, respectively. Filament operation was in both the on-and-off modes. The multiplier voltage was 2692 V, and the scan range was either 79 to 500 or 92 to 300 amu, depending on the mixtures being analyzed. The injection volume was either 10 µL or 20 µL, depending on the concentration of the sample.

The instrument was tuned with polyethylene glycol (PEG) tuning solution to give maximum abundance of ions. It should be noted that the thermospray ion source should be cleaned approximately once a week to remove nonvolatile chloride salts resulting from the use of HCl as the mobile phase. Also, since HCl possesses corrosive effects on metal surfaces, water was flushed through both the HPLC and thermospray system at the end of the day. As long as these cleaning and flushing procedures were followed, no detrimental effects of the thermospray or chromatographic equipment were observed.

Actual Waste Sample

The waste sample represented a composite of several segments of actual waste obtained by core drilling the waste in Tank 101-SY. This material was highly radioactive, contained a high concentration of nitrate and nitrite, and the OH⁻ concentration was 2 M. The TOC was 1.5 to 2.1%.

The actual waste sample was passed through a Bio-Rad analytical grade cation exchange column (AG 50W-X8, 50-100 mesh, hydrogen form) in a remote handling hot cell which removed almost all of the radioactivity due to primary fission products in the waste (sometimes down nearly background levels) before being brought to the instruments for analysis. The hot-cell facilities are used for the preparation, e.g., sample dissolution, dilution, and solvent extraction, and occasionally, the analysis of nuclear wastes. For highly radioactive wastes, e.g. 3 to 11 R/h, the hot cell 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 processed in the hot cell, the procedure is both time consuming and difficult. These procedures can not be performed by just anyone, anywhere, in any laboratory, when highly radioactive samples are involved. Special training is required. Sample turnaround is much lower when using the hot cell facilities. Wastes with low-to-moderate specific or total radioactivity, ≤ 1 R/h, may be prepared and analyzed outside the hot cell in a radiation hood or glove box. The actual cutoff levels that differentiate lab bench work, glove-box work, and hot-cell work is usually site specific, based upon local practice or the judgment of the resident health physicist.

A 1-g aliquot of the waste sample was weighed and placed in a 25.0 mL volumetric flask. The sample was then neutralized with 0.001 N HCl to the pH of the mobile phase using an Orion extended scale pH meter. The solution was then diluted to volume using Milli-Q water. An aliquot of the solution was filtered into an LC vial using a Gelman Acrodisc LC13, 0.45 μ m syringe-tip filter. Approximately 20 μ L was used for HPLC or thermospray LC/MS analysis.

A.6 Electrospray MS-Determination of Low Molecular Weight Acids

The mass spectrometer used in these studies was assembled from Extrel components and is described in detail elsewhere (Smith et al. 1987). The important features of the instrument are a differentially pumped atmospheric pressure inlet suitable for use with electrospray ionizations and a rf only quadrupole for ion confinement while the neutral gas is pumped away, followed by an analysis quadrupole. The sample was introduced through a sheath-flow interface described elsewhere. The concentration for all samples was 1 mg/mL of the free acid in water. The sample was infused at a

2 of 2

rate of 0.2 $\mu\text{L}/\text{min}$. through the 50 μm i.d. central capillary. Methanol was used in the sheath at rate of 3 $\mu\text{L}/\text{min}$. The electrospray tip was biased to approximately -4 kV, adjusted to optimize the analyte response. The spectra were obtained in the negative ion mode, single scan spectra, and were acquired at a dwell of 50 ms/amu.

A.7 Liquid Chromatography-Determination of HEDTA and EDTA

Chemicals and Reagents

Tetrasodium ethylenediaminetetraacetic acid (EDTA) dihydrate and trisodium hydroxyethylenediaminetetraacetic acid (HEDTA) hydrate were obtained from Aldrich (Milwaukee, Wisconsin). Dodecyltrimethylammonium bromide was obtained from Kodak Chemicals (Eastman Kodak Co., Rochester, New York). The water was purified by a Milli-Q system. All other chemicals were reagent grade.

Simulated Waste Mixture Preparation

Table 3.6.2 lists the concentrations of the constituents of the simulated waste mixture recipe (reference recipe) along with the composition of four variant recipes. The variant compositions were chosen to be the same as in the reference recipe except for the concentrations of the AlO_2^- and the chelators (EDTA and HEDTA). In two of the four variant compositions the AlO_2^- and the chelator concentrations were both changed by a factor of 50% above and below the reference recipe concentrations. In the remaining two variant recipes, the concentration of AlO_2^- and the chelators were alternately changed to 50% high and low respectively, and 50% low and high respectively. The compositions of the variants were chosen arbitrarily, but with a great enough change in compositions from the reference to insure observation of the effect of these changes. The AlO_2^- concentration was varied because it is thought to play an important role in chelator decomposition.

To further replicate conditions in the waste storage tanks the simulated waste material (SWM) were heated for 60 days at 60°C. Samples for these analyses were taken at day 16 and day 41 of heating.

High Performance Liquid Chromatography

A model 510 solvent delivery pump, a model 712 WISP autosampler, and a model 484 variable wavelength UV absorption detector (Waters Associates, Milford, Massachusetts) were used. The column was an Adsorbosphere C-8 (25 cm x 4.6 mm, particle size 5 μm) equipped with an Adsorbosphere C-8 guard column cartridge (Alltech, Deerfield, Illinois).

The mobile phase was 0.002 M dodecyltrimethylammonium bromide, and 0.05 M potassium dihydrogen phosphate (pH 6.5, adjusted with 6N sodium hydroxide). The chromatography was performed at ambient temperature with a flow rate of 2 mL/min. The eluant's absorbance was monitored at 280 nm. The chromatographic data were collected and processed by Maxima 820, v3.02, software (Dynamic Solutions, Ventura, California) on a model APC IV NEC computer (Boxborough, Massachusetts).

Calibration Standards

To 129 mg of tetrasodium EDTA dihydrate and 117 mg of trisodium HEDTA hydrate in a 10 mL volumetric flask were added water, 3 mL, and 0.5M copper(II) sulfate, 2 mL. After total dissolution of the chelators, the volume was taken to 10 mL with water. This gave a stock solution of 0.03 M EDTA and 0.03 M HEDTA. Further serial dilutions gave solutions of 0.012M, 0.006 M, and 0.003 M of both chelators. Another calibration standard for HEDTA was similarly prepared from 87.5 mg of trisodium HEDTA hydrate. Serial dilutions of this standard gave solutions of 0.009 M, 0.018 M, and 0.023 M of HEDTA.

To one gram of simulated waste mixture in a 25 mL volumetric flask were added water, 5 mL, and 0.5 M copper(II) sulfate, 2 mL. The pH was adjusted to 6.5 by the dropwise addition of 1.5 N phosphoric acid. The pH was monitored by means of pH indicator strips (Baxter, McGaw Park, IL). Typically one gram of simulated waste mixture required about 7 mL of acid. After the desired pH had been attained, the sample was diluted to 25 mL with water. A 5-mL aliquot of solution was placed in a centrifuge tube and spun in a centrifuge (IEC, model HN-S, Needham Heights, Massachusetts) for 10 min at 1500 rpm. This was necessary to remove a precipitate, probably the hydroxide or oxide of aluminum, that formed upon addition of the phosphoric acid. After centrifuging, a portion of the supernatant was transferred to a WISP autosampler vial for analysis.

Quantitation

Calibration Curves for both chelator were obtained by plotting the peak areas of the calibration standards against the concentrations of the calibration standards. The data were then fitted to a straight line by linear regression.

Concentrations of each chelator in simulated waste mixture (SWM) were calculated based on the corresponding calibration curve.

A.8 References

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Appendix B

List of Waste Tank 101-SY Window C and E Samples and Location Within Tank

Appendix B

List of Waste Tank 101-SY Window C and E Samples and Location Within Tank

Sample #	Segments & Location
Window C Composites	
1073	Composite of segments 4-8, top of convective layer
1091	Composite of segments 9-14, bottom of convective layer
961	Composite of segments 14-18, top of nonconvective layer
1078	Composite of segments 19-22, bottom nonconvective layer
Window E Core Composites	
1197	Core composite 1, bulk sample, convective layer
1199	Core composite 1, bulk sample, convective layer
1215	Core composite 2, bulk sample, convective layer
1214	Core composite 2, bulk sample, convective layer
1196	Core composite 3, bulk sample, non-convective layer
1198	Core composite 3, bulk sample, non-convective layer not analyzed
1299	Core composite 4, bulk sample, non-convective layer
1306	Core composite 4, bulk sample, non-convective layer
Window E Segments	
R2458	From Segment 4, convective layer
R4259	From Segment 6, convective layer
R4260	From Segment 9, convective layer
R4261	From Segment 11, convective layer
R4262	From Segment 16, nonconvective layer
R4263	From Segment 17, nonconvective layer
R42664	From Segment 22R, nonconvective layer and bottom most segment

Appendix C

Analytical Data Obtained from Window E Core Composites

Appendix C

Analytical Data Obtained from Window E Core Composites

Table C.1. Total Organic Determination for Window E Core Composite Samples.
These samples were lost before analysis was complete.

<u>Sample</u>	<u>% TOC Before Leaching</u>	<u>%TOC After^(a)</u>
1197/C	1.3%	0.19%
1199/C	0.83	0.10
1214/C	1.4	0.052
1215/C	1.0	0.11
1196/NC	1.6	0.19
1299/NC	1.5	0.17
1306/NC	1.4	0.073

(a) Calculated using sample weights prior to leach

C Convective

NC Nonconvective

Table C.2. Amount of Water-Soluble Organic Carbon ($\mu\text{g C/g}$ sample) Accounted for by Chelators, Oxalate, Formic Acid, Acetic Acid, and Glycolic Acid in Previous Samples. Derivatization Performed in Hot Cell Facilities

<u>Sample</u>	<u>Chelators</u>	<u>Acetic + Glycolic Oxalate + Formic</u>	<u>% Water-Soluble Organic Carbon^(a)</u>
1197/C	1054	1640	24
1199/C	1663	890	36
1215/C	3002	880	44
1214/C	1216	660	14
1196/NC	1121	730	14
1299/NC	982	1620	20
1306/NC	749	500	11

(a) Based on % in water leachate

C Convective

NC Nonconvective

Table C.3. Results of Derivatization GC/MS Analyses in Core Composite Samples, lost from Hot Cell Before Analysis was Complete. Concentration of Major Components (μg Carbon/g sample). Derivatization Performed in Hot Cell Facilities

<u>Sample #</u>	<u>NIDA</u>	<u>NTA</u>	<u>CA</u>	<u>ED3A</u>	<u>EDTA</u>	<u>HEDTA</u>
1197/C	750	54	10	90	120	10
1199/C	760	337	15	153	338	20
1215/C	2610	242	20	40	70	10
1214/C	940	165	10	20	51	10
1196/NC	226	87	30	134	480	10
1198/NC	Not analyzed					
1299/NC	222	110	40	260	290	20

Appendix D

Wt% Solids of Core Segment Samples

Appendix D

Wt% Solids of Core Segment Samples

Table D.1. Wt% Solids of Core Segment Samples

<u>Sample</u>	<u>% Solids</u>	<u>%H₂O</u>
R4258/C	60.72	39.28
R4259/C ⁽¹⁾	59.00	41.00
R4260/C	58.02	41.98
R4261/C	72.68	27.32
R4262/NC	68.79	31.21
R4263/NC	68.67	31.33
R4264/NC	71.08	28.92

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