Pacific Northwest National Laboratory

Operated by Battelle for the
U.S. Department of Energy

Speciation of Organic Carbon in Hanford Waste Storage Tanks: Part 1

C. D. Carlson

February 1997

RECEIVED
MAR 14 1997
OSTI

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

PNNL-11480

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor Battelle Memorial Institute, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or Battelle Memorial Institute. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PACIFIC NORTHWEST NATIONAL LABORATORY

operated by

BATTELLE

for the

UNITED STATES DEPARTMENT OF ENERGY

under Contract DE-AC06-76RLO 1830

Printed in the United States of America

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831;
prices available from (615) 576-8401.

Available to the public from the National Technical Information Service,
U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161

The document was printed on recycled paper.

Speciation of Organic Carbon in Hanford Waste Storage Tanks: Part 1

C.D. Carlson

February 1997

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

Pacific Northwest National Laboratory
Richland, Washington 99352

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**

Summary

This report is the first in a series to report on speciation of organic carbon in Hanford waste storage tanks. The comparison of the existing total organic carbon with oxalate and limited analyses of other organic species (acetate, formate, and normal paraffin hydrocarbons [NPH]) are reported. All of the data have been previously reported by the Grout and Characterization programs; the information includes all of the publicly available data through October 1996.

Oxalate data were reported for 33 tanks, TOC data were reported for 82 tanks, and both oxalate and TOC data were available for 27 tanks. Of these 27 tanks, seven were found to have greater than 80% of the TOC identified as oxalate: 241-BY-104, 241-BY-105, 241-BY-106, 241-BY-110, 241-S-109, and 241-SX-108. Eighty percent accountability has been tentatively established as a minimum goal of the Organic Safety Program for speciation of TOC. Accountability of TOC through speciation will allow more accurate estimate of the potential energy content of the wastes as currently stored.

Of the remaining 19 tanks, seven had between 40 and 80% of the TOC identified as oxalate, and eleven had less than 35% of the TOC identified. Of these, only five tanks had segment results that were greater than 1% TOC, and none was above 2%. Since the current safety criterion outlined in the Safety Analysis (Webb et al. 1995) is 4.5% TOC, it may be determined that the further analyses of these tank wastes are not necessary. If additional analyses are deemed necessary, minimal work may be required, possibly limited to ion chromatography (IC), ion pair chromatography and capillary zone electrophoresis (CZE).

Additional speciation work is planned for this fiscal year in both the Organic Tanks Safety and Characterization programs. The Characterization program reports acetate and formate data in addition to the oxalate data for all the tank cores it processes. The Organic Tanks Safety Program will perform organic speciation on up to 50 tanks this fiscal year. This report will be updated periodically to include the new data.

Acknowledgments

This report is a compilation of data from numerous sources and could not have been accomplished without assistance. I would like to thank Joe Meacham for providing the direction and funding and Rich Hallen for his help as a technical reviewer and as the project manager. I would also like to thank Dan Reynolds for his help in finding many of the obscure sources of data which were available and Dr. Leon Stock for his timely comments and insights. Finally, I would like to thank Harry Babad for his assistance and review, much of which came after his retirement and was performed on his own time.

Contents

1. Introduction	1.1
2. Data	2.1
2.1 Tanks with Greater Than 80% of the TOC Identified	2.1
2.1.1 Tank 241-BY-105	2.1
2.1.2 Tank 241-BY-106	2.2
2.1.3 Tank 241-BY-110	2.2
2.1.4 Tank 241-C-106	2.5
2.1.5 Tank 241-S-109	2.7
2.1.6 Tank 241-SX-108	2.7
2.1.7 Tank 241-BY-104	2.8
2.1.8 Tank 241-C-103	2.8
2.2 Tanks with Between 80 and 40% of the TOC Identified	2.10
2.2.1 Tank 241-S-107	2.10
2.2.2 Tank 241-AW-101	2.11
2.2.3 Tank 241-BY-108	2.11
2.2.4 Tank 241-S-102	2.13
2.2.5 Tank 241-U-107	2.14
2.2.6 Tank 241-S-101	2.14
2.2.7 Tank 241-AN-107	2.16
2.3 Tanks with Less Than 40% of the TOC Identified	2.16
3. Summary and Conclusions	3.1
4. References	4.1
Appendix: Organic Carbon Data	A.1

Figures

1	Oxalate as a Percentage of Measured TOC for Tank 241-BY-105	2.2
2	Organic Species as a Percentage of Measured TOC for Tank 241-BY-106.....	2.3
3	Organic Species as a Percentage of Measured TOC for Tank 241-BY-110 (Core 92)	2.4
4	Organic Species as a Percentage of Measured TOC for Tank 241-BY-110 (Core 95)	2.4
5	Organic Species as a Percentage of Measured TOC for Tank 241-BY-110 (Core 96)	2.5
6	Organic Species as a Percentage of Measured TOC for Tank 241-BY-110 (Core 101)	2.6
7	Percent TOC as Oxalate in Liquid Grab Samples from Tank 241-C-106	2.6
8	Percent TOC as Oxalate in Solid Grab Samples from Tank 241-C-106.....	2.6
9	Oxalate as a Percentage of Measured TOC for Tank 241-S-109.....	2.7
10	Oxalate as a Percentage of Measured TOC for Tank 241-SX-108	2.8
11	Oxalate as a Percentage of Measured TOC for Tank 241-BY-104 (Core 116).....	2.9
12	Oxalate as a Percentage of Measured TOC for Tank 241-BY-104 (Core 117).....	2.9
13	Oxalate as a Percentage of Measured TOC for Tank 241-S-107.....	2.10
14	Oxalate as a Percentage of Measured TOC for Tank 241-AW-101	2.11
15	Oxalate as a Percentage of Measured TOC for Tank 241-BY-108 (Core 98).....	2.12
16	Oxalate as a Percentage of Measured TOC for Tank 241-BY-108 (Core 104).....	2.12
17	Oxalate as a Percentage of Measured TOC for Tank 241-S-102 (Core 125)	2.13
18	Oxalate as a Percentage of Measured TOC for Tank 241-S-102 (Core 130)	2.14
19	Oxalate as a Percentage of Measured TOC for Tank 241-U-107	2.15
20	Oxalate as a Percentage of Measured TOC for Tank 241-S-101	2.15

Tables

1 Concentrations of Oxalate at 24°C	1.3
2 Average TOC with Less Than 40% of the TOC Identified/	2.17

Abbreviations

CZE	capillary zone electrophoresis
EDTA	ethylenediaminetetraacetate
GC-MS	derivatization gas chromatography-mass spectrometry
HEDTA	N-(2-hydroxyethyl)ethylenediaminetriacetate
IC	ion chromatography
IPC	ion pair chromatography
LC-MS	liquid chromatography-mass spectrometry
NPH	normal paraffin hydrocarbons
TBP	tributyl phosphate
TCD	Tank Characterization Database
TOC	total organic carbon
TWRS	Tank Waste Remediation System
ww	wet weight basis

Segment Descriptions

DL	drainable liquids
UH	upper half
LH	lower half
LL	liner liquid
WS	whole segment
top ¼	top quarter
2nd ¼	second quarter
3rd ¼	third quarter
4th ¼	bottom quarter

Analysis abbreviations

BDL	below detection limit
NA	not analyzed

1. Introduction

The Organic Safety Program, under the Tank Waste Remediation System (TWRS), is addressing the issues associated with the presence of organic species in the Hanford waste storage tanks. These organic species, when mixed with the oxidizers in the tanks (nitrates and nitrites), have the potential to react and burn uncontrollably, which raises a concern about the release of radioactively and chemically hazardous waste. The focus of the Organic Safety Program is to determine the actual probability that a reaction will occur and its extent, and to develop some potential mitigation strategies.

To accurately assess the potential for uncontrolled organic oxidation, the actual organic species present in the tanks must be determined. Past safety assessments (e.g., SARR-033 Rev. 1) have been based on total organic carbon (TOC) with an acetate energy equivalent, which does not accurately describe the wastes as they are currently stored. Initially, the main organic complexants added to the tanks were glycolate, citrate, N-(2-hydroxyethyl)ethylenediaminetriacetate (HEDTA), and ethylenediaminetetraacetate (EDTA) (Webb et al. 1995), in addition to organic solvents (normal paraffin hydrocarbons [NPH] and tributyl phosphate [TBP]). Because the tanks contain radioactive species, various oxidizing agents, and elevated temperatures, it has been hypothesized that these organic compounds would decompose or age to other compounds. This degradation, or aging, would eventually lead to the formation of very simple compounds such as formate, oxalate, or carbonate (Meisel et al. 1993; Barefield et al. 1996; Camaioni et al. 1996). As the organic species decompose, the other species that they form show a net reduction in the amount of energy available for reaction. While the total amount of carbon in the tank would not change, the energy available for release during oxidation reactions with nitrates and nitrites would be reduced, because the final degradation species, such as oxalate and formate, have a low energy content per carbon atom (Burger 1995). The final species in the degradation of organic species would be the inorganic species carbonate, which has no fuel value.

To fully characterize the organic species in the tanks, many different analytical procedures must be used. Some of these procedures are well established for this mission and are relatively easy to perform, such as ion chromatography to determine low molecular weight carboxylic acids (e.g., formate, oxalate, acetate). Other available techniques are very complex and time-consuming and/or require further development to identify and quantitate the organic species present (e.g., capillary zone electrophoresis [CZE], ion pair chromatography [IPC], derivatization gas chromatography-mass spectrometry [GC-MS], liquid chromatography-mass spectrometry [LC-MS]) (Campbell et al. 1996). As a cost-savings measure, a scenario has been developed in which the analyses are performed in order of increasing expense and complexity and continued until at least 80% of the TOC is identified. This report evaluates the data that have already been collected by other programs (Characterization and Grout). The majority of the data described in this report will be for oxalate, with some EDTA, HEDTA, glycolate, and citrate concentrations. All of the results will be compared with the TOC values obtained by the hot persulfate-coulometry method (Baldwin et al. 1994). From these data, a more accurate estimate of the amount of energy (and energy density) available for reaction can be calculated.

The information available included data on both solids and supernatant solutions. Using the current safety criteria, if greater than 20% water is present, then the tanks are conditionally safe regardless of the carbon content. Since any supernatant solution will be greater than 20% moisture, this portion of any tank would be conditionally safe. As mentioned previously, the high-energy species are the chelators and chelator fragments, while the low energy species include oxalate. The data in this report show that the oxalate is mainly found in the solid samples due to the low solubility in these solutions (see below), and that the chelators (unidentified TOC) are mainly in solution. Since the high-

energy species are in solution, they will be conditionally safe because of the moisture content, while the TOC in the solids has greater amounts of oxalate, making the total energy available for reaction below the propagation threshold.

In order to keep the tanks in the conditionally safe category, the water content must be kept above this threshold value. There are two ways in which water could leave the tanks and allow a situation in which the wastes would be less than 20%, either through removal (e.g., salt-well pumping or leaking to the ground) or evaporation. If the supernatant solution is removed from the tank, the soluble organic species would be removed as well, and only the organic species present in the solids would be of concern. If, on the other hand, the wastes dry out, then the total amount of organic in the tank will be important, in addition to the location of the supernatant liquid (as interstitial liquid or as discrete layers). In a dry-out scenario, if the supernatant solution is in a discrete layer, the organic species would be concentrated in layers, allowing for a potential burn situation. In the following sections, the amount of TOC identified is based on the species found in the solids only. In the remaining reports in this series, the estimate of the TOC identified if dry-out occurs will also be presented.

In all cases, the percent of organic carbon as oxalate in liquid samples was found to be very low. This was expected because of the solubility of various organic species (Barney 1994, 1995, 1996). Oxalate has a very low solubility in high-concentration salt solutions, while the organic complexants have very high solubilities. This led to low percentages of TOC identified in liquid samples when only oxalate data were available. Generally, the most important information was obtained from the solid phases, partly due to the solubility issues, but, more importantly, due to the fact that if the moisture content of a waste is greater than 20%, propagating reactions will not occur (Webb 1995). So if the waste fraction is a liquid, the moisture content is always greater than 20% and of little consequence to the tank safety issues.

Part of the basis for resolving the Organic Tanks Safety issues is that the majority of the organic complexants will be present in the liquid phase. As mentioned in the previous paragraph, Barney (1994, 1995, 1996) has performed studies on the solubility of various organic species. All of the common complexants are highly soluble, while oxalate is very insoluble. Table 1 shows the concentration of oxalate at various sodium hydroxide concentrations as determined by Barney. In contrast, EDTA and NTA are two orders of magnitude more soluble under the same conditions. This low solubility has caused some concern that the reported results may be at or above the solubility limits of oxalate, rendering the results unreliable. This could be the case with some of the results for supernatant solutions, but the results described here were all less than the solubility limits for the given nitrate and nitrite levels.

To determine the concentrations of oxalate in solid samples, 0.5 g of the sample was washed with 100 mL of distilled water. Thus, if all of the solids were sodium hydroxide, the resulting solution would be 0.0125 M in sodium hydroxide. The maximum amount of oxalate (as the sodium salt) that could dissolve in a solution of this concentration would be 0.11 g. The 0.5-g sample would mean 7.3% or 73,000 ppm of oxalate. All of the results in the databases were much less than this amount, and because the oxalate solubility increases slightly with a decrease in the hydroxide concentration, the solubility limit of oxalate was not a limiting factor in these results.

At the end of each tank description is a description of representativeness of the results for the tank. The number of segments are reported along with the total volume of the waste in each tank. For all except the 55,000 gallon tanks, a segment represents approximately 50 kgal of waste.

Table 1. Concentrations of Oxalate at 25°C(a)

NaOH Concentration (molarity)	Oxalate Concentration (molarity)	Oxalate concentration (ppm)	Carbon concentration (ppm)
Pure Water	0.27	24,000	6500
3.0×10^{-5}	0.0085	748	204
0.001	0.0086	757	206
0.01	0.0083	730	199
0.1	0.0081	713	194
0.5	0.0075	660	180
1	0.0057	501	137
2	0.0036	317	86
3	0.00213	187	51
(a) With the exception of pure water, all solutions contained 4.0 <u>M</u> sodium nitrate and 1.0 <u>M</u> sodium nitrite.			

In preparing this report, oxalate data were reported for 33 tanks, TOC data were reported for 82 tanks, and both were reported for 27 tanks. In addition, NPH data are available for a number of tanks, but only those having oxalate data were used. All of the oxalate data were obtained at the 222S Laboratory. Additional data from other programs may be available in other reports, as may raw data from the 222S Laboratory. In the next revision of this report, information from any of these additional sources will be added.

2. Available Characterization Data

Each tank that has data available will be addressed separately, followed by a summary of all of the tanks. The tanks for which information has been published include 241-A-101, 241-A-102, 241-AN-107, 241-AP-102, 241-AP-105, 241-AP-106, 241-AW-101, 241-B-106, 241-BX-109, 241-BY-104, 241-BY-105, 241-BY-106, 241-BY-110, 241-C-103, 241-C-106, 241-S-101, 241-S-102, 241-S-107, 241-S-109, 241-SX-108, 241-U-102, 241-U-105, 241-U-106, 241-U-107, 241-U-108, and 241-U-109. The tanks that have more than 80% of the TOC accounted for will be presented first (Tanks 241-BY-104, 241-BY-105, 241-BY-106, 241-BY-108, 241-BY-110, 241-S-109, and 241-SX-108), followed by the remaining tanks for which oxalate data are available. Most of the data were obtained from the Tank Characterization Database (TCD) (PNNL 1996), but the information on the AP tanks was collected from reports generated by the Grout Program (Terry 1994a, 1994b, 1994c), and the results for AN-107 were reported in Toste et al. (1985). The data are presented in tabular form in the appendix. Data are reported only if both the TOC and oxalate values are available. The TOC data listed for each tank are on a wet weight basis (ww). For all core samples, the segments are numbered sequentially from the top of the tank. The subsegments for each core are identified with the following letters: WS - whole segment, UH - upper half, LH - lower half, DL - drainable liquids, LL - liner liquid, top ¼ - top quarter, 2nd ¼ - second quarter, 3rd ¼ - third quarter, 4th ¼ - bottom quarter. Special designations include the letters A and R after the segment number, indicating duplicate analyses and repeat analyses, respectively.

2.1 Tanks with Greater Than 80% of the TOC Identified

This section will describe the tanks in which greater than 80% of the TOC has been identified as oxalate or various organic species. As stated, in all cases, the average TOC accounted for is greater than 80% except for Tank 241-BY-104. In this tank, all of the upper segments showed a high oxalate content, but the segment nearest the bottom showed a much lower oxalate concentration. Because the bottom layer is far from any credible reaction initiator, and the rest of the tank is well above 80% of the measured TOC as oxalate, this tank was included in this section.

Based on the programmatic criterion of making sufficiently accurate estimates of the energy content when 80% of all of the organic carbon (measured as TOC) has been identified, the tanks in this grouping have enough information available to make some judgments about their relative safety. The remaining tanks may require additional characterization to determine their relative safety.

2.1.1 Tank 241-BY-105

The TCD provided information for three segments from this tank (Core 108). All three contained solids, while only the first two segments had drainable liquids. Figure 1 shows the percent TOC as oxalate in each segment. The TOC values ranged from 0.2 to 0.7% (ww) in the core.

The drainable liquids showed that less than 10% of the TOC was oxalate, which is expected because the oxalate is not very soluble in supernatant solutions. The complexants, however, are very soluble. In the solids, oxalate made up more than 90% of the TOC in segments 1 and 2; in segment 3, only 54% of the TOC was oxalate. Overall, 84% of the TOC could be accounted for by the oxalate in the sample. The lower value for %TOC accounted for in the third segment appears to be an anomaly, and

Figure 1. Oxalate as a Percentage of Measured TOC for Tank 241-BY-105 (Core 108)

its contribution to the overall contents in the tank is small. Since the contents of the tank total 695 kgal (Hanlon 1996), three segments may not be representative of the entire tank. These data should be representative of the upper portions of the tank.

2.1.2 Tank 241-BY-106

The TCD report from this tank (Core 121) provided information for ten segments, but analyses were reported for only four of the segments (3, 4, 8, and 10). All four of these segments report the results from the solids present, but only segment 10 reported results from drainable liquids. The percent TOC accounted for as oxalate, acetate, and formate in each segment can be seen in Figure 2. The TOC values ranged from 0.1 to 0.6% (ww) in the core.

The analyses of organic species in the drainable liquid from segment 10 showed 30% of the measured TOC accounted for as acetate and formate, with oxalate below the detection limit. Again, the absence of oxalate in the liquids can be explained by the low solubility, and the remaining TOC would be the more complex organics (e.g., complexants). For the solids, all of the segments showed that nearly 80% of the TOC could be accounted for as oxalate, acetate, and formate. The average of all four of the segments was 88% of the TOC identified. This core had 10 segments, which should be representative of the 842 kgal (Hanlon 1996) of waste in the tank.

2.1.3 Tank 241-BY-110

The TCD results from this tank (Cores 92, 95, 96, and 101) provided information for nine segments; but only Core 101 showed analytical results for all of the segments. Drainable liquids were only

Figure 2. Organic Species as a Percentage of Measured TOC for Tank 241-BY-106 (Core 121)

reported for segment 4 of Core 101. The percent TOC accounted for as oxalate and NPH species from each segment can be seen in Figures 3 through 6. The TOC values ranged from 0.1 to 4.3% (ww) in each segment.

The results for Core 101 show that the average of all segments is 75% of the TOC accounted for by the NPH and oxalate, assuming any number greater than 100% is only 100%. In this calculation, the result from segment 4 was not used, since neither oxalate nor NPH values were reported. The last segment reported has only 15% of the TOC identified, but, as noted earlier, this accounts for a small amount of the tank contents. Using all but the last segment gives an average of 85% of the TOC accounted for. The data from Cores 95 and 96 show that the upper levels have well above 80% of the TOC identified. The only core with an upper segment that has a very low amount of TOC identified is Core 92. The upper half of segment 6 has a TOC value of 1400 ppm and a carbon from oxalate and acetate of 849 ppm. The average for the segments reported in the core is still very high, so the overall core is well above the 80% threshold value. The nine segments retrieved from core 101 should be representative of the 507 kgal (Hanlon 1996) of waste in this tank. There is some discrepancy between the same segments of different cores, but this is probably due to the way the tanks are filled. The inlets are located at discreet points in the tank, and when waste is introduced into the tanks, it must flow out to the rest of the tank. If the wastes are relatively dilute solutions, the waste composition at a definite horizontal layer should be the same. If the wastes are more viscous or precipitate solids upon cooling, the layers will not be horizontal, providing for differences during core sampling at the same height from the bottom of the tank. Relatively small variations are not unexpected. Another possible cause of the discrepancies could be the uncertainties in the analytical data, which are not discussed in this report.

Figure 3. Organic Species as a Percentage of Measured TOC for Tank 241-BY-110 (Core 92)

Figure 4. Organic Species as a Percentage of Measured TOC for Tank 241-BY-110 (Core 95)

Figure 5. Organic Species as a Percentage of Measured TOC for Tank 241-BY-110 (Core 96)

2.1.4 Tank 241-C-106

The TCD results from this tank are all from grab samples from two different risers. Both liquid and solid sample results are reported. Values were reported only for oxalate and TOC, not for any additional organic species. The results from analyses of these samples are graphically depicted in Figures 7 and 8. The TOC values ranged from 0.2 to 5.5% (ww) in the samples.

Figure 6. Organic Species as a Percentage of Measured TOC for Tank 241-BY-110 (Core 101)

Figure 7. Percent TOC as Oxalate in Liquid Grab Samples from Tank 241-C-106

In all of the solid grab samples from this tank, the oxalate numbers were more than 80% of the TOC. This shows that the solid phase contains low energy content organic species that would not support any propagating reactions. The liquid samples all showed less than 50% of the carbon as oxalate, indicating that some complexants/NPH/TPB are still present, but in the liquid phase with high water content. Since these samples were all grab samples and the tank contains 245 kgal (Hanlon 1996), the probability that the solid samples are representative of the whole tank is not very great. The only thing that can be said is that since the top layer of the waste is relatively low in reactive organic species, the bulk may not have the same characteristics.

Figure 8. Percent TOC as Oxalate in Solid Grab Samples from Tank 241-C-106 (starred samples showed more carbon as oxalate than the TOC results)

2.1.5 Tank 241-S-109

The TCD results from this tank (Cores 158 and 160) indicated that only four segments were recovered. For all four segments, only solids data were reported. The oxalate numbers for four of the subsegments (half segments) were reported as the detection limits, so these numbers are actually only maximum possible values, not a definitive observation of oxalate. The percentages of TOC accounted for as oxalate are shown in Figure 9. The TOC values ranged from 0.02 to 0.2% (ww) in the core.

All of the samples with the oxalate value above the detection limit had carbon from oxalate exceeding 80% of the measured TOC, and in most cases it exceeded the measured TOC value. It appears that most of the organic species in this tank have degraded to oxalate. Since this tank contains 570 kgal of solids (Hanlon 1996), the four subsegments do not represent a very large fraction of the total tank contents, and the results may not be representative of the whole tank.

2.1.6 Tank 241-SX-108

The TCD results from this tank were from the analyses performed on two auger samples composed of solids only. All of the samples showed oxalate results that had more carbon than was measured by TOC. The results can be seen in Figure 10. The TOC values ranged from 0.01 to 0.2% (ww) in the core.

Figure 9. Oxalate as a Percentage of Measured TOC for Tank 241-S-109 (Cores 158 and 160)

Figure 10. Oxalate as a Percentage of Measured TOC for Tank 241-SX-108.(1995 auger samples)

Because the oxalate numbers are so much higher than the TOC numbers, there appears to be a recovery problem with the TOC results. This concern will be addressed in the discussion at the end of the report. For this tank, the oxalate numbers are very high, indicating that the TOC will have very low energy content. Since this tank contains only 92 kgal of waste (Hanlon 1996), the auger sample should be representative of the entire tank contents.

2.1.7 Tank 241-BY-104

The TCD provided information for eight and five segments from this tank (Cores 116 and 117, respectively). No drainable liquids were reported in the database. The segments were divided into quarters for analysis. The percentages of TOC accounted for as oxalate are shown in Figures 11 and 12. The TOC values ranged from 0.3 to 2.6% (ww) in the core.

As can be seen in Figure 11, the majority of the TOC in the upper segments can be accounted for by oxalate, but the very bottom of the tank has very little oxalate. A concern is that the TOC for the bottom layer is higher than the rest of the tank by 30 to 300%, except for the very top layer (segment 2 in this case). In segment 2 this higher TOC value is probably due to the large amount of interstitial liquid, in which the organic species are very soluble. This tank contains 130 kgal of waste (Hanlon 1996), and the four segments from each core should be representative of the entire contents of the tank.

2.1.8 Tank 241-C-103

The organic speciation of Tank 241-C-103 has been well documented (Postma et al. 1994). Essentially all of the organic species (NPH, TBP, etc.) have been identified, and the safety issue for the tank has been closed.

Figure 12. Oxalate as a Percentage of Measured TOC for Tank 241-BY-104 (Core 117)

Figure 11. Oxalate as a Percentage of Measured TOC for Tank 241-BY-104 (Core 116)

2.2 Tanks with Between 80 and 40% of the TOC Identified

Of the remaining 19 tanks with some oxalate information, seven have between 40 and 80% of the measured TOC identified. In many of these cases, the analysis of the samples by additional methods to give formate and acetate values could be all that is needed to reach the 80% goal for speciation for the organic carbon. Since ion chromatography (IC) is a well-studied and relatively simple technique, the results could be available relatively quickly.

2.2.1 Tank 241-S-107

The TCD results from this tank were from the analyses performed on three cores (Cores 105, 110, and 111), and only solids data for TOC and oxalate were reported. The results can be seen in Figure 13; the TOC values ranged from 0.3 to 0.7% (ww) in the core.

The reproducibility of the values for both TOC and oxalate was not very good for these cores. The TOC and oxalate values differed by as little as 10% and as much as two orders of magnitude between replicates. In some cases, one value was close to the detection limit, and the duplicate was two orders of magnitude higher. In one quarter of the samples, if the higher oxalate values were used, the carbon from oxalate would account for more than 80% of the measured TOC. This indicates that a reanalysis of the samples from these cores by IC, rather than an extensive organic speciation, may provide enough information. Since this tank contains 419 kgal of waste (Hanlon 1996), the eight core segments reported should be representative of the tank contents.

Figure 13. Oxalate as a Percentage of Measured TOC for Tank 241-S-107 (Cores 105, 110, and 111)

2.2.2 Tank 241-AW-101

The TCD results for this tank were from the analyses performed on one core (Core 132) where both drainable liquids and solids were reported. The results for composite samples can be seen in Figure 14. The TOC values ranged from 0.2 to 0.5% (ww) in the core. The composite samples show that the vast majority of the organic carbon is in the form of oxalate. This tank contains over 1100 kgal of waste (Hanlon 1996), but 1044 kgal are supernatant solution, so the composite results from the core are representative of the material in the entire tank.

2.2.3 Tank 241-BY-108

The TCD results from this tank were from the analyses performed on two cores (98 and 104) where both drainable liquids and solids were reported. The results for composite samples can be seen in Figures 15 and 16. The TOC values ranged from 0.1% to 2.0% (ww) in the core. For all of the drainable liquid samples (from segments 2 and 3 of Core 98) the oxalate value was below detection limit, so the value on the graph is actually a maximum value.

The two cores show very different results for oxalate content. Core 98 has all of the values for oxalate at less than 70% of the measured TOC, while in Core 104 segment 2 the oxalate value is above 80%. Both of the cores show the trend of decreasing TOC identification as the sample is taken from deeper in the tank. When looking at the actual values, both the oxalate and the TOC numbers vary throughout the cores, indicating that any problem with the data is due either to sampling or to the

Figure 14. Oxalate as a Percentage of Measured TOC for Tank 241-AW-101 (Core 132)

Figure 15. Oxalate as a Percentage of Measured TOC for Tank 241-BY-108 (Core 98)

Figure 16. Oxalate as a Percentage of Measured TOC for Tank 241-BY-108 (Core 104)

heterogeneity of the tank waste. As mentioned earlier, the decreasing oxalate could be due to poor mixing in the tank, with the oxalate forming in the solution (through organic degradation/aging) and depositing in the upper layers. The 237 kgal of waste (Hanlon 1996) in this tank is well represented by the four segments analyzed in each core.

2.2.4 Tank 241-S-102

The TCD results for this tank were from the analyses performed on two cores (Cores 125 and 130) where both drainable liquids and solids were reported. The results for composite samples can be seen in Figures 17 and 18. The TOC values ranged from 0.08 to 1.1% (ww) in the core. For all of the drainable liquid samples (from segments 2 and 3 of Core 98) the oxalate value was below the detection limit, so the value on the graph is actually a maximum value.

The results show that, while some of the quarter segments have oxalate values approaching 100% of the TOC, the majority are well below 80% and the average is 52%. In Figure 18, the results from composite samples of the saltcake and sludge fractions of the core are shown. The sludge has a slightly higher ratio of oxalate to other organics, as would be expected since the saltcake should be composed mainly of species soluble in alkaline media. The 780 kgal of waste (Hanlon 1996) in this tank is well represented by the 11 segments analyzed in these two cores.

Figure 17. Oxalate as a Percentage of Measured TOC for Tank 241-S-102 (Core 125) (slck = salt cake)

Figure 18. Oxalate as a Percentage of Measured TOC for Tank 241-S-102 (Core 130)
(sltck = saltcake) (QS = quarter segment)

2.2.5 Tank 241-U-107

The TCD results from this tank were from the analyses performed on three cores (Cores 129, 134, and 135) where both drainable liquids and solids were reported. One of the cores had results reported on six segments, while the others reported results only on three segments. The liner liquid sample (from segment 5A of Core 134) had a carbon from oxalate value that was greater than the TOC. The liner liquid is the material that is observed in the space between the core and the core container. This solution is typically sample rinse solution, hydrostatic head fluid of condensate, and is usually not used for determining the contents of the tanks even if analyses are performed on the sample. The results are diagrammed in Figure 19. The TOC values ranged from 0.05 to 0.9% (ww) in the core.

In this tank, all of the drainable liquid oxalate values were low, while the remainder of the samples (liner liquid and solids) showed relatively high oxalate values. The average for this tank is 53% of the measured organic carbon as oxalate. The results from these cores may not be representative of the entire tank, because only five segments are reported and the tank contains 553 kgal of waste.

2.2.6 Tank 241-S-101

The TCD results from this tank were from the analyses performed on two cores (Cores 138 and 142) where both drainable liquids and solids were reported. The results for composite samples can be seen in Figure 20. The TOC values ranged from 0.03 to 0.3% (ww) in the core. In the drainable liquids sample (from segment 9 of Core 138) the oxalate value was below the detection limit, so the value on the graph is actually a maximum value.

Figure 19. Oxalate as a Percentage of Measured TOC for Tank 241-U-107

Figure 20. Oxalate as a Percentage of Measured TOC for Tank 241-S-101 (Cores 138 and 142)

The results from the composite samples show that oxalate makes up less than 60% of the TOC measured in the tank, so further characterization will be required. Again, this characterization may be accomplished quickly and inexpensively using IC. The results reported for this tank should be representative, because nine segments were used to make the composite samples and the tank contains 511 kgal of waste (Hanlon 1996).

2.2.7 Tank 241-AN-107

The information from this tank was obtained from work reported at the Twenty-Fourth Hanford Life Sciences Symposium held in 1985 (Toste et al. 1985). The study was performed to identify the organic species that could be toxic or promote the transport of radionuclides in the environment. The samples were methylated subsequent to analysis. The analytical methods included gas chromatography (GC), gas chromatography/mass spectrometry (GC/MS), and gas chromatography/Fourier transform infrared spectroscopy (GC/FTIR).

The species identified included (in order of decreasing concentration) citric acid, N-(2-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA), ethylenediaminetetraacetic acid (EDTA), ethylenediaminetriacetic acid (ED3A), methane tricarboxylic acid, nitrilotriacetic acid (NTA), N-(2-hydroxyethyl)ethylenediamine-N,N'-diacetic acid (HEDDA), N-(2-hydroxyethyl)-N'-(methyl) ethylenediamine-N,N'-diacetic acid (MeHEDD'A), N-(methyl) ethylenediamine-N,N'-diacetic acid (MeEDD'A), iminodiacetic acid (IDA), and N-(2-hydroxyethyl)iminodiacetic acid (HEIDA). The measured TOC for the sample was 44,000 g/mL (ww), and the total carbon content of the chelators and chelator fragments found was 17,7000 g/mL, for a total of 40.3% of the TOC identified.

The most obvious test to perform on this sample would be IC, to determine the oxalate and perhaps the acetate and formate content. Unfortunately, this sample was tested over ten years ago and will have changed due to aging; so any new results cannot be compared with the old results. These data could be used to show the effect of aging on an actual sample if a new sample of AN-107 were to be tested for the previously mentioned analytes. The samples used in the study were from a composite of the waste. Since the results are only reported for the solution, the results should be representative of the supernatant solution in the tank.

2.3 Tanks with Less Than 40% of the TOC Identified

The remaining 12 tanks have very little of the organic carbon identified. All of these tanks that have high TOC will require extensive characterization for their potential to propagate reactions can be more accurately evaluated. For most of the tanks, the only organic carbon identified is oxalate, but in three (241-AP-102, 241-AP-105, and 241-AP-106) the speciation also includes EDTA, HEDTA, citrate, and glycolate. Table 2 shows the average TOC identified for these tanks.

For Tank 241-BX-109 the TOC values are very low (450 µg/g), and the detection limit for the oxalate is very high (2170 µg/g). The oxalate content could be high enough that all of the organic carbon is oxalate, but that determination cannot be made without further work. Because of the remaining uncertainty in the majority of the TOC in these tanks, all of these tanks are essentially uncharacterized with respect to the organic carbon present.

Table 2. Average TOC with Less Than 40% of the TOC Identified

Tank	Average TOC Identified	Average TOC Value (wt%)
241-AP-102	32%	0.35
241-AP-105	25%	0.28
241-U-108	27%	0.51
241-U-105	25%	1.20
241-A-102	21%	1.62
241-U-102	17%	0.90
241-U-106	13%	1.22
241-AP-106	8.8%	0.05
241-A-101	BDL(a)	0.50
241-U-109	BDL	0.41
241-B-106	BDL	0.06 (1.1 in top segment)
241-BX-109	BDL	0.04
(a) Oxalate values are all below detection limit.		

3. Summary and Conclusions

The information compiled here shows that seven tanks have undergone sufficient analyses to make predictions based on the theoretical energy content of the organic species present. Of the remaining tanks, only six have greater than 1.0% TOC by weight. Since the criteria are 4.5% TOC, it may be determined that additional analyses are not needed. If additional data are required, eight tanks may require very little additional analysis to make the reactivity predictions. This additional analysis may be limited to IC and CZE; in many cases, simple IC should be sufficient to bring the total of identified species up to more than 80%. IC can detect acetate, formate, and glycolate, and, with some method development, will be able to identify citrate and iminodiacetic acid (IDA). Acetate, formate, and glycolate have been observed in fairly high concentrations in some of the tanks with more extensive analyses (e.g., BY-106 and AP-102.) CZE could provide additional and corroboratory information on a large number of complexant species and small organic acids. In the remaining tanks, extensive work may be needed to identify a sufficient fraction of the organic carbon that is present.

While compiling these data, several problems were encountered with their reproducibility, and trends were noted. One such trend was that the oxalate values as a fraction of the TOC in the bottom segment of many tanks were lower than in all of the other segments. As discussed in Section 1, this could be due to a number of things, including low moisture content (more compact solids). Since the degradation of organics appears to be faster in solution, a high solid-to-liquid ratio would produce less aging.

In several of the tank segments, the actual difference between duplicate measurements was as high as two orders of magnitude. This could easily be explained by the fact that scientists at the 222S Laboratory have reported seeing crystals of sodium oxalate in tank samples. If the samples were not well homogenized, a crystal of sodium oxalate could have been chosen with one sample and not with the duplicate. In Tank 241-S-107, the oxalate result for segment 2 of Core 111 was 11,700 $\mu\text{g/g}$, and the duplicate sample showed 362 $\mu\text{g/g}$ with a detection limit of 196 $\mu\text{g/g}$. Many other samples showed differences of two times and more. Crystals of sodium oxalate in a non-homogeneous mixture could easily give this kind of discrepancy. Unfortunately, this brings into question a large number of the data. All of the data with a relative percent difference (RPD) outside of an accepted range, typically 20%, should be considered suspect and not used for decision-making.

Another disturbing finding was that the carbon from oxalate in some of the samples was much higher than the TOC values. One of the easiest explanations would again be that single crystals of oxalate are not included in TOC samples but added in the IC samples. It is also possible that this could be due to some of the oxalate remaining unreacted during the hot persulfate analysis for TOC. This problem may be reduced by using the combustion method, although this causes problems with the recovery of other species. This problem occurs most often when the oxalate values are very high ($>20,000 \mu\text{g/g}$), which could cause the oxalate to be close to the solubility limit in the persulfate solution.

In all of the BY tanks that had oxalate data, the oxalate numbers at the bottom of every core were lower than in the rest of the tank. The initial layers in the tanks are complexant-poor, and that, in conjunction with the stagnant nature of tanks, could give low oxalate numbers. Other possibilities include differing rates of degradation due to temperature and radiation dose (Camaioni et al. 1996).

The 222S Laboratory at the Hanford Site routinely reports acetate and formate concentrations with all of the other IC data. In addition, CZE and other speciation techniques are being performed on up to 50 tanks this fiscal year as a part of the Organic Tanks Safety Program. When additional data become available, new versions of this report will be issued.

4. References

- Baldwin DL, RW Stromat, and WI Winters. 1994. "Comparative Study of Total Organic Carbon (TOC) Methods for High-Level Mixed Wastes." *Proceedings of the International Topical Meeting on Nuclear and Hazardous Wastes - Spectrum 94, August 14-18*. American Nuclear Society, La Grange, Illinois, pp. 27-34. (PNL-SA-23718, Pacific Northwest Laboratory, Richland, Washington.)
- Barefield EK, D Boatright, A Deshpande, F Doctorovich, CL Liotta, HM Neuman, and S Seymore. 1996. *Mechanisms of Gas Generation from Simulated SY Tank Farm Wastes: FY 1995 Progress Report*. PNNL-10822, Pacific Northwest National Laboratory, Richland, Washington.
- Barney GS. 1994. *The Solubilities of Significant Organic Compounds in HLW Tank Supernate Solutions*. WHC-SA-2565-FP, Westinghouse Hanford Company, Richland, Washington.
- Barney GS. 1995. *The Solubilities of Significant Organic Compounds in HLW Tank Supernate Solutions - FY 1995 Progress Report*. WHC-EP-0899, Westinghouse Hanford Company, Richland, Washington.
- Barney GS. 1996. *Solubilities of Significant Organic Compounds in HLW Tank Supernate Solutions - FY 1996 Progress Report*. WHC-EP-0899-1, Westinghouse Hanford Company, Richland, Washington.
- Burger LL. 1995. *Calculation of Reaction Energies and Adiabatic Temperatures for Waste Tank Reactions*. PNL-8557 Rev. 1, Battelle Pacific Northwest National Laboratory, Richland, Washington.
- Camaioni DM, WD Samuels, JC Linehan, SA Clauss, AK Sharma, KL Wahl, JA Campbell. 1996. *Organic Tanks Safety Program FY 96 Waste Aging Studies*. PNNL-11312, Pacific Northwest National Laboratory, Richland, Washington.
- Campbell JA, KL Wahl, SA Clauss, KE Grant, V Hoopes, GM Mong, J Rau, and R Steele. 1996. *Organic Tanks Safety Program: Advanced Organic Analysis FY 1996 Progress Report*. PNNL-11309, Pacific Northwest National Laboratory, Richland, Washington.
- Hanlon BM. 1996. *Waste Tank Summary Report for Month Ending September 30, 1996*. WHC-EP-0182-102, Westinghouse Hanford Company, Richland, Washington.
- Meisel D, CD Jonah, S Kapoor, MS Matheson, and MC Sauer Jr. 1993. *Radiolytic and Radiolytically Induced Generation of Gases from Synthetic Wastes*. ANL-93/43, Argonne National Laboratory, Argonne, Illinois.
- Pacific Northwest National Laboratory (PNNL). December 31, 1996. *Tank Characterization Database, Version 2.6*. PNNL, Richland, Washington.
- Postma AK, DB Bechtold, GL Borsheim, JM Grigsby, RL Guthrie, M Kummerer, MG Plys, and DA Turner. 1994. *Safety Analysis of Exothermic Reaction Hazards Associated With the Organic Liquid Layer in Tank 241-C-103*. WHC-SD-WM-SARR-001, Westinghouse Hanford Company, Richland, Washington.
- Terry TL. 1994a. *Tank 241-AP-102 Characterization and Grout Program Test Results*. WHC-SD-WM-TRP-168, Westinghouse Hanford Company, Richland, Washington.
- Terry TL. 1994b. *Tank 241-AP-105 Characterization Test Results*. WHC-SD-WM-TRP-169, Westinghouse Hanford Company, Richland, Washington.
- Terry TL. 1994c. *Tank 241-AP-106 Characterization Results*. WHC-SD-WM-TRP-170, Westinghouse Hanford Company, Richland, Washington.

Toste AP, TR Pahl, RB Lucke, and RB Myers. 1985. *Proceedings of the Twenty-Fourth Hanford Life Sciences Symposium*, p. 133. Battelle Memorial Institute, Columbus, Ohio.

Webb AB, JL Stewart, DA Turner, MG Plys, G Malinovic, JM Grigsby, DM Camaioni, PG Heasler, WD Samuels, and JJ Toth. 1995. *Preliminary Safety Criteria for Organic Watch List Tanks at the Hanford Site*. WHC-SD-WM-SARR-033 Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Appendix
Organic Carbon Data

Appendix

Organic Carbon Data

In these tables, all solids data are expressed in $\mu\text{g/g}$ and all liquids data are expressed in $\mu\text{g/mL}$.
The abbreviations used in these tables are as follows:

Segment Descriptions

DL	drainable liquids
LH	lower half
LL	liner liquid
UH	upper half
WS	whole segment
top $\frac{1}{4}$	top quarter
2 nd $\frac{1}{4}$	second quarter
3 rd $\frac{1}{4}$	third quarter
4 th $\frac{1}{4}$	bottom quarter

Analysis abbreviations

BDL	below detection limit
IC	ion chromatography
NA	not analyzed

Table A.1. Tank 241-A-101 Grab Samples

Grab Sample	State	TOC	Carbon from Oxalate	% TOC from Oxalate
1A-96-1	liquid	2080	292	14
1A-96-2	liquid	5340	292	5
1A-96-3	liquid	4770	120	2
1A-96-3	solid	NA	4888	

Table A.2. Tank 241-A-102 Grab Sample

Grab Sample	State	TOC	Carbon from Oxalate	% TOC from Oxalate
96-Aug-003	solid	16250	11910	73

Table A.3. Tank 241-AP-102 Liquids from Core Samples

Segment	TOC	Carbon from Oxalate	Carbon from EDTA	Carbon from HEDTA	Carbon from Citrate	Carbon from Glycolate	Sum of Carbon Identified	%TOC Identified
1	3180	218	188	42	215	352	1015	32
4	3240	218	217	65	226	352	1078	33
9	3420	218	123	42	211	352	946	28
10	4270	191	208	36	205	352	993	23
11	3440	191	210	39	160	352	952	28
13A	3060	218	221	40	156	352	987	32
13B	3290	218	260	59	185	352	1075	33
Average	3280	208	198	46	198	352	1001	30

Table A.4. Tank 241-AP-105 Liquid Core Samples

Segment	TOC	Carbon from Oxalate	Carbon from EDTA	Carbon from HEDTA	Carbon from Citrate	Carbon from Glycolate	Sum of Carbon Identified	%TOC Identified
2	2850	95	55	10	150	208	518	18
4	3240	109	62	11	256	256	693	21
6	2620	55	58	7	229	192	541	21
7	2530	82	52	8	178	192	511	20
9A	2720	327	38	2	88	160	615	23
9B	2870	245	40	3	76	160	525	18
11	2830	82	57	11	209	192	550	19
Average	2750	118	53	8	184	200	563	20

Table A.5. Tank 241-AP-106 Liquid Core Samples

Segment	TOC	Carbon from Oxalate	Carbon from EDTA	Carbon from HEDTA	Carbon from Citrate	Carbon from Glycolate	Sum of Carbon Identified	%TOC Identified
1	462	19	BDL	BDL	BDL	22	41	9
2	449	25	BDL	BDL	BDL	19	44	10
3A	343	19	BDL	BDL	BDL	19	38	11
3B	652	19	BDL	BDL	BDL	22	41	6
4	320	22	BDL	BDL	BDL	29	51	16
5	555	22	BDL	BDL	BDL	16	38	7
6	328	19	BDL	BDL	BDL	16	35	11
Average	497	21	BDL	BDL	BDL	20	41	8

Table A.6. Tank 241-AW-101 Core 132

Segment	TOC	Carbon from Oxalate	% TOC from Oxalate
composite-solid	4890	3275	67
composite-liquid	2410	BDL (<112)	< 4.7
composite-solid	4535	3190	70
composite-liquid	3440	BDL (<150)	< 4.3

Table A.7. Tank 241 -B-106 Core Samples

Core	Segment	TOC Average	Carbon in Oxalate	% TOC as Oxalate
93	1-UH	11700	BDL (<232)	<2
93	1-LH	1093	BDL (<252)	<23
93	2-UH	280	BDL (<131)	<47
93	2-LH	250	BDL (<113)	<45
93	Composite	569	BDL (<137)	<24
94	1-UH	707	BDL (<222)	<31
94	1-UH	289	BDL (<248)	<86
94	2-LH	166	BDL (<119)	<72
94	Composite	441	BDL (<121)	<27
94	2-UH	364	BDL (<223)	<61

Table A.8. Tank 241-BX-109 Solid Grab Samples

Sample	Segment	TOC Average	Carbon from Oxalate	% TOC as Oxalate
grab	composite	440	BDL (<580)	<132

Table A.9. Tank 241-BY-104 Core Samples

Core	Segment	TOC	Carbon from Oxalate	% TOC from Oxalate
116	2 - top 1/4	26300	15136	58
116	3 - UH	NA	2945	--
116	3 - LH	4100	4636	113
116	4 - top 1/4	5740	5155	90
116	4 - 2nd 1/4	5680	4555	80
116	4 - 3rd 1/4	5760	NA	--
116	5 - top 1/4	6290	4527	72
116	5 - 2nd 1/4	6300	4664	74
116	5 - 3rd 1/4	5440	3600	66
116	5 - 4th 1/4	6270	4336	69
116	6 - top 1/4	4900	4500	92
116	6 - 2nd 1/4	3990	3600	90
116	6 - 3rd 1/4	5280	4118	78
116	6 - 4th 1/4	6050	5073	84
116	7 - top 1/4	6810	5864	86
116	7 - 2nd 1/4	7140	6000	84
116	7 - 3rd 1/4	8460	7064	83
116	7 - 4th 1/4	12500	1173	9
116	8 - top 1/4	14800	971	7
116	8 - 4th 1/4	6910	1017	15
117	1 - UH	NA	611	--
117	2 - top 1/4	3390	2782	82
117	2 - 4th 1/4	10400	7773	75
117	3 - UH	NA	2114	--
117	3 - 3rd 1/4	6260	3327	53
117	4 - UH	NA	303	--
117	5 - top 1/4	3000	2165	72
117	5 - 3rd 1/4	3240	2348	72

Table A.10. 241-BY-105 Core 108 Samples

Segment	TOC	Oxalate from Carbon	% TOC from Oxalate
1A - WS	6880	7118	103
1A - DL	1970	BDL	--
1R - WS	5560	5100	92
1R - DL	1920	BDL	--
1B - WS	6970	6382	92
1R - WS	4060	3818	94
2AR - WS	2180	2414	111
2AR - DL	2240	BDL	--
2R - WS	4830	4745	98
1 - WS	3460	4255	123
1 - DL	1920	156	8
2 - WS	4080	3409	84
3 - WS	668.5	365	55

Table A.11. 241-BY-106 Core 121 Samples

Segment	TOC	Carbon from Oxalate	Carbon from Acetate	Carbon from Formate	Total Carbon from IC	% TOC Identified
3 - UH	2770	2427	BDL	173	2600	94
3 - LH	3640	2945	BDL	212	3157	87
4 - UH	2020	1445	BDL	141	1586	79
4 - LH	3470	2809	BDL	169	2978	86
8 - UH	5410	3600	283	273	4156	77
8 - LH	5860	4773	325	298	5396	92
10B - UH	1320	401	328	316	1045	79
10B - LH	1090	766	213	212	1191	109
10B - DL	2460	BDL	560	193	753	31

Table A.12. Tank 241-BY-108 Core Samples

Core	Segment	TOC	Carbon from Oxalate	%TOC from Oxalate
98	2 - top 1/4	3610	2206	61
98	2 - 3rd 1/4	5760	3818	66
98	2 - 4th 1/4	9410	5291	56
98	2 - DL	2720	BDL	--
98	3 - top 1/4	4040	2809	70
98	3 - 3rd 1/4	3800	1991	52
98	3 - 4th 1/4	3140	826	26
98	3 - DL	2530	BDL	--
98	4 - top 1/4	11500	529	4
98	4 - 2nd 1/4	20800	4309	21
98	4 - 3rd 1/4	5770	687	12
98	4 - 4th 1/4	3440	211	6
104	2 - top 1/4	2420	2389	99
104	2 - 2nd 1/4	4540	4091	90
104	2 - 3rd 1/4	2840	2945	104
104	2 - 4th 1/4	2060	2247	109
104	3 - 3rd 1/4	1540	1115	72
104	3 - 4th 1/4	6400	3027	47
104	4 - top 1/4	4860	3436	71
104	4 - 3rd 1/4	2560	1936	76
104	4 - 4th 1/4	2440	1039	43
104	5 - top 1/4	4140	1778	43
104	5 - 2nd 1/4	15300	BDL	--
104	5 - 3rd 1/4	13400	2007	15
104	5 - 4th 1/4	7650	421	6

Table A.13. Tank 241-BY-110 Core Samples

Core	Segment	TOC	Carbon from Oxalate	Carbon from Acetate	Total from IC	Carbon from Hexadecane	% TOC Identified
92	4-WS	43900	7091	528	7619	NA	17
	5-WS	3240	2918	400	3318	NA	102
	6-UH	1400	404	446	849	NA	61
	6-LH	910	305	454	760	NA	83
	7-WS	2020	365	408	773	NA	38
	4-6 composite	2130	2266	BDL	2266	NA	106
95	1-WS	2880	2130	BDL	2130	NA	74
	4-WS	3130	2727	416	3144	NA	100
	5-UH	2420	2678	469	3147	NA	130
	5-LH	998.5	1004	460	1464	NA	147
	6-WS	394	387	438	826	NA	210
	7-WS	734.5	168	340	508	NA	69
	4-7 composite	1420	1020	BDL	1020	NA	72
96	1-WS	2360	2422	488	2910	NA	123
	2-WS	3700	2836	421	3258	NA	88
	3 - top 1/4	2040	1994	278	2271	NA	111
	3 - 2nd 1/4	11600	11045	392	11438	NA	99
101	2 - WS	3610	1636	NA	1947	311	54
	3 - WS	3370	4445	NA	4751	306	141
	4 - WS	3500	BDL	NA	BDL	BDL	--
	4 - DL	NA	393	NA	393	BDL	--
	5 - WS	12400	10855	NA	11179	325	90
	6 - UH	6260	BDL	NA	BDL	BDL	--
	6 - LH	10400	BDL	NA	BDL	BDL	--
	6 - WS	NA	6082	NA	6082	BDL	--
	6A - top 1/4	NA	9327	NA	9327	BDL	--
	6 - WS	NA	BLD	NA	467	467	--
	7 - top 1/4	5300	5400	NA	5979	579	113
	7 - 2nd 1/4	6380	6245	NA	6784	539	106
	7 - 3rd 1/4	28700	25827	NA	26490	663	92
	7 - 4th 1/4	5260	4391	NA	5118	727	97
	7 - WS	4860	3573	NA	3958	386	81
	8 - top 1/4	5140	4391	NA	4996	605	97
	8 - 2nd 1/4	4380	4364	NA	5015	652	114
	8 - 3rd 1/4	6090	1691	NA	2167	476	36
	8 - 4th 1/4	6140	4418	NA	5032	613	82
	9 - top 1/4	9220	2324	NA	2903	579	31
	9 - 2nd 1/4	9000	207	NA	682	475	8
	9 - 3rd 1/4	10800	234	NA	760	526	7
	9 - 4th 1/4	13300	1527	NA	1965	438	15
	5-9 composite	9040	5482	NA	5482	BDL	61

Table A.14. Core 241-C-106 Auger Samples

Auger Sample	State	TOC	Carbon from Oxalate	% TOC from Oxalate
6C-96-4	liquid	2315	603	26
6C-96-5	liquid	3300	1003	30
6C-96-7	liquid	2045	842	41
6C-96-11	liquid	2070	904	44
6C-96-12	liquid	2515	813	32
6C-96-13	liquid	1950	897	46
6C-96-15	liquid	NA	959	--
6C-96-3	solid	55400	85445	154
6C-96-4	solid	15600	21873	140
6C-96-7	solid	22650	18716	83
6C-96-10	solid	26950	21131	78
6C-96-11	solid	18650	41475	222
6C-96-13	solid	14750	14656	99

Table A.15. Tank 241-S-101 Core Samples

Core	Segment	State	TOC	Carbon from Oxalate	% TOC from Oxalate
138	2R1-LH	solid	NA	3226	
138	5-UH	solid	NA	959	
138	5-LH	solid	NA	769	
138	6-UH	solid	NA	1081	
138	6-LH	solid	NA	398	
138	7-UH	solid	NA	BDL (<119)	
138	7-LH	solid	NA	BDL (<80)	
138	8-UH	solid	NA	BDL (<70)	
138	8-LH	solid	NA	BDL (<84)	
138	9-WS	liquid	NA	BDL (<0)	
138	9-WS	liquid	267	BDL (<148)	<55
138	9-UH	solid	NA	BDL (<81)	
138	9-LH	solid	NA	BDL (<77)	
138	Composite	solid	852	369	43
142	1-UH	solid	NA	3638	
142	2-UH	solid	NA	3760	
142	2-LH	solid	NA	3694	
142	3-UH	solid	NA	4001	
142	3-LH	solid	NA	4205	
142	4-UH	solid	NA	4418	
142	4-LH	solid	NA	2956	
142	5-UH	solid	NA	2057	
142	5-LH	solid	NA	2349	
142	6-LH	solid	NA	260	
142	6-UH	solid	NA	477	
142	7-UH	solid	NA	139	
142	7-LH	solid	NA	BDL (<109)	
142	8-UH	solid	NA	BDL (<59)	
142	8-LH	solid	NA	375	
142	Composite	solid	3135	1782	57

Table A.16. Tank 241-S-102 Core Samples

Core	Segment	State	TOC	Carbon from Oxalate	%TOC from Oxalate
125	2 - UH	solid	1285	862	67
125	3 - UH	solid	2239	283	13
125	4 - LH	solid	2335	1061	45
125	5 - UH	solid	1550	828	53
125	5 - LH	solid	2100	812	39
125	6 - QSA	solid	786	425	54
125	6 - QSB	solid	3220	1217	38
125	8 - LH	solid	7940	4936	62
125	9 - UH	solid	6870	4555	66
125	9 - LH	solid	4940	3818	77
125	10 - UH	solid	4900	3436	70
125	10 - LH	solid	6860	2945	43
125	11 - UH	solid	2120	982	46
125	11 - DL	liquid	3095	BDL	--
125	11 - LL	liquid	2690	BDL	--
125	7 - DL	liquid	2690	BDL	--
125	Saltcake	solid	1995	884	44
125	Sludge	solid	5760	3982	69
130	2 - UH	solid	1455	1399	96
130	3 - UH	solid	1130	897	79
130	4 - UH	solid	1745	1085	62
130	5 - DL	liquid	5175	BDL	--
130	5 QSA	solid	1700	597	35
130	5 QSB	solid	2290	1276	56
130	5 QSC	solid	3260	802	25
130	6 - UH	solid	2595	1167	45
130	6 - LH	solid	2930	720	25
130	6A - DL	liquid	5495	BDL	--
130	6A - LL	liquid	4950	BDL	--
130	7 - UH	solid	2520	849	34
130	8 - UH	solid	3000	1121	37
130	8A - QS:A	solid	9000	8463	94
130	8A - QS:B	solid	13000	8018	62
130	8A - QS:C	solid	6460	4331	67
130	9 - UH	solid	6870	3627	53
130	9 - LH	solid	4945	2809	57
130	10 - UH	solid	4900	3237	66
130	10 - LH	solid	6900	3136	45
130	10 - DL	liquid	3500	223	6
130	11 - UH	solid	11100	8659	78
130	11 - LH	solid	7950	5836	73
130	saltcake	solid	1940	797	41
130	sludge	solid	4900	2945	60

Table A.17. Tank 241-S-107 Core Samples

Core	Segment	TOC	Carbon from Oxalate	% TOC from Oxalate
105	105, 2-LH	4530	3674	84
105	105, 3-UH	7380	870	14
105	105, 4-UH	832	494	57
105	105, 5-UH	2230	1315	81
105	105, 8-UH	305	39	13
110	110, 2-LH	6970	3729	62
110	110, 3-UH	3700	288	8
110	110, 4-UH	1010	412	60
110	110, 5-LH	860	592	49
110	110, 8-LH	397	736	130
111	111, 2-LH	3890	3191	43
111	111, 4-UH	1510	679	43
111	111, 5-LH	977	146	13
C105	Composite	1420	546	36
C110	Composite	1620	646	46

Table A.18. Tank 241-S-109 Core Samples

Core	Segment	TOC	Carbon from Oxalate	% TOC from Oxalate
158	1-LH	990	855	86
158	1-UH	1855	2117	114
158	2-LH	796	766	96
158	2A-LH	673	1031	153
158	2B-LH	387	626	162
158	2B-UH	517	410	79
158	3-LH	754	634	84
158	3-UH	383	596	156
158	3A-LH	497	465	94
158	4-LH	672	678	101
160	1-LH	365	399	109
160	2-LH	249	336	135
160	2B-LH	977	1592	163
160	2B-UH	338	363	107
160	3-LH	216	233	108

Table A.19. Tank 241-SX-108 Auger Samples

Auger Sample	TOC	Carbon from Oxalate	%TOC from Oxalate
95-AUG-042-UH	148	397	268
95-AUG-042-LH	91	844	931
95-AUG-043-LH	1675	1867	111

Table A.20. Tank 241-U-102 Core Samples

Core	Segment	TOC	Carbon from Oxalate	% TOC from Oxalate
143	1 - UH	7430	1841	25
143	1 - LH	4200	BDL	--
143	2 - UH	7440	905	12
143	2 - LH	8190	1492	18
143	3 - UH	10200	1500	15
143	3 - LH	9460	BDL	--
143	4 - UH	9540	2504	26
143	4 - LH	10700	2305	22
143	5 - WS	4390	483	11
143	5A - UH	4140	420	10
143	5B - UH	9210	1380	15
143	5B - LH	10900	1912	18
143	6 - UH	8890	1677	19
143	Composite	8750	1451	17
144	1 - LH	5960	2550	43
144	1 - DL	17800	BDL	--
144	2 - UH	7150	1085	15
144	2 - LH	5560	758	14
144	3 - UH	3980	584	15
144	3 - LH	3750	488	13
144	4 - UH	6900	1271	18
144	4 - LH	9390	1784	19
144	5 - UH	11800	2716	23
144	5 - LH	8850	1579	18
144	6 - UH	11200	2005	18
144	6 - LH	7680	1154	15
144	6A - UH	5570	706	13
144	Composite	9220	1628	18

Table A.21. Tank 241-U-105 Core Samples

Core	Segment	TOC	Carbon from Oxalate	%TOC from Oxalate
131	1 - UH	11750	2397	20
131	2 - UH	11250	2727	24
131	3 - UH	8830	2228	25
131	4 - UH	11700	2018	17
131	4 - LH	11750	1964	17
131	5 - UH	7710	1675	22
131	6 - UH	8680	1391	16
131	7 - UH	9500	1724	18
131	7 - LH	12500	2236	18
131	8 - UH	9900	2037	21
131	8 - LH	15200	5945	39
131	9 - UH	13900	5209	37
131	9 - LH	18000	7145	40
133	1 - DL	1351	BDL	--
133	1 - LL	1250	5	0.42
133	2 - WS	10100	4282	42
133	3 - WS	11600	1789	15
133	4 - WS	5550	1347	24
133	5 - WS	12900	2667	21
133	6 - WS	15400	2809	18
133	8 - UH	10200	2345	23
133	8 - LH	12600	4173	33
133	9 - UH	9000	3791	42
133	9 - LH	14100	8782	62
136	3 - UH	9470	1895	20
136	4 - UH	10100	1527	15
136	4 - LH	13200	1664	13
136	5 - UH	12300	1500	12
136	5 - L H	14200	2073	15
136	6 - WS	11500	1582	14
136	7 - UH	23000	2918	13
136	7 - LH	19100	2359	12
136	9 - UH	1400	2645	189
136	9A - UH	9800	5782	59
136	9A - LH	16200	1336	8

Table A.22. Tank 241-U-106 Core Samples

Core	Segment	TOC	Carbon from Oxalate	% TOC from Oxalate
147	1 - WS	47800	148	0.31
147	2 - UH	26500	2547	10
147	2 - DL	33400	2727	8
147	3 - UH	26300	2542	10
147	3 - LH	17100	3000	18
147	4 - UH	25800	2864	11
147	4 - LH	25100	2891	12
147	5 - UH	15400	2043	13
147	5 - LH	9040	2809	31
147	Composite	19500	2918	15
148	1 - DL	33400	256	0.77
148	2 - UH	23200	1939	8
148	2 - LH	25000	2495	10
148	2 - DL	41800	166	0.40
148	3 - UH	25600	2684	10
148	3 - LH	25800	2809	11
148	4 - UH	25700	2891	11
148	4 - LH	25200	2864	11
148	5 - UH	15600	1669	11
148	5 - LH	8940	603	7
148	Composite	22400	2367	11

Table A.23. Tank 241-U-107 Core Samples

Core	Segment	TOC	Carbon from Oxalate	% TOC from Oxalate
129	3R - UH	882	676	77
129	1 - DL	3120	171	5
129	2 - UH	4940	2564	52
129	2 - LH	1920	777	40
129	2 - DL	4850	143	3
129	3 - UH	1220	--	--
129	3 - LH	1380	--	--
134	5A - LL	675	1419	210
134	5B - DL	3690	--	--
134	6A - LL	1790	79	4
134	6A - WS	1220	--	--
134	6A - DL	1050	--	--
134	2 - UH	767	704	92
134	3 - UH	1900	900	47
134	4 - top 1/4	3680	709	19
134	4 - 2nd 1/4	3640	815	22
134	4 - 4th 1/4	5160	1658	32
134	5 - top 1/4	9040	4173	46
134	5 - 2nd 1/4	5150	2468	48
135	1R - DL	3200	163	5
135	2A - WS	1180	--	--
135	2A - DL	4760	985	21
135	2R - UH	506	254	50
135	2R - LH	919	225	24
135	1 - DL	3230	147	5
135	1 - LL	937	540	58

Table A.24. Tank 241-U-108 Core Samples

Core	Segment	TOC	Carbon from Oxalate	% TOC from Oxalate
141	1-DL	7090	BDL (<119)	<2
141	1-LH	6280	3420	54
141	2-UH	3265	1009	31
141	3-UH	2670	842	32
141	3A-UH	2965	378	13
141	4-LH	4850	947	20
141	4-UH	3590	845	24
141	4A-LH	4460	830	19
141	4A-UH	4500	814	18
141	5-LH	3840	775	20
141	5-UH	4640	935	20
141	6-LH	2815	749	27
141	6-UH	3330	728	22
141	7-LH	5265	1022	19
141	7-UH	6315	1419	22
141	8-LH	4655	1048	23
141	8-UH	5825	1266	22

Table A.24 (contd)

Core	Segment	TOC	Carbon from Oxalate	% TOC from Oxalate
141	9-UH	2460	2227	91
141	composite	5090	1247	24
145	1-DL	7015	201	3
145	2-UH	2685	640	24
145	3-LH	3260	686	21
145	3-UH	3180	809	25
145	4-LH	3865	843	22
145	4-UH	2935	644	22
145	5-LH	5555	1461	26
145	5-UH	3710	915	25
145	6-LH	4105	1007	25
145	6-UH	4885	1271	26
145	7-LH	5300	1059	20
145	7-UH	4605	1095	24
145	8-LH	4590	1272	28
145	8-UH	2890	744	26
145	9-LH	2795	754	27
145	9-UH	5220	4246	81
145	composite	4645	1351	29
146	1-DL	7105	BDL (<147)	<2
146	1-UH	3960	740	19
146	2-LH	1745	BDL (<608)	<35
146	2-UH	2805	656	23
146	3-LH	2440	BDL (<401)	<16
146	3-UH	2850	797	28
146	3A-UH	2675	543	20
146	4-LH	4210	1151	27
146	4-UH	2620	709	27
146	5-LH	4090	1051	26
146	5-UH	4865	1253	26
146	6-LH	4435	941	21
146	6-UH	4200	1139	27
146	7-LH	6870	1390	20
146	7-UH	5355	1047	20
146	8-LH	3290	1737	53
146	8-UH	5995	1220	20
146	9-LH	5360	1810	34
146	9-top 1/4	11150	5550	50
146	composite	3680	1194	32

Distribution

No. of
Copies

No. of
Copies

Offsite

2 Office of Scientific and Technical Information

S. F. Agnew
Los Alamos National Laboratory
PO Box 1664
Los Alamos, NM 87545

E. C. Ashby
Boggs Chemistry Building
Georgia Institute of Technology
225 North Avenue
Atlanta, GA 30332-0399

H. Babad
2540 Cordoba Ct
Richland, WA 99352

K. K. Bandyopadhyay
Brookhaven National Laboratory
Upton, NY 11973

D. O. Campbell
102 Windham Road
Oak Ridge, TN 37830

H. K. Fauske
Fauske and Associates, Inc.
16W070 W. 83rd St
Burr Ridge, IL 60521

C. W. Forsberg
Oak Ridge National Laboratory
P.O. Box 2008, MS-6495
Oak Ridge, TN 37831-6495

B. C. Hudson
P.O. Box 271
Lindsborg, KA 67456

M. S. Kazimi
Department of Nuclear Engineering
Massachusetts Institute of Technology
77 Massachusetts Ave.
Cambridge, MA 02139

J. L. Kovach
Nuclear Consulting Services, Inc.
P.O. Box 29151
Columbus, OH 43229-0151

S. Kress
102-B Newridge Road
Oak Ridge, TN 37830-8118

T. E. Larson
2711 Walnut St.
Los Alamos, NM 87544

M. Plys
Fauske and Associates, Inc.
16W070 W. 83rd St.
Burr Ridge, IL 60521

A. K. Postma
G & P Consulting Inc.
3640 Ballard Road
Dallas, OR 97338

D. A. Powers
Nuclear Facilities Safety Dept.
Sandia National Laboratories
P.O. Box 5800, MS-0744
Albuquerque, NM 87185-0744

W. Schulz
727 Sweetlead Drive
Wilmington, DE 19808

No. of
Copies

S. E. Slezak
806 Hermosa NE
Albuquerque, NM 87110

Onsite

6 DOE Richland Operations Office

S. O. Branch	S7-54
R. G. Harwood	S7-54
W. F. Hendrickson	S7-54
D. H. Irby	S7-54
J. K. McClusky	T6-30
J. C. Peschong	S7-53

7 Hanford Contractors

G. S. Barney	T5-12
D. B. Bechtold	T6-09
R. J. Cash	S7-14
J. M. Grigsby	A3-37
N. W. Kirch	R2-11
J. E. Meacham	S7-14
L. M. Stock	S7-14

No. of
Copies

33 Pacific Northwest National Laboratory

S. Q. Bennett	K7-90
J. W. Brothers (3)	K9-20
S. A. Bryan	P7-25
D. M. Camaioni	K2-44
J. A. Campbell	P8-08
C. D. Carlson (10)	P7-25
P. M. Daling	K8-07
R. T. Hallen	P8-38
P. G. Heasler	K5-12
V. L. Hunter	K7-97
M. A. Lilga	P8-38
L. R. Pederson	K2-44
W. E. Samuels	K2-44
R. D. Scheele	P7-25
C. S. Simmons	K9-33
J. J. Toth	K7-94
T. W. Wood	K7-94
Information Release (5)	K1-06