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ENGINEERING DATA TRANSMITTAL

Page 1 of 4
 1. EDT **616012**

2. To: (Receiving Organization) Distribution	3. From: (Originating Organization) Data Assessment and Interpretation	4. Related EDT No.: N/A
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16. KEY										
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2	1	Cog. Eng. W.I. Winters	<i>W.I. Winters</i>	6/25/96						
2	1	Cog. Mgr. J.G. Kristofzski	<i>J.G. Kristofzski</i>	6-26-96						
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18. A.E. Young <i>A.E. Young</i> Signature of EDT Originator Date <i>6-25-96</i>	19. N/A Authorized Representative Date for Receiving Organization	20. <i>J.G. Kristofzski</i> J.G. Kristofzski Cognizant Manager Date <i>6/26/96</i>	21. DOE APPROVAL (if required) Ctrl. No. <input type="checkbox"/> Approved <input type="checkbox"/> Approved w/comments <input type="checkbox"/> Disapproved w/comments
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Tank Characterization Report for Single-Shell Tank 241-C-103

W. I. Winters
Westinghouse Hanford Company, Richland, WA 99352
U.S. Department of Energy Contract DE-AC06-87RL10930

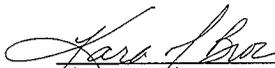
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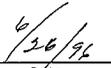
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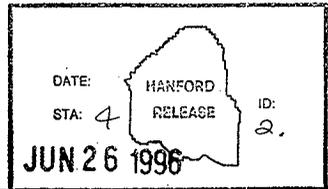
Abstract: This document summarizes the information on the historical uses, present status, and the sampling and analysis results of waste stored in Tank 241-C-103. This report supports the requirements of Tri-Party Agreement Milestone M-44-09.

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Tank Characterization Report for Single-Shell Tank 241-C-103

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EXECUTIVE SUMMARY

This tank characterization report summarizes the information on the historical uses, current status, and sampling and analysis results of waste stored in single-shell underground tank 241-C-103. This report supports requirements of the *Hanford Federal Facility Agreement and Consent Order* (Ecology et al. 1994), Milestone M-44-09.

Tank 241-C-103 is one of 16 single-shell underground high-level radioactive waste storage tanks located in the 200 East Area C Tank Farm on the Hanford Site. It is the third tank in a three-tank cascade series. The tank went into service in August 1946, receiving metal waste from the bismuth phosphate process used at B Plant (Agnew 1993). The tank also received cladding waste from the PUREX Plant (Agnew et al. 1994). Transfers of PUREX sludge supernate (AR solids) from tank 241-C-106 are expected to have left a high-level strontium layer on top of the PUREX cladding waste sludge (Agnew 1993).

Wastes from other tanks in the 241-C Tank Farm, destined as feed for the 242-S Evaporator, were received from 1973 to 1978 (Agnew et al. 1994). The separable organic material in the tank probably originated in PUREX; it is thought to have been originally approximately 70 percent normal paraffin hydrocarbon (NPH) and 30 percent tributyl phosphate (TBP) (Carothers 1993). In 1979, the tank was declared out of service (Agnew et al. 1994).

A description and status of tank 241-C-103 are provided in Tables ES-1 and ES-2 and Figure ES-1. The tank has an operating capacity of 2,010 kL; it currently contains an

Table ES-1. Description and Status of Tank 241-C-103.

TANK DESCRIPTION	
Type	Single-shell
Constructed	1943 and 1944
In-service	1946
Diameter	22.9 m
Maximum operating depth	5.18 m
Capacity	2,010 kL
Bottom Shape	Dish
Ventilation	Passive
TANK STATUS	
Total waste volume	738 kL
Sludge volume	235 kL
Drainable interstitial liquid	0
Aqueous layer volume	485 kL
Organic layer volume	18.2 kL
Waste surface level (October 31, 1995)	175 cm
Temperature (April 1995 to April 1996) ¹	Range 38.8 to 49.5 °C Mean 45.4 °C
Integrity	Sound
Watch List	Organics
SAMPLING DATES	
Grab Sample	December 1993
Push-mode Sample	October 1994 to February 1995
Vapor Sample	May 12 to 25, 1994
Core Sample (Historical) ²	May 1986
Grab Sample (Historical)	1990
SERVICE STATUS	
Out of service	1979
Interim Stabilization	n/a
Intrusion Prevention	n/a

Note:

¹The temperature is the average of the first three thermocouples.

²Pre-May 1989 data may not be acceptable for some regulatory uses because adequate quality control information for the data is not available to assess data quality and permit confident decisions.

Table ES-2. Major Analytes and Analytes of Concern. (4 sheets)

Analyte	Concentration	Relative Standard Deviation (Mean) ¹	Inventory Estimate
SLUDGE LAYER²			
Metals	µg/g	%	kg²
Aluminum	193,000	0.1	60,800
Chromium	970	5.9	305
Iron	15,800	9.2	4,980
Sodium	26,400	1.7	8,310
Zinc	824	23.8	259
Zirconium	11,400	9.4	3,590
Anions	µg/g	%	kg
Chloride	632	38.9	199
Cyanide	98.4	8	31.0
Fluoride	1,070	14.8	337
Nitrate	1,730	36.6	545
Nitrite	17,600	49.1	5,540
Oxalate	2,710	28.7	853
Phosphate	3,240	12.9	1,020
Sulfate	2,790	28.3	879
Radionuclides	µCi/g	%	Ci
¹³⁷ Cs	122	25.6	38,400
¹⁵⁴ Eu	10.6	40.9	3,340
⁹⁰ Sr	4,190	39.4	1.32E+06
Total Alpha	9.74	23.6	3,070

Table ES-2. Major Analytes and Analytes of Concern. (4 sheets)

Analyte	Concentration	Relative Standard Deviation (Mean) ¹	Inventory Estimate
Carbon	µg C/g	%	kg C
Total Inorganic Carbon	4,960	9.2	1,560
Total Organic Carbon	8,210	10.8	2,590
Physical Properties			
Density	1.34 g/mL	---	
Percent Water	57.7%	34.9%	
AQUEOUS LAYER⁴			
Metals	µg/mL	%	kg ⁵
Chromium	57.0	11	27.6
Nickel	72.1	10	35.0
Phosphorus	2,530	21	1,230
Potassium	323	0	157
Silver	11.8	0	5.72
Sodium	32,700	10	15,900
Uranium	2,100	15	1,020
Zirconium	301	14	146
Anions	µg/mL	%	kg
Chloride	404	6.4	196
Cyanide	26.9	2	13.0
Fluoride	1,160	6.7	563
Nitrate	2,140	14.3	1,040
Nitrite	21,200	12.9	10,300
Oxalate	3,210	7.1	1,560
Phosphate	2,250	13.1	1,090
Sulfate	3,220	3.87	1,560

Table ES-2. Major Analytes and Analytes of Concern. (4 sheets)

Analyte	Concentration	Relative Standard Deviation (Mean) ¹	Inventory Estimate
Radionuclides	μCi/mL	%	Ci
¹³⁷ Cs	57.9	0.43	28,100
Total Alpha	0.0435	---	21.1
Total Beta	70.6	---	34,200
Carbon	μg C/mL	%	kg
Total Inorganic Carbon	6,850	9.6	3,320
Total Organic Carbon	6,640	5.9	3,220
Physical Properties			
Density at 44 °C	1.076 g/mL	---	
Percent Water	86.2%	2.2%	
pH	10.0	---	
ORGANIC LAYER²			
Organic Compounds	μg/g	%	kg
Normal Paraffin Hydrocarbon	3.33E+05	Not reported	5,260
Tributyl Phosphate	6.4E+05	Not reported	10,100
Dibutyl Butylphosphonate	26,000	Not reported	411
Radionuclides	μCi/g	%	Ci
Gross Alpha	5.47E-04	Not reported	0.00864
Gross Beta	1.05	Not reported	16.6
²⁴¹ Am	2.11E-04	6.9	0.00333
¹³⁷ Cs	0.0413	2.4	0.652
^{239/240} Pu	1.94E-04	3	0.00306

Table ES-2. Major Analytes and Analytes of Concern. (4 sheets)

Analyte	Concentration	Relative Standard Deviation (Mean) ¹	Inventory Estimate
Metals	μL/g	%	kg
Silver	0.9	0	0.0142
Cadmium	2.1	0	0.0332
Potassium	23	25	0.363
Sodium	70	3	1.11
Nickel	9.9	8	0.156
Phosphorus	605	6	9.56
Other	μg NH₄/g	%	kg²
Ammonia	24.0	Not reported	0.379
Physical Properties			
Density at 44 °C	0.868 g/mL		
Percent water	1.31 %		

Notes:

¹Relative standard deviation (Mean) = the standard deviation (Mean), divided by the mean, times one hundred, based on the entire data set for a given analyte.

²Bell 1995a, Bell 1995b, and Bell 1995c.

³Inventory estimates for the sludge layer are calculated using a volume of 235 kiloliters.

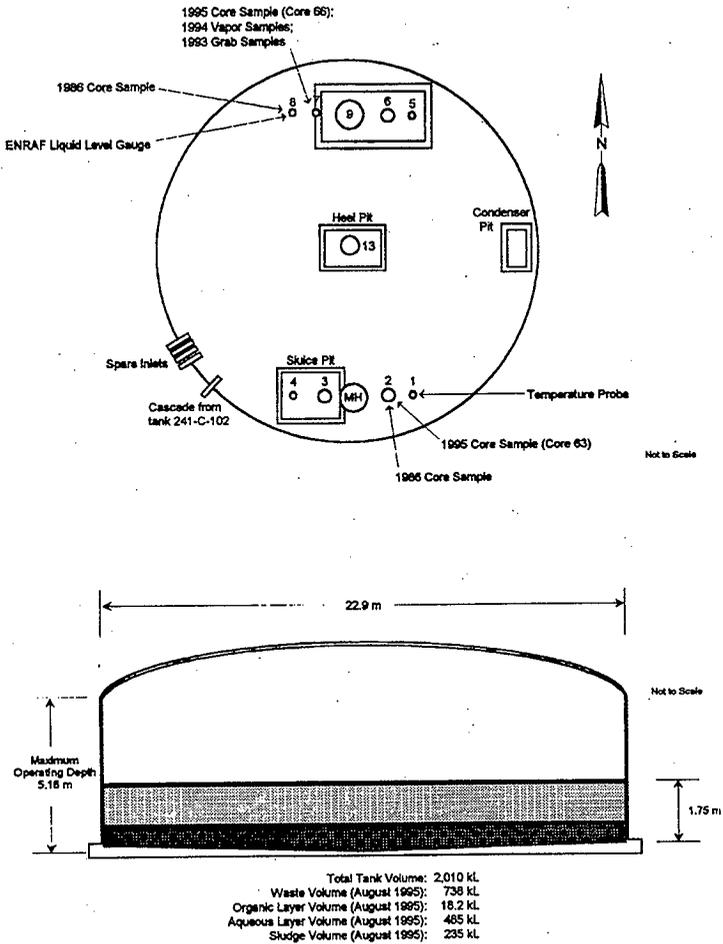
⁴Results for lithium, anions, total inorganic and organic carbon, and percent water taken from sources as noted in footnote (2). All others were taken from Pool and Bean (1994).

⁵Inventory estimates for the aqueous layer are calculated using a volume of 485 kiloliters.

⁶Pool and Bean 1994.

⁷Inventory estimates for the organic layer are calculated using a volume of 18.2 kiloliters.

Figure ES-1. Profile of Tank 241-C-103.



estimated 738 kL of waste. According to Hanlon (1995), it is composed of an estimated 503 kL of supernate and 235 kL of sludge. The supernate is divided into a 485 kL aqueous layer and an 18 kL organic layer.

This report summarizes the collection and analysis of data from three sampling events. The first event, a grab sampling of the organic and aqueous layers, took place in 1993. It was conducted in accordance with the *Organic Layer Sampling for SST 241-C-103 Background and Data Quality Objectives and Analytical Plan* (Wood et al. 1993). Seven grab samples were removed from the liquid in the tank, one from the aqueous layer and six from the organic layer. A complete set of analyses was performed on the samples, including gas chromatograph/mass spectrometry (GC/MS), radiochemistry, inductively coupled plasma (ICP) spectrometry, ion chromatography (IC), and physical tests for viscosity, density, and pH (Pool and Bean 1994).

The second sampling event involved several samples of the tank headspace, obtained from November 1993 through May 1994; the bulk of information came from the May 1994 sample. The vapor sampling operations were performed to satisfy requirements listed in *Tank 241-C-103 Vapor and Gas Sampling Data Quality Objectives* (Osborne et al. 1994). Data from this and other sampling events were used to compile a report which characterized the headspace of tank 241-C-103 (Huckaby and Story 1994).

The third sampling event comprised two core samples of four segments each obtained in 1994 and 1995 to satisfy the requirements of the *Tank Safety Screening Data Quality*

Objective (Babad and Redus 1994), the *Data Quality Objective to Support Resolution of the Organic Fuel Rich Tank Safety Issue* (Babad et al. 1994), and the *Interim Data Quality Objectives for Waste Pretreatment and Vitrification* (Kupfer et al. 1994). However, the requirements of the pretreatment DQO were not implemented in the Sample and Analysis Plan because the pretreatment program decided that only archived sample material was needed at this time. This sampling event resulted in the acquisition of core numbers 63 and 66 using the push-mode core sampling method. Analyses performed included total alpha activity, energetics by differential scanning calorimetry (DSC), moisture content by thermogravimetric analysis (TGA), and secondary analytes (Bell 1995c).

Only one moisture content result from the nonorganic samples (13.47 weight percent) violated the 17 weight percent safety screening requirement. This result came from the first analysis of the upper half sample from core 63, segment 4. The average of three TGA runs was 23.2 percent, and this was verified by two gravimetric runs that averaged 25.2 percent. The overall mean weight percent water content was 57.7 percent for the sludge fraction of the tank and 86.2 percent for the aqueous layer fraction.

Two exothermic reactions were detected which exceeded the -481 J/g (dry weight basis) data quality objective (DQO) limit, one each from the sludge and aqueous layers. A DSC result of -784 J/g (dry weight) was found in the aqueous layer sample from core 63, segment 4. The highest exothermic reaction from the sludge samples was -540 J/g (dry weight) from the lower half sample of core 63, segment 3. However, both samples had percent water results well above the 17 weight percent criteria. Neither sample had a cyanide or total organic

carbon (TOC) result above its respective DQO limit although the overall TOC concentration of the aqueous phase did exceed the 30,000 $\mu\text{g/g}$ DQO criteria when calculated on a dry weight basis. Considering that the aqueous phase contains 86.2 percent water, this does not pose a safety concern.

The highest total alpha activity, 19.6 $\mu\text{Ci/g}$, came from the upper half solids of core 63, segment 3; it was roughly half the notification limit. The average of all sludge samples was approximately one-fifth of the total alpha criteria for criticality consideration.

The 1993 sampling event substantiated the presence of an organic layer that has a flash point of approximately 118 °C. The organic analyses performed in 1994 showed this layer was composed of approximately 64 weight percent TBP and 33 weight percent NPH. These concentrations are the reverse of that indicated by historical records, suggesting that much of the NPH has been removed by evaporation. The organic analyses also show dibutyl butylphosphonate (DBBP) to be present in significant quantities (~ 3 weight percent). Records indicated that limited quantities of DBBP may have been used at PUREX (Klem 1988). Specific analytes in the organic layer exceeding the decision criteria based on the data quality objective in use at the time of analyses were viscosity and total alpha and beta. Additional radionuclide analyses were performed for ^{90}Sr and the actinides because the radionuclide screening tests thresholds were exceeded. The viscosity result was greater than 1 centipose indicating the organic may not be thoroughly mixed from thermal effects. The criteria for transuranics (TRU), ^{137}Cs , and ^{90}Sr activities were used in calculating the radiological risk implications of a pool fire.

The organic vapor analysis showed that the fuel content of the headspace was about 3.8 percent of the lower flammability limit (LFL), well below the operational limit of 25 percent of the LFL. However, the concentration of several toxic vapors (ammonia, nitrous oxide, TBP, acetonitrile, n-butanol, 2-hexane propane nitrile, benzene, NPH, and 1,3-butadiene), identified in the tank headspace, were large enough to warrant further consideration from a personnel health perspective (Mahlum et al. 1994).

The heat load in the tank produced by radioactive decay is estimated to be 9,270 watts, less than the 11,700 watts level that classifies high-heat tanks (Boyles 1994). Surveillance data showed a high temperature of 49.4 °C on November 1, 1995.

In summary, the only issue of immediate safety concern is the possibility of toxic vapors in the tank headspace. Although exothermic reactions and high TOC values were noted, these would pose a potential danger only if the weight percent water in the tank dropped considerably.

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LIST OF TERMS

ACL	Analytical Chemistry Laboratory
ANOVA	analysis of variance
AR	PUREX sludge washed in AR vault
C	Celsius
cal/g	calories per gram
CCT	Carbotrap/Carbotrap C
Ci	curies
Ci/L	curies per liter
cm	centimeter
CWP	cladding waste PUREX
DBBP	dibutyl butylphosphonate
DBP	dibutyl phosphate
DQO	data quality objective
DSC	differential scanning calorimetry
EDTA	ethylenediaminetetraacetic acid
g/mL	grams per milliliter
GC/MS	gas chromatography/mass spectroscopy
GEA	gamma energy analysis
HDW	Hanford Defined Wastes
HEDTA	N-(hydroxyethyl)-ethylenediaminetriacetic acid
HHF	hydrostatic head fluid
HLRF	High-Level Radiochemistry Facility
HTCE	Historical Tank Content Estimate
IC	ion chromatography
ICP	inductively coupled plasma
kg	kilograms
kg C	kilograms of carbon
kL	kiloliters
kW	kilowatts
LFL	lower flammability limit
m	meters
mg/L	milligrams per liter
mg/m ³	milligrams per cubic meter
mm	millimeters
mm Hg	millimeters of mercury
mol/L	moles per liter
mR/hr	milliroentgen per hour
NPH	normal paraffin hydrocarbons
NTA	nitrilotriacetate
OSHA	Occupational Safety and Health Administration
OVS	OSHA versatile sampler

LIST OF TERMS (Continued)

ppm	parts per million
ppmv	parts per million volume
RPD	relative percent difference
RSD	relative standard deviation
TBP	tributyl phosphate
TCP	Tank Characterization Plan
TGA	thermogravimetric analysis
TIC	total inorganic carbon
TLM	Tank Layer Model
TOC	total organic carbon
TST	triple sorbent trap
WSTRS	Waste Status and Transaction Record Summary
wt%	weight percent
$\mu\text{Ci/g}$	microcuries per gram
$\mu\text{Ci/mL}$	microcuries per milliliter
$\mu\text{g C/g}$	micrograms of carbon per gram
$\mu\text{g C/mL}$	micrograms of carbon per milliliter
$\mu\text{g/g}$	micrograms per gram
$\mu\text{g/mL}$	micrograms per milliliter
$\mu\text{g NH}_3/\text{g}$	micrograms of ammonia per gram
μmol	micromoles
ΔH	change in enthalpy

1.0 INTRODUCTION

This tank characterization report presents an overview of single-shell tank 241-C-103 and its waste components. It provides estimated concentrations and inventories for the waste constituents based on the latest available sampling and analysis activities and background tank information. The tank 241-C-103 organic and aqueous layers were grab sampled in 1993 in accordance with the requirements listed in the *Organic Layer Sampling for SST 241-C-103 Background, Data Quality Objectives, and Analytical Plan* (Wood et al. 1993). The tank was sampled again in 1994 and 1995 to satisfy the requirements of the *Tank Safety Screening Data Quality Objective* (Babad and Redus 1994), the *Data Quality Objective to Support Resolution of the Organic Fuel Rich Tank Safety Issue* (Babad et al. 1994), and the *Interim Data Quality Objectives for Waste Pretreatment and Vitrification* (Kupfer et al. 1994). However, pretreatment program requirements were later modified to require only the acquisition of archive material for possible testing at a later time. Vapor samples were taken in 1994 in accordance with the *Tank 241-C-103 Vapor and Gas Sampling Data Quality Objectives* (Osborne et al. 1994). In addition, two historical sampling events are discussed.

1.1 PURPOSE

This report summarizes information about the use and contents of tank 241-C-103. When possible, this information will be used to assess issues associated with safety, operations, environmental, and process activities. This report also provides a reference point for more detailed information about tank 241-C-103.

1.2 SCOPE

Tank 241-C-103 was grab sampled in 1993 to address an unreviewed safety question concerning the possibility of a pool fire in an organic-rich waste tank with subsequent loss of containment and release of radioactivity to the surrounding environment (Pool and Bean 1994).

Push-mode core samples were taken in 1994 and 1995 to comply with the requirements of the tank safety screening program, to further address the question of pool fires in organic-rich waste tanks, and to gather information for future retrieval and vitrification activities. In addition, vapor samples were taken to increase the available information concerning vapor headspace and to evaluate the flammability and toxic properties of these gases.

Two historical sampling events are also discussed; one in 1986 and one in 1990. In each event, samples were taken to compare data from tanks that were similarly sampled and analyzed. This information was to be used for future retrieval, process, and disposal activities (Weiss and Schull 1988, Edrington 1991).

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2.0 HISTORICAL TANK INFORMATION

This section describes historical information about tank 241-C-103. The first part details the current condition of the tank. This is followed by a discussion of the tank's background, transfer history, and the process sources that contributed to the tank waste, including an estimate of the current contents based on the process history. Events that may be related to tank safety issues, such as potentially hazardous tank contents (organics) or off-normal operating temperatures, are included. The final part of the section summarizes available surveillance data for the tank.

2.1 ESTIMATED TANK CONTENTS

Tank 241-C-103 contained an estimated 738 kL of noncomplexed waste as of August 31, 1995 (Hanlon 1995). The amount of the various waste phases in the tank is shown in Table 2-1. Tank 241-C-103 is identified as sound; partial isolation was completed in December 1982. It has not been interim stabilized. The tank was placed on the Organics Watch List in January 1991. In September 1992, an unreviewed safety question involving tank 241-C-103 was declared because of an organic layer covering the waste surface. The unreviewed safety question was closed in May 1994 (Grumbly 1994).

Table 2-1. Tank Contents Summary.¹

Waste Form	Volume (kiloliters)
Total waste	738
Supernatant	503
Sludge	235
Salt cake	0
Drainable interstitial liquid	0
Pumpable liquid remaining	503

Note:

¹Hanlon (1995)

2.2 TANK DESIGN AND BACKGROUND

The 241-C Tank Farm consists of 12 first-generation 2,010-kL tanks and four 208-kL tanks. The tanks were designed for nonboiling waste with a maximum fluid temperature of 104 °C. A typical tank has 9 to 13 risers, which range from 5 cm to 1.1 m in diameter, and provide surface level access to the underground tank. Generally, there is one riser through the center of the tank dome, five each on opposite sides of the tank and the remaining one to three are scattered on the dome.

Tank 241-C-103 entered service in August 1946 through the cascade from tank 241-C-102. It is the third in a three-tank cascading series. The tanks are connected by a 7.6 cm-diameter cascade line. The cascade overflow height is approximately 4.78 m from the tank bottom and 0.6 m below the top of the steel liner. The tank is constructed of 30 cm-thick reinforced concrete with a 0.64 cm mild carbon steel liner on the bottom and sides and a 38 cm-thick domed concrete top. The tank has a dished bottom with a 1.2 m radius knuckle and a 5.18 m operating depth. The tank is set on a reinforced concrete foundation. It is covered with approximately 2.2 m of overburden.

The surface level is monitored through riser 8. Liquid and solid waste volume is determined by an ENRAF gauge. Tank temperatures are monitored by a temperature probe inserted through riser 1. A list of tank 241-C-103 risers is shown in Table 2-2. The riser configuration is shown in Figures 2-1 and 2-2.

Table 2-2. Tank 241-C-103 Riser and Piping Configuration.¹

Riser Number	Diameter (cm)	Description and Comments
1	10	Temperature probe (bench mark)
2	30	Breather filter, carbon filter
3	30	Sluicing access (weather covered)
4	10	Recirculating dip leg (weather covered)
5	10	Recirculating dip leg (weather covered)
6	30	Sluicing access (weather covered)
7	30	Observation port
8	10	Liquid level gauge
9	107	Manhole (weather covered)
13	30	Saltwell screen
Nozzle Number	Diameter (cm)	Description and Comments
B	8	Cascade inlet
C1	8	Spare
C2	8	Spare
C3	8	Spare
C4	8	Spare

Note:

¹Alstad (1993)

Figure 2-1. Tank 241-C-103 Riser Configuration.

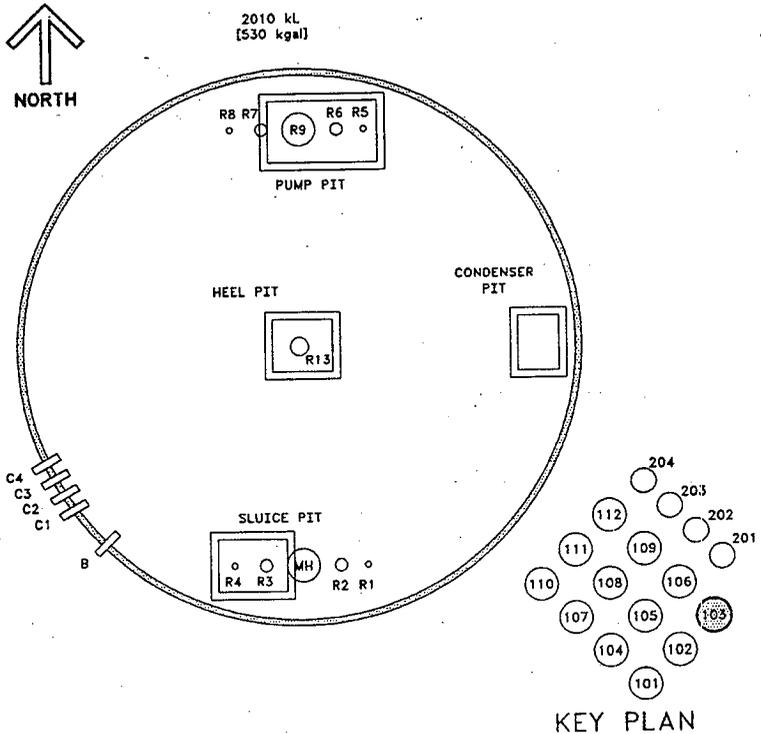
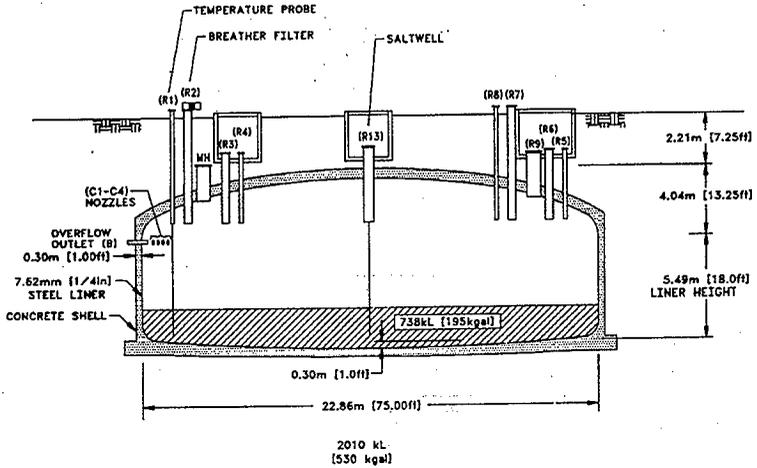


Figure 2-2. Tank 241-C-103 Cross Section.



2.3 PROCESS KNOWLEDGE

This section provides the transfer history of tank 241-C-103 and an estimate of its contents based on transfer history.

2.3.1 Waste Transfer History

Tank 241-C-103 went into service in 1946 receiving metal waste from the other two tanks in this cascade. The metal waste originated from the bismuth phosphate separations process used at B Plant (Agnew 1993). Because tank 241-C-103 is the final tank in a cascade series, most of the metal waste solids would have settled in the first two tanks. Tank 241-C-103 was filled in October 1946 and stood idle until it was sluiced in 1953; it was declared empty in August 1953 (Rodenhizer 1987). The tank was refilled with uranium recovery waste (Agnew et al. 1994). This uranium recovery waste was removed during 1957 for ferrocyanide scavenging in the CR vault, then directed to other tanks in the 241-C Tank Farm.

Tank 241-C-103 received cladding waste transfers directly from the PUREX Plant during 1960 (Agnew et al. 1994). Solids settling from the cladding waste stored in tank 241-C-103 are believed to account for a sludge layer of about 132 kL predicted to reside in the bottom of the tank (Agnew et al. 1995). From 1963 to 1966, the tank received PUREX high-level and organic wash wastes transferred from tanks in the 241-A Tank Farm. In 1969, most of this waste was transferred to tank 241-C-105, a feed tank for the B Plant cesium recovery operation. This waste is not expected to have contributed to the sludge residing in the tank.

During 1970 and 1971, the tank received B Plant low-level waste and PUREX sludge supernatant (Agnew et al. 1994). Agnew (1993) suggests that a high-strontium sludge layer (washed PUREX sludge or AR solids) is expected in the tank resulting from PUREX sludge supernatant transfers from tank 241-C-106. Most of the supernatant from transfers this period were removed by 1971 thereby reducing the tank's waste volume to 348 kL.

From 1973 to 1978, the tank received waste transfers from other tanks in the 241-C Tank Farm (Agnew et al. 1994). Most transfers were a mixture of dilute wastes to be concentrated in the B-Plant evaporator. The tank is believed to have received an organic layer during a transfer from tank 241-C-102 in the fourth quarter of 1975 (Agnew 1993). This organic layer floats on the aqueous layer; its thickness is not determined although it is expected to be less than 33 cm. The organic layer originated from PUREX organic wash waste; it is thought to be a solvent mixture of 70 volume percent NPH and 30 volume percent TBP (Carothers 1993).

The waste volume of tank 241-C-103 was reduced to 757 kL during a final transfer of supernatant in 1979 to tank 241-C-104. Subsequently, the tank was inactive (Agnew et al. 1994). Based on the transfer history, the supernatant remaining in the tank is a mixture of wastes received by the tank from 1973 to 1978. The waste include PUREX cladding,

PUREX high-level, organic wash, PUREX sludge supernatant, B Plant high-level, B Plant low-level, decontamination, N-Reactor, ion exchange, REDOX high-level, REDOX ion exchange, uranium recovery, laboratory, and flush water wastes.

The transfer history of tank 241-C-103 is summarized in Table 2-3 and shown in Figure 2-3.

Table 2-3. Summary of Tank 241-C-103 Waste Transfer History.^{1,2}

Waste Type	Time Period	Estimated Volume Received (kiloliters)	Comments
Metal waste	1946	2,010	Removed in 1953.
Uranium recovery waste	1954	1,800	Waste removed for scavenging.
PUREX high-level and organic wash wastes	1957 to 1966	6,880	Not expected to have contributed to current waste.
PUREX cladding waste	1960	1,810	Transfers associated with a 132 kL (35 kgal) solids volume measurement.
B Plant low-level waste and PUREX sludge supernate	1970 to 1971	3,320	Transfers associated with sludge volume increase; believed to represent 91 kL (24 kgal) of AR solids. ³
Various supernates from C Farm tanks	1973 to 1978	17,400	Transfer from tank 241-C-102 in 1975 creates floating organic layer in tank 241-C-103. ²

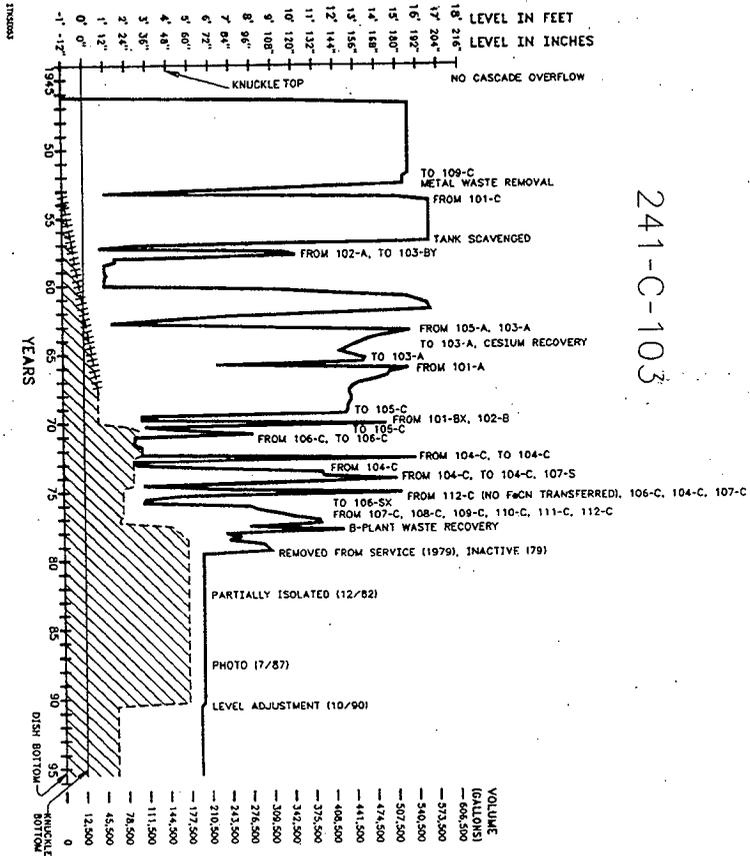
Notes:

¹Agnew et al. (1994)

²Waste volumes and types are best estimates based on historical data.

³Agnew (1993)

Figure 2-3. Tank 241-C-103 Level History.



2.3.2 Historical Estimation of Tank Contents

An estimate of the current contents of tank 241-C-103, based on historical data, is available from the *Historical Tank Content Estimate for the Northeast Quadrant of the Hanford 200 East Areas* (HTCE) (Brevick et al. 1994a). The data used for the estimate are from the *Waste Status and Transaction Record Summary for the Northeast Quadrant* (WSTRS) (Agnew et al. 1994), *Hanford Defined Wastes Chemical and Radionuclide Composition* (HDW) (Agnew 1995), and the *Tank Layer Model for Northeast, Southwest, and Northwest Quadrants* (TLM) (Agnew et al. 1995). The WSTRS is a compilation of available waste transfer and volume status data. An HDW list provides the assumed typical compositions for Hanford waste types. In most cases, the available data are incomplete thereby reducing the usefulness of the transfer data and the modeling results derived from it. The TLM takes the WSTRS data, models the waste deposition processes, and, using additional data from the HDW (which may introduce error), generates an estimate of the tank contents. Therefore, these model predictions can only be considered an estimate that requires further evaluation using analytical data.

Based on the HTCE, tank 241-C-103 contains three sludge layers that are covered by supernatant composed of organic and aqueous layers. Figure 2-4 shows the estimated waste types and volumes for the tank layers. The CWP (Cladding Waste PUREX) is rich in aluminum, sodium nitrate, sodium nitrite, and uranium. Cesium and strontium are present but in such quantities that the activity in this layer will be low. The strontium concentration is estimated to be larger than the cesium concentration. The AR waste (waste originating from washed PUREX sludge in AR vault) has significant concentrations of sodium, aluminum, nitrates, silicates, and sulfates. The cesium and strontium concentrations are extremely high, especially the strontium concentration which is approximately 47 times greater than the cesium concentration; therefore, the associated activity for this waste layer will be much larger than the CWP waste layer. This waste layer does not have uranium. This is significant because the CWP waste type contains uranium. The layer above the AR waste layer is unknown; however, Agnew et al. (1995) suggest this waste may be PUREX cladding waste or AR solids. The top waste layer in tank 241-C-103 is supernatant. Table 2-4 provides an estimate of the expected sludge constituents and their concentrations. An estimate of the constituents and concentrations of the supernatant are not yet available.

2.4 SURVEILLANCE DATA

Tank 241-C-103 surveillance consists of surface level measurements (liquid and solid), and temperature monitoring inside the tank (waste and headspace). Liquid level measurements are used to determine whether a major leak exists or, there are intrusions into the tank. Solid surface level measurements provide physical changes or consistency of the solid layers of a tank. In-tank photography also can be used to resolve measurement anomalies and determine tank integrity.

Figure 2-4. Tank Layer Model.

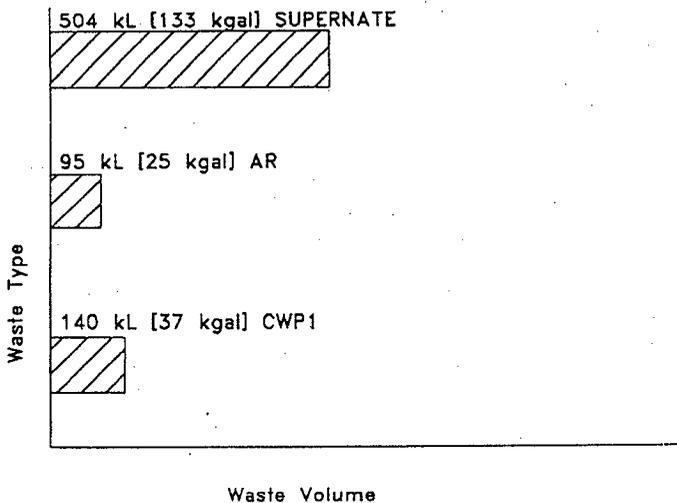


Table 2-4. Tank 241-C-103 Inventory Estimate.^{1,2,3} (2 sheets)

Solids Composite Inventory Estimate			
Physical Properties			
Total solid waste	8.89E+05 kg (195 kgal)		
Heat load	7.90 kW (2.70E+04 BTU/hr)		
Bulk density	1.20 (g/cc)		
Water wt%	72.8		
Total organic carbon wt% carbon (wet)	1.10		
Chemical Constituents	mole/L	ppm	kg
Na ⁺	3.04	5.81E+04	5.16E+04
Al ³⁺	1.20	2.69E+04	2.39E+04
Fe ³⁺ (total Fe)	0.199	9.23E+03	8.21E+03
Cr ³⁺	7.31E-03	316	281
Bi ³⁺	1.26E-04	21.8	19.4
La ³⁺	4.99E-07	5.75E-02	5.11E-02
Hg ²⁺	4.81E-04	80.1	71.2
Zr (as ZrO(OH) ₂)	4.43E-05	3.35	2.98
Pb ²⁺	2.26E-02	3.88E+03	3.45E+03
Ni ²⁺	1.85E-02	904	804
Sr ²⁺	1.66E-07	1.21E-02	1.07E-02
Mn ⁴⁺	9.35E-04	42.7	37.9
Ca ²⁺	4.11E-02	1.37E+03	1.22E+03
K ⁺	1.10E-02	356	316
OH	4.85	6.85E+04	6.09E+04
NO ₃ ⁻	0.660	3.40E+04	3.02E+04
NO ₂ ⁻	0.530	2.03E+04	1.80E+04
CO ₃ ²⁻	0.159	7.93E+03	7.05E+03

Table 2-4. Tank 241-C-103 Inventory Estimate.^{1,2,3} (2 sheets)

Chemical Constituents	mole/L	ppm	kg
PO ₄ ³⁻	1.37E-02	1.08E+03	960
SO ₄ ²⁻	6.45E-02	5.15E+03	4.58E+03
Si (as SiO ₃ ²⁻)	0.307	7.17E+03	6.37E+03
F ⁻	8.17E-03	129	115
Cl ⁻	3.74E-02	1.10E+03	979
C ₆ H ₅ O ₇ ³⁻	5.02E-03	789	701
EDTA ⁴⁻	3.01E-02	7.21E+03	6.40E+03
HEDTA ³⁻	5.72E-02	1.30E+04	1.16E+04
glycolate ⁻	6.41E-02	3.99E+03	3.55E+03
acetate ⁻	9.57E-03	469	417
oxalate ²⁻	4.27E-07	3.12E-02	2.77E-02
DBP	4.28E-03	946	841
butanol	4.28E-03	264	234
NH ₃	2.79E-02	394	350
Fe(CN) ₆ ⁴⁻	0	0	0
Radiological Constituents			
Pu		1.15 (μCi/g)	17.0 (kg)
U	2.07E-02 (M)	4.10E+03 (μg/g)	3.64E+03 (kg)
Cs	6.67E-02 (Ci/L)	55.4 (μCi/g)	4.93E+04 (Ci)
Sr	1.54 (Ci/L)	1.28E+03 (μCi/g)	1.14E+06 (Ci)

Notes:

- EDTA = ethylenediaminetetraacetic acid
- HEDTA = N-(hydroxyethyl)-ethylenediaminetetraacetic acid
- NTA = nitrilotriacetate
- DBP = dibutylphosphate

¹The HTCE predictions have not been validated and should be used with caution.

²Small differences appear to exist among the inventory above and the inventories calculated from the two sets of concentrations. These differences are being evaluated.

³Agnew et al. (1996)

2.4.1 Surface Level Readings

The tank 241-C-103 waste surface level is measured with an ENRAF gauge. A Food Instrument Corporation gauge was used before August 1994 [Hanlon 1995]. The ENRAF gauge is monitored automatically by the Tank Monitor and Control System. The surface level on November 1, 1995 was 175 cm. A level history graph, based on quarterly volume measurements from the time the tank went into service until 1993, is shown in Figure 2-3.

2.4.2 Internal Tank Temperatures

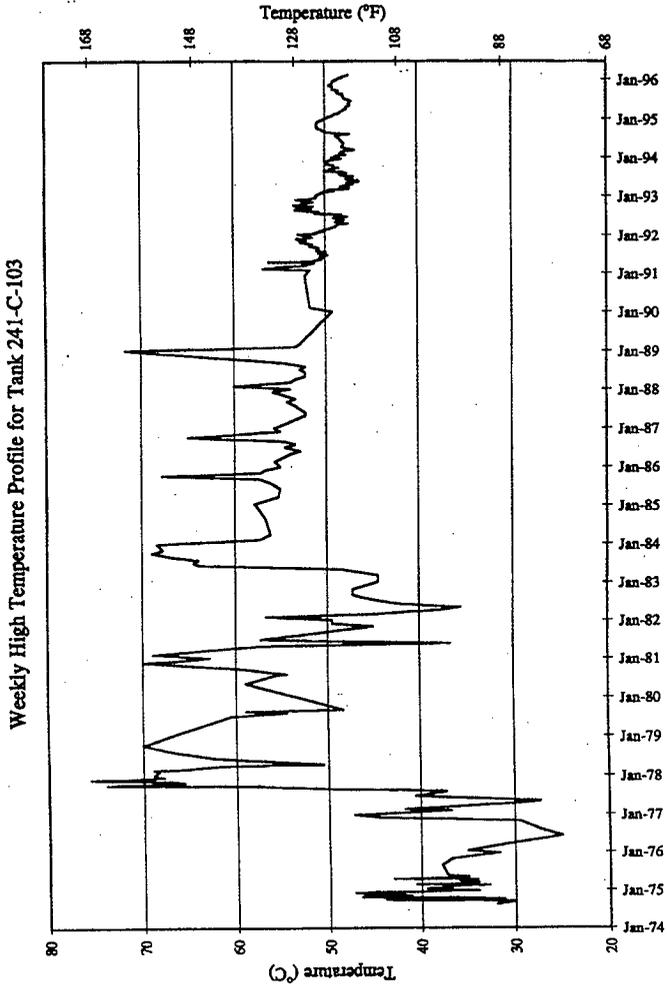
The waste temperature in tank 241-C-103 is monitored by a single thermocouple tree with 14 thermocouples. The maximum temperature measured in the tank on November 1, 1995 was 49.4 °C at thermocouple 1 which is 36.9 cm above the tank bottom (Tran 1993). Thermocouples are generally spaced 60 cm apart (Tran 1993). The tank level history indicates that thermocouple 1 was consistently in or near the solids level; thermocouple 2 was in or near the solids level from 1988 to 1990 and in or near the liquid level thereafter; and thermocouple 3 has been consistently in or near the liquid level. Estimated elevations for thermocouples 4 and 5 indicate they are in the headspace (Brevick et al. 1994b).

The first 4 thermocouples have similar temperature readings (Brevick et al. 1994b) as do thermocouples 5 through 11. Thermocouples 12, 13, and 14 have a few sporadic readings. The mean temperature from thermocouples 1 through 4 is 48.9 °C, the median is 46.7 °C, the minimum is 35 °C, and the maximum is 60 °C. The mean temperature for the last year (April 1995 to April 1996) was 45.4 °C and the range was 38.8 °C to 49.5 °C. Brevick et al. (1994b) contains plots of individual thermocouple readings. Figure 2-5 shows the weekly maximum temperatures from 1974 to 1994.

2.4.3 Tank 241-C-103 Photographs

The 1987 photographic montage of the tank 241-C-103 interior shows a brown mottled waste layer covered by liquid waste. Equipment visible in the tank include a liquid level gauge, spare inlet nozzles, an overflow inlet nozzle, and a temperature probe. Some unknown equipment can be seen in the tank. They appear to be pieces of equipment that were cut off and allowed to drop into the tank. Although there were minor adjustments in the waste volume after the photographs were taken, the picture should represent the current tank contents. The photographic montage is not included in this document because only the supernate waste layer is visible.

Figure 2-5. Tank 241-C-103 Weekly High Temperature Plot.



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3.0 TANK SAMPLING OVERVIEW

This section describes the three sampling events used to the characterize the contents of tank 241-C-103; all were governed by data quality objectives. Two core samples were obtained, one in 1994 and one in 1995, in accordance with the following data quality objectives: *Tank Safety Screening Data Quality Objective* (Babad and Redus 1994), *Data Quality Objective to Support Resolution of the Organic Fuel Rich Tank Safety Issue* (Eiabad et al. 1994), and *Interim Data Quality Objectives for Waste Pretreatment and Vitrification* (Kupfer et al. 1994). Grab samples were obtained in 1993 as directed in the *Organic Layer Sampling for SST 241-C-103 Background, Data Quality Objectives, and Analytical Plan* (Wood et al. 1993) and vapor samples were obtained in 1994 as mandated in *Data Quality Objectives for Generic In-Tank Health and Safety Issue Resolution* (Osborne et al. 1994). Descriptions of two other sampling events used for historical comparisons are briefly discussed as well. For a detailed discussion of sampling and analytical procedures, refer to the *Tank Characterization Reference Guide* (De Lorenzo et al. 1994).

3.1 DESCRIPTION OF 1994/1995 CORE SAMPLING EVENT

Two core samples were obtained from tank 241-C-103 using the push-mode sampling method. Segment 1 of core 63 was removed from riser 2 on October 28, 1994 and was received by the 222-S Laboratory on October 31, 1994. After removing the segment, problems with the sampling truck resulted in approximately a three-month delay before sampling was resumed. Segments 2 and 3 of core 63 were not obtained until January 17, 1995; segment 4 was obtained on January 18. Segments 1 and 2 of core 66 were removed from riser 7 were on February 6, 1995; segments 3 and 4 were obtained on February 7, 1995. Hereafter, throughout the rest of the document, the 1994/1995 sampling event is referred to as the 1995 sampling event.

Hydrostatic head fluid (HHF) with a lithium bromide tracer was used in the collection of all core samples (Schreiber 1995). A field blank of deionized water was created and delivered to the 222-S Laboratory with the core samples.

The flammability of tank vapors were checked before core sampling using a flammable gas meter to ensure that vapors were less than 25 percent of the flammability limit. This was done to meet operational safety requirements and to satisfy the safety screen DQO for flammability.

The sampling and analytical plan for the core samples was initially outlined in *Tank 241-C-103 Tank Characterization Plan* (Schreiber 1994). Segment 1 of core 63 was taken according to the procedures contained in that document. While the sampling truck was out of commission, the Pretreatment Program requested that earlier required analyses be deleted from the tank characterization plan. Consequently, the remaining segments were acquired according to the revised tank characterization plan (Schreiber 1995).

3.1.1.1 Sample Handling

All segments were received by the 222-S Laboratory within three days of sampling. Table 3-1 lists the segments, sample types amount and percent recovered, and drill string dose rates (Bell 1995a and 1995c). Video recordings or color photographs were taken of each segment immediately following extrusion and may be viewed by contacting program support personnel at the 222-S Laboratory.

The four segments from core 63 were extruded within one week of receipt by the laboratory. Segment 1 was composed completely of drainable liquid, segments 2 and 4 contained both drainable liquid and sludge, and segment 3 contained sludge only. The presence of a separable (presumably organic) layer floating on top of an aqueous layer was noted in the first two segments. The layers were separated, and a subsample of the aqueous layer was submitted for analysis. At the time of extrusion, the drainable liquid from segment 2 appeared to be one phase. It was not until subsampling the following week that a possible separable organic layer was discovered, presumably after the layers had time to settle and separate. Even after separation, the two layers were difficult to distinguish because of similarities in color and densities (Bell 1995a). What appeared to be an organic layer may have been fine solids that had settled out with time. Small amounts of liner liquid (5 mL or less) were collected from each segment; no analyses were performed.

All four segments from core 66 were extruded on February 27, 1995. Segments 1 and 2 were composed entirely of drainable liquid, while segments 3 and 4 contained drainable liquid and sludge. The organic layer was separated and archived, while a subsample of the aqueous layer was submitted for analysis. An anomaly was observed during the extrusion of segment 4. Although the sampler valve was closed prior to extrusion, 125 grams of olive-green liner liquid were collected. Neither this liner liquid nor the minor amounts of liner liquid from segments 1 and 3 were analyzed.

Segment subsampling was performed as directed in Schreiber (1995 and 1994). Figure 3-1 shows the sampling and analysis scheme for the sludge from core samples, and Figure 3-2 shows the sampling and analysis scheme for the core sample drainable liquid. Any aqueous layer recovered was separated from the sludge to form a subsegment. The sludge segments 2 and 3 from core 63 were separated into equal subsegments and designated as upper and lower half subsamples. Segment 4 from core 63 and segments 3 and 4 from core 66 were not split but were designated the "upper half" subsample. Each subsample was homogenized before aliquots were removed for analysis. A homogenization test was performed on the upper half subsample from segment 4 of core 63. In this test, the subsample was homogenized then two aliquots were taken from different locations and analyzed in replicate for several metals (see Section 5.1.3.2). Material was then removed from each sludge subsample and aqueous layer subsample for analysis and archiving. Sludge core composites for the pretreatment and process development work were made by combining portions of the half segments. Likewise, aqueous layer composites were made for each core.

Table 3-1. Tank 241-C-103 Sampling Summary. (2 sheets)

Segment	Sample Type	Amount Recovered	Percent Recovery	Drill String Dose Rate (mR/hr)	Description
Core 63 (Riser 2)					
1	Drain. liquid	225.8 g (220 mL)	71%	220	Entirely drainable liquid. A dark brown organic layer floated on a light brown aqueous layer. The organic layer was roughly 20 mL. About 5 mL of liner liquid were gathered.
2	Drain. liquid	173.62 g (150 mL)	95%	1,600	Drainable liquid was dark brown and may have contained organic and aqueous layers. 2 mL of liner liquid were recovered.
	Sludge	160.3 g			Dark brown, moist sludge with a smooth consistency.
3	Sludge	405.6 g	100%	2,400	Completely soft, dark brown sludge that was moist with a crumbly consistency. After being split into half segments, the lower half portion appeared to be slightly drier with some pitting on its surface. 4 mL of liner liquid were obtained.
4	Drain. liquid	73.06 g (60 mL)	84%	800	Drainable liquid was dark brown. Roughly 7 g of liner liquid were collected.
	Sludge	236.3 g			Sludge was moist and dark brown on the outside. The interior was cream-colored and somewhat drier than the dark material.

Table 3-1. Tank 241-C-103 Sampling Summary. (2 sheets)

Segment	Sample Type	Amount Recovered	Percent Recovery	Drill String Dose Rate (mR/hr)	Description
Core 66 (Riser 7)					
1	Drain. liquid	195.55 g (200 mL)	100%	250	Entirely drainable liquid. A separable dark brown organic layer floated on top of a light brown aqueous layer. Organic layer was roughly 25 mL. 11.85 mL of liner liquid were collected.
2	Drain. liquid	330.36 g (310 mL)	100%	270	Drainable liquid was light brown. No organic material was visible. No liner liquid was collected.
3	Drain. liquid	280.19 g (240 mL)	95%	900	Drainable liquid was dark brown with no organic material visible. 4.85 g of liner liquid were recovered.
	Sludge	43.66 g			Sludge was soft and dark brown.
4	Drain. liquid	89.80 g (85 mL)	80%	900	Drainable liquid was medium to dark brown in color. Although the sampler valves were closed upon extrusion, 135 mL of olive green liner liquid was collected.
	Sludge	58.24 g			Sludge was moist and dark brown.

Note:

Drain. = drainable

Figure 3-1. Sludge Sampling and Analysis Scheme.

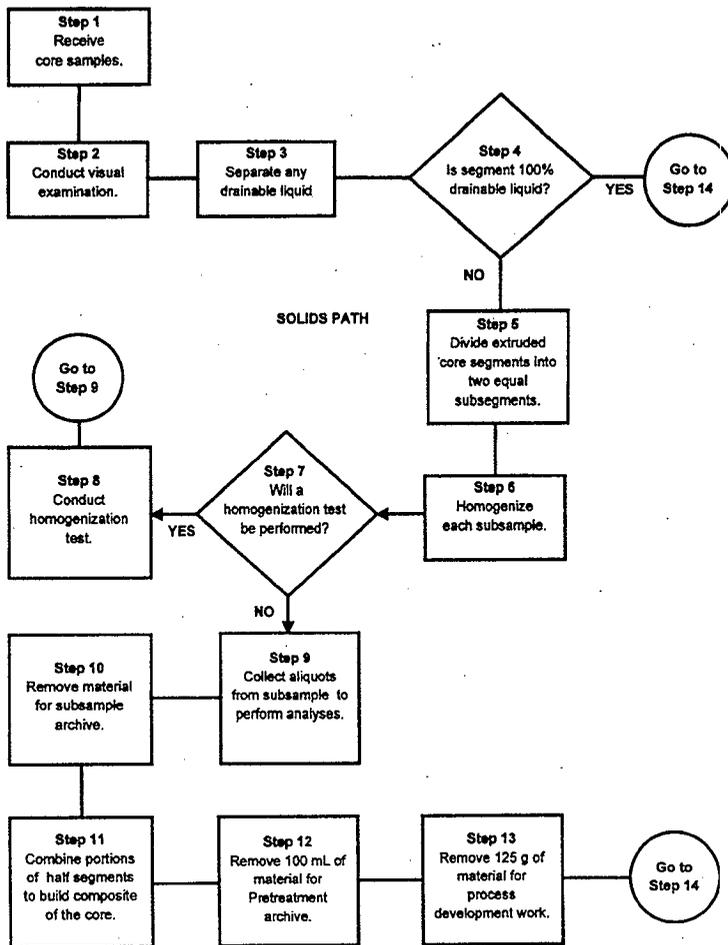
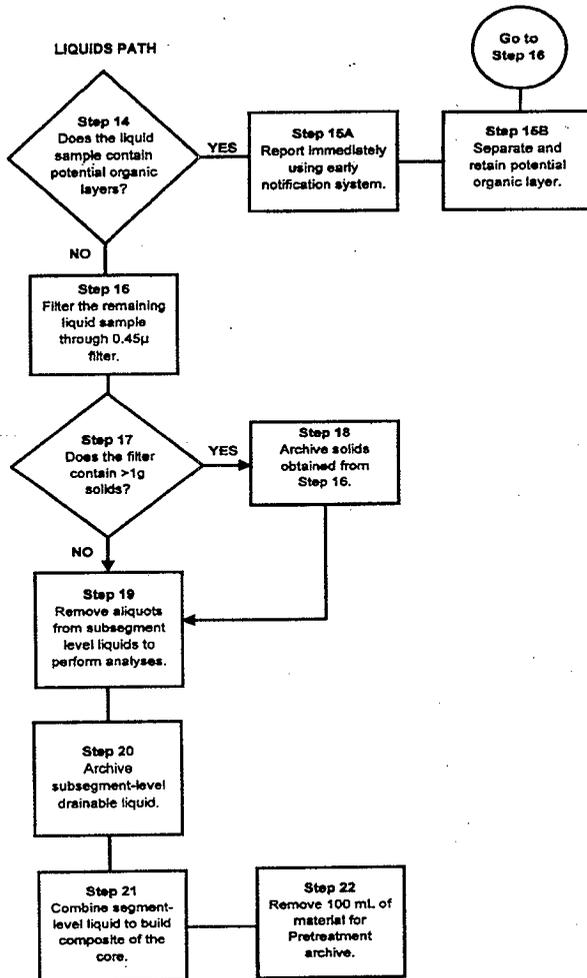


Figure 3-2. Drainable Liquid Sampling and Analysis Scheme.



As discussed in Schreiber (1995), the Pretreatment Program determined that it was no longer necessary to run all the analyses that they had required earlier. Consequently, it directed that only 100 mL of material from each of the sludge and aqueous layer composites be archived for program use. The program also requested archiving 125 mL of material from the sludge core composite for process development work.

Unique circumstances warranted special procedures for a majority of the core segments. Radiation levels for these segments were higher than those of typical tank waste samples; therefore, separate aliquots were taken from the sludge subsamples for direct analysis and fusion dissolution. This was an effort to reduce sample sizes and dose rates (Bell 1995a). For the same reason, two subsamples were removed for analysis from the drainable liquid for all segments except the first one in each core.

3.1.2 Sample Analysis

All analyses were performed on subsamples of the segments; no analyses were run on the composites. Drainable liquid subsamples were analyzed directly or after dilution in water or acid. Depending on the analysis sludge subsamples were analyzed directly or after a fusion or water digestion.

Initially, only the primary analyses listed in the safety screening and organic DQOs were performed. These analyses included TGA, DSC, total alpha activity, TOC, and a determination of the lithium content to gauge the amount of sample contamination by the hydrostatic head fluid. Because the analytical results from the primary analyses exceeded several action limits, secondary analyses for nitrite, nitrate, bromide, hydroxide, cyanide, and percent water (by gravimetry) were performed subsequently on selected samples. Because samples from this tank had very high dose rates, analyses for nitrate, nitrite, and hydroxide were only performed on the upper half of each sludge core sample to comply with the As Low As Reasonably Achievable principle (Bell 1995b). The analyses for hydroxide were performed on a water-digested aliquot of the sludge sample because a procedure for direct analysis on solid samples was not available. Smaller aliquots were taken for fusion dissolutions in an effort to reduce dose rates. This increased dilution factors which in turn raised detection limits (Bell 1995b).

During the bromide determination by ion chromatography (IC), additional analyses for sulfate, phosphate, fluoride, chloride, and oxalate were performed because they required minimal additional effort (Bell 1995c). Likewise, results for total inorganic carbon (TIC) were collected when obtaining the required TOC measurements. Radiochemical analyses were performed for ^{90}Sr and ^{137}Cs to better understand the nature of the radiological hazards associated with the core samples and to support shipment of samples to Pacific Northwest National Laboratory for waste pretreatment development work (Bell 1995c). Because ^{137}Cs was evaluated by gamma energy analysis (GEA), additional radionuclides analyzed by the same method were also obtained. These extra radionuclides included ^{154}Eu , ^{155}Eu , and ^{60}Co . The samples used for the radiochemical analyses were prepared using a potassium hydroxide fusion digestion in nickel crucibles. To perform the homogenization test on segment 4 of

core 63, aluminum, calcium, chromium, iron, sodium, zinc, and zirconium were determined by inductively coupled plasma (ICP) on similarly fusion-digested samples. Except for these samples used for the homogenization test, fusion digestions were performed in duplicate.

Table 3-2 provides analysis information on tank 241-C-103 samples. The table lists segments, sample type and number, and the analyses that were performed. Analytical procedures and procedure numbers are in Appendix D.

Table 3-2. Tank 241-C-103 Sample Analysis Summary. (2 sheets)

Segment	Sample Type	Sample Number	Analyses
Core 63 (Riser 2)			
1	Drainable liquid	S94T000200	TGA, DSC, TIC, TOC, Li, IC ¹
2	Drainable liquid	S95T000049	TGA, DSC, TIC, TOC, Li, IC
		S95T000112	TOC
	Sludge: upper half	S95T000045	TGA, DSC, TIC, TOC
		S95T000054	Total Alpha, GEA ² , ⁹⁰ Sr, Li
		S95T000872	IC, OH ⁻
		S95T000525	OH ⁻
	Sludge: lower half	S95T000038	TGA, DSC, TIC, TOC
		S95T000053	Total Alpha, GEA, ⁹⁰ Sr, Li
3	Sludge: upper half	S95T000047	TGA, DSC, TIC, TOC
		S95T000056	Total Alpha, GEA, ⁹⁰ Sr, Li
		S95T000871	IC, OH ⁻
		S95T000526	OH ⁻
	Sludge: lower half	S95T000046	TGA, DSC, TIC, TOC
		S95T000566	TGA, DSC
		S95T000055	Total Alpha, GEA, ⁹⁰ Sr, Li
		S95T000863	CN ⁻
4	Drainable liquid	S95T000052	TGA, DSC, TIC, TOC, IC
		S95T000051	IC, CN ⁻ , Li
	Sludge: upper half ³	S95T000048	TGA, DSC, TIC, TOC
		S95T000057	Total Alpha, GEA, ⁹⁰ Sr, Li
		S95T000094	ICP ⁴
		S95T000095	
		S95T000527	IC, OH ⁻
		S95T000887	Gravimetric

Table 3-2. Tank 241-C-103 Sample Analysis Summary. (2 sheets)

Segment	Sample Type	Sample Number	Analyses
Core 66 (Riser 7)			
1	Drainable liquid	S95T000218	TGA, DSC, TOC, Li, IC
2	Drainable liquid	S95T000214	TGA, DSC, TOC, IC
		S95T000217	Li
3	Drainable liquid	S95T000220	TGA, DSC, TOC, IC
		S95T000221	Li
	Sludge: upper half ³	S95T000224	TGA, DSC, TIC, TOC
		S95T000226	Total Alpha, Li
4	Drainable liquid	S95T000222	TGA, DSC, TOC, IC
		S95T000223	Li
	Sludge: upper half ³	S95T000225	TGA, DSC, TIC, TOC
		S95T000227	Total Alpha, Li
		S95T000529	IC, OH ⁴
Field blank	Drainable liquid	S95T000212	IC, TOC

Notes:

¹Ion chromatography included analyses for bromide, chloride, fluoride, nitrate, nitrite, oxalate, phosphate, and sulfate.

²Gamma energy analysis included analyses for ⁶⁰Co, ¹³⁷Cs, ¹⁵⁴Eu, and ¹⁵²Eu.

³Upper half: all sludge was combined into a single subsample and designated "upper half."

⁴Inductively coupled plasma included analyses for aluminum, calcium, chromium, iron, lithium, sodium, zinc, and zirconium.

3.2 DESCRIPTION OF 1993 GRAB SAMPLING EVENT

On December 15, 1993, seven grab samples were obtained from riser 7 of tank 241-C-103 using the "bottle-on-a-string" sampling technique. The samples were collected with 100-ml glass bottles. Six grab samples were taken at the waste surface (organic layer) and one was obtained approximately 60 centimeters below the surface (aqueous layer) (Huckaby 1994). No problems were documented.

Five organic layer samples and the single aqueous layer sample were delivered to Pacific Northwest National Laboratory for analysis. The sixth organic layer sample was sent to the 222-S Laboratory for adiabatic calorimetry testing. However, adiabatic calorimetry analyses were not performed, and the sample was archived. The sampling and analytical plan for the

1993 grab sampling event is outlined in the *Organic Layer Sampling for SST 241-C-103 Background, and Data Quality Objectives, and Analytical Plan* (Wood et al. 1993). The sampling and analytical results are published in *Waste Tank Organic Safety Project: Analysis of Liquid Samples from Hanford Waste Tank 241-C-103* (Pool and Bean 1994).

3.2.1 Sample Handling

The six grab samples (five organic and one aqueous) sent to Pacific Northwest National Laboratory were received in two shipments on December 15, 1993. Upon receipt, the samples were logged into the Pacific Northwest National Laboratory Analytical Chemistry Laboratory Information Management System. Laboratory tracking numbers were assigned as shown in Table 3-3 (Pool and Bean 1994). The six samples were unloaded in the ACL Shielded Analytical Laboratory hot cells. Each of the collection bottles was filled to capacity. All samples were red in color and appeared to be composed of a single phase. The organic samples were much darker in color than the aqueous sample (Pool and Bean 1994).

Table 3-3. Sample Identification Numbers for the 1993 Grab Samples.

Waste Layer	Laboratory Identification Number	Client Identification Number
Organic	94-02001	X-11
Organic	94-02002	X-12
Organic	94-02003	X-13
Organic	94-02004	X-14
Organic	94-02005	X-15
Aqueous	94-02006	X-17

3.2.2 Sample Analysis

The following sample breakdown discussion was taken from Pool and Bean (1994). Organic samples X-11, X-12, X-14, and X-15 were subsampled for flash point, GS/MS, total alpha, total beta, GEA, and Karl Fischer water determinations. Aliquots of samples X-11 and X-12 were sent to the Pacific Northwest National Laboratory High-Level Radiochemistry Facility for physical testing. Aliquots from samples X-14 and X-15 were water leached, with the resulting leachates underwent IC and ICP analyses. Aliquots from these samples were also leached with 2 percent nitric acid for ICP analysis. Reagent blanks were provided with each preparation type.

A subsample of the aqueous sample, X-17, was sent to the High-Level Radiochemistry Facility for physical testing. Water and nitric acid dilutions were performed for IC and ICP analyses, respectively. Duplicate pH determinations were done in the hot cell. The sample was analyzed remotely for hydroxide, total carbon, TOC, and TIC. Aliquots were taken for GEA, total alpha, total beta, volatile organic, headspace, and GC/MS analyses. Finally, DSC and TGA determinations were performed.

Analytical procedures and procedure numbers for the grab sample analysis are in Appendix D. Subsample identification information was unavailable.

3.3 DESCRIPTION OF 1994 VAPOR SAMPLING EVENT

Tank 241-C-103 headspace gas and vapors were characterized in a series of samplings from November 1993 to May 1994. The bulk of the data used in the characterization was derived from the May 1994 sampling event (Huckaby and Story 1994, Mahon et al. 1994). Selected data from three other sampling events, November 1993 (Huckaby 1993), December 1993 (Ligotke et al. 1994a), and April 1994 (Rasmussen and Einfeld 1994), have been incorporated when more recent data were not available. All headspace sampling events were governed by *Tank 241-C-103 Vapor and Gas Sampling DQOs* (Osborne et al. 1994). This information may also be used to support evaluation of flammability based on vapor composition as required by the safety screening DQO.

Headspace samples were removed from riser 7 between May 12 and 25, 1994 using the vapor sampling system. For detailed descriptions about the system, refer to DeFord (1993) and Mahon et al. (1994). Gases and vapors were drawn from the waste tank through the vapor sampling system by an air pump mounted on a mobile laboratory truck. The system used a heated sampling probe and heated sample transfer lines to transfer gases and vapors from the waste tank headspace to a heated sampling manifold inside the mobile laboratory (Huckaby and Story 1994). Mahon et al. (1994) describes the May 1994 sampling event in detail, including flow rates and flow durations for all samples, relevant meteorological and tank headspace temperature data, and chain-of-custody documentation.

Table 3-4 lists the laboratory responsible for the analysis of each respective device, the sampling devices, and the target analytes (Huckaby and Story 1994). Analytical methodology is also discussed in Huckaby and Story (1994). Because sampling and analysis of tank vapor was in the development stage, a quality assurance plan was not approved for vapor analyses performed by Oregon Graduate Institute of Science and Technology. However, the sampling and analysis data were subjected to a peer review (Story 1994) and the results were found to be acceptable.

Table 3-4. Sampling Devices and Targeted Analytes.

Laboratory	Sampling Device	Targeted Analytes
Oregon Graduate Institute of Science and Technology	SUMMA ¹ canister	Hydrogen, carbon monoxide, carbon dioxide, methane, and nitrous oxide; volatile organic vapors
Pacific Northwest National Laboratory	OSHA versatile sampler sorbent trap	Aerosol particles and semivolatile organic vapors
	Silica gel sorbent trap	Water vapor
	Acidified carbon sorbent trap	Ammonia
	Triethanolamine sorbent trap	Nitrogen dioxide
	Oxidation bed + triethanolamine sorbent trap	Nitric oxide
	Metal hydroxide-carbon sorbent trap	Sulfur dioxide and sulfur trioxide
	Hydrated calcium oxide-sodium hydroxide sorbent trap	Hydrogen cyanide
Oak Ridge National Laboratory	Triple sorbent trap	Organic vapors and gases
	Carbotrap/Carbotrap C ² traps	Tributyl phosphate and dibutyl butylphosphonate

Notes:

OSHA = Occupational Safety and Health Administration

¹SUMMA is a registered trademark of Moletrics, Inc., Cleveland, Ohio.

²Carbotrap and Carbotrap C are registered trademarks of Supleco, Bellefonte, Pennsylvania.

3.4 DESCRIPTION OF HISTORICAL SAMPLING EVENTS

Results from historical sampling events are compared with recent analytical results to corroborate data and to identify data trends. Because tank 241-C-103 was actively receiving waste until 1978, sampling events prior to this date no longer represent the current tank contents. Two historical sampling events have been identified for this tank: a grab sampling in 1990, and a core sampling in 1986.

Although the tank 241-C-103 headspace has been sampled extensively in the past, samples prior to 1992 should be used with caution because of poor sampling techniques (Huckaby and

Story 1994). For this reason, historical headspace sampling events prior to 1992 are not discussed in this report. Headspace sampling events between 1992 and those mentioned in this report are addressed in Huckaby and Story (1994).

Data from sampling and analysis events prior to 1990 may not be acceptable for some regulatory evaluations and decisions.

3.4.1 1990 Grab Sampling Event

Four grab samples were obtained from tank 241-C-103 in the second half of 1990 to measure of the chemical, radiochemical, and thermodynamic properties of the tank supernate (Edrington 1991). The sampling riser is not known. The samples were part of a comparison study between selected BY and C Farm tanks. Initially, two samples were taken, one each from the top and bottom of the supernate. Chemical, radiochemical, and thermodynamic (TGA and DSC) analyses were performed. The tank was resampled because the top layer did not contain any of the expected organic liquid. The only analyses run on the second set of samples were TGA and DSC, and they were run only on the top supernate sample. The analytical results from this sampling event are tabulated in Appendix B. Comparisons between this sampling event and the 1995 drainable liquid results are shown in Table 5-2.

3.4.2 1986 Core Sampling Event

Two core samples were taken in May 1986 from tank 241-C-103. The first core sample was obtained from riser 2; the second was obtained from riser 8. Each core sample consisted of four segments. Analyses were performed on drainable liquid and sludge core composites at the 222-S Laboratory, and the results were published in *Data Transmittal Package for 241-C-103 Waste Tank Characterization* (Weiss and Schull 1988). These results are tabulated in Appendix B, and comparisons between them and the 1995 core sampling results are shown in Section 5.2. Weiss and Schull (1988) also includes sample observations and sample breakdown and preparation procedures. In this sampling event NPH was used as a hydrostatic head fluid. Pre-May 1989 data may not be acceptable for some regulatory uses because adequate quality control information for the data is not available to assess data quality and permit confident decisions.

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4.0 ANALYTICAL RESULTS

This section provides the analytical results associated with the sampling of tank 241-C-103. All three sampling events used to characterize the tank waste (a core sampling in 1995, a vapor sampling in 1994, and a grab sampling in 1993) were governed by DQOs. Data locations for this document are shown in Table 4-1.

Table 4-1. Analytical Data Presentation Tables.

Sample Type	Table
Sludge chemical data summary	4-2
Sludge percent water results	4-3
Sludge DSC results	4-4
Aqueous layer chemical data summary	4-5
Aqueous layer headspace analysis	4-6
Aqueous layer percent water results	4-7
Aqueous layer DSC results	4-8
Organic layer analytical data	4-9 through 4-19
Vapor sample analytical data	4-20 through 4-36
1995 raw analytical data	Appendix A

4.1 SLUDGE ANALYTICAL RESULTS

The analytical results pertaining to the sludge are summarized in Section 4.1. The data were originally reported in three documents: *45-Day Safety Screen Results for Tank 241-C-103, Push-Mode Core Samples 63 and 66* (Bell 1995a); *90-Day Safety Screen Results for Tank 241-C-103, Push-Mode, Cores 63 and 66* (Bell 1995b); and *Final Report for Tank 241-C-103, Push-Mode Cores 63 and 66* (Bell 1995c).

Bell (1995a) reported the results of the safety screening primary analyses (TGA, DSC, and total alpha activity) for all eight segments (four from each core). Bell (1995b) reported the remaining primary analytical data required by the organics DQO (lithium and TOC) and results from certain secondary analyses. Secondary analyses for nitrite, nitrate, bromide, hydroxide, cyanide, and percent water (by gravimetry) were required because results from primary analyses had exceeded DQO-defined decision limits. Hydroxide, nitrite, and nitrate were analyzed because the energy equivalent of the TOC assay by the hot persulfate method (based on sodium acetate and nitrate reactions) was greater than 125 percent of any exotherm present (as determined by DSC). The bromide concentration was evaluated because the notification limit for lithium was exceeded on one of the duplicates from segment 4 of

core 66. Analyses for cyanide were performed because two DSC values exceeded the notification limit of -481 J/g . Finally, a percent water measurement by gravimetry was obtained on the upper half sludge from segment 4 of core 63 because the TGA water estimate was below 17 weight percent.

Bell (1995c) transmitted additional extrusion information and analytical data not provided in the earlier data packages. The extra analytes evaluated, TIC, sulfate, phosphate, fluoride, chloride, oxalate, ^{90}Sr , ^{137}Cs , ^{154}Eu , ^{155}Eu , and ^{60}Co , were not required by a DQO but were performed because they required little additional effort. The additional anions were measured during the collection of required bromide results; TIC results were obtained during the TOC measurement; and ^{154}Eu , ^{155}Eu , and ^{60}Co values were acquired during the gamma energy analysis for ^{137}Cs . Although not DQO driven, ^{90}Sr and ^{137}Cs were analyzed to better understand the high dose rates and radiological hazards associated with these samples and to support transfer of these samples for pretreatment research work at Pacific Northwest National Laboratory (Bell 1995c). The ICP analyses for aluminum, calcium, chromium, iron, sodium, zinc, and zirconium were also conducted for the homogenization test.

More discussion of DQO requirements and decision limits, including specific samples which exceeded thresholds, is provided in Section 5.5. The data from these reports are tabulated in Appendix A. Analyte composition means derived using the data from Appendix A are provided in Sections 4.1.1 and 4.2.1. Physical data about the sludge have been compiled in Section 4.1.2.

4.1.1 Chemical Data Summary

Table 4-2 shows overall composition means for all analytes measured in the sludge. The means reported are actually weighted means and were derived by determining a segment mean, such that each subsegment (if sampled) was weighted equally. Then, respective segment means from a given core were averaged so that a core mean was produced that gave equal emphasis to each of four segments in a core. Finally, an overall mean was determined by simply averaging the two core means. When results for greater than half of the samples for a given analyte were reported as less-than values, the overall mean was recorded as a less-than value. Conversely, when half or more samples had detected results, the overall mean was reported as a detected value. The less than value was included in the averaging. When results for analytes, such as metals, were not obtained for all segments, it is possible that biases in the mean estimates were introduced because of inaccurate weighting of the segments. For these analytes, the data from the 1986 core composite results may be a more accurate estimate of the average waste composition. However, this pre-1990 data may not be acceptable for some regulatory uses.

All information in Table 4-2 was taken from Appendix A, except the density value. The first two columns of Table 4-2 contain the analyte and overall mean. The third column, Relative Standard Deviation, displays the relative standard deviation (RSD) for the mean of all the results. The RSD is defined as the standard deviation of the mean divided by the mean and multiplied by 100. It is determined using standard analysis of variance statistical

techniques. The projected inventories listed in the final column were derived by multiplying the overall mean in $\mu\text{g/g}$ or $\mu\text{Ci/g}$ by the density and the sludge volume of 235,000 L. Density was not determined for sludge in the 1995 analysis. Consequently, the 1.34 g/mL density average measured on the 1986 core samples was estimated to be the sludge density, and it was used for all projected inventory calculations.

Table 4-2. Chemical Data Summary for the Sludge in Tank 241-C-103. (2 sheets)

Analyte	Overall Mean	Relative Standard Deviation (Mean)	Projected Inventory ¹
METALS	$\mu\text{g/g}$	%	kg
Aluminum	1.93E+05	0.1	60,800
Calcium	< 3,800	---	< 1,200
Chromium	970	5.9	305
Iron	15,800	9.2	4,980
Sodium	26,400	1.7	8,310
Zinc	824	23.8	259
Zirconium	11,400	9.4	3,590
ANIONS	$\mu\text{g/g}$	%	kg
Chloride	414	26.5	130
Cyanide	98.4	8	31.0
Fluoride	1,070	14.8	337
Hydroxide ²	< 26,300	---	< 8,280
Nitrate	1,730	36.6	545
Nitrite	17,600	49.1	5,540
Oxalate	2,710	28.7	853
Phosphate	3,240	12.9	1,020
Sulfate	2,790	28.3	879

Table 4-2. Chemical Data Summary for the Sludge in Tank 241-C-103. (2 sheets)

Analyte	Overall Mean	Relative Standard Deviation (Mean)	Projected Inventory ¹
RADIONUCLIDES	$\mu\text{Ci/g}$	%	Ci
¹³⁷ Cs	122	25.6	38,400
⁶⁰ Co	1.89	36.8	595
¹⁵⁴ Eu	10.6	40.9	3,340
¹⁵⁵ Eu	8.93	50.3	2,810
⁹⁰ Sr	4,190	39.4	1.32E+06
Total Alpha	9.74	23.6	3,070
CARBON	$\mu\text{g C/g}$	%	kg C
Total Inorganic Carbon	4,960	9.2	1,560
Total Organic Carbon	8,210	10.8	2,590
PHYSICAL PROPERTIES			
Density	1.34 ³ g/mL	---	n/a
Percent Water	57.7	34.9	

Notes:

n/a = not applicable

¹Projected sludge inventory estimates are derived using 1986 sludge density measurements.²The large < value was caused by the large dilution associated with the water leach. Thus, the hydroxide level was too low to be determined. However, pH measurements in the sludge and supernate layers from 1986 data indicate that the hydroxide concentration is very low.³Because density was not determined on the 1995 core samples, the average density value from the 1986 core samples, 1.34 grams per milliliter, was used as the sludge density value.**4.1.2 Physical Data Summary**

The sludge in tank 241-C-103 was evaluated for percent water by TGA and energetics by DSC. No other physical tests were requested or performed.

4.1.2.1 Thermogravimetric Analysis. During TGA, the mass of a sample is measured while its temperature is increased at a constant rate. Nitrogen is passed over the sample during heating to remove gaseous matter. Any decrease in sample weight represents a loss of gaseous matter from the sample through evaporation or through a reaction that forms gas

phase products. The moisture content is estimated by assuming that all TGA sample weight loss up to a certain temperature (typically 150 to 200 °C) is caused by water evaporation. Procedure LA-560-112, Rev. A-2 was used for the analysis.

TGA results for all samples but one were substantially higher than the 17 weight percent water limit required by the safety screening DQO. The exception was the upper half sample from segment 4 of core 63, which had a result of 13.47 percent. However, the duplicate measured 26.37 percent, which resulted in an average percent water of 19.92 for that sample. A third analysis was run on the sample because of the large relative percent difference (RPD) (64.8 percent) between the first two results. This analysis gave a result of 29.70 percent, which agreed with the duplicate value. It is also worth noting that this sample contained 73.06 g of drainable liquid out of a total 236.3 g of sample recovered. This represents an additional 18.9 weight percent water over that measured by TGA. Because the DQO notification limit had been exceeded, a secondary analysis for percent water by gravimetry was performed on this sample. The analysis was run twice yielding an average of 25.15 percent water. This compared favorably with the later TGA measurements on the sample. The gravimetric results for segment 4 of core 63 were included in the derivation of the percent water mean because this method uses a larger sample size and is subject to less sample heterogeneity problems.

Two other samples exhibited high RPDs between their original and duplicate results: the core 63 segment 3 lower half sample (35.3 percent) and the core 66 segment 3 upper half sample (13.5 percent). A rerun conducted on the core 63 segment 3 lower half sample gave a similar analytical result and a higher RPD (45.8 percent). Additional runs were not made on these samples because of the high dose rates and because results were well above the 17 weight percent water criteria. The large RPD values indicate sample heterogeneity and/or subsampling variability at the 15 to 30 milligram level, the sample size required for the TGA instrument (Bell 1995a).

Table 4-3 provides the sludge TGA data. All samples exhibited a large weight loss between ambient temperature and 150 °C. This weight loss is attributed to water vaporization. A second weight loss region with an approximate temperature range of 220 to 480 °C was displayed in TGA scans from the upper half sample of core 63 segment 4. This second endothermic reaction is not shown in Table 4-3 because it does not correspond to water loss. However, it can be observed in the raw data plots included in Bell (1995a).

Table 4-3. Sludge Percent Water Results for Tank 241-C-103.

Sample Number	Sample Location	Temperature Range	Result	Duplicate	Sample Mean	Overall Mean
		(°C)	% H ₂ O			
Thermogravimetric Analysis Results						
S94T000045	core 63 segment 2 upper ½	ambient to 150 (duplicate: ambient to 120)	63.09	61.30	62.20	57.7
S95T000038	core 63 segment 2 lower ½	ambient to 130 (duplicate: ambient to 150)	56.63	54.05	55.34	
S95T000047	core 63 segment 3 upper ½	ambient to 140	49.75	51.26	50.50	
S95T000046	core 63 segment 3 lower ½	ambient to 90 (duplicate: ambient to 130)	30.82	44.04	37.43	
S95T000566	core 63 segment 3 lower ½	scan was unavailable	43.23	27.20	35.21	
S95T000048	core 63 segment 4 upper ½	ambient to 70 (duplicate: ambient to 100)	13.47	26.37	19.92	
S95T000887 ¹	core 63 segment 4 upper ½	n/a	25.30 ¹	25.0 ¹	25.15 ¹	
S95T000224	core 66 segment 3 upper ½	ambient to 140 (duplicate: ambient to 90)	79.15	69.13	74.14	
S95T000225	Core 66 segment 4 upper ½	ambient to 130 (duplicate: ambient to 90)	76.46	73.49	74.97	
RSD (Mean) = 34.9						

Notes:

n/a = not applicable

¹Data based on gravimetric weight percent water measurement.

4.1.2.2 Differential Scanning Calorimetry. In a DSC analysis, heat absorbed or emitted by a substance is measured while the substance is exposed to a linear increase in temperature. Nitrogen is passed over the sample to remove any gases being released. The onset temperature for an endothermic or exothermic event is determined graphically.

The DSC analyses for tank 241-C-103 were performed using procedure LA-514-113, Rev. B-1 on a Mettler¹ DSC 20 instrument. Individual wet weight DSC exothermic values were converted to a dry weight basis using the respective sample average percent water as determined by TGA. This conversion is demonstrated in the following equation:

$$\text{Exotherm dry weight} = \frac{\text{exotherm wet weight}}{\left(1 - \frac{\% \text{ H}_2\text{O}}{100}\right)}$$

Although exothermic reactions were noted in samples from segments 2 and 3 of core 63, only one exceeded the safety screening DQO notification limit of -481 J/g on a dry weight basis. The wet weight result of -337.6 J/g for the lower half sample from segment 3 converted to -540 J/g dry weight. However, this result was from the duplicate run. The original run did not show an exothermic reaction. A rerun was not performed because of the sample's high dose rates (Bell 1995c). No exothermic behavior was found for core 66.

Table 4-4 shows the sludge DSC results. Exothermic reactions are denoted by a negative change in the enthalpy (ΔH) value.

4.1.3 Hydrostatic Head Fluid Contamination Check for the 1995 Sludge Results

Hydrostatic head fluid was used during the 1995 push-mode sampling event. Lithium bromide was added to the fluid as a tracer, and its presence in the core samples indicates contamination by the hydrostatic head fluid. Since hydrostatic head fluid is essentially water, the significance of contamination is the possibility of a high bias in the analytical percent water results. This check, through analyses for lithium and bromide, was prescribed by the Tank Characterization Plan (Schreiber 1995) that established notification limits of 100 $\mu\text{g/g}$ for lithium and 1,200 $\mu\text{g/g}$ for bromide.

The analytical results for lithium and bromide were not included in Table 4-2 because they are not inherent constituents of the tank waste. The only sludge subsample to have a lithium value over the notification limit was the duplicate for segment 4 of core 66, which had a result of 106.8 $\mu\text{g/g}$, although the mean was below the limit (98.94 $\mu\text{g/g}$). Confirming this, the only bromide results above the limit were from the same subsegment. Both sample and duplicate values were above the limit, with a mean of 1,710 $\mu\text{g/g}$. Utilizing lithium bromide correction calculations, the weight percent water value for this subsegment changed from the original 74.97 percent to 73.46 percent. This is a two percent difference and was

¹Mettler is a trademark of Mettler Instrument Corporation, Hightown, New Jersey.

statistically insignificant at the 0.05 confidence level (p -value = 0.553, see Section 5.3 for an explanation of p -values) using standard analysis of variance techniques. Because the affect on the overall weight percent water mean of 57.7 for the sludge would have been less than one percent, and all but one original percent water values were well above the safety screening criteria of 17 percent (Babad and Redus 1994), the corrections were not applied.

Table 4-4. Sludge Differential Scanning Calorimetry Results for Tank 241-C-103.

Sample Number	Sample Location	Run	Transition 1		Transition 2	
			Temp. range (°C)	ΔH (J/g) ¹	Temp. range (°C)	ΔH (J/g) ¹
S95T000045	core 63 ² segment 2 upper ½	1	ambient-160	1,190	220-440	-95.8 (-253)
		2	ambient-160	1,041	250-440	-119.4 (-316)
S95T000038	core 63 segment 2 lower ½	1	ambient-160	1,072	240-440	-97.3 (-218)
		2	ambient-160	1,162	270-450	-101.4 (-227)
S95T000047	core 63 segment 3 upper ½	1	ambient-160	751.9	---	---
		2	ambient-180	644.5	---	---
S95T000046	core 63 ² segment 3 lower ½	1	ambient-160	797.1	---	---
		2	ambient-160	922.0	210-470	-337.6 (-540)
S95T000048	core 63 segment 4 upper ½	1	ambient-140	521.5	220-330	495.3
		2	ambient-130	582.9	220-330	470.1
S95T000224	core 66 segment 3 upper half	1	ambient-140	1,276	---	---
		2	ambient-140	1,080	---	---
S95T000225	core 66 segment 4 upper ½	1	ambient-130	1,467	---	---
		2	ambient-130	1,439	---	---

Notes:

Temp. = temperature
() = dry weight values

¹Wet weight

²Analysis precision was outside the quality control limit (see Section 5.1.2 and Appendix A).

4.2 AQUEOUS LAYER ANALYTICAL RESULTS

This section summarizes the analytical results pertaining to the aqueous layer. Because the aqueous layer was obtained during the 1995 core sampling event, the results were reported in Bell (1995a, 1995b, and 1995c). As discussed in Section 3.1, there was a three-month delay in sampling between removing of the first segment from core 63 and the acquisition of the remaining segments. Segment 1 contained only aqueous and organic liquids. Because of this delay, the original safety screening analysis results for segment 1 were reported in the *45-Day Safety Screening for Tank C-103 Push-Mode Sample, Riser 2* (Bell 1994). The Bell data were later included in Bell (1995a). The raw data (see Section 4.1) have been tabulated in this document in Appendix A. Further discussion of DQO requirements and action limits is provided in Section 5.5. Section 4.2.1 summarizes the aqueous layer chemical data from Appendix A, and Section 4.2.2 provides relevant physical data.

All aqueous layer data for 1995 are reported in this section. Results from a 1993 sampling and analysis event are included if data from the 1995 event were not available for a particular analyte. One aqueous layer sample was recovered in the 1993 event (Pool and Bean 1994). The 1993 sampling event concentrated on characterizing the organic layer, and the organic results are discussed in Section 4.3. Applicable analytical results from the single aqueous sample are discussed in Section 4.2.1.

The total supernate volume currently in the tank is estimated to be $5.03E+05$ L (Hanlon 1995). This volume consists of an aqueous layer and an organic layer. To calculate projected inventory values for the waste in the tank, both the aqueous layer and organic layer volumes are needed. The organic layer volume is estimated from the amount of organic waste recovered from the 1995 core sampling event. Approximately 20 and 25 mL of organic layer waste were recovered from segment 1 of cores 63 and 66, respectively, yielding an average of 22.5 mL. This average organic volume recovered from the sampler can be converted to a thickness, knowing the sampler diameter (2.54 cm), as follows:

$$22.5 \text{ mL} \times \frac{1 \text{ cm}^3}{1 \text{ mL}} \times \frac{1}{\pi (1.27 \text{ cm})^2} = 4.44 \text{ cm}$$

Assuming this thickness represents the thickness of the tank organic layer, and knowing that 2.54 cm of tank waste is equivalent to a volume of 10,400 L, the tank organic layer volume can be estimated as follows:

$$4.44 \text{ cm} \times \frac{10,400 \text{ L}}{2.54 \text{ cm}} = 18,200 \text{ L}$$

The 4.44 cm organic layer thickness is consistent with the estimates of 3.8 cm to 5.1 cm made during sampling (Huckaby 1994). Because the total supernate volume estimate is $5.03E+05$ L and the organic layer volume estimate is 18,200 L, the remaining aqueous layer volume can be estimated to be $4.85E+05$ L.

4.2.1 Chemical Data Summary

Table 4-5 provides overall composition means for the aqueous layer analytes. For the 1995 results, means were derived using the same equal weighting method as that used in determining the sludge means: segment means were first calculated, then core means, and finally an overall mean. When results for greater than 50 percent of the samples for a given analyte were reported as less-than values, the overall mean was recorded as a less-than value. On the other hand, when 50 percent or more of the samples for a given analyte had detected results, the overall mean was reported as a detected value.

All data listed in Table 4-5 for the anions, TIC, TOC, and percent water are from Appendix A (1995 sampling event). The data for the other analytes are from the single grab sample obtained in 1993. Since the 1993 mean estimate is based on a single sample and a duplicate pair, the variability estimate given in column three for these analytes is actually an RPD rather than an RSD. The only exceptions were ^{137}Cs and ^{60}Co , which had RSDs determined. The projected inventories listed in the final column are derived by multiplying the overall mean in $\mu\text{g/mL}$ or $\mu\text{Ci/mL}$ by the aqueous layer volume, $4.85\text{E}+05\text{ L}$.

During the 1993 analysis, determinations of the extractable organic and volatile organic constituents of the aqueous phase were performed by GC/MS. The extractable organic components were removed from the aqueous sample using methylene chloride. The resulting solvent, bearing a sample of the organic substances contained by the aqueous layer, was subjected to the GC/MS gas analysis. The results showed that the major organic constituents of the aqueous phase were dibutyl butylphosphonate and tributyl phosphate, with average concentrations of $7\ \mu\text{g/mL}$ and $80\ \mu\text{g/mL}$, respectively. Normal paraffin hydrocarbon was found just above detection levels with an estimated concentration of 1 to $3\ \mu\text{g/mL}$.

To perform the GC/MS analysis on the aqueous phase for the volatile organic components, $40\ \mu\text{L}$ of sample were placed in a 2-mL vial and heated to 40, 70, and $100\ ^\circ\text{C}$. Then the vapors in the sample headspace were analyzed. The organic constituents of the headspace did not change appreciably as the temperature was elevated. The primary components of the headspace were NPH and related species and TBP. Table 4-6 shows the results of the aqueous phase headspace analysis.

Table 4-5. Chemical Data Summary for the Aqueous Layer
in Tank 241-C-103. (2 sheets)

Analyte	Overall Mean	RSD (Mean)	Projected Inventory
METALS	µg/mL	%	kg
Calcium ¹	5.38	100	2.61
Cadmium ¹	0.861	50	0.418
Chromium ¹	57.0	11	27.6
Iron ¹	3.23	0	1.57
Molybdenum ¹	10.8	0	5.24
Nickel ¹	72.1	10	35.0
Phosphorus ¹	2,350	21	1,230
Potassium ¹	323	0	157
Silver ¹	11.8	0	5.72
Sodium ¹	32,700	10	15,900
Uranium ¹	2,100	15	1,020
Zirconium ¹	301	14	146
ANIONS	µg/mL	%	kg
Chloride	404	6.4	196
Cyanide	26.9	2	13.0
Fluoride	1,160	6.7	563
Nitrate	2,140	14.3	1,040
Nitrite	21,200	12.9	10,300
Oxalate	3,210	7.1	1,560
Phosphate	2,250	13.1	1,090
Sulfate	3,220	3.87	1,560
RADIONUCLIDES	µCi/mL	%	Ci
¹³⁷ Cs ¹	57.9	0.43	28,100
⁶⁰ Co ¹	0.0511	1.37	24.8
Total Alpha ¹	0.0435	---	21.1
Total Beta ¹	70.6	---	34,200

Table 4-5. Chemical Data Summary for the Aqueous Layer in Tank 241-C-103. (2 sheets)

Analyte	Overall Mean	RSD (Mean)	Projected Inventory
CARBON	$\mu\text{g C/mL}$	%	kg C
Total Inorganic Carbon	6,850	9.6	3,320
Total Organic Carbon	6,640	5.9	3,220
PHYSICAL PROPERTIES			
Density at 44 °C ¹	1.076 g/mL	---	n/a
Percent Water	86.2%	2.2	n/a
pH ¹	10.0	---	n/a

Notes:

n/a = not applicable

¹The results for these analytes were taken from the 1993 sampling event data. A RPD between the initial and duplicate runs was calculated instead of a RSD.

Table 4-6. 1993 Aqueous Sample Headspace Analysis.¹

Component	Concentration at 40 °C (mg/L)	Concentration at 70 °C (mg/L)	Concentration at 100 °C (mg/L)
Tridecane	0.001	0.002	0.02
Tetradecane	0.001	0.01	0.01
Dibutyl butylphosphonate	---	0.002	0.01
Tributyl phosphate	0.004	0.07	0.24

Note:

¹Pool and Bean (1994)

4.2.2 Physical Data Summary

As a part of the 1995 sampling event, TGA and DSC were performed on aqueous layer samples. In addition, a viscosity determination was done during the 1993 sampling event.

4.2.2.1 Thermogravimetric Analysis. The TGA on the aqueous layer samples was performed using the same procedure that was used on sludge samples. Results were well above the safety screening DQO notification limit of 17 weight percent, ranging from 80 to 90 percent. The overall mean was determined in the same manner as the chemical data means.

The segment means were averaged to form a core mean, and each segment had equal weight. Then the two core means were averaged. Table 4-7 shows the aqueous layer TGA results.

Table 4-7. Aqueous Layer Thermogravimetric Analysis Results for Tank 241-C-103.

Sample Number	Sample Location	Temperature Range	Result	Duplicate	Sample Mean	Overall Mean
		(°C)	% H ₂ O			
S94T000200	core 63 segment 1	Ambient to 100 (duplicate: ambient to 120)	88.29	88.57	88.43	86.2
S95T000049	core 63 segment 2	Ambient to 100	81.66	87.30	84.48	
S95T000052	core 63 segment 4	Ambient to 280 (duplicate: ambient to 110)	82.12	77.85	79.98	
S95T000218	core 66 segment 1	Ambient to 110	87.79	88.10	87.94	
S95T000214	core 66 segment 2	Ambient to 100	87.86	87.28	87.57	
S95T000220	core 66 segment 3	Ambient to 100	87.47	86.99	87.23	
S95T000222	Core 66; segment 4	Ambient to 140	89.50	89.38	89.44	
RSD (Mean) = 2.2						

4.2.2.2 Differential Scanning Calorimetry. As with the sludge, DSC analyses for tank 241-C-103 liquid were performed using procedure LA-514-113, Rev. B-1 on a Mettler™ DSC 20 instrument. Only segment 4 of core 63 exhibited exothermic behavior. The initial and duplicate runs gave exothermic reactions of -156.8 and -52.7 J/g, respectively. Converting these wet weight results into dry weight values using the equation in Section 4.1.2.2 yielded -784 and -263 J/g for an average of -523 J/g. A third run was performed, and the wet weight result of -46.2 J/g was consistent with the duplicate result. The -784 J/g sample result exceeded the -481 J/g safety screening limit (dry weight basis).

Table 4-8 displays the aqueous layer DSC results. Exothermic reactions are denoted by a negative change in enthalpy (ΔH) value. Only one transition range was observed for all samples except for the core 63 segment 4 sample, which displayed three transitions. The second transition for that sample is not shown in Table 4-8. The transition was endothermic, with an enthalpy value of 56.9 J/g for the original run, 19.7 J/g for the duplicate, and 10.6 J/g for the third run.

Table 4-8. Aqueous Layer Differential Scanning Calorimetry Results for Tank 241-C-103.

Sample Number	Sample Location	Run	Transition 1		Transition 3	
			Temp. range (°C)	ΔH (J/g)	Temp. range (°C)	ΔH ¹ (J/g)
S94T000200	core 63 segment 1	1	ambient-140	1,538	---	---
		2	ambient-150	1,631	---	---
S95T000049	core 63 segment 2	1	ambient-140	1,559	---	---
		2	ambient-140	1,323	---	---
S95T000052	core 63 ² segment 4	1	ambient-140	1,128	300-430	-156.8 (-784)
		2	ambient-140	1,547	280-400	-52.7 (-263)
		3	ambient-140	1,331	280-380	-46.2 (-231)
S95T000218	core 66 segment 1	1	ambient-140	1,653	---	---
		2	ambient-140	1,390	---	---
S95T000214	core 66 segment 2	1	ambient-140	1,532	---	---
		2	ambient-140	1,587	---	---
S95T000220	core 66 segment 3	1	ambient-140	1,579	---	---
		2	ambient-140	1,523	---	---
S95T000222	core 66 segment 4	1	ambient-140	1,214	---	---
		2	ambient-140	1,264	---	---

Notes:

Temp. = temperature
 () = dry weight values

¹Based on wet weight

²Analysis precision was outside the quality control limit (see Section 5.1.2 and Appendix A).

4.2.2.3 Viscosity. A viscosity determination was made on the aqueous layer sample obtained in 1993 (Pool and Bean 1994). The viscosity analysis was performed according to procedure PNL-ALO-502, using a Bohlin² CS viscometer modified for glovebox operation. Shear stress as a function of shear rate was obtained by measuring the shear stress produced at a specific shear rate; then viscosity as a function of shear rate was calculated from the data.

The viscosity of the aqueous sample increased as the shear rate increased. At 25 °C, the viscosity of the aqueous layer increased from 1.5 to 4.5 centipoise over the shear rate range from 25 to 500 second⁻¹ (s⁻¹). At 40 °C, the viscosity of the sample exhibited essentially Newtonian behavior with a viscosity of between 1.5 and 2 centipoise over a shear rate range from 25 to 200 s⁻¹. Higher shear rate ranges could not be achieved at this temperature because of the low viscosity of the sample.

4.2.3 Hydrostatic Head Fluid Contamination Check for the 1995 Aqueous Results

Hydrostatic head fluid was used in the 1995 push-mode sampling event. The possibility of a high bias in the analytical percent water results was investigated for the aqueous results. This check, through analyses for lithium and bromide, was prescribed by the Tank Characterization Plan (Schreiber 1995) which established notification limits of 100 µg/ml for lithium and 1,200 µg/ml for bromide.

As with sludge results, the only aqueous subsample to have a lithium and/or bromide value over the notification limit was the subsample for segment 4 of core 66. The mean result for lithium was 225 µg/ml, and the mean result for bromide was 2,820 µg/ml. Using lithium bromide correction calculations, the percent water value for this subsegment changed from the 89.44 percent to 88.54 percent. The difference between the corrected and uncorrected results was one percent, and this was found to be statistically significant at the 0.05 confidence level (p-value = 0.009; see Section 5.3 for an explanation of p-values). Because the affect on the overall percent water mean for the aqueous portion would have been less than one percent, and all original percent water values were well above the safety screening criteria of 17 percent (Babad and Redus 1994), the correction was not applied.

4.3 ORGANIC LAYER ANALYSIS BY PACIFIC NORTHWEST NATIONAL LABORATORY

Tank 241-C-103 was grab sampled in December of 1993 to satisfy the requirements listed in Appendix B of Wood et al. (1993). Five samples of the organic layer and one sample of the underlying aqueous layer were obtained. The organic samples were analyzed for flash point, GC/MS, total alpha, total beta, GEA, and Karl Fischer water determinations.

²Bohlin is a trademark of Bohlin Instruments, Inc., Cranbury, New Jersey.

Table 4-9 lists the analytes for which an inventory estimate could be calculated. The inventory was based on an estimated organic layer volume of 18,200 L (see Section 4.2 for organic layer volume derivation) and a density of 0.868 g/mL. Where more than one analytical or digestion method was used to analyze a waste component, the higher value was used to calculate the inventory. Where duplicate results were reported, an average was calculated. Relative standard deviations are presented in the table when available.

Table 4-9. Summary of Inventory Estimates of Organic Layer.¹ (2 sheets)

Analyte	Concentration	Relative Standard Deviation	Inventory Estimate
Organic Compounds	μg/g	%	kg
NPH	3.33E+05	Not reported	5,260
TBP	6.4E+05	Not reported	10,100
DBBP	26,000	Not reported	411
Radionuclides	μCi/g	%	Ci
Gross Alpha	5.47E-04	Not reported	0.00864
Gross Beta	1.05	Not reported	16.6
²⁴¹ Am	2.11E-04	6.9	0.00333
⁶⁰ Co	7.45E-04	1.6	0.0118
¹³⁷ Cs	0.0413	2.4	0.652
¹⁵⁴ Eu	3.17E-04	2.3	0.00501
¹⁵⁵ Eu	3.15E-04	4.4	0.00498
²³⁸ Pu	9.02E-05	6	0.00142
^{239/240} Pu	1.94E-04	3	0.00306
⁹⁰ Sr	0.546	Not reported	8.61
Metals	μg/g	%	kg
Ag	0.9	0	0.0142
Al	1.8	29	0.0284
B	1.4	69	0.0221
Ca	2.0	0	0.0316
Cd	2.1	0	0.0332
Cu	2.2	3	0.0348
Fe	0.33	15	0.00521
K	23	25	0.363

Table 4-9. Summary of Inventory Estimates of Organic Layer.¹ (2 sheets)

Analyte	Concentration	Relative Standard Deviation	Inventory Estimate
Metals (Continued)	µg/g	%	kg
Na	70	3	1.11
Ni	9.9	8	0.156
P	605	6	9.56
Other	µg NH₃/g	%	kg
Ammonia	24.0	Not reported	0.379

Note:

¹Pool and Bean (1994)

4.3.1 Flash Point of Organic Layer

Flash point analyses were performed using an International Standards Organization 9001 quality certified Grabner Instruments CCA-FLP Miniflash Flash Point Tester Instrument. An n-dodecane standard was supplied by PETROLAB Corporation. The check standard was used before and after all analyses as a performance check.

Flash points of the samples were obtained by successively heating the samples beginning at a temperature estimated to be close to, but less than, the flash point of the sample, until a flash occurred. Additional portions of the same sample then were heated at successively lower temperatures, beginning at a temperature greater than the flash point obtained in the first stage of the analysis, until no flash occurred. The flash point results are expressed as means of the highest nonflash number and the lowest flash temperature rounded up to the nearest whole number. Results of the flash point test are shown in Table 4-10. The n-dodecane standard, certified at 84.4 ± 1 °C, exhibited a flash point of 85 °C showing that the results of the flash point test were accurate within the range of the standard. The flash point of the organic layer agrees with the expected flash point of a 70 percent TBP/30 percent NPH mixture.

Table 4-10. Flash Point Measurements of 241-C-103 Organic Layer.¹

Sample	No Flash Temperature (°C)	Flash Temperature (°C)	Approximate Flash Point (°C)
X-11	116	118	117
X-12	118	120	119
X-14	118	119	118
X-15	118	121	119
Mean Value = 118			

Note:

¹Pool and Bean (1994)

4.3.2 Gas Chromatography/Mass Spectroscopy of Organic Layer

Each of four samples was diluted 10,000X with methylene chloride prior to analysis by GC/MS. The DBBP and TBP standards were used for quality control. The results of the analyses are shown in Tables 4-11 and 4-12. Results are not reported for specific samples; however, similar results were shown by all four organic samples. The "weight percent" column in Table 4-11 reports the weight percent of the particular component in relation to the total amount of carbon expected in the sample. The "relative weight percent" column reports the weight of the component in relation to the weight of the sample. Not all components are named precisely because of the difficulty and expense of distinguishing one alkane from another. However, components with attached functional groups such as nitrile are identified. Table 4-12 shows the concentrations of tentatively identified compounds found in the headspace above the samples at various temperatures.

A 5 μ L sample of the organic layer was examined for inorganic species using a scanning electron microscope. The results, which are semiquantitative because of incomplete sample transfer, showed concentrations of 8,950 ppm and 75,100 ppm for silicon and phosphorus, respectively. Other inorganic species included sulfur, nickel, calcium, chromium, and titanium.

Table 4-11. Components of Organic Layer as Determined by Gas Chromatography/Mass Spectroscopy.¹

Component	Retention Time (minutes)	Weight Percent ²	Relative Weight Percent ³
Dodecane	10.51	2.8	3.8
Alkane	10.74	0.2	0.3
Alkane	11.85	1.1	1.5
Tridecane	12.38	11.4	15.5
Alkane	13.23	0.5	0.6
Alkane	13.72	1.0	1.3
Tetradecane	14.17	6.0	8.1
Alkane	15.17	0.7	1.0
Pentadecane	15.84	0.9	1.2
Total Alkane	n/a	24.6	33.4
DBBP	17.60	1.9	2.6
TBP	18.09	47.2	64.0
Total		73.7	100.0

Note:

n/a = not applicable

¹Pool and Bean (1994)²Weight percent of component relative to total amount of carbon³Weight percent of component relative to the weight of sample

Table 4-12. Concentrations of Tentatively Identified Compounds Found in Headspace of Organic Fraction.¹ (2 sheets)

Component	Retention Time (minutes)	Concentration (mg/L)		
		40 °C	70 °C	100 °C
Hexanenitrile	7.494	---	0.01	0.06
Ketone	7.983	---	0.02	0.17
Alkane	8.461	---	0.01	0.10
Ketone	10.206	---	0.01	0.12
Heptanenitrile	10.923	---	0.02	0.10
Branched Alkane	11.235	---	0.01	0.14
Decane	11.525	---	0.02	0.12
Alkane	11.609	---	0.01	0.06
Branched Alkane	12.087	---	0.01	0.03
Octanenitrile	13.459	---	0.01	0.04
Undecane	13.887	0.06	0.22	1.46
Branched Alkane	15.031	---	0.06	0.18
Branched Alkane	15.250	---	0.03	0.32
Branched Alkane	15.375	---	0.02	0.17
Alkane	15.75	---	0.07	0.18
Ketone	15.769	---	---	0.76
Dodecane	15.95	0.32	2.4	13.8
Alkane	16.185	0.05	0.32	2.2
Alkane	16.77	---	0.13	0.72
Alkane	17.28	0.08	0.62	3.6
Alkane	17.662	---	---	0.12
Tridecane	17.87	0.46	4.2	18.2
Alkane	18.101	---	0.10	0.64
Alkane	19.09	0.07	0.36	0.64
Tetradecane	19.51	0.22	1.2	6.4
Alkane	20.47	0.03	0.11	0.68
Pentadecane	21.10	0.02	0.12	0.70

Table 4-12. Concentrations of Tentatively Identified Compounds Found in Headspace of Organic Fraction.¹ (2 sheets)

Component	Retention Time (minutes)	Concentration (mg/L)		
		40 °C	70 °C	100 °C
DBBP	22.72	0.01	0.04	0.58
TBP	23.20	0.14	0.78	8.4

Notes:

¹Pool and Bean (1994)²Dashes indicate compound was not detected.**4.3.3 Infrared Analysis of Organic Layer for Nitroalkanes**

Sample numbers X-11 and X-12 were analyzed and compared to waste simulants by Fourier transform infrared spectroscopy for nitroalkanes. Infrared absorption bands characteristic of primary and secondary nitroalkanes were not observed. However, absorption bands that could be assigned to nitro-organic complexes were observed. The upper band of nitroalkane concentration was determined to be 0.01 weight percent or 2 micromole nitroalkane per gram.

4.3.4 Physical Properties of Organic Layer

4.3.4.1 Viscosity. At 25 °C, the viscosity of the organic sample was approximately 4 centipoise over a shear rate range from 25 s⁻¹ to 300 s⁻¹. The viscosity dropped slightly when the temperature was increased to 40 °C (2.5 centipoise over the same shear rate range). The organic layer sample viscosity was found to be Newtonian over the shear rate range.

4.3.4.2 Density. The densities of the organic samples were calculated from measured masses of specific volumes of the sample at 25 °C and at 44 °C. The samples were placed in tared 10-mL volumetric flasks. The mass of the sample was then determined using a Mettler™ balance. The samples were held at 40 °C for one hour prior to measuring the density at 44 °C. The density of the waste sample was 0.876 g/mL at 25 °C, and 0.868 g/mL at 44 °C. The difference is statistically significant. Organic layer inventory values provided in this report were calculated using the density measured at 44 °C because this temperature is more representative of the current tank waste temperature.

4.3.4.3 Water Content. The water content of the organic layer samples was determined by Karl Fischer coulometric titration. Quality control procedures included a blank, a certified standard in duplicate, and triplicate analyses for all samples. The blanks before and after analysis were zero, and recoveries for the standards ranged between 97.6 and 99.1 percent. The results of the water content analyses are shown in Table 4-13.

Table 4-13. Water Content of Organic Layer Samples.¹

Sample Number	Weight Percent Water	Standard Deviation
X-11	1.32	0.01
X-12	1.31	0.02
X-14	1.24	0.003
X-15	1.38	0.02
Grand average	1.31	0.06

Note:

¹Pool and Bean (1994)

4.3.5 Radiochemistry of Organic Layer

The analytical plan for tank 241-C-103 called for a phased approach to the radiochemical analyses of the organic layer. Initial measurements of gross alpha, gross beta, and gamma energy analysis were performed to determine the necessity for performing more extensive analyses. If threshold activities (Wood et al. 1993) for gross alpha and gross beta were exceeded, further investigations were to be scheduled. The threshold for gross alpha was exceeded by a factor of 50; for gross beta by a factor of 40.

4.3.5.1 Gross Alpha and Gross Beta. Four organic samples (X-11, X-12, X-14, and X-15) were analyzed for gross alpha and gross beta. The analyses were run in one batch for each analyte. Each batch included a sample duplicate, method blank, and a blank spike. The method blank and the blank spike were prepared with a simulated waste matrix. The aliquots were 0.044 g which corresponds to a volume of 0.051 mL. The samples were weighed onto a planchet, evaporated to dryness, and counted on a gas proportional counter for the gross beta analysis and on a zinc sulfide scintillation counter for the gross alpha analysis. The residual solids were less than 1 mg. Gross beta and gross alpha activities were identical for all four samples. The standard deviations of the samples were all within the precision of the methods, the activities were well above the threshold activities. Activities in the method blanks were well below the activities of the samples; therefore, background was not a factor. The blank spike recoveries were 108 percent and 107 percent for the alpha and beta analyses, respectively, indicating a slight upward bias on the results.

The gross alpha detector is calibrated with ²³⁹Pu (an alpha emitter), and the gross beta detector is calibrated with ⁹⁰Sr/⁹⁰Y (both beta emitters). Other alpha or beta emitters in a sample could have different counting efficiencies. For this reason, Pool and Bean (1994) caution that the total alpha and beta results found in their report should be considered qualitative. Table 4-14 shows the results of the gross alpha and gross beta analyses.

Table 4-14. Gross Alpha and Gross Beta Activities of Organic Layer.¹

Analyte	Average Result ($\mu\text{Ci/g}$)	Threshold Level ($\mu\text{Ci/g}$)	Factor Above Threshold
Gross Alpha Activity	$5.47\text{E-}04 \pm 2.2\text{E-}05^2$	1.1E-05	50
Gross Beta Activity	$1.05 \pm 3.7\text{E-}02^2$	2.7E-02	40

Note:

¹Pool and Bean (1994)

²Propagated error estimates from counting and analysis

4.3.5.2 Gamma Energy Analysis. Gamma energy analysis was performed on four of the organic waste samples (X-11, X-12, X-14, and X-15) using 10-mL aliquots. The results for each radionuclide shown in Table 4-15 are an average of all four samples, plus the duplicate which was performed on sample X-11. The data suggest that the samples come from a homogeneous source. The values in the table were corrected for radioactive decay to January 1, 1993.

Table 4-15. Gamma Energy Analysis of Organic Layer.¹

Radionuclide	Activity ($\mu\text{Ci/g}$)	Relative Standard Deviation (%)
⁶⁰ Co	7.45E-04	1.6
¹³⁷ Cs	4.13E-02	2.4
¹⁵⁴ Eu	3.17E-04	2.3
¹⁵⁵ Eu	3.15E-04	4.4
²⁴¹ Am	2.11E-04	6.9

Note:

¹Pool and Bean (1994)

4.3.5.3 Radioisotope Analysis. The four organic samples (X-11, X-12, X-14, and X-15) were subsampled for radioisotopic analysis. Aliquots of 0.44 g or 0.051 mL, nominal, were obtained. Each analytical batch included a sample duplicate, method blank, and method blank spike. The method blank and method blank spike were prepared with a simulated organic matrix. The organic matrix of the samples was destroyed prior to commencing the analytical procedures. The ⁹⁰Sr activity was separated and determined by gas proportional counter; the alpha activities (Pu and Am isotopes) were separated and determined by alpha energy analysis. All samples exhibited nearly identical results for the ⁹⁰Sr analysis, averaging 0.545 $\mu\text{Ci/g}$. The ⁹⁰Sr activity accounts for about half of the gross beta activity; ⁹⁰Y, which exists in secular equilibrium with ⁹⁰Sr, accounts for most of the remaining half.

Table 4-16 shows the average values of the radioisotopic analysis of the alpha-emitting isotopes. The total, 4.63E-04 $\mu\text{Ci/g}$, represents approximately 85 percent of the total alpha activity. The difference may be attributed to the presence of other alpha emitting isotopes and errors associated with the measurements.

Table 4-16. Activities of Alpha-emitting Radionuclides.¹

Radionuclide	Average Activity ($\mu\text{Ci/g}$)	Relative Standard Deviation (%)
²³⁸ Pu	9.02E-05	6
^{239/240} Pu	1.94E-04	3
²⁴¹ Am	1.79E-04	2
Total	4.63E-04	---

Note:

¹Pool and Bean (1994)

4.3.6 Inorganic Analyses of the Organic Layer

The analytical plan, as outlined in Wood et al. (1993), called for inorganic analysis of the organic phase if the water content was above one percent. As discussed in Section 4.3.4.3, the water content was 1.31 percent. Analytical procedures for anions, cations, and ammonia were performed. Anions were measured by IC, cations by ICP spectrometry, and ammonia by ion selective electrode. The IC was performed using 100:1 water to organic sample volume, and the ICP was performed using 10:1 water to organic sample volume and a 10:1 2 percent HNO₃ extraction. The results of the inorganic analyses are shown in Tables 4-17 through 4-19.

Table 4-17. Ion Chromatographic Analysis of Organic Layer.¹

Anion	Sample Number X-14 ($\mu\text{g/mL}$)	Sample Number X-15 ($\mu\text{g/mL}$)
F ⁻	< 26, < 24	< 23, < 24
Cl ⁻	< 26, < 24	< 23, < 24
NO ₂ ⁻	< 51, < 47	< 47, < 49
NO ₃ ⁻	< 51, < 47	< 47, < 49
SO ₄ ²⁻	< 51, < 47	< 47, < 49

Notes:

All results were less than the detection limit ("<" denotes result below the detection limit)

¹Pool and Bean (1994)

Table 4-18. Inductively Coupled Plasma Analysis of Organic Layer.¹

Cation	2 Percent HNO ₃ Extract		Water Extract	
	Concentration in Aqueous Phase (µg/g)	Relative Standard Deviation (%)	Concentration in Aqueous Phase (µg/g)	Relative Standard Deviation (%)
Ag	0.9	0	0.33	17
Al	1.8	29	---	---
B	1.2	11	1.4	69
Ca	2.0	0	---	---
Cd	2.1	0	---	---
Cu	2.2	3	---	---
Fe	0.33	15	---	---
K	<DL	---	23	25
Na	70	3	39	6
Ni	9.9	8	---	---
P	605	6	450	4
Si	---	---	1.5	38
Ti	---	---	0.07	16

Note:

¹Pool and Bean (1994)

Table 4-19. Ion Selective Electrode Ammonia Results for Organic Layer.¹

Sample Number	µg/mL NH ₃	Dilution Factor	µg NH ₃ /g in Sample
X-14	2.85	9.25	26.4
X-14	2.43	9.66	23.5
Blank	<0.06	---	---
X-15	2.19	9.75	21.3
X-15	2.55	9.63	24.6

Note:

¹Pool and Bean (1994)

4.4 VAPOR SAMPLE ANALYSIS

This section reports the results of the May 12 to May 25, 1994 vapor sample and analysis event for tank 241-C-103 headspace gases and vapors. It also includes selected data from the November 1993, December 1993, and April 1994 sampling events when more recent data was not available.

The reports, from which information was extracted and the type of information extracted, are listed below. In addition, the reports also discuss laboratory quality control, reasons for omitting data and general data quality.

Vapor Characterization of Tank 241-C-103 (Huckaby and Story 1994): vapor sampling results and analytical procedures, most notably GC/MS.

Tank 241-C-103 Vapor and Gas Sampling Data Quality Objectives (Osborne et al. 1994): objectives of the sampling and analysis events.

Quality Assurance Project Plan for Waste Tank Vapor Characterization (Suydam 1993): quality assurance guidelines.

Evaluation of the Capabilities and Use of the Vapor Sampling System for Tank Headspace Sampling and Characterization (Mahon et al. 1994): documentation of the May 1994 sampling event, meteorological and tank headspace temperature data, and detailed discussions of the tests and procedures used to ensure the validity of samples collected with the vapor sampling system.

Vapor Characterization of Tank 241-C-103: Data Report for OVS Samples Collected from Sample Job 7B, Parts I & II, Received 5/18/94 and 5/24/94 (Clausen et al. 1994): sample analyses.

Analysis of Tank 241-C-103 Headspace Components from sampling Job 7B (Jenkins et al. 1994): sample analyses.

Vapor Space Characterization of Waste Tank 241-C-103: Inorganic Sample Results from Sample Job 7B (Ligotke et al. 1994b): sample analyses.

Hanford Tank 103C analyses and Method Validation Development Phase (Rasmussen and Einfeld 1994): sample analyses.

4.4.1 Inorganic Gases and Vapors

4.4.1.1 Water Vapor. Water vapor is the most abundant vapor constituent in the headspace of tank 241-C-103. Water vapor was estimated from the gravimetric analysis of 50 inorganic gas sorbent traps to be 42.2 mg/L (standard deviation for the data $[\sigma] = 2.4$ mg/L), assuming the tank headspace was nominally 38 °C. This corresponds to a water partial

pressure in the headspace of 45.4 mmHg, to a dewpoint of 36.3 °C, and to a relative humidity of 91 percent. Therefore the headspace is almost saturated with water vapor. The gas and vapor concentrations are for humid tank air at the temperature and pressure recorded for tank 241-C-103 at the time the samples were collected (see Section 4.4).

Individual sample gravimetric results are given by Ligothke et al. (1994b). Some of the gravimetric data were eliminated. For reasons explained in that document, valid data are summarized in Table 4-20, which groups samples according to date and headspace elevation.

Water vapor trip blanks indicated no adverse handling effects, and no correction was applied to account for the small deviations observed. Given the $\sigma = 2.4$ mg/L as a measure of uncertainty in the water vapor measurements, the results in Table 4-20 are self-consistent. There is not a statistically significant difference in the headspace water vapor content at the three different sample elevations or over the length of time of the sampling period.

Table 4-20. Summary of Water Vapor Data.

Date (1994)	Elevation Above Waste (m)	Number of Samples	Mean (mg/L)	Standard Deviation (mg/L)
May 12	0.79	9	43.2	0.6
May 19	0.79	17	41.1	2.5
May 20	2.92	5	45.2	1.3
May 20	5.05	5	44.4	1.8
May 25	0.79	14	41.0	1.7
Total:		50	42.2	2.4

4.4.1.2 Ammonia. Ammonia vapor in tank 241-C-103 headspace was 304 ppmv ($\sigma = 11$ ppmv) using 35 sorbent traps. This value incorporates the results of samples collected from the three headspace elevations as well as all spiked and unspiked samples collected during May 1994. Table 4-21 summarizes results from the six sets of ammonia samples. The concentrations reported in have been adjusted for water vapor content. Ligothke et al. (1994b) provides individual results for all samples.

Analyses of spiked and unspiked ammonia samples are also summarized in Table 4-21. The average ammonia trapped in these 15 samples was 42.6 μ mol, which is between the 24.2 and 48.2 μ mol spike levels. Given the uncertainties associated with the sample volumes, analytical measurements, and spike amounts, there is no significant difference in the observed ammonia concentrations in the unspiked and spiked samples. The results are in very good agreement, and clearly indicate that the extraction of ammonia is not affected by the chemical matrix of the tank headspace.

Unspiked samples were collected on May 19 and 20, 1994 to determine whether ammonia was subject to vertical stratification within the headspace. As indicated in Table 4-21, the differences between ammonia concentrations observed at 0.79, 2.92, and 5.05 m above the waste surface are statistically indistinguishable and suggest the tank headspace is vertically mixed.

These ammonia concentrations exceed the notification limits (Tusler 1994) of 250 ppm or one-half of the National Institute of Occupational Safety and Health limits for immediately dangerous to life and health for ammonia.

Table 4-21. Summary of Ammonia Analyses.

Date (1994)	Elevation Above Waste (m)	Spike (ppmv of Sample) ¹	Number of Samples	Mean (ppmv)	Standard Deviation (ppmv)
May 12	0.79	0	10	310	9
May 19	0.79	170	5	300	19
May 19	0.79	338	5	300	16
May 19	0.79	0	5	296	7
May 20	2.92	0	5	307	3
May 20	5.05	0	5	307	5
Total:			35	304	11

Note:

$$^1\text{Spike ppm} = 10^6 * (\text{volume of ammonia vapor spike}) / (\text{sample volume})$$

4.4.1.3 Hydrogen. Hydrogen gas in the tank 241-C-103 headspace was 782 ppmv ($\sigma = 63$ ppmv) from 35 SUMMA³ canister samples. This value incorporates the results of samples collected from the three headspace elevations, and the results of six samples collected during a different sampling event which occurred in April 1994. Table 4-22 summarizes results from the six sets of hydrogen samples. Individual sample results are given by Einfeld (1994) and Rasmussen and Einfeld (1994).

The sample means, as reported in Table 4-22 for May 19 and 20 indicate no statistically significant stratification of hydrogen over the three elevations of headspace sampled (see Table 4-22).

³SUMMA is a registered trademark of Moletrics, Inc., Cleveland, Ohio.

Table 4-22. Summary of Hydrogen Analyses.^{1,2}

Date (1994)	Elevation Above Waste (m)	Number of Samples	Mean (ppmv)	Standard Deviation (ppmv)
April 7	0.79	6	724	7
May 16	0.79	4	803	26
May 19	0.79	3	718	11
May 20	2.92	3	732	49
May 20	5.05	3	714	26
May 25	0.79	16	833	43
Total:		35	782	63

Notes:

¹Einfeld (1994)

²Rasmussen and W. Einfeld (1994)

4.4.1.4 Nitrous Oxide. Nitrous oxide vapor in the tank 241-C-103 headspace was 763 ppmv ($\sigma = 51$ ppmv) from 37 SUMMA™ canister samples. This value incorporates the sample results collected from the three headspace elevations and the six sample results collected during the April 1994 sampling event. Table 4-23 summarizes results from the six sets of nitrous oxide samples. Individual sample results are given by Einfeld (1994) and Rasmussen and Einfeld (1994).

Comparing nitrous oxide concentration averages at the three headspace elevations is consistent with the comparisons of ammonia and hydrogen previously discussed; no statistically significant vertical stratification of nitrous oxide is observed.

Table 4-23. Summary of Nitrous Oxide Analyses.^{1,2}

Date (1994)	Elevation Above Waste (m)	Number of Samples	Mean (ppmv)	Standard Deviation (ppmv)
April 7	0.79	6	772	12
May 16	0.79	6	737	14
May 19	0.79	3	710	18
May 20	2.92	3	696	6
May 20	5.05	3	686	6
May 25	0.79	16	805	34
Total:		37	763	51

Notes:

¹Einfeld (1994)

²Rasmussen and W. Einfeld (1994)

4.4.1.5 Carbon Monoxide. Carbon monoxide gas in the tank 241-C-103 headspace was 26.7 ppmv ($\sigma = 2.3$ ppmv) from 36 SUMMA™ canister samples. This value incorporates the sample results collected from the three headspace elevations, and the results of six sample results collected in April 1994. Table 4-24 summarizes results from the six sets of carbon monoxide samples. Individual sample results are given in Einfeld (1994) and Rasmussen and Einfeld (1994).

Comparing carbon monoxide concentration averages at the three headspace elevations is consistent with the comparisons of ammonia, hydrogen, and nitrous oxide previously discussed; no statistically significant vertical stratification of carbon monoxide is observed.

Table 4-24. Summary of Carbon Monoxide Analyses.^{1,2}

Date (1994)	Elevation Above Waste (m)	Number of Samples	Mean (ppmv)	Standard Deviation (ppmv)
April 7	0.79	6	22.3	0.5
May 16	0.79	5	26.3	0.6
May 19	0.79	3	26.7	0.6
May 20	2.92	3	26.3	0.6
May 20	5.05	3	26.3	0.6
May 25	0.79	16	28.6	0.6
Total:		36	26.7	2.3

Note:

¹Einfeld (1994)

²Rasmussen and Einfeld (1994)

4.4.1.6 Nitrogen Dioxide and Nitric Oxide. Neither concentration or a concentration limit has been established for nitrogen dioxide in the tank 241-C-103 headspace. The weight of evidence suggests that nitrogen dioxide concentrations are indeed low, but Ligothke et al. (1994b) has suggested the nitrogen dioxide sorbent trap samples may be affected by the presence of ammonia; thereby raising a sampling interference issue. Ligothke et al. explains that inconsistent levels of nitrite, the ion that is extracted from the sorbent traps and is related to nitrogen dioxide in the sample, were measured in the trip blanks carried on May 25, 1994.

Because nitrogen dioxide sorbent trap samples collected in April 1994 were downstream of ammonia sorbent traps, they were consequently protected from potential interferences from ammonia. However, water vapor condensation in the ammonia sorbent traps which were upstream of the nitrogen dioxide/nitric oxide traps may have absorbed nitrogen dioxide. Analysis of these nitrogen dioxide samples suggests the concentration of nitrogen dioxide is less than 0.06 ppmv (see Table 4-25).

Table 4-25 also summarizes analytical results for the May 1994 nitrogen dioxide sorbent traps. These sorbent traps were not downstream of ammonia sorbent traps, and condensation of water vapors upstream of the sorbent media was prevented. If it is determined that ammonia does not interfere with collecting nitrogen dioxide and laboratory tests are planned, the upper concentration of nitrogen dioxide in the tank 241-C-103 headspace would be established as less than 0.04 ppmv.

Results of the spike addition study for nitrogen dioxide are not conclusive for the following reasons: (1) trip blank contaminant nitrite concentration variations are significant; and (2) spike blank recoveries average 153 percent, presumably caused by the higher than average nitrite contamination levels.

Table 4-25. Summary of Nitrogen Dioxide Analyses.^{1,2}

Date (1994)	Number of Samples	Mean (ppmv)
April 17	5	< 0.04
May 12	3	< 0.004
May 25	10	< 0.06

Note:

¹Einfeld (1994)

²Rasmussen and Einfeld (1994)

From the eight sorbent traps collected in May 1994, the nitric oxide concentration in the tank 241-C-103 headspace is estimated to be 1.5 ppmv ($\sigma = 0.3$). Table 4-26 summarizes the results from the two sets of nitric oxide sorbent trap samples. Ligothke et al. (1994b) provide individual sample results.

The design of nitric oxide sorbent trap sampling is such that if ammonia interferes with the nitrogen dioxide sampling, it also interferes with nitric oxide sampling. Therefore, until the ammonia interference issue is resolved, the values provided in Table 4-26 should be considered subject to change.

Nitric oxide sorbent trap samples collected on May 12, 1994, corrected for nitrite contamination levels, indicate incomplete adsorption of the analyte. The breakthrough sorbent section was found to contain about seven percent of the analyte. Because similar data are not yet available for the May 25, 1994 samples, this correction was applied to all the results reported in Table 4-26.

Two sets of spiked nitric oxide samples were collected on May 25, 1994. These correspond to two amounts of nitrite (the absorbed form of nitric oxide) added to the sorbent traps. The lower spike level was slightly higher than the observed tank nitric oxide concentration. Analysis of the spiked samples indicated the analytical recovery of analyte was not diminished by the sample chemical matrix. For more information, refer to Ligothke et al. (1994b).

Table 4-26. Summary of Nitric Oxide Analyses.¹

Date (1994)	Number of Samples	Mean (ppmv)	Standard Deviation (ppmv)
May 12	3	1.33	0.06
May 25	5	1.63	0.31
Total	8	1.5	0.3

Note:

¹Ligotke et al. (1994b)

4.4.1.7 Sulfur Oxides. No significant quantities of sulfur oxides were observed in tank 241-C-103. Three sulfur oxide sorbent trap samples were collected May 12, 1994 and analyzed at Pacific Northwest National Laboratory. Ligotke et al. (1994b) report that trace contamination of sulfur oxides was present in the sorbent media. This contamination validated that analytical detection limits were unaffected by vapor sampling. Analysis of the samples and blanks indicated slightly more sulfur oxides in the samples than in the blanks, but the difference was not significant given analytical standard deviations. It was determined that the sulfur oxides concentration in the tank headspace was conservatively ≤ 0.02 ppmv.

4.4.1.8 Hydrogen Cyanide. Five sorbent trap hydrogen cyanide samples were collected during May 1994. Ligotke et al. (1994b) report that the hydrogen cyanide measured in the samples was about the same as that measured in the trip blanks. Conservative assumptions described in their report place the hydrogen cyanide concentration at ≤ 0.04 ppmv.

4.4.2 Organic Vapors

4.4.2.1 Aromatic Hydrocarbons. The benzene concentration in the tank 241-C-103 headspace measured between less than 0.01 and 0.33 ppmv from 16 SUMMA™ canister and four triple sorbent trap (TST) samples. Table 4-27 shows the results of four sets of samples. Note that the May 16, 1994 SUMMA™ canister samples were analyzed for benzene by the EPA TO-14 methodology and a direct injection methodology.

The toluene concentration in the tank 241-C-103 headspace was measured between 0.020 and 0.057 ppmv from 12 SUMMA™ canister and four TST samples. Table 4-27 shows the results of the three sets of samples.

SUMMA™ canister spike additions were used by Rasmussen and Einfeld (1994) to establish that benzene is completely recovered from SUMMA™ canisters filled with the tank 241-C-103 chemical matrix. SUMMA™ canisters were analyzed by the EPA TO-14 method for toluene (EPA 1988). Although SUMMA™ canisters were not spiked with

toluene, toluene would be expected to behave much like benzene. Therefore, total recovery of toluene from SUMMA™ canisters would be expected. For individual sample analyses, refer to Rasmussen and Einfeld (1994).

Triple sorbent trap samples were spiked at two levels of benzene and at two levels of toluene. However, the spike levels of both compounds were too large, relative to the observed tank compound concentrations, to properly address matrix interference effects. Analytical error associated with measuring relatively large spike amounts was greater than the amounts of benzene and toluene collected from the tank sample. Rasmussen and Einfeld (1994) discuss TST, spiked TST blank analyses, and surrogate recoveries.

Table 4-27. Summary of Aromatic Hydrocarbon Analyses.

Compound	Method	Date (1994)	Number of Samples	Mean (ppmv)	Standard Deviation (ppmv)
Benzene	SUMMA™	April 7 ^{1,2}	6	0.33	0.11
		May 16 ²	6	0.071	0.015
		May 16 ³	6	< 0.01	---
		May 25 ³	4	< 0.01	---
	TST	May 16	4	0.08	0.03
Toluene	SUMMA™	April 7 ^{1,2}	6	0.057	0.016
		May 16 ²	6	0.020	0.004
	TST	May 17	4	0.03	0.02

Notes:

¹Rasmussen and Einfeld (1994)

²EPA TO-14 methodology

³Direct injection methodology

4.4.2.2 Butanal, n-Butanol, and 1,3-Butadiene. Table 4-28 summarizes butanal, n-butanol, and 1,3-butadiene concentrations measured in the tank 241-C-103 headspace. Butanal measured between 1.2 and 4.7 ppmv, n-butanol between 13.1 and 28.4 ppmv, and 1,3-butadiene at or below 0.060 ppmv. Results are based on analysis of SUMMA™ canister and TST samples.

Tank 241-C-103 headspace SUMMA™ canister samples were spiked and analyzed to determine the recovery efficiency of these analytes from the tank chemical matrix. Recovery efficiencies (Rasmussen and Einfeld 1994) were 73.6 percent for butanal, 43.2 percent for n-butanol, and 86.9 percent for 1,3-butadiene. These average recoveries were used to

correct direct injection method analyses of the May 16 and 25, 1994 SUMMA™ canister samples. Rasmussen and Einfeld (1994) justify and discuss the analyses and corrections applied.

Jenkins et al. (1994) discuss the analysis of butanal and n-butanol in TST samples. Triple sorbent trap samples were spiked with n-butanol, but the spiked amounts were not appropriate for evaluating the recovery of n-butanol.

Given that sampling and analysis techniques were different and multiple independent laboratories were used, the agreement between the SUMMA™ and TST results for butanal and n-butanol is very good.

Table 4-28. Butanal, Butanol, and 1,3-Butadiene Analyses.

Compound	Method	Date (1994)	Number of Samples	Mean (ppmv)	Standard Deviation (ppmv)
Butanal (butyraldehyde)	SUMMA™	May 16	6	4.7	0.7
		May 25	4	4.4	0.7
	TST	May 17	4	1.2	0.8
n-Butanol	SUMMA™	May 16	6	13.1	2.5
		May 25	4	13.1	2.5
	TST	May 17	4	28.4	6.1
1,3 Butadiene	SUMMA™	April 7 ¹	6	< 0.020	---
		May 16 ¹	5	0.060	0.020
		May 16 ²	6	< 0.05	---
		May 25 ²	4	< 0.05	---

Notes:

¹EPA TO-14 methodology

²Direct injection methodology

4.4.2.3 Halogenated Compounds. Table 4-29 summarizes vinylidene (1,1-dichloroethene) and methylene chloride (dichloromethane) concentrations measured in the tank 241-C-103 headspace. Vinylidene chloride, which was not detected in SUMMA™ canister or TST samples, was conservatively estimated to be less than 0.02 ppmv. Averaged methylene chloride measurements are as high as 1.62 ppmv, but this is thought to be a contaminant of the vapor sampling system. The uncertainty of this highest methylene chloride measurement, as indicated by σ , was also relatively high.

Table 4-29. Summary of Halogenated Compound Analyses.

Compound	Method	Date (1994)	Number of Samples	Mean (ppmv)	Standard Deviation (ppmv)
Vinylidene Chloride (1,1-Dichloroethene)	SUMMA™	April 7 ^{1,2}	6	< 0.02	---
		May 16 ²	6	< 0.02	---
		May 16 ³	6	< 0.02	---
		May 25 ³	4	< 0.02	---
	TST	May 17	4	< 0.009	---
Methylene Chloride (Dichloromethane)	SUMMA™	April 7 ^{1,2}	6	0.30	0.14
		May 16 ²	6	0.061	0.030
		May 16 ³	6	< 0.02	---
		May 25 ³	4	< 0.02	---
	TST	May 17	4	1.62	1.47

Notes:

¹Rasmussen and Einfeld (1994)

²EPA TO-14 methodology.

³Direct injection methodology.

The analytical limit of detection for vinylidene chloride from SUMMA™ canister samples by the direct injection method was 0.02 ppmv, and by the EPA TO-14 methods was estimated by Rasmussen and Einfeld (1994) to be about 0.01 to 0.02 ppmv. The limit of detection for vinylidene chloride from TST samples was estimated by Jenkins et al. (1994) to be about 0.009 ppmv.

Methylene chloride was used as a solvent to degrease parts in the vapor sampling system transfer tubing and manifold. It was detected in samples from a January 1994 sampling event (it is not well detected by the gas chromatograph/flame ionization detector of the vapor sampling system), but was associated with its use as a cleaning solvent. It was observed in the cleanliness test of the vapor sampling system at the start of the May 1994 sampling event. It is believed to have been inadvertently reintroduced to the vapor sampling system when the electrically heated transfer tube between tank 241-C-103 and the mobile laboratory (which had been cleaned before the use of methylene chloride as a cleaning solvent was eliminated) was replaced at the start of the May 1994 sampling event.

4.4.2.4 Ketones. Table 4-30 summarizes the acetone (propanone), 2-pentanone, 2-hexanone, 2-heptanone, and 2-octanone concentrations measured in the tank 241-C-103 headspace. Acetone is the most abundant ketone, exhibiting concentrations of 8.8 and 19.4 ppmv from TST and SUMMA™ canister samples, respectively. Both acetone and 2-hexanone are on the preliminary list of compounds of toxicological concern (Huckaby 1994).

SUMMA™ canister tank headspace samples were spiked with acetone and 2-hexanone to establish the recovery of these compounds. Rasmussen and Einfeld (1994) report acetone was extracted with 69.6 percent efficiency, and 2-hexanone was extracted with 50.8 percent efficiency. Values reported in Table 4-30 have been corrected for these factors. The precision of SUMMA™ canister analyses was excellent, and there was agreement between analyses of individual samples in each set and between the sample set averages of May 17 and 25, 1994.

Triple sorbent trap samples were spiked with each of the five ketones listed in Table 4-30. Jenkins et al. (1994) reports that only the tank headspace concentrations of 2-hexanone, 2-heptanone, and 2-octanone were properly within the range of the spike additions. For these three compounds, unspiked and (corrected) spiked sample results agreed, and indicate chemical matrix effects for these compounds were small. All five ketones, measured quantitatively in unspiked TST samples, were within or acceptably near the instrument calibration range.

4.4.2.5 Nitriles. Table 4-31 summarizes the nitrile concentrations measured in tank 241-C-103 headspace. Acetonitrile and propanenitrile were the most abundant nitriles, and measured in the 9.1 to 13.2 ppmv range and 3.3 to 5.3 ppmv range, respectively. Acetonitrile and propanenitrile are on the preliminary list of compounds of toxicological concern.

SUMMA™ canister tank headspace samples were spiked with acetonitrile and propanenitrile to establish recovery of these compounds. Rasmussen and Einfeld (1994) report acetonitrile was extracted with 41.3 percent efficiency, and propanitrile was extracted with 64.6 percent efficiency. Values reported in Table 4-31 have been corrected for these factors. Triple sorbent trap samples were spiked with each of the nitriles listed in Table 4-31. Jenkins et al. (1994) report that only the tank headspace concentrations of pentanenitrile, hexanenitrile, heptanenitrile, and octanenitrile were properly within the range of the spike additions. For these four nitriles, unspiked and (corrected) spiked sample results agreed, and indicate chemical matrix effects for these compounds are small. All nitriles, measured quantitatively in unspiked TST samples, were within or acceptably near the instrument calibration range.

Table 4-30. Summary of Ketone Analyses.

Compound	Method	Date (1994)	Number of Samples	Mean (ppmv)	Standard Deviation (ppmv)
Acetone (Propanone)	SUMMA™	May 16	6	19.4	2.0
		May 25	4	19.2	2.0
	TST	May 17	4	8.8	3.9
2-Pentanone	TST	May 17	4	1.09	0.64
2-Hexanone	SUMMA™	May 16	6	0.59	0.05
		May 25	4	0.57	0.04
	TST	May 17	4	0.51	0.12
2-Heptanone	TST	May 17	4	0.56	0.10
2-Octanone	TST	May 17	4	0.25	0.04

Table 4-31. Summary of Nitrile Analyses.

Compound	Method	Date (1994)	Number of Samples	Mean (ppmv)	Standard Deviation (ppmv)
Acetonitrile (Ethanenitrile)	SUMMA™	May 16	6	13.2	1.2
		May 25	4	12.7	1.2
	TST	May 17	4	9.1	2.2
Propanenitrile	SUMMA™	May 16	6	5.3	0.7
		May 25	4	5.1	0.7
	TST	May 17	4	3.3	0.3
Butanenitrile	TST	May 17	4	2.4	0.8
Pentanenitrile	TST	May 17	4	1.0	0.1
Hexanenitrile	TST	May 17	4	0.79	0.1
Heptanenitrile	TST	May 17	4	0.60	0.04
Octanenitrile	TST	May 17	4	0.32	0.09
Nonanenitrile	TST	May 17	4	0.14	0.02

4.4.2.6 Normal Paraffin Hydrocarbons and Alkanes. Tables 4-32 and 4-33 summarize measured tank 241-C-103 headspace concentrations of quantified volatile alkanes and semivolatile alkanes, respectively. Only straight-chain (normal) alkanes were quantitatively analyzed; branched alkanes are discussed briefly in Section 4.4.2.8. N-hexane, n-dodecane, and n-tridecane are on the preliminary list of compounds of toxicological concern (Huckaby 1994).

Table 4-32. Summary of Volatile Alkane Analyses.

Compound	Method	Date (1994)	Number of Samples	Mean (ppmv)	Standard Deviation (ppmv)
Methane	SUMMA™	Nov. 1993 ¹	18	16.0	1.6
n-Hexane	SUMMA™	May 16	6	0.72	0.07
		May 25	4	0.71	0.1
	TST	May 17	4	0.80	0.06
n-Heptane	TST	May 17	4	0.66	0.14
n-Octane	TST	May 17	4	0.33	0.09
n-Nonane	TST	May 17	4	0.28	0.08

Note:

¹Einfeld (1994)

SUMMA™ canister tank headspace samples were spiked with hexane, and it was determined that hexane was extracted with 95.4 percent ($\sigma = 9.3$) efficiency. The precision of individual samples in each set was good, and the agreement between the sample set averages of May 17 and May 25, 1994 was also good.

Triple sorbent trap samples were spiked with n-hexane, n-heptane, n-octane, and n-nonane. Jenkins et al. (1994) report that the tank headspace concentrations of these alkanes were all within the range of the spike additions. For these four compounds, unspiked and (corrected) spiked sample results agreed, and indicate chemical matrix effects for these compounds are small. Each of these alkanes were within or acceptably near the instrument calibration range.

Jenkins et al. (1994) also spiked TSTs with n-dodecane and n-tridecane. However, the amounts of these compounds in unspiked and spiked TSTs were much higher than the calibration range of the instrument and have not been included here. Deuterated n-dodecane and n-tridecane spiked OSHA versatile sampler (OVS) trap samples were analyzed by Clausen et al. (1994), who concluded matrix effects were not significant.

The semivolatile alkane results shown in Table 4-33 are those of Jenkins et al. (1994), Claus et al. (1994), and Ligothke et al. (1994a). These alkanes are the major components of NPH solvents used in the PUREX process. The consistency of these results was very good. Measurement of the NPH using OVS samples lowered into the tank 241-C-103 headspace were similar to the measurements of both OVS trap and Carbotrap/Carbotrap C (CCT) samples collected using the vapor sampling system. From the large number and agreement of these sample results, a high degree of confidence can be placed in the established concentrations of semivolatile alkanes.

Table 4-34 shows the data from Table 4-33 in mass concentrations. Table 4-35 presents the average total NPH mass concentrations from each set of samples.

4.4.2.7 Tributyl Phosphate and Dibutyl Butylphosphonate. Headspace concentrations of tributyl phosphate and dibutyl butylphosphonate were measured in the May 16, 1994 samples. Although results were reported at that time, subsequent experience indicated these compounds were not properly represented in the samples. Specifically, the particulate filters, used to protect the sampling devices from radiolytic particles, have been shown to adsorb substantial quantities of tributyl phosphate (Jenkins et al. 1995); and the reported values of tributyl butylphosphate and dibutyl butylphosphonate should be invalid because they are biased low.

4.4.2.8 Tentatively Identified Organic Compounds. In addition to the positively identified, quantitatively analyzed compounds discussed in preceding sections, many other compounds were tentatively identified. Jenkins et al. (1994) and Rasmussen and Einfeld (1994) provide lists of compounds tentatively identified by GC/MS analysis of the TST and SUMMA™ canister samples, respectively.

Many of the tentatively identified compounds are semivolatile branched alkanes and alkenes that were probably impurities of the PUREX process NPH diluent. Alternately, these may be products resulting from the radiolysis and oxidation of TBP and NPH, either in PUREX or in tanks. Alkanes, alkenes, alcohols, ketones, aldehydes, acids, and esters are among the many compounds.

Table 4-33. Semivolatile Alkane Concentrations.

Compound	Method	Elevation above waste (m)	Date (1994)	Number of Samples	Mean (ppmv)	Standard Deviation (ppmv)
n-Decane	CCT	0.79	May 16	10	0.57	0.06
n-Undecane	OVS	0.79	May 16	9	3.7	0.1
		0.79	May 19	5	3.6	0.2
		2.92	May 20	5	3.5	0.2
		5.05	May 20	5	3.3	0.3
	CCT	0.79	May 16	10	4.6	0.7
n-Dodecane	OVS	0.63 ^{1,2}	December 2 (1993)	9	46.4	10.4
		0.79	May 16	5	45.6	7.4
		0.79	May 19	5	40.3	3.4
		2.92	May 20	5	36.2	3.0
		5.05	May 16	5	38.0	4.8
	CCT	0.79	May 16	10	40.3	7.2
n-Tridecane	OVS	0.63 ^{1,2}	December 2 (1993)	9	63.0	13.5
		0.79	May 16	5	53.6	10.6
		0.79	May 19	5	44.4	4.3
		2.92	May 20	5	40.1	3.6
		5.05	May 20	5	44.9	5.6
	CCT	0.79	May 16	10	52.0	3.7
n-Tetradecane	OVS	0.63 ^{1,2}	December 2 (1993)	9	13.9	4.2
		0.79	May 16	5	5.8	1.0
		0.79	May 19	5	6.0	0.5
		2.92	May 20	5	5.6	0.3
		5.05	May 20	5	6.0	0.6
	CCT	0.79	May 16	10	10.0	1.0

Notes:

¹OVS lowered into headspace

²Ligoške et al. (1994a)

Table 4-34. Semivolatile Alkane Mass Concentrations. (2 sheets)

Compound	Method	Elevation above waste (m)	Date (1994)	Number of Samples	Mean (mg/m ³)	Standard Deviation (mg/m ³)
n-Decane	CCT	0.79	May 16	10	3.06	0.32
n-Undecane	OVS	0.79	May 16	9	21.8	0.9
		0.79	May 19	5	21.7	1.2
		2.92	May 20	5	20.9	1.2
		5.05	May 20	5	19.7	2.8
	CCT	0.79	May 16	10	27.4	4.4
n-Dodecane	OVS	0.63 ^{1,2}	December 2 (1993)	9	301	68
		0.79	May 16	5	297	49
		0.79	May 19	5	262	22
		2.92	May 20	5	236	20
	5.05	May 16	5	248	45	
CCT	0.79	May 16	10	261	47	
n-Tridecane	OVS	0.63 ^{1,2}	December 2 (1993)	9	443	95
		0.79	May 16	5	377	75
		0.79	May 19	5	314	30
		2.92	May 20	5	283	26
	5.05	May 20	5	317	52	
CCT	0.79	May 16	10	365	26	

Table 4-34. Semivolatile Alkane Mass Concentrations. (2 sheets)

Compound	Method	Elevation above waste (m)	Date (1994)	Number of Samples	Mean (mg/m ³)	Standard Deviation (mg/m ³)
n-Tetradecane	OVS	0.63 ^{1,2}	December 2 (1993)	9	105	32
		0.79	May 16	5	44	7.6
		0.79	May 19	5	45	3.6
		2.92	May 20	5	42	2.4
		5.05	May 20	5	46	6.8
	CCT	0.79	May 16	10	75	7.5

Notes:

¹OVS lowered into headspace

²Ligotke et al. (1994a)

Table 4-35. Average Total Semivolatile NPH Mass Concentrations.

Method	Elevation above waste (m)	Date (1994)	Number of Samples	Mean (mg/m ³)	Standard Deviation (mg/m ³)
OVS	0.63 ^{1,2}	December 2, 1993	9	850	138
OVS	0.79	May 16	9	704	108
	0.79	May 19	5	644	55
	2.92	May 20	5	582	47
	5.05	May 20	5	630	107
CCT	0.79	May 16	10	731	85
Liquid Sample ³	---	December 15, 1993	1	1,260	---

Notes:

¹OVS traps were lowered into the headspace.

²Ligotke et al. (1994a)

³Pool and Bean (1994) analyzed headspace vapors above the organic liquid waste sample.

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5.0 INTERPRETATION OF CHARACTERIZATION RESULTS

The purpose of Section 5.0 is to evaluate the overall quality and consistency of the available results for tank 241-C-103 and to assess and compare these results with historical information and program requirements.

5.1 ASSESSMENT OF SAMPLING AND ANALYTICAL RESULTS

This section evaluates sampling and analysis factors that may impact data interpretation. These factors are used to assess the overall data quality and consistency and to identify limitations in data use. Some consistency checks were not possible because of the lack of analyses.

5.1.1 Field Observations

Segment 1 of core 63 was obtained from riser 2 about three months prior to the removal of segment 2 and the remainder of core 63. Because segment 1 and a substantial portion of segment 2 were drainable liquids, it is likely that the waste contents of these segments may have intermingled in the tank between the two sampling events, thereby creating an unknown bias in the analytical results. For this reason, caution should be used when interpreting drainable liquid results from these two segments and when attempting to distinguish between them. Possible contamination occurred to segment 4 of core 66 by hydrostatic head fluid, but the effect on the overall mean percent water results for the sludge and aqueous portions was estimated to be less than one percent. The efficiency of the sample recovery varied from 71 to 100 percent with an average of 91 percent. This recovery was considered good for this type of waste.

5.1.2 Quality Control Assessment

This section reviews the quality control data pertinent to the 1995 event. The assessment included an evaluation of appropriate blanks, duplicate analyses, spike and standard recoveries performed in conjunction with the chemical analyses. Although the quality control information for the 1993 organic layer sampling event and for the 1994 vapor sampling event was limited, all pertinent quality control tests were conducted for the 1995 core sampling event, allowing a full assessment regarding the accuracy and precision of the data. The 1995 samples which had one or more quality control results outside the specified criteria have been identified by footnoting in the Appendix A tables.

The spike and standard results provide an estimate of analysis accuracy. For the 1995 sampling event, total alpha activity results had two standards and one spike slightly outside the limits. The low spike recovery was caused by partial dissolution of the sample mount. Any other deviations were not significant enough to affect the criticality evaluation. For the 1993 grab sampling event, all standards were within the limits.

Analytical precision is estimated by the relative percent difference (RPD), which is defined as the absolute value of the difference between the primary and duplicate samples, divided by their mean, multiplied by one hundred.

In the 1995 sampling results, DSC had one of seven aqueous portion samples and two of seven sludge samples exceeding the criterion. A rerun was conducted on only one of these three samples because of the high dose rates associated with them. The results of the rerun were satisfactory. Total alpha analyses were conducted only on the sludge samples, and one RPD exceeded the criteria out of seven samples. Reruns were not requested because of the very high beta to alpha activity ratio in these samples. For percent water, all RPDs met the criterion for the aqueous layer results; two of seven RPDs for the sludge results did not. A rerun was conducted on one sludge sample; it agreed with the duplicate result. Further reruns were not conducted because of the high dose rate of the samples and because the results were well above the 17 percent notification limit. The high RPD values indicate that sample heterogeneity exists at the 15 to 30 mg sample size level used for DSC/TGA measurement. The RPDs were available for most analytes from the 1993 sampling event. The RPDs for metals listed in Table 4-5 were outside the limits, but all other aqueous phase analytes met the criterion. For the organic phase, the target level was met for all analytes except aluminum which may have had contamination problems. The only measure of precision for the 1994 vapor sample results were standard deviations (see Section 4.4 vapor analyte tables).

In summary, the majority of the quality control data met program and laboratory criteria. Data outside the criteria have been flagged in Appendix A. However, when making important decisions, it is advisable for data users to refer to original data reports for more detailed quality information for testing.

5.1.3 Data Consistency Checks

Checks, which were performed to help assess data consistency and quality included comparing different analytical methods and a homogenization test. These are described below. Other checks were not possible: total alpha and total beta could not be compared to the sum of individual alpha and beta emitters because of a lack of data, and a mass and charge balance was not conducted on the 1995 data because ICP data was available from only one subsegment.

5.1.3.1 Comparison of Results from Different Analytical Methods. The following data consistency checks compare the results of two different analytical methods for a given analyte. A close correlation between the two strengthens the credibility of both results, whereas a poor correlation brings the reliability of the data into question.

For comparative purposes, the segments 1 and 2 aqueous layer results (1995 data) from core 63 were analyzed for TOC by the direct persulfate oxidation and furnace oxidation methods. As a basis for comparison, an RPD was calculated between the two methods for each segment. This resulted in RPDs of 4.5 and 2.8 percent, indicating consistency between the two methods. It should be noted that the persulfate TOC method does not oxidize NPH type organics; therefore agreement between the two methods indicates there are not significant quantities of aliphatic hydrocarbons in the aqueous phase (or other organic species not oxidized by persulfate).

The TGA sludge results from core 63, segment 4 (1995 data) yielded a sample result of 13.47, a duplicate result of 26.37, and a rerun (triplicate) result of 29.70 (not included in the data summary tables of Bell 1995a). This gave an overall mean of 23.18 weight percent. Because one result was below the 17 percent notification limit, weight percent water by gravimetry was performed which resulted in a mean of 25.15 percent. These two means have an RPD of 8.2 percent which lends credibility to the percent water data.

Both phosphorus as determined by ICP and phosphate as determined by IC were conducted on the aqueous layer from the 1993 sampling event (Pool and Bean 1994). The ICP phosphorus result was 2,350 $\mu\text{g/g}$, which converted to a phosphate value of 7,200 $\mu\text{g/g}$. The RPD of 113 percent between the derived value of 7,200 $\mu\text{g/g}$ and the IC phosphate result of 2,000 $\mu\text{g/g}$ draws into question the reliability of these results. The IC phosphate did agree more with the 1995 value of 3,240 $\mu\text{g/g}$. The higher ICP phosphorus result could also indicate that phosphorus is present as a specie other than phosphate, such as organic phosphates or pyrophosphates.

5.1.3.2 Homogenization Test. To evaluate the adequacy of the laboratory homogenization procedure on the samples taken in the 1995 event, two aliquots were removed from different locations of the homogenized upper half sludge of segment 4, core 63. Fusion digests for ICP were conducted in replicate for each of the two aliquots. Except for zinc, which had an RPD between the two aliquots of 47.7 percent, the remaining detected analytes all had RPDs less than 21.1 percent (Bell 1995c). This indicates a fair degree of sample homogenization was achieved and that sample heterogeneity, for analytical methods that use sample sizes comparable to ICP (0.25 g to 1 g), should not be a primary source of variability in estimating analyte concentrations. However, greater errors from sample heterogeneity may be expected for methods (DSC/TGA) that use very small (10 to 20 mg) sample sizes.

5.1.4 Data Limitations

In some cases, data limitations impacted the treatment of data and may have introduced an unknown amount of error in the concentration estimates. For example, because analyses for

the determination of the metals content were not performed on the 1995 aqueous layer samples, concentration estimates for metals were based on results from a 1993 sampling event. However, only one aqueous layer sample was taken in 1993, and it is not known whether the sample was taken from the same riser, or depth, as the 1995 samples. In the 1995 sampling event, analytical results from both cores, or from all segments, were not available for all analytes. The sludge metals content is based solely on an analysis of one segment, segment 4 of core 63, and the radionuclides were examined only in core 63. Because these results may not represent the entire tank contents, extrapolating them to tank inventories may result in estimate errors. Inventory estimates based on composites should be more representative of the entire tank contents than results from a single sample.

5.2 COMPARISON OF ANALYTICAL RESULTS FROM DIFFERENT SAMPLING EVENTS

Comparisons were possible between the 1995 analytical results and data from several historical samplings. Recent sludge data were compared with results from a 1986 core sampling, and current aqueous layer data were compared to results from a 1990 grab sample analysis and the 1986 core sampling. In addition, the data from the 1993 aqueous layer grab sampling, which have not already been discussed in Section 4.2, are compared in this section with corresponding results from the 1995 analysis. The 1990 and 1986 results are taken from Appendix C.

Table 5-1 compares sludge data from core sampling events in 1995 and 1986. The data should be similar because no changes to the tank waste have taken place since 1978. However, a comparison of metals is not valid because the 1995 values are based on a single sample from segment 4 of core 63. Because the waste composition changes significantly with depth (see Section 5.3), results based on one segment would be expected to be different than an average of several segments. As stated above, the 1986 sampling results are based on composites rather than segment analysis and may be more accurate than the metal and radionuclide data from 1995. Except for aluminum, iron, and zinc, the results agree to within a factor or two. This is reasonable considering the differences in the material sampled and analyzed. The lower ^{60}Co values for the 1995 results are probably caused by radioactive decay. Excellent agreement was found for ^{137}Cs , total alpha, zirconium.

Table 5-2 provides the aqueous layer data comparison. Because transfers into and out of the tank ceased in 1978, data from the 1986 and 1990 sampling events should be similar to the 1995 results. Data for the 1986 and 1990 sampling events were taken from Appendix C. Conversions were performed where needed for the units to match. RSDs of all detected data were calculated for each analyte to measure variability between sampling events. The RSDs were less than 50 percent except for calcium, iron, uranium, nitrate, and sulfate. The 1990 sulfate result is roughly a factor of 10 high, and may be a reporting error. The aqueous results agree reasonably well considering the differences in sampling and analysis for the four sampling events.

Table 5-1. Comparison of Sludge Data from 1995 and 1986.

Analyte	1986 Result	1995 Result	Ratio
INORGANIC CONSTITUENTS	$\mu\text{E/g}$	$\mu\text{E/g}$	1986/1995
Aluminum	14,500	1.93E+05	0.08
Calcium	11,100	< 3,800	---
Chromium	618	970	0.64
Iron	86,800	15,800	5.49
Sodium	50,500	26,400	1.91
Zinc	175	824	0.21
Zirconium	12,300	11,400	1.08
Nitrate	2,810	1,730	1.62
RADIONUCLIDES	$\mu\text{Ci/g}$	$\mu\text{Ci/g}$	
^{137}Cs	108	122	0.89
^{60}Co	5.03	1.89	2.66
^{90}Sr	2,920	4,190	0.70
Total Alpha	10.5 ($^{239/240}\text{Pu}$ + ^{241}Am)	9.74	1.08
ORGANIC CONSTITUENTS	$\mu\text{E/g}$	$\mu\text{E/g}$	
Total Organic Carbon	3,270	8,210	0.40

5.3 TANK WASTE PROFILE

Based on the process history of the tank, three distinct layers of waste were expected in tank 241-C-103: an upper organic layer of uncertain depth, a supernatant layer comprising about two-thirds of the waste volume, and a lower sludge layer. The sludge layer itself was expected to be somewhat layered with PUREX cladding waste on the bottom, PUREX sludge in the middle, and unknown waste on the top. The supernate consists of various wastes. The visual descriptions of the samples verified the presence of a thin organic layer overlying an aqueous layer in the supernate. The descriptions of segment 1 samples from both cores indicated the organic layer was a dark brown liquid, and the aqueous layer was a lighter brown color. A supernate layer did exist over the sludge in the tank, but substantial drainable liquid portions were also found in all sludge segments except one. The sludge portion was described in all segments as being dark brown with the exception of segment 4, core 63, which revealed a cream-colored interior. Also, the sludge portion appears to begin

at a lower depth for core 66 than for core 63. Core 63 had some sludge extruded from segment 2, whereas none was found in segment 2 of core 66 and very little was found in segment 3.

The 1995 sampling event met the tank characterization plan requirement of sampling from two risers located approximately 180 degrees apart and near the tank outer edge (Schreiber 1995). The sampling analyses from these two risers provided limited information on the spatial distribution of several analytes in the tank waste (Bell 1995a, 1995b, and 1995c), allowing a statistical analysis of these data.

A statistical procedure known as the analysis of variance (ANOVA) was conducted on the 1995 sludge and aqueous layer data to determine whether there were any horizontal or vertical differences in analyte concentrations. The ANOVA models were random effects nested models; the particular model used depended on whether a specific analyte had data from one or both cores. When a segment was subsampled into upper and lower halves (sludge only), the results were combined to simplify the analysis. Only analytes in which all values were detected were used in this analysis (except nitrate, in which the data from core 63, segment 4 were deleted from the analysis).

Table 5-2. Aqueous Layer Historical Data Comparison. (2 sheets)

Analyte	1986 Result	1990 Result	1993 Result	1995 Result	RSD (Data)
	µg/mL	µg/mL	µg/mL	µg/mL	%
INORGANIC CONSTITUENTS					
Calcium	16	3.18	5.38	---	84
Cadmium	< 10.2	1.06	0.861	---	15
Chromium	105	83.7	57.0	---	29
Iron	9.29	4.24	3.23	---	58
Molybdenum	Not reported	12.7	10.8	---	11
Nickel	90.2	82.7	72.1	---	11
Phosphorus	1,530	Not reported	2,530	---	35
Potassium	358	281	323	---	12
Silver	31.4	25.4	11.8	---	44
Sodium	39,300	38,200	32,700	---	10
Uranium	6,820	Not reported	2,100	---	75
Zirconium	281	313	301	---	5
Cyanide	Not reported	31.0	Not reported	26.9	10
Nitrate	6,820	4,510	2,640	2,140	53

Table 5-2. Aqueous Layer Historical Data Comparison. (2 sheets)

Analyte	1986 Result	1990 Result	1993 Result	1995 Result	RSD (Data)
Nitrite	Not reported	30,200..	24,700	21,200	18
Phosphate	Not reported	2,170	2,150	2,250	2
Sulfate	Not reported	28,100	3,230	3,220	125
RADIONUCLIDES	$\mu\text{Ci/mL}$	$\mu\text{Ci/mL}$	$\mu\text{Ci/mL}$	$\mu\text{Ci/mL}$	%
¹³⁷ Cs	21.7	63.0	57.9	---	47
⁶⁰ Co	< 0.0483	0.0705	0.0511	---	23
Total Alpha	< 0.0360 (^{239/240} Pu + ²⁴¹ Am)	0.0244 (^{239/240} Pu + ²⁴¹ Am)	0.0435	---	40
ORGANIC CONSTITUENTS	$\mu\text{g/mL}$	$\mu\text{g/mL}$	$\mu\text{g/mL}$	$\mu\text{g/mL}$	%
Total Organic Carbon	7,290	7,450	7,190	6,640	5
PHYSICAL PROPERTIES					
Density	1.10 g/mL	1.06 g/mL	1.076 g/mL	---	2
Percent Water	Not reported	91%	76.9%	86.2%	8
pH	9.72	9.5	10.0	---	3

The ANOVA generates a p-value which is compared with a standard significance level ($\alpha = 0.05$). If a p-value is below 0.05, there is sufficient evidence to conclude that the sample means are significantly different from each other. However, if a p-value is above 0.05, there is not sufficient evidence to conclude that the samples are significantly different from each other.

The tests were conducted on all analytes having sufficient data to support a statistical analysis. Some analytes had more data than others. For the sludge portion of the tank contents, 16 analytes had enough data to provide information on vertical differences (all anions except hydroxide and cyanide, all radionuclides, TIC, TOC, and percent water), and 11 analytes had sufficient data to provide information on horizontal as well as vertical differences (all anions except hydroxide and cyanide, total alpha activity, TIC, TOC, and percent water). The results of the ANOVA tests for the sludge portion indicated that none of the 11 analytes providing horizontal information on the tank contents showed significant differences between the two cores (all p-values > 0.05). This was contrasted by 15 of 16 analytes showing significant vertical differences. The single exception was TIC, with a p-value of 0.106. For the aqueous portion of the tank contents, 10 analytes had sufficient

data to provide information of vertical differences (all anions except hydroxide and cyanide, TIC, TOC, and percent water), and nine analytes had sufficient data to provide information on horizontal as well as vertical differences (all anions except hydroxide and cyanide, TOC, and percent water). The results for the aqueous portion indicated that four of nine analytes showed significant horizontal differences. The four analytes were chloride (p-value = 0.013), fluoride (p-value = 0.028), oxalate (p-value = 0.035), and sulfate (p-value = 0.018). On the segment level, 9 of 10 analytes showed significant vertical differences, the single exception being sulfate (p-value = 0.106).

Although it was not shown statistically, a visual study of the sludge data in Appendix A indicate that all seven anions appear to decrease in concentration as a function of depth. No obvious trends are apparent for TIC, TOC, percent water, or the six radionuclides. The concentration seemed to be highest for the six radionuclides in segment 3 of core 63, which coincides with the expected high concentrations of cesium and strontium in the AR waste (see Section 2.3.2). Overall trends were much less clear for most drainable liquid analytes. Analytes such as fluoride and nitrate also appeared to decrease as a function of depth, but most others showed no trend or a trend was apparent in the data from one core but not the other.

In summary, the information provided by the tank waste history, the visual descriptions, and the statistical analysis indicated vertical heterogeneity within the sludge and aqueous layers, and perhaps some horizontal differences in the aqueous layer as well. This was in addition to the obvious heterogeneity of waste within the tank comprising the organic, aqueous, and sludge portions.

5.4 COMPARISON OF TRANSFER HISTORY AND ANALYTICAL RESULTS

The historical tank content estimate (HTCE) data for tank 241-C-103 were compared to analytical data from the 1995 sampling in Table 5-3. These data are available for the sludge inventory of the tank only; therefore, this comparison was limited to sludge data.

A comparison of sludge inventories from the historical tank content estimate and analytical results generally demonstrated little agreement, particularly for inventories of key analytes of the waste types predicted to constitute most of the sludge. Analytical results show higher inventories than predicted for aluminum and nitrite, and even higher inventories of sulfate and ¹³⁷Cs. However, the analytical results showed lower inventories than predicted for iron, hydroxide, nitrate, and ⁹⁰Sr, and even lower for sodium. The analytical results also showed higher inventories than predicted for zirconium, phosphate, oxalate, and total organic carbon. These discrepancies are in large part likely caused by the data difficulties already discussed in Section 5.1.4 because the metals content for the sludge is based only on the analysis of segment 4 from core 63.

Table 5-3. Comparison of Historical Tank Content Estimate and Analytical Data. (2 sheets)

Analyte	Historical Tank Content Estimate Solids Inventory ¹	1995 Core Sample Sludge Results
Water weight percent	72.8	57.7
Metals	kg	kg
Aluminum	23,900	60,800
Iron	8,210	4,980
Sodium	51,600	8,310
Anions	kg	kg
Cl ⁻	979	199
OH ⁻	60,900	< 8,280
NO ₃ ⁻	30,200	545
NO ₂ ⁻	18,000	5,540
PO ₄ ³⁻	960	1,020
SO ₄ ²⁻	4,580	879
Radiological Constituents	CI	CI
¹³⁷ Cs	49,300	38,400
⁹⁰ Sr	1.14E+06	1.32E+06

Note:

¹Agnew (1996)

Despite disparities between analytical results and historical estimates, the aluminum and iron results, which are from analyses of only one subsegment from the lower depths of the sludge, tend to support the prediction that a bottom layer comprised of mostly PUREX cladding waste exists. In addition, the higher ⁹⁰Sr results in segments 2 and 3 of core 63 were consistent with the prediction that AR solids (washed PUREX sludge) comprise a waste layer on top of the PUREX cladding waste.

5.5 EVALUATION OF PROGRAM REQUIREMENTS

The two push-mode core samples retrieved from tank 241-C-103 in late 1994 and early 1995 were taken to meet the requirements of the safety screening DQO (Babad and Redus 1994), the organic DQO (Babad et al. 1994), and the pretreatment DQO (Kupfer et al. 1994). Although a wide array of analyses were requested in the pretreatment DQO, it was determined by the Pretreatment Program that these analyses were not necessary for samples

retrieved from tank 241-C-103. The Pretreatment Program requested only that a 125 mL composite sample for process development and a 100 mL composite sample for archive be obtained from this core sampling event (Schreiber 1995). Evaluation of data in terms of operational and environmental requirements was not required. The process development work on the tank 241-C-103 samples has not taken place; therefore a discussion of process development issues is not possible.

5.5.1 Safety Evaluation

Data criteria identified in the safety screening and organic DQOs are used to assess the safety of waste in tank 241-C-103. For a proper safety assessment, both DQOs require samples from two widely spaced risers. The set of primary analyses required by the DQOs was similar. Both DQOs dictated that DSC be performed to evaluate fuel content and that TGA be performed to determine the weight percent water. The safety screening DQO also required analysis of total alpha activity and vapor flammability, and the organic DQO required a determination of the TOC content using the hot persulfate method. For each required analysis, the pertinent DQO established a notification threshold which, if exceeded, could warrant further investigation to evaluate the tank safety conditions. Table 5-4 compares the notification thresholds of the DQOs with the analytical results from the 1995 core and 1994 vapor sampling events.

Exothermic reactions, as measured by DSC, were noted in sludge samples from segments 2 and 3 of core 63. Of these, only one exceeded the DQO notification limit of -481 J/g on a dry weight basis. The duplicate sample from the lower half of segment 3 of core 63 exhibited a wet weight exothermic result of -337.6 J/g (-540 J/g on a dry weight basis). However, the initial sample did not show an exothermic reaction, and reruns were not performed because of the sample's high dose rates (Bell 1995a). The moisture level for this portion of the segment was about 36 percent. Only one aqueous sample, segment 4 of core 63, exhibited exothermic behavior. The initial, duplicate, and triplicate runs yielded wet-weight, exothermic results of -156.8 J/g (-784 J/g on a dry weight basis), -52.7 J/g (-263 J/g on a dry weight basis), and -46.2 J/g (-231 J/g on a dry weight basis) respectively. This sample was about 80 percent water, well above the minimum DQO criteria of 17 percent. The oxidant (nitrate and nitrite) concentration levels in the waste are relatively near or below the TOC oxidation stoichiometric requirements. This lack of excess oxidant, along with other factors, may be affecting the reproducibility of the exothermic reactions.

Table 5-4. Comparison of Analytical Results with Decision Criteria of Safety Screening and Organic Data Quality Objectives.^{1,2} (2 sheets)

Applicable DQO	Primary Decision Variable	Decision Criteria Threshold	Analytical Values	
			Sludge	Aqueous Layer
Safety screening; organic	Total fuel content	-481 J/g ³	-540 J/g ³ (duplicate, lower half of segment 3, core 63)	-784 J/g ³ (result, segment 4, core 63)
Safety screening; organic	Percent moisture	17 wt%	57.7 wt% (mean)	86.2 wt% (mean)
Safety screening	Total alpha	(1 g/L) ⁴ sludge=45.9 μCi/g liquid=57.2 μCi/g	9.74 μCi/g (mean)	0.0404 μCi/g ⁵ (mean)
Safety screening	Flammable gas	≤ 25% LFL	Vapor = 3.8% LFL	
Safety screening; organic	TOC ⁶	30,000 μg C/g	19,400 μg C/g ⁷	48,100 μg C/g ⁷

Notes:

¹Babad et al. (1994)

²Babad and Redus (1994)

³Negative values denote exothermic reactions. Only the specific subsegment with the largest dry-weight, exothermic values, are listed.

⁴Although the actual decision criterion listed in the DQO is 1 g/L, total alpha is measured in μCi/g rather than g/L. To convert the notification limit for total alpha into a number more readily usable by the laboratory, it was assumed that all alpha decay originates from ²³⁹Pu. Using the sludge density of 1.34 g/mL and the specific activity of ²³⁹Pu (0.0615 Ci/g), the sludge decision criterion may be converted to 45.9 μCi/g as shown:

$$2\left(\frac{1 \text{ g}}{\text{L}}\right) \left(\frac{1 \text{ L}}{10^3 \text{ mL}}\right) \left(\frac{1 \text{ mL}}{\text{density g}}\right) \left(\frac{0.0615 \text{ Ci}}{1 \text{ g}}\right) \left(\frac{10^6 \mu\text{Ci}}{1 \text{ Ci}}\right) = \frac{61.5 \mu\text{Ci}}{\text{density g}}$$

Similarly, using the aqueous layer density of 1.076 g/mL, the aqueous decision criterion may be converted to 57.2 μCi/g.

⁵Results taken from the 1993 sampling event data reported in Pool and Bean (1994). The aqueous value was converted from the 0.0435 μCi/mL value reported in Table 4-5 using a density value of 1.076 g/mL.

Table 5-4. Comparison of Analytical Results with Decision Criteria of Safety Screening and Organic Data Quality Objectives.^{1,2} (2 sheets)

⁶Analyzed using the hot persulfate method

⁷Because the TOC sludge and aqueous analytical results were given on a wet weight basis, they were converted to a dry weight basis using the following equation to compare them to the decision criteria of 30,000 µg C/g. (The aqueous TOC value was first converted from 6,640 µg/mL using a density value of 1.076 g/mL).

$$\frac{X \text{ } \mu\text{g (wet weight)}}{1 - (\% \text{ water}/100)} = X \text{ } \mu\text{g (Dry weight)}$$

To determine the fuel source for these exothermic reactions, secondary analyses for cyanide were performed on the lower-half subsegment of segment 3 and on the aqueous layer from segment 4 of core 63 because the notification limit for DSC was exceeded. Results on both samples are far below the notification limit of 39,000 µg/g or 39,000 µg/mL. According to the organic DQO (Babad et al. 1994), TOC is a primary analyte and was analyzed on all subsegments. After conversion to a dry weight basis, the TOC duplicate sludge result from the lower half of segment 3 of core 63 was 16,000 µg C/g. Similarly, the dry weight TOC aqueous result for segment 4 of core 63 was 25,500 µg C/g. Neither result exceeded the TOC limit of 30,000 µg C/g. As noted in Table 5-7, the overall TOC mean for the aqueous portion was 48,100 µg C/g on a dry weight basis. This level of TOC in the tank would only be a safety concern if the tank dried out substantially. The furnace oxidation method of TOC analysis compared well with the persulfate oxidation method (see Section 5.1.3.1), indicating that other sources of organic fuel are not present. Secondary analyses for hydroxide, nitrate, and nitrite were also performed because the energy equivalent of TOC by the persulfate oxidation method was greater than 125 percent. As noted above, the nitrate/nitrite oxidant level is lower than that found in most tank waste and may be a limiting factor in potential organic/nitrate reactions. This low nitrate may explain the smaller observed exothermic reactions compared to that expected based on TOC (acetate)-nitrate reactions.

The average moisture contents of sludge (57.7 percent) and aqueous samples (86.2 percent) were substantially higher than the DQO minimum limit of 17 weight percent, as measured by TGA. The only individual sample exhibiting a TGA moisture content below 17 percent was the upper half sludge sample from segment 4 of core 63. The initial sample showed a result of 13.47 percent. However, the duplicate and triplicate measured 26.37 and 29.70 percent, respectively. Because the DQO notification limit had been exceeded, a secondary analysis for percent water by gravimetry was performed on the same sample. This analysis was run twice, yielding an average of 25.15 percent water, which agreed with the duplicate and triplicate TGA values. Although the moisture level was low, no exothermic reactions were observed in the sample, indicating that the fuel level was low in this area. Also, this segment had an aqueous phase that contained 82.1 percent water which would account for an additional 18.9 weight percent water for the segment.

The criticality issue is assessed using the total alpha concentration. The safety screening criterion is 1 g/L. However, because the laboratory reports total alpha in units of $\mu\text{Ci/g}$, the 1 g/L threshold can be converted to 45.9 $\mu\text{Ci/g}$ for the sludge using the sludge density of 1.34 g/mL and to 57.2 $\mu\text{Ci/g}$ for the aqueous layer using the aqueous layer density of 1.076 g/mL. Total alpha results for the sludge and aqueous phases of the waste were well below their respective threshold limit.

The flammability of gas in the tank headspace is an additional safety screening consideration. As shown in Table 5-5, hydrogen, organic vapor, and ammonia fuel represent a combined total of 3.8 percent of the LFL, well below the safety screening limit of 25 percent of the LFL (Huckaby and Story 1994). At the reported concentrations, hydrogen, organic vapor, and ammonia do not represent a flammability hazard.

Vapor data from tank 241-C-103 were evaluated by a toxicology review panel (Mahlum et al. 1994). This panel concluded that concentrations of acetone, hexane, nitric oxide, nitrogen dioxide, sulfur dioxide, butanal and vinylidene chloride were not unacceptable. Ammonia, nitrous oxide, tributyl phosphate, acetonitrile, n-butanol, 2-hexanone, propane nitrile, benzene methylene chloride (may be an artifact), NPHs, and 1,3 butadiene are greater than one-half of the recommended exposure limit for noncarcinogens or greater than one-tenth of the recommended exposure limit for carcinogens therefore, they should receive further consideration. For more definitive toxicological evaluation, the panel recommended additional biological characterization of tank vapors.

Table 5-5. Tank 241-C-103 Vapor Flammability Results.

Analyte	LFL	Average Concentration	Concentration as Percent of LFL
H ₂	40,000 ppmv	782 ppmv	2.0%
Total organics ¹	46,000 mg/m ³	721 mg/m ³	1.6%
NH ₃	150,000 ppmv	304 ppmv	0.2%
Total:			3.8%

Note:

¹A conservative assumption, that the LFL of the organic vapor mixture is that of the semivolatiles alkanes (n-undecane, n-dodecane, n-tridecane, and n-tetradecane), is made.

Table 5-6 lists the decision criteria applicable to organic layer analyses at the time of the 1993 sampling event (Wood et al. 1993). The TRU, ¹³⁷Cs, and ⁹⁰Sr dose rates exceeded the criteria for allowable exposure in the event of a pool fire. Viscosity is measured to help determine the degree of thermal stagnation or mixing. The threshold of 1 centipoise was appropriate for this measurement because values below this would ensure essentially complete mixing in the organic layer. The viscosity exceeded the threshold of 1 centipoise,

indicating that complete thermal mixing may not be occurring. This information has been used to evaluate the risk of organic solvent fires in tank 241-C-103 (Meacham et al. 1995).

Table 5-6. Decision Thresholds Applicable to the 1993 Organic Layer Sampling Event.

Decision Variable	Decision Threshold	Analytical Values
Dose	TRU: 1.0E-08 Ci/L ⁹⁰ Sr: 2.4E-05 Ci/L ¹³⁷ Cs: 2.4E-05 Ci/L	4.75E-07 Ci/L ¹ 4.74E-04 Ci/L 3.58E-05 Ci/L
Criticality	1 g/L ²³⁹ Pu	2.74E-06 g/L
Deflagration	≥ 75 cal/g	not analyzed
Stagnation and Mixing	1 centipoise	4 centipoise at 25 °C 2.5 centipoise at 40 °C

Notes:

Cal/g = calories per gram

¹The TRU analytical value was derived by summing the extraction chromatography ²³⁸Pu and ^{239/240}Pu results and the GEA ²⁴¹Am result. The ²⁴¹Am result from GEA was used instead of the number from extraction chromatography because it was larger and provided the most conservative estimate.

Another factor in assessing the tank waste safety is the heat generation and waste temperature. Heat is generated in the tanks from radioactive decay. Column 2 of Table 5-7 lists the radionuclides analyzed in the sludge layer from 1995 sampling event. Because radionuclides were not evaluated in the supernate layer in the 1995 sampling event, column 3 lists the radionuclides analyzed from the 1993 supernate sampling event. Column 4 totals the values from these two events, and column 5 converts the values to watts, providing an overall estimate of the tank heat load. Because ⁹⁰Sr was not analyzed in the 1993 event, it was assumed that the difference between the total beta result and the sum of the ¹³⁷Cs and ⁶⁰Co results would represent the ⁹⁰Sr concentration. The calculated estimate of 9,270 watts was below the criteria of < 11,700 watts that separates a high from a low heat load tank. In a comparison, the HTCE estimate was 8,300 watts. Because an upper temperature limit is exhibited (see Section 2), it may be concluded that any heat generated from radioactive sources throughout the year is dissipated.

Table 5-7. Tank 241-C-103 Projected Heat Load.

Radionuclide	1995 Sludge Result	1993 Aqueous Result	Total	Total
	Ci	Ci	Ci	Watts
¹³⁷ Cs	38,400	28,100	66,500	314
⁶⁰ Co	595	24.8	620	9.5
¹⁵⁴ Eu	3,340	---	3,340	30.2
¹⁵⁵ Eu	2,810	---	2,810	2.0
⁹⁰ Sr	1.32E+06	6,100 (estimated)	1.33E+06	8,910
Total				9,270

5.5.2 Pretreatment

The 1986 analysis data report (Weiss and Schull 1988) provide results for water and acid soluble fractions that may support pretreatment evaluation. Appendix C represents the total composition based on the sum of the sample treatments.

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6.0 CONCLUSIONS AND RECOMMENDATIONS

Waste characterization for tank 241-C-103 was based on three different sampling events: a 1995 core sampling event, a 1994 vapor sampling event, and a 1993 grab sampling event. In 1995, the tank was sampled in accordance with the safety screening DQO (Babad and Redus, 1994) and organic DQO (Babad et al. 1994) which specified the analyses and decision criteria to govern the results. In 1994, vapor sampling was conducted in accordance with the tank 241-C-103 vapor and gas sampling DQO (Osborne et al. 1994). In 1993, the organic layer was sampled according to a DQO specifically addressing the sampling of that layer (Wood et al. 1993). The tank was also sampled in 1986, and a composite of the aqueous and sludge layers was analyzed.

In evaluating the data against the safety screening criteria, only the sludge from the lower half of segment 3 of core 63 (-540 J/g) and the drainable liquid from segment 4 of core 63 (-784 J/g) were found to contain waste that exceeded the safety screening energetics limit of -481 J/g for a dry sample. Replicate analyses of these wastes gave results that were below the criteria, and the moisture levels for both samples were well above the safety screen 17 weight percent criteria. The ratio of the exothermic to endothermic enthalpy was < 1 for both samples indicating that reaction propagation in the waste is not possible in its present condition. The nitrate and nitrite concentration for this waste was low and may be impacting the reproducibility of the exothermic reaction and DSC analyses. The nitrate and nitrite molar concentrations for these waste samples are near or below the oxidation stoichiometric requirements.

Secondary analyses (cyanide, nitrate and nitrite) were performed in support of the organic DQO because the energy equivalent of the TOC results based on acetate/nitrate reactions was not within 125 percent of the observed exothermic reaction for the DSC analysis. Cyanide concentrations were low and do not contribute to the fuel value of the waste. The nitrate and nitrite concentrations were relatively low and may result in nonstoichiometric reactions with the organics. The ion chromatography results indicate that approximately 10 percent of the organic is oxalate, which has a lower fuel value than the acetate used for evaluating the TOC equivalent energy. Although the average TOC concentrations for the sludge on a dry weight basis (19,400 $\mu\text{g/g}$) is below the organic DQO criteria (30,000 $\mu\text{g/g}$), the aqueous phase dry weight TOC result (48,100 $\mu\text{g/g}$) exceeded the limit. This poses no problem considering that the aqueous phase contains 86.2 percent water.

The average moisture content of tank sludge was 57.7 weight percent. Only the material in the upper half of segment 4 of core 63 had a single TGA moisture result less than 17 weight percent, but this material did not exhibit an exotherm. Additional gravimetric analyses using larger sample sizes indicated that the moisture content was 25.5 weight percent. In addition, the segment contained drainable liquid that would add an additional 18.9 weight percent water for the waste found in that segment. Lithium and bromide analysis indicated that hydrostatic head fluid may have contaminated only segment 4 of core 66. Further evaluation shows that this contamination was not substantial (approximately 1 or 2 percent dilution), and no adjustments were made to the data for this segment.

The estimated heat load based on radiological results from the 1993 and 1995 data indicate the heat load for the tank is 9,270 watts, well below the 11,700 watts criteria separating high from low heat load tanks. Tank temperature monitoring indicates that the mean temperature is 48.9 °C and, as expected based on the composition, does not show any evidence of temperature excursions. Because of these conditions, the potential for a propagating reaction in the sludge and aqueous phases in tank 241-C-103 is highly unlikely.

The highest total alpha result found was the 19.1 $\mu\text{Ci/g}$ result for segment 3 of core 63. This is well below the 45.9 $\mu\text{Ci/g}$ criticality criteria established by the safety screen DQO. The actinide levels in the sludge exceeded 100 nCi/g and would be designated a TRU waste.

The organic characterization in the 1993 data showed that the organic layer in the tank was about 64 weight percent TBP and 2.6 weight percent DBBP in NPH. This data indicates that the TBP has concentrated from the original process operating solvent which was 30 percent TBP in NPH. The DBBP, which was used only occasionally in limited quantities (Klem 1988) at PUREX, is not a normal component of PUREX solvent. Infrared analysis of the organic indicated that any nitration products of the organic were low, approximately 0.01 weight percent. The flash point of the organic was 118 °C, which agrees with what is expected for this TBP/NPH concentration. Because the total alpha and beta activities exceeded the DQO thresholds, additional specific radionuclide analyses were performed. All metal and radionuclide concentrations in the organic were low. The viscosity results for the organic were above the DQO criteria of 1 centipoise indicating that the organic may not be thoroughly mixed from thermal effects.

The vapor in the headspace of the tank was analyzed for its flammability and toxicological properties. The LFL for the vapor, based on the composition of the gases determined in the 1994 sampling and analysis activities, was 3.8 percent. This is well below the 25 percent LFL safety criteria. The vapor data from tank 241-C-103 were evaluated by a toxicology review panel. Their report indicated that the concentrations of the following components merited further consideration: ammonia, nitrous oxide, TBP, acetonitrile, n-butanol, 2-hexane, propane nitrile, benzene, NPHs, 1,3-butadiene, and methylene chloride (possible artifact of method). For a more definitive toxicological evaluation, the panel recommended additional biological characterization of the vapors.

The analytical results from the 1995 sampling event did not agree well quantitatively with the historical tank content estimates. However, the high aluminum concentrations in the lower layers support the historical tank content estimate prediction that the lower sludge layer is PUREX cladding waste. In addition, the higher ^{90}Sr results in segments 2 and 3 support the prediction that a washed PUREX sludge layer is above the cladding waste. The inventories, based on the 1995 sampling event, may be biased because not all segments of the waste were analyzed for those analytes. In these cases, the 1986 results in which composites were used may provide a more accurate estimate of the average tank waste composition. In addition, the 1986 analyses were performed in such a manner that solubility information is available that is useful to pretreatment evaluations. However, data from sampling and analysis events before 1990 may not be acceptable for some regulatory evaluations and decisions.

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APPENDIX A

1995 ANALYTICAL DATA RESULTS

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A.1 INTRODUCTION

Appendix A presents the chemical and radiological characteristics of the waste in tank 241-C-103 in terms of the specific metal, ion, radionuclide, and carbon concentrations.

The data table for each analyte lists the following: the analyte, sample number and location, an analytical data result, the result of duplicate analysis, a mean value for the sample (sample plus duplicate divided by two), an overall analyte mean, an error estimate given as the relative standard deviation (RSD), and the projected tank inventory for the particular analyte. The data are listed in standard notation for values greater than 0.001 and less than 100,000. Values outside these limits are listed in scientific notation.

A.2 COLUMN HEADINGS

The "Analyte" column contains the abbreviation of the analyte or physical characteristic, information about the measurement method, and where applicable, information about the method of sample digestion. The analyte and method are presented as follows: "method.analyte" or "method.digestion.analyte." For example, the specific concentration of aluminum was determined by the inductively coupled plasma method and digested by fusion; therefore, the analyte is denoted as ICP.f.Al.

The "Sample Number" column lists the laboratory sample number which is different from the number assigned to the samples at the tank farm. For sampling rational, locations, and descriptions of sampling events see Section 3.0.

The "Sample Location" column specifies the core and segment numbers from which the samples were obtained.

The "Segment Portion" column specifies the portion of the segment from which the sample was obtained.

The "Result" column lists the specific concentration of the analyte determined at the sampling location. The "Duplicate" column lists the results of the duplicate analyses on the individual samples.

The "Sample Mean" column averages the values in the "Result" and "Duplicate" columns. In the data package, three significant figures were usually given in the data package; in some cases, four were used. Thus, the mean column sometimes lists three or four significant figures, depending on the available data. In some cases, it will appear that the result and duplicate were rounded down rather than rounded up in calculating the mean, but this is reflecting significant figures not shown on the laboratory summary sheets. This information may be obtained from the following three data packages: the *45-Day Safety Screen Results for Tank 241-C-103, Push Mode Cores 63 and 66*, Westinghouse Hanford Company, Richland, Washington (Bell 1995a); the *90-Day Safety Screen Results for Tank 241-C-103, Push Mode Cores 63 and 66*, Westinghouse Hanford Company, Richland, Washington (Bell

1995b); and the *Final Report for Tank 241-C-103, Push Mode Cores 63 and 66*, Westinghouse Hanford Company, Richland, Washington (Bell, K.E., 1995c). Numbers that are preceded by a less than symbol (<) indicate that although the analyte was noted, it was below the analytical instrument's calibrated detection limit for the sample. The values listed are the detection limit and are used in all calculations. When a value less than the detection unit was given along with a detected value, the values were averaged together and reported as a detected mean. When both values given were less than the detection limit, they were averaged and reported as a nondetected mean.

The "Overall Mean" column lists the calculated weighted mean for the sludge and/or drainable liquid results. To obtain a weighted overall mean, the sample means are calculated, then segment means, and finally core means. This resulted in a calculated mean which was spatially balanced as much as possible. When over half of the sample means were reported as less than values, the overall weighted mean was considered a less than value. When half or more of the sample means were detected values, the weighted mean was considered a detect.

The column titled "RSD" (mean) is the variability estimate for the analyte. It is defined as the standard deviation divided by the mean, multiplied by one hundred. It is determined using standard analysis of variance statistical techniques. The RSDs were calculated only for those analytes in which all values were detected with the exception of nitrate and ¹⁵⁵Eu. The nondetected values in these cases were deleted from the analysis.

The final column lists the estimated total inventory for a given analyte based on the analyte concentration and specific waste phase volume. It is calculated for the sludge layer metals, ions, TIC, and TOC as follows:

$$\text{Analyte Concentration } \left(\frac{\mu\text{g}}{\text{g}} \right) * \left(\frac{1 \text{ kg}}{1.0\text{E}+09 \mu\text{g}} \right) * \left(\frac{1.34 \text{ g}}{\text{ml}} \right) * \left(\frac{1,000 \text{ ml}}{\text{L}} \right) * (2.35\text{E}+05 \text{ L}) = \text{Inventory (kg)}$$

Similarly, the total inventory in curies for the radionuclides was calculated as follows:

$$\text{Analyte Concentration } \left(\frac{\mu\text{Ci}}{\text{g}} \right) * \left(\frac{1 \text{ Ci}}{1.0\text{E}+06 \mu\text{Ci}} \right) * \left(\frac{1.34 \text{ g}}{\text{ml}} \right) * \left(\frac{1,000 \text{ ml}}{\text{L}} \right) * (2.35\text{E}+05 \text{ L}) = \text{Inventory (Ci)}$$

The total inventory for the anions, TIC, and TOC from the aqueous layer samples was calculated as follows:

$$\text{Analyte Concentration } \left(\frac{\mu\text{g}}{\text{ml}} \right) * \left(\frac{1 \text{ kg}}{1.0\text{E}+09 \mu\text{g}} \right) * \left(\frac{1,000 \text{ ml}}{\text{L}} \right) * (4.85\text{E}+05 \text{ L}) = \text{Inventory (kg)}$$

The sludge density value was obtained from *Data Transmittal Package for 241-C-103 Waste Tank Characterization*, (Weiss and Schull 1988), and the sludge and aqueous layer volumes were obtained from *Waste Tank Summary Report for Month Ending August 31, 1995* (Hanlon 1995). The aqueous layer volume of $4.85E+05$ L is derived from the Hanlon pumpable liquid volume by subtracting the organic layer volume, 18,200 L.

The four quality control parameters assessed on tank 241-C-103 samples were standard recoveries, spike recoveries, duplicate analyses (RPDs), and blanks. The quality control results were summarized in Section 5.1.2. Specific information is provided with each appendix table. Sample and duplicate pairs, in which any quality control parameter was outside its specified limit, are footnoted in the "Sample Mean" column as follows:

"a" indicates the standard recovery was below the quality control limit.

"b" indicates the standard recovery was above the quality control limit.

"c" indicates the spike recovery was below the quality control limit.

"d" indicates spike recovery was above the quality control limit.

"e" indicates the RPD was outside the quality control limit.

"f" indicates there was some blank contamination.

The quality control criteria specified in the Tank Characterization Program (Schreiber 1995) and DOE (1995) are summarized as follows:

Sludge samples:

Ninety to 110 percent recovery for standards and spikes, less than or equal to 10 percent for RPDs and less than or equal to 5 percent of the analyte concentration for blanks. These criteria applied to DSC, TGA, total alpha activity, TOC, lithium, bromide, cyanide, nitrate, nitrate, hydroxide, chromium, and iron results. For the gravimetric percent water data, the standard must be between 80 to 120 percent recovery, and the RPD must be less than or equal to 20 percent. All other analytes were subject to and met the internal laboratory criteria.

Liquid samples:

Ninety to 110 percent recovery for standards and spikes, less than or equal to 10 percent for RPDs, and less than or equal to 5 percent of the analyte concentration for blanks. These criteria applied to DSC, TGA, TOC, lithium, bromide, cyanide, nitrate, nitrite, and hydroxide results. All other analytes were subject to and met the internal laboratory criteria.

Table A-1. Tank 241-C-103 Analytical Data: ALUMINUM.¹

Analyte	Sample Number	Sample Location	Segment Portion	Result	Duplicate	Sample Mean	Overall Mean	RSD (Mean)	Projected Inventory
Sludge				µg/g	µg/g	µg/g	µg/g	%	kg
ICP.f.A1	S95T000094	core 63, seg. 4	upper half	1.92E+05	1.94E+05	1.93E+05	1.93E+05	0.1	60,800
	S95T000095	core 63, seg. 4	upper half	1.93E+05	1.94E+05	1.93E+05	05		

Notes: f = fusion digestion

¹Bell (1995c)

Table A-2. Tank 241-C-103 Analytical Data: CALCIUM.¹

Analyte	Sample Number	Sample Location	Segment Portion	Result	Duplicate	Sample Mean	Overall Mean	RSD (Mean)	Projected Inventory
Sludge				µg/g	µg/g	µg/g	µg/g	%	kg
ICP.f.Ca	S95T000094	core 63, seg. 4	upper half	< 3,431	< 3,431	< 3,431	< 3,800	---	< 1,200
	S95T000095	core 63, seg. 4	upper half	< 4,167	< 4,167	< 4,167			

Note: ¹Bell (1995c)

Table A-3. Tank 241-C-103 Analytical Data: CHROMIUM.¹

Analyte	Sample Number	Sample Location	Segment Portion	Result µg/g	Duplicate µg/g	Sample Mean µg/g	Overall Mean µg/g	RSD (Mean) %	Projected Inventory kg
ICP.f.Cr	S95T000094	core 63, seg. 4	upper half	864.2	957.2	910.7 ^o	970	5.9	305
	S95T000095	core 63, seg. 4	upper half	1,020	1,030	1,030			

Note: ¹Bell (1995c)

Table A-4. Tank 241-C-103 Analytical Data: IRON.¹

Analyte	Sample Number	Sample Location	Segment Portion	Result µg/g	Duplicate µg/g	Sample Mean µg/g	Overall Mean µg/g	RSD (Mean) %	Projected Inventory kg
ICP.f.Fe	S95T000094	core 63, seg. 4	upper half	14,100	14,400	14,300	15,800	9.2	4,980
	S95T000095	core 63, seg. 4	upper half	17,100	17,200	17,200			

Note: ¹Bell (1995c)

Table A-5. Tank 241-C-103 Analytical Data: LITHIUM.^{1,2}

Analyte	Sample Number	Sample Location	Segment Portion	Result µg/g	Duplicate µg/g	Sample Mean µg/g	Overall Mean µg/g	RSD (Mean) %	Projected Inventory kg
Sludge									
ICP.f.Li	S95T000054	core 63, seg. 2	upper half	< 95.2	< 95.2	< 95.2	< 86.3	---	< 27.2
	S95T000053	core 63, seg. 2	lower half	< 94.1	< 93.4	< 93.8			
	S95T000056	core 63, seg. 3	upper half	< 82.5	< 88.6	< 85.6			
	S95T000055	core 63, seg. 3	lower half	< 71.2	< 91.6	< 81.4			
	S95T000057	core 63, seg. 4	upper half	< 81.62	< 75.00	< 78.31			
	S95T000226	core 66, seg. 3	upper half	< 79.4	< 71.8	< 75.6			
	S95T000227	core 66, seg.4	upper half	91.08	106.8	98.94 ^o			
	Aqueous Layer			µg/ml	µg/ml	µg/ml	µg/ml	%	kg
ICP.d.Li	S94T000200	core 63, seg. 1		0.671	0.6424	0.657	35.6	78.5	17.3
	S95T000049	core 63, seg. 2		3.19	3.05	3.12			
	S95T000051	core 63, seg. 4		19.9	19.9	19.9			
	S95T000218	core 66, seg. 1		4.08	4.22	4.15			
	S95T000217	core 66, seg. 2		2.08	2.17	2.125			
	S95T000221	core 66, seg. 3		22.1	22.3	22.2			
	S95T000223	core 66, seg. 4.		227	223	225			

Notes:

d = direct

¹Added as a tracer to the HHF, thus, not a tank waste constituent.

²Bell 1995b.

Table A-6. Tank 241-C-103 Analytical Data: SODIUM.¹

Analyte	Sample Number	Sample Location	Segment Portion	Result µg/g	Duplicate µg/g	Sample Mean µg/g	Overall Mean µg/g	RSD (Mean) %	Projected Inventory kg
ICP.f.Na	S95T000094	core 63, seg. 4	upper half	26,000	25,900	26,000	26,400	1.7	8,310
	S95T000095	core 63, seg. 4	upper half	26,900	26,800	26,800			

Note: ¹Bell (1995c)

Table A-7. Tank 241-C-103 Analytical Data: NICKEL.^{1,2}

Analyte	Sample Number	Sample Location	Segment Portion	Result µg/g	Duplicate µg/g	Sample Mean µg/g	Overall Mean µg/g	RSD (Mean) %	Projected Inventory kg
ICP.f.Ni	S95T000094	core 63, seg. 4	upper half	28,800	29,400	29,100	32,600	10.7	10,300
	S95T000095	core 63, seg. 4	upper half	36,200	35,900	36,000			

Notes: ¹Fusion was conducted in a nickel crucible; thus, these results are not reliable.

²Bell (1995c)

Table A-8. Tank 241-C-103 Analytical Data: ZINC.¹

Analyte	Sample Number	Sample Location	Segment Portion	Result	Duplicate	Sample Mean	Overall Mean	RSD (Mean)	Projected Inventory
Sludge				µg/g	µg/g	µg/g	µg/g	%	kg
ICP.f.Zn	S95T000094	core 63, seg. 4	upper half	628.8	626.2	627.5	824	23.8	259
	S95T000095	core 63, seg. 4	upper half	1,040	998.8	1,020			

Note: ¹Bell (1995c)

Table A-9. Tank 241-C-103 Analytical Data: ZIRCONIUM.¹

Analyte	Sample Number	Sample Location	Segment Portion	Result	Duplicate	Sample Mean	Overall Mean	RSD (Mean)	Projected Inventory
Sludge				µg/g	µg/g	µg/g	µg/g	%	kg
ICP.f.Zr	S95T000094	core 63, seg. 4	upper half	10,300	10,400	10,300	11,400	9.4	3,590
	S95T000095	core 63, seg. 4	upper half	12,500	12,500	12,500			

Note: ¹Bell (1995c)

Table A-10. Tank 241-C-103 Analytical Data: BROMIDE,^{1,2}

Analyte	Sample Number	Sample Location	Segment Portion	Result µg/g	Duplicate µg/g	Sample Mean µg/g	Overall Mean µg/g	RSD (Mean) %	Protected Inventory kg
Sludge	S95T000872	core 63, seg. 2	upper half	< 156.9	< 149.4	< 153.2	< 627	---	< 197
	S95T000871	core 63, seg. 3	upper half	< 210.9	< 203.8	< 207.4			
	S95T000527	core 63, seg. 4	upper half	< 292.2	< 275.2	< 283.7			
	S95T000528	core 66, seg. 3	upper half	413	329	371 ^c			
	S95T000529	core 66, seg. 4	upper half	1,740	1,680	1,710			
Aqueous Layer									
IC.d.Br	S94T000200	core 63, seg. 1		< 888.	< 888.	< 888.	< 1,090	---	< 548
	S95T000049	core 63, seg. 2		< 1,110	< 1,110	< 1,110			
	S95T000051	core 63, seg. 4		< 606	< 606	< 606			
	S95T000052	core 63, seg. 4		268	260	264			
	S95T000218	core 66, seg. 1		< 889	< 889	< 889			
	S95T000214	core 66, seg. 2		< 888	< 888	< 888			
	S95T000220	core 66, seg. 3		< 889	< 889	< 889			
	S95T000222	core 66, seg. 4		2,820	2,810	2,820			

Notes: w = water digestion

¹Added as a tracer to the HHF, thus, not a tank waste constituent.

²Bell (1995b)

Table A-11. Tank 241-C-103 Analytical Data: CHLORIDE.¹

Analyte	Sample Number	Sample Location	Segment Portion	Result	Duplicate	Sample Mean	Overall Mean	RSD (Mean)	Projected Inventory
Sludge	S95T000872	core 63, seg. 2	upper half	467	456	461.5	414	26.5	130
	S95T000871	core 63, seg. 3	upper half	290	273	281.5			
	S95T000527	core 63, seg. 4	upper half	176	195	185.5			
	S95T000528	core 66, seg. 3	upper half	670	509	589.5			
	S95T000529	core 66, seg. 4	upper half	496	397	446.5			
Aqueous Layer									
IC.d.Cl	S94T000200	core 63, seg. 1		418	430	424	404	6.4	196
	S95T000049	core 63, seg. 2		439	465	452			
	S95T000051	core 63, seg. 4		410	402	406			
	S95T000052	core 63, seg. 4		443	406	424.5			
	S95T000218	core 66, seg. 1		396	401	398.5			
	S95T000214	core 66, seg. 2		373	381	377			
	S95T000220	core 66, seg. 3		385	376	380.5			
S95T000222	core 66, seg. 4		360	352	356				

Note:

¹Bell (1995c)

Table A-12. Tank 241-C-103 Analytical Data: CYANIDE.¹

Analyte	Sample Number	Sample Location	Segment Portion	Result	Duplicate	Sample Mean	Overall Mean	RSD (Data)	Projected Inventory
Sludge				$\mu\text{g/g}$	$\mu\text{g/g}$	$\mu\text{g/g}$	$\mu\text{g/g}$	%	kg
Microdst/Spec.CN	S95T000863	core 63, seg. 3	lower half	92.8	104	98.4 ²	98.4	8	31.0
Aqueous Layer									
Microdst/S pec.CN	S95T000051	core 63, seg. 4		26.6	27.2	26.9	26.9	2	13.0

Notes: Microdst/Spec = microdistillation/spectrophotometric

¹Bell (1995b)

Table A-13. Tank 241-C-103 Analytical Data: FLUORIDE.¹

Analyte	Sample Number	Sample Location	Segment Portion	Result	Duplicate	Sample Mean	Overall Mean	RSD (Mean)	Projected Inventory
Sludge				µg/g	µg/g	µg/g	µg/g	%	kg
IC.w.F.	S95T000872	core 63, seg. 2	upper half	1,090	1,070	1,080	1,070	14.8	337
	S95T000871	core 63, seg. 3	upper half	1,020	1,020	1,020			
	S95T000527	core 63, seg. 4	upper half	641.0	650.0	645.5			
	S95T000528	core 66, seg. 3	upper half	1,590	1,300	1,440			
	S95T000529	core 66, seg.4	upper half	998	1,010	1,000			
Aqueous Layer									
IC.d.F.	S94T000200	core 63, seg. 1		1,240	1,240	1,240	1,160	6.7	562
	S95T000049	core 63, seg. 2		1,190	1,190	1,190			
	S95T000051	core 63, seg. 4		1,240	1,240	1,240			
	S95T000052	core 63, seg. 4		1,330	1,340	1,340			
	S95T000218	core 66, seg. 1		1,170	1,140	1,160			
	S95T000214	core 66, seg. 2		1,090	1,120	1,100			
	S95T000220	core 66, seg. 3		1,080	1,120	1,100			
S95T000222	core 66, seg. 4		991	955	973				

Note: ¹Bell (1995c)

Table A-14. Tank 241-C-103 Analytical Data: HYDROXIDE.^{1,2}

Analyte	Sample Number	Sample Location	Segment Portion	Result µg/g	Duplicate µg/g	Sample Mean µg/g	Overall Mean µg/g	RSD (Mean) %	Projected Inventory kg
Pot. Tit. w. OH ⁻ Sludge	S95T000525	core 63, seg. 2	upper half	< 27,700	No result	< 27,700	< 26,300	---	< 8,280
	S95T000872	core 63, seg. 2	upper half	< 4,900	< 4,670	< 4,790			
	S95T000526	core 63, seg. 3	upper half	< 17,000	< 3.78E+05	< 1.98E+05			
	S95T000871	core 63, seg. 3	upper half	< 6,590	< 6,370	< 6,480			
	S95T000527	core 63, seg. 4	upper half	< 15,100	No result	< 15,100			
	S95T000528	core 66, seg. 3	upper half	< 8,570	< 8,720	< 8,650 ^a			
	S95T000529	core 66, seg. 4	upper half	< 7,760	7,550	< 7,660			

Notes:

Pot. Tit. = Potentiometric Titration

¹The free hydroxide was too low to titrate, based on the pH of 9.8 from the 1986 sampling event. The high < values are the result of performing the titration on water digested samples.

²Bell (1995b)

Table A-15. Tank 241-C-103 Analytical Data: NITRATE.¹

Analyte	Sample Number	Sample Location	Segment Portion	Result	Duplicate	Sample Mean	Overall Mean	RSD (Mean)	Projected Inventory
Sludge				µg/g	µg/g	µg/g	µg/g	%	kg
IC.w.NO ₃	S95T000872	core 63, seg. 2	upper half	1,690	1,710	1,700	1,730	36.6	545
	S95T000871	core 63, seg. 3	upper half	688	643	666			
	S95T000527	core 63, seg. 4	upper half	< 365.3	< 344.1	< 354.7			
	S95T000528	core 66, seg. 3	upper half	3,270	2,710	2,990 ^a			
	S95T000529	core 66, seg.4	upper half	2,190	2,020	2,100			
	Aqueous Layer				µg/ml	µg/ml	µg/ml	µg/ml	%
IC.d.NO ₃	S94T000200	core 63, seg. 1		2,590	2,630	2,610	2,140	14.3	1,040
	S95T000049	core 63, seg. 2		2,630	2,600	2,620			
	S95T000051	core 63, seg. 4		< 606	< 606	< 606			
	S95T000052	core 63, seg. 4		339	322	330			
	S95T000218	core 66, seg. 1		2,510	2,470	2,490			
	S95T000214	core 66, seg. 2		2,430	2,420	2,420			
	S95T000220	core 66, seg. 3		2,370	2,370	2,370			
	S95T000222	core 66, seg. 4		2,230	2,290	2,260			

Note: ¹Bell (1995b)

Table A-16. Tank 241-C-103 Analytical Data: NITRITE.¹

Analyte	Sample Number	Sample Location	Segment Portion	Result	Duplicate	Sample Mean	Overall Mean	RSD (Mean)	Projected Inventory
Sludge				µg/g	µg/g	µg/g	µg/g	%	kg
IC.w.NO ₂	S95T000872	core 63, seg. 2	upper half	19,600	19,300	19,400	17,600	49.1	5,540
	S95T000871	core 63, seg. 3	upper half	7,250	7,570	7,380			
	S95T000527	core 63, seg. 4	upper half	2,340	2,410	2,380			
	S95T000528	core 66, seg. 3	upper half	32,300	26,500	29,400*			
	S95T000529	core 66, seg. 4	upper half	22,300	21,000	21,600			
Aqueous Layer									
IC.d.NO ₂	S94T000200	core 63, seg. 1		26,400	25,500	26,000	21,200	12.9	10,300
	S95T000049	core 63, seg. 2		24,400	23,900	24,200			
	S95T000051	core 63, seg. 4		6,220	6,310	6,260			
	S95T000052	core 63, seg. 4		6,700	6,700	6,700			
	S95T000218	core 66, seg. 1		24,200	24,100	24,200			
	S95T000214	core 66, seg. 2		22,900	23,800	23,400			
	S95T000220	core 66, seg. 3		24,000	24,000	24,000			
	S95T000222	core 66, seg. 4		22,800	22,200	22,500			

Note: ¹Bell (1995b)

Table A-17. Tank 241-C-103 Analytical Data: OXALATE.¹

Analyte	Sample Number	Sample Location	Segment Portion	Result	Duplicate	Sample Mean	Overall Mean	RSD (Mean)		Projected Inventory
								µg/g	µg/g	
IC.w. Oxalate	S95T000872	core 63, seg. 2	upper half	2,610	2,720	2,660	2,710		28.7	853
	S95T000871	core 63, seg. 3	upper half	1,960	1,930	1,940				
	S95T000527	core 63, seg. 4	upper half	1,290	1,340	1,320				
	S95T000528	core 66, seg. 3	upper half	4,300	3,550	3,920				
	S95T000529	core 66, seg. 4	upper half	3,030	2,900	2,960				
Aqueous Layer										
IC.d. Oxalate	S94T000200	core 63, seg. 1		3,390	3,320	3,360	3,210		7.1	1,560
	S95T000051	core 63, seg. 4		3,360	3,360	3,360				
	S95T000052	core 63, seg. 4		3,730	3,550	3,640				
	S95T000218	core 66, seg. 1		3,180	3,090	3,140				
	S95T000214	core 66, seg. 2		3,110	3,090	3,100				
	S95T000220	core 66, seg. 3		2,950	2,960	2,960				
	S95T000222	core 66, seg. 4		2,720	2,740	2,730				

Note: ¹Bell (1995c)

Table A-18. Tank 241-C-103 Analytical Data: PHOSPHATE.

Analyte	Sample Number	Sample Location	Segment Portion	Result $\mu\text{g/g}$	Duplicate $\mu\text{g/g}$	Sample Mean $\mu\text{g/g}$	Overall Mean $\mu\text{g/g}$	RSD (Mean) %	Projected Inventory kg
Sludge	S95T000872	core 63, seg. 2	upper half	2,940	3,180	3,060	3,240	12.9	1,020
	S95T000871	core 63, seg. 3	upper half	2,880	2,910	2,900			
	S95T000527	core 63, seg. 4	upper half	2,490	2,560	2,520			
	S95T000528	core 66, seg. 3	upper half	4,880	3,990	4,440			
	S95T000529	core 66, seg. 4	upper half	2,730	2,990	2,860			
Aqueous Layer									
IC.d.PO ₄ ³	S94T000200	core 63, seg. 1		2,060	2,090	2,080	2,250	13.1	1,090
	S95T000049	core 63, seg. 2		2,480	2,400	2,440			
	S95T000051	core 63, seg. 4		3,130	3,140	3,140			
	S95T000052	core 63, seg. 4		3,230	3,040	3,140			
	S95T000218	core 66, seg. 1		2,020	1,990	2,000			
	S95T000214	core 66, seg. 2		1,870	1,940	1,900			
	S95T000220	core 66, seg. 3		2,000	2,080	2,040			
S95T000222	core 66, seg. 4		1,850	1,800	1,820				

Note: 'Bell (1995c)

Table A-19. Tank 241-C-103 Analytical Data: SULFATE.¹

Analyte	Sample Number	Sample Location	Segment Portion	Result	Duplicate	Sample Mean	Overall Mean	RSD (Mean)	Projected Inventory
IC. w. SO ₄ ²⁻	S95T000872	core 63, seg. 2	upper half	2,820	2,880	2,850	2,790	28.3	879
	S95T000871	core 63, seg. 3	upper half	2,030	1,990	2,010			
	S95T000527	core 63, seg. 4	upper half	1,270	1,280	1,280			
	S95T000528	core 66, seg. 3	upper half	4,430	3,670	4,050			
	S95T000529	core 66, seg. 4	upper half	3,080	2,980	3,030			
Aqueous Layer									
IC. d. SO ₄ ²⁻	S94T000200	core 63, seg. 1		3,350	3,360	3,360	3,220	3.8	1,560
	S95T000049	core 63, seg. 2		3,360	3,370	3,360			
	S95T000051	core 63, seg. 4		3,260	3,280	3,270			
	S95T000052	core 63, seg. 4		3,060	3,420	3,510			
	S95T000218	core 66, seg. 1		3,220	3,170	3,200			
	S95T000214	core 66, seg. 2		3,050	3,080	3,060			
	S95T000220	core 66, seg. 3		3,100	3,130	3,120			
S95T000222	core 66, seg. 4		2,940	2,920	2,930				

Note:

¹Bell (1995c)

Table A-20. Tank 241-C-103 Analytical Data: CESIUM-137.¹

Analyte	Sample Number	Sample Location	Segment Portion	Result μCi/g	Duplicate μCi/g	Sample Mean μCi/g	Overall Mean μCi/g	RSD (Mean)		Projected Inventory
								%	Ci	
Sludge							122	25.6		38,400
GEA.f. ¹³⁷ Cs	S95T000054	core 63, seg. 2	upper half	133	131	132				
	S95T000053	core 63, seg. 2	lower half	139.0	130.0	134.5				
	S95T000056	core 63, seg. 3	upper half	167.0	154.0	160.5				
	S95T000055	core 63, seg. 3	lower half	169	215	192				
	S95T000057	core 63, seg. 4	upper half	55.4	59.0	57.2				

Note:

¹Bell (1995c)

Table A-21. Tank 241-C-103 Analytical Data: COBALT-60.¹

Analyte	Sample Number	Sample Location	Segment Portion	Result μCi/g	Duplicate μCi/g	Sample Mean μCi/g	Overall Mean μCi/g	RSD (Mean)		Projected Inventory
								%	Ci	
Sludge							1.89	36.8		595
GEA.f. ⁶⁰ Co	S95T000054	core 63, seg. 2	upper half	1.800	2.310	2.055				
	S95T000053	core 63, seg. 2	lower half	2.48	2.20	2.34				
	S95T000056	core 63, seg. 3	upper half	3.650	3.700	3.675				
	S95T000055	core 63, seg. 3	lower half	2.500	2.590	2.545				
	S95T000057	core 63, seg. 4	upper half	0.360	0.338	0.349				

Note:

¹Bell (1995c)

Table A-22. Tank 241-C-103 Analytical Data: EUROPIUM-154.¹

Analyte	Sample Number	Sample Location	Segment Portion	Result	Duplicate	Sample Mean	Overall Mean	RSD (Mean)		Projected Inventory
								$\mu\text{Ci/g}$	$\mu\text{Ci/g}$	
Studge GEA.f. ¹⁵⁴ Eu	S95T000054	core 63, seg. 2	upper half	14.00	8.950	11.47	10.6		40.9	3,340
	S95T000053	core 63, seg. 2	lower half	12.70	11.80	12.25				
	S95T000056	core 63, seg. 3	upper half	22.4	19.4	20.9				
	S95T000055	core 63, seg. 3	lower half	14.20	18.70	16.45				
	S95T000057	core 63, seg. 4	upper half	1.04	1.20	1.12				

Note: ¹Bell (1995c)

Table A-23. Tank 241-C-103 Analytical Data: EUROPIUM-155.¹

Analyte	Sample Number	Sample Location	Segment Portion	Result	Duplicate	Sample Mean	Overall Mean	RSD (Mean)		Projected Inventory
								$\mu\text{Ci/g}$	$\mu\text{Ci/g}$	
Studge GEA.f. ¹⁵⁵ Eu	S95T000054	core 63, seg. 2	upper half	9.020	8.450	8.735	8.93		50.3	2,810
	S95T000053	core 63, seg. 2	lower half	9.21	9.19	9.20				
	S95T000056	core 63, seg. 3	upper half	22.40	19.90	21.15				
	S95T000055	core 63, seg. 3	lower half	< 8.09	17.0	12.5				
	S95T000057	core 63, seg. 4	upper half	0.882	1.120	1.001				

Note: ¹Bell (1995c)

Table A-24. Tank 241-C-103 Analytical Data: STRONTIUM-89/90.¹

Analyte	Sample Number	Sample Location	Segment Portion	Result μCi/g	Duplicate μCi/g	Sample Mean μCi/g	Overall Mean μCi/g	RSD (Mean) %	Projected Inventory Ci
Beta f. ⁹⁰ Sr	S95T000054	core 63, seg. 2	upper half	4,820	4,580	4,700	4,190	39.4	1.32E+06
	S95T000053	core 63, seg. 2	lower half	5,010	4,500	4,760			
	S95T000056	core 63, seg. 3	upper half	6,990	6,520	6,760			
	S95T000055	core 63, seg. 3	lower half	6,610	8,800	7,700			
	S95T000057	core 63, seg. 4	upper half	573.0	618.0	595.5			

Note: ¹Bell (1995c)

Table A-25. Tank 241-C-103 Analytical Data: TOTAL ALPHA.¹

Analyte	Sample Number	Sample Location	Segment Portion	Result μCi/g	Duplicate μCi/g	Sample Mean μCi/g	Overall Mean μCi/g	RSD (Mean) %	Projected Inventory Ci
Sludge APC.f. Total Alpha	S95T000054	core 63, seg. 2	upper half	13.6	12.9	13.2	9.74	23.6	3,070
	S95T000053	core 63, seg. 2	lower half	14.1	13.8	13.9			
	S95T000056	core 63, seg. 3	upper half	18.5	19.6	19.1			
	S95T000055	core 63, seg. 3	lower half	13.2	14.4	13.8			
	S95T000057	core 63, seg. 4	upper half	1.90	1.57	1.73 ^a			
	S95T000226	core 66, seg. 3	upper half	6.73	4.97	5.85 ^a			
	S95T000227	core 66, seg. 4	upper half	11.2	12.7	11.9 ^a			

Notes: APC = alpha proportional counting
¹Bell (1995c)

Table A-26. Tank 241-C-103 Analytical Data: TOTAL INORGANIC CARBON.¹

Analyte	Sample Number	Sample Location	Segment Portion	Result µg C/g	Duplicate µg C/g	Sample Mean µg C/g	Overall Mean µg C/g	RSD (Mean) %	Projected Inventory kg C
Sludge									
Acid/ Coul. TIC	S95T000045	core 63, seg. 2	upper half	4,860	5,190	5,020	4,960	9.2	1,560
	S95T000038	core 63, seg. 2	lower half	6,380	6,760	6,570			
	S95T000047	core 63, seg. 3	upper half	5,850	5,740	5,800			
	S95T000046	core 63, seg. 3	lower half	6,210	6,020	6,120			
	S95T000048	core 63, seg. 4	upper half	3,900	5,080	4,490			
	S95T000024	core 66, seg. 3	upper half	4,850	4,370	4,610			
	S95T000025	core 66, seg. 4	upper half	4,520	4,280	4,400			
	Aqueous Layer				µg C/ml	µg C/ml	µg C/ml	µg C/ml	%
Acid/ Coul. TIC	S94T000200	core 63, seg. 1		5,630	5,430	5,530	6,850	19.6	3,320
	S95T000049	core 63, seg. 2		5,420	5,540	5,480			
	S95T000052	core 63, seg. 4		9,740	9,340	9,540			

Notes: Acid/Coul. = acid/coulometry
¹Bell (1995c)

Table A-27. Tank 241-C-103 Analytical Data: TOTAL ORGANIC CARBON.¹

Analyte	Sample Number	Sample Location	Segment Portion	Result µg C/g	Duplicate µg C/g	Sample Mean µg C/g	Overall Mean µg C/g	RSD (Mean) %	Projected Inventory kg C
Persulf/ Coul. TOC	S95T000045	core 63, seg. 2	upper half	7,650	9,330	8,490*	8,210	10.8	2,590
	S95T000038	core 63, seg. 2	lower half	10,700	9,790	10,200*			
	S95T000047	core 63, seg. 3	upper half	7,340	7,850	7,600			
	S95T000046	core 63, seg. 3	lower half	8,860	8,940	8,900			
	S95T000048	core 63, seg. 4	upper half	4,360	4,650	4,500* ^c			
	S95T000224	core 66, seg. 3	upper half	8,760	9,050	8,900			
	S95T000225	core 66, seg. 4	upper half	8,460	9,930	9,200*			
	Aqueous Layer								
Persulf/ Coul. TOC	S94T000200	core 63, seg. 1		7,630	7,110	7,370	6,640	5.9	3,220
	S95T000049	core 63, seg. 2		7,370	7,420	7,400			
	S95T000052	core 63, seg. 4		4,560	4,540	4,550			
	S95T000218	core 66, seg. 1		7,200	7,340	7,270			
	S95T000214	core 66, seg. 2		7,130	6,800	6,970*			
	S95T000220	core 66, seg. 3		6,750	6,760	6,760			
	S95T000222	core 66, seg. 4		5,950	6,070	6,970			
	S95T000200	core 63, seg. 1		7,810	7,610	7,710			
Fur/Oxid .TOC	S95T000112	core 63, seg. 2		7,560	7,660				

Notes: Persulf/Coul = Persulfate/Coulometry
 Fur/Oxid = Furnace Oxidation

¹Bell (1995b)

Table A-28. Tank 241-C-103 Analytical Data: THERMOGRAVIMETRIC ANALYSIS.¹

Analyte	Sample Number	Sample Location	Segment Portion	Result %	Duplicate %	Sample Mean %	Overall Mean %	RSD (Mean) %
Sludge								
Mettler™, TG A (% H ₂ O)	S95T000045	core 63, seg. 2	upper half	63.09	61.30	62.20	57.7	34.9
	S95T000038	core 63, seg. 2	lower half	56.63	54.05	55.34		
	S95T000047	core 63, seg. 3	upper half	49.75	51.26	50.50		
	S95T000046	core 63, seg. 3	lower half	30.82	44.04	37.43°		
	S95T000566	core 63, seg. 3	lower half	43.23	27.20	35.21°		
	S95T000048	core 63, seg. 4	upper half	13.47	26.37	19.92°		
	S95T000224	core 66, seg. 3	upper half	79.15	69.13	74.14°		
	S95T000225	core 66, seg. 4	upper half	76.46	73.49	74.97		
	S95T000887	core 63, seg. 4	upper half	25.30	25.0	25.15		
Grav. (% H ₂ O)								
Aqueous Layer								
Mettler™, TG A (% H ₂ O)	S94T000200	core 63, seg. 1		88.29	88.57	88.43	86.2	2.2
	S95T000049	core 63, seg. 2		81.66	87.30	84.48		
	S95T000052	core 63, seg. 4		82.12	77.85	79.98		
	S95T000218	core 66, seg. 1		87.79	88.10	87.94		
	S95T000214	core 66, seg. 2		87.86	87.28	87.57		
	S95T000220	core 66, seg. 3		87.47	86.99	87.23		
	S95T000222	core 66, seg. 4		89.50	89.38	89.44		

Notes:

Grav = gravimetry
 'Bell (1995a), Bell (1995b), and Bell (1995c)

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APPENDIX B

HISTORICAL ANALYTICAL RESULTS

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Table B-1. Tank 241-C-103 1990 Aqueous Layer Results. (2 sheets)

Analyte	R8108	R8109	Mean
Metals	µg/g	µg/g	µg/g
Aluminum	10	9	10
Arsenic	0.12 mg/L	0.12 mg/L	0.12 mg/L
Cadmium	1	1	1
Calcium	3	3	3
Chromium	81	77	79
Copper	3	2	2
Iron	4	4	4
Magnesium	2	2	2
Manganese	0.3	0.2	0.2
Molybdenum	12	12	12
Nickel	80	76	78
Potassium	270	260	265
Selenium	0.03 mg/L	0.03 mg/L	0.03 mg/L
Silicon	22	21	21.5
Silver	24	24	24
Sodium	36,000	36,000	36,000
Tin	5	5	5
Zirconium	300	290	295
Anions	µg/g	µg/g	µg/g
Carbonate	0.4 mol/L	0.4 mol/L	0.4 mol/L
Cyanide	5.5 ¹	52.9 ²	29.2
Nitrate	4,300	4,200	4,250
Nitrite	30,000	27,000	28,500
Phosphate	2,100	2,000	2,050
Sulfate	26,000	27,000	26,500
Radionuclides	µCi/L	µCi/L	µCi/L
^{89/90} Sr	2,500	3,300	2,900
⁹⁹ Tc	37	67	52
^{239/240} Pu	24	24	24
²⁴¹ Am	0.3	0.5	0.4
⁶⁰ Co	74	67	70.5
¹³⁷ Cs	64,000	62,000	63,000

Table B-1. Tank 241-C-103 1990 Aqueous Layer Results. (2 sheets)

Analyte	R8108	R8109	Mean
Physical Properties			
Percent H ₂ O	91%	91%	91%
pH	9.5	9.5	9.5
Specific Gravity	1.07	1.06	1.06
TOC	7.46 g C/L	7.44 g C/L	7.45 g C/L

Notes:

¹This result is taken from sample R8346, which was obtained during a second sampling of tank 241-C-103. The second sampling was required because the organic layer was not sampled during the first. Sample R8346 is that organic layer.

²This result is taken from sample R8347, also obtained during the second sampling of the tank. The sample was acquired from the bottom portion of the aqueous layer.

Table B-2. Tank 241-C-103 1986 Sludge Results. (2 sheets)

Analyte	Core Composite Riser 2	Core Composite Riser 8	Mean
Metals	$\mu\text{g/g}$	$\mu\text{g/g}$	$\mu\text{g/g}$
Aluminum	15,300	13,700	14,500
Barium	4,920	5,010	4,970
Bismuth	680	766	723
Boron	0	4.85	2.43
Cadmium	570	448	509
Calcium	10,700	11,500	11,100
Chromium	731	504	618
Cobalt	54.2	71.5	62.9
Copper	1,530	181	856
Iron	1.05E+05	68,600	86,800
Lead	4,370	2,750	3,560
Magnesium	5,810	6,570	6,190
Manganese	2,560	2,400	2,480
Nickel	3,270	2,430	2,850
Phosphorus	4,090	4,260	4,180
Potassium	1,450	1,360	1,410
Silicon	68,000	73,200	70,600
Silver	373	69.5	221
Sodium	40,300	60,700	50,500
Strontium	138	96.9	117
Uranium	2,190	4,690	3,440
Zinc	269	80.3	175
Zirconium	15,500	9,130	12,300
Anions	$\mu\text{g/g}$	$\mu\text{g/g}$	$\mu\text{g/g}$
Nitrate	1,790	3,830	2,810
Radionuclides	$\mu\text{Ci/g}$	$\mu\text{Ci/g}$	$\mu\text{Ci/g}$
^{239/240} Pu	11.5	6.43	8.97
¹⁴ C	3.81E-04	2.90E-04	3.36E-04
⁹⁰ Sr	4,160	1,680	2,920
⁹⁹ Tc	0.467	0.196	0.332
²⁴¹ Am	1.57	1.44	1.51

Table B-2. Tank 241-C-103 1986 Sludge Results. (2 sheets)

Analyte	Core Composite Riser 2	Core Composite Riser 8	Mean
Radionuclides (Cont'd)	$\mu\text{Ci/g}$	$\mu\text{Ci/g}$	$\mu\text{Ci/g}$
^{60}Co	6.75	3.31	5.03
^{137}Cs	139	77	108
^{129}I	2.30E-05	0	1.15E-05
Total Gamma	226	105	166
Physical Properties			
TOC	3,900 $\mu\text{g/g}$	2,630 $\mu\text{g/g}$	3,270 $\mu\text{g/g}$
pH	9.8	9.8	9.8
Bulk Density	1.13 g/mL	1.54 g/mL	1.34 g/mL

Table B-3. Tank 241-C-103 1986 Aqueous Layer Results. (2 sheets)

Analyte	Core Composite Riser 2	Core Composite Riser 8	Mean
Metals	mg/L	mg/L	mg/L
Aluminum	< 13.9	< 13.9	< 13.9
Barium	2.17	5.12	3.65
Bismuth	161	76.4	119
Boron	4.48	5.26	4.87
Cadmium	< 10.2	< 10.2	< 10.2
Calcium	15.2	16.7	16
Chromium	66.6	143	105
Copper	197	4.83	101
Iron	9.69	8.88	9.29
Lead	< 33.2	< 33.2	< 33.2
Magnesium	5.49	8.49	6.99
Manganese	< 82	< 82	< 82
Nickel	60.4	120	90.2
Phosphorus	1,450	1,600	1,530
Potassium	351	364	358
Silicon	129	135	132
Silver	23.6	39.1	31.4
Sodium	40,200	38,300	39,300
Strontium	0.477	0	23.9
Uranium	2,630	11,000	6,820
Zinc	7.3	0	3.65
Zirconium	359	202	281
Anions	mol/L	mol/L	mol/L
Nitrate	0.0754	0.144	0.110
Radionuclides	μCi/L	μCi/L	μCi/L
^{239/240} Pu	33.2	33.7	33.5
¹⁴ C	0.969	0.631	0.800
⁹⁰ Sr	1,950	2,630	2,290
⁹⁹ Tc	37.0	35.7	36.4
²⁴¹ Am	< 3.74	< 1.31	< 2.53
⁶⁰ Co	< 57.3	< 39.3	< 48.3

Table B-3. Tank 241-C-103 1986 Aqueous Layer Results. (2 sheets)

Analyte	Core Composite Riser 2	Core Composite Riser 8	Mean
Radionuclides (Cont'd)	$\mu\text{Ci/L}$	$\mu\text{Ci/L}$	$\mu\text{Ci/L}$
^{137}Cs	22,100	21,200	21,700
^{129}I	0.270	0.040	0.155
Total Gamma	22,200	21,300	21,800
Physical Properties			
TOC	7.37 g/L	7.2 g/L	7.29 g/L
pH	9.91	9.52	9.72
Density	1.11 g/mL	1.08 g/mL	1.10 g/mL

Note:

mg/L = milligrams per liter.

APPENDIX C
ANALYTICAL METHODS AND PROCEDURES

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Table C-1. 1995 Sampling Event Analytical Methods and Procedure Numbers.¹

Method	Analyte	Procedure Number
Inductively coupled plasma	Aluminum, Calcium, Chromium, Iron, Sodium, Zinc, Zirconium	LA-505-151, Rev. A-1 LA-505-161, Rev. A-1
	Lithium	LA-505-151, Rev. D-1 LA-505-161, Rev. A-1
Gamma energy analysis	Cesium-137, Cobalt-60, Europium-154, Europium-155	LA-548-121, Rev. D-1
High level beta counting	Strontium-90	LA-220-101, Rev. D-1
Ion chromatography	Bromide, Chloride, Fluoride, Nitrate, Nitrite, Oxalate, Phosphate, Sulfate	LA-533-105, Rev. C-2
Titration	Hydroxide	LA-211-102, Rev. B-1
Microdistillation/ Spectrophotometric	Cyanide	LA-695-102, Rev. C-0
Persulfate/Coulometry	Total organic carbon, Total inorganic carbon	LA-342-100, Rev. A-0
Furnace Oxidation	Total organic carbon	LA-344-105, Rev. B-3
Thermogravimetric Analysis	Percent moisture	LA-560-112, Rev. A-2
Gravimetric	Percent moisture	LA-564-101, Rev. F-1
Differential Scanning Calorimetry	Fuel content, energetics	LA-514-113, Rev. B-1
Total Alpha	Alpha (fissile actinides)	LA-508-101, Rev. D-2

Note:

¹Bell (1995a, 1995b, and 1995c)

Table C-2. Analytical Procedures for 1993 Aqueous Layer Analyses.¹

Analyte	Procedure	Procedure Number
Organic Compounds	Gas Chromatograph/Mass Spectrometry	Not Available
Energetics	Differential Scanning Calorimetry/Thermogravimetric Analyzer	PNL-ALO-508, rev.0
Viscosity	Cone and Plate Viscometer	PNL-ALO-502
Density	Cone and Plate Viscometer	PNL-ALO-502
Gross Alpha	Source Preparation Scintillation Counter	PNL-ALO-460 PNL-ALO-461
Gross Beta	Source Preparation Beta Proportional Counting	PNL-ALO-462 PNL-ALO-463
Total Carbon, Total Inorganic Carbon, Total Organic Carbon	Hot Persulfate Oxidation/Coulometry	PNL-ALO-381, rev.0
Anions	Ion Chromatography	PNL-ALO-212
Cations	Inductively Coupled Plasma Spectrometry	PNL-ALO-211
pH	Direct	PNL-ALO-225

Note:

¹Pool and Bean (1994)

Table C-3. Analytical Procedures for 1993 Organic Layer Analyses.¹

Analyte	Procedure	Procedure Number
Flash Point	CCA-FLP Miniflash Closed Cup Tester	PNL-ALO-234
Organic Compounds	Gas Chromatograph/Mass Spectrometry	Not Available
Nitroalkanes	Infrared Analysis	Not Available
	Fourier Transform Infrared Spectroscopy	
Viscosity	Cone and Plate Viscometer	PNL-ALO-502
Density	Cone and Plate Viscometer	PNL-ALO-502
Gross Alpha	Source Preparation Scintillation Counter	PNL-ALO-460 PNL-ALO-461
Gross Beta	Source Preparation Beta Proportional Counting	PNL-ALO-462 PNL-ALO-463
Gamma Energy (⁶⁰ Co, ¹³⁷ Cs, ¹⁵⁴ Eu, ¹⁵⁵ Eu, ²⁴¹ Am)	Gamma Energy Analysis - Track Detector	PNL-ALO-450
Radioisotope Analysis ⁹⁰ Sr	Source Preparation Beta Proportional Counting	PNL-ALO-476 PNL-ALO-463
Radioisotope Analysis ²³⁸ Pu, ^{239/240} Pu, ²⁴¹ Am	Separation Alpha Energy Analysis	PNL-ALO-417 PNL-ALO-496
Water Content	Coulometric Karl Fischer Titration	Not Available
Anions	Ion Chromatography	PNL-ALO-212
Cations	Inductively Coupled Plasma Spectrometry	PNL-ALO-211
NH ₃	Ion Selective Electrode	PNL-ALO-226

Note:

¹Pool and Bean (1994)

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APPENDIX D

SELECTED THERMOGRAVIMETRIC AND

DIFFERENTIAL SCANNING CALORIMETRY GRAPHS

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Figure D-1. Typical Thermogravimetric Analysis Graph.

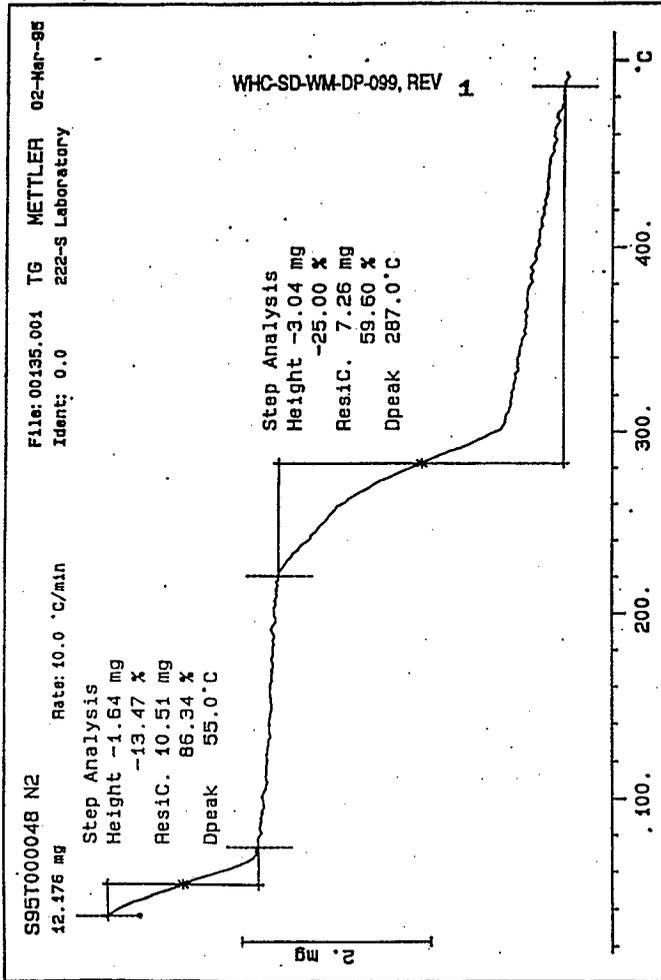


Figure D-2. Typical Differential Scanning Calorimetry Graph.

