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1	1	QA K. K. CUTSFORTH	Kimberly Cutsforth	1/13/95		Proj. S. C. GOHEEN	[signature]	1/12/95		1	1
		Safety				Proj. R. A. JENKINS	see attachment			1	1
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11. Receiver Remarks:		12. Major Assm. Dwg. No.: N/A
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1		Cog.Eng. C. S. HOMI	[signature]	1/9/95	[illegible]	Proj. J. W. OSBORNE				1	
1		Cog. Mgr. C. S. HALLER	[signature]	1/9/95		Proj. D. L. EDWARDS				1	
1		QA K. K. CUTSFORTH				Proj. S. C. GOHEEN				1	
		Safety				Proj. R. A. JENKINS	[signature]	1/9/95		1	
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Document Title:	TANK 241-T-111 TANK CHARACTERIZATION PLAN
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This document was reviewed following the procedures described in WHC-CM-3-4 and is:

APPROVED FOR PUBLIC RELEASE

WHC Information Release Administration Specialist:

Kara M. Broz — January 13, 1995

SUPPORTING DOCUMENT

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3. Number	WHC-SD-WM-TP-200
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6. Author

Name: C. S. HOMI

Signature 1/9/95

Organization/Charge Code 71520/N4168

7. Abstract

This document is a plan which serves as the contractual agreement between the Characterization Program, Sampling Operations, Oak Ridge National Laboratory, and PNL tank vapor program. The scope of this plan is to provide guidance for the sampling and analysis of vapor samples from tank 241-T-111.

8. RELEASE STAMP

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Tank 241-T-111
Tank Characterization Plan

Prepared for the U.S. Department of Energy
Office of Environmental Restoration
and Waste Management

by

Los Alamos Technical Associates
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Kennewick, Washington 99336

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LIST OF ABBREVIATIONS

244	Lanthanum Fluoride Waste
2C	Second-Cycle Decontamination Waste
DNFSB	Defense Nuclear Facilities Safety Board
DOE	Department of Energy
DQO	Data Quality Objective
DST	Double-Shell Tank
NCPLX	Non-complexed Waste
RCRA	Resource Conservation and Recovery Act
SST	Single-Shell Tank
T-111	Tank 241-T-111
TCP	Tank Characterization Plan
TIC	Total Inorganic Carbon
TOC	Total Organic Carbon
TWRS	Tank Waste Remediation System
WHC	Westinghouse Hanford Company

1.0 INTRODUCTION

The Defense Nuclear Facilities Safety Board (DNFSB) has advised the Department of Energy (DOE) to concentrate the near-term sampling and analysis activities on the identification and resolution of safety issues (Conway 1993). The data quality objective (DQO) process was chosen as a tool to be used to identify the sampling and analytical needs for the resolution of safety issues. As a result, a revision in the Federal Facility Agreement and Consent Order (Tri-Party Agreement) milestone M-44-00 has been made, which states that "A Tank Characterization Plan (TCP) will also be developed for each double-shell tank (DST) and single-shell tank (SST) using the DQO process . . . Development of TCPs by the DQO process is intended to allow users (e.g., Hanford Facility user groups, regulators) to ensure their needs will be met and that resources are devoted to gaining only necessary information." This document satisfies that requirement for tank 241-T-111 (T-111) sampling activities.

2.0 SPECIFIC TANK CHARACTERIZATION OBJECTIVES

2.1 APPLICABLE DATA QUALITY OBJECTIVES

The sampling and analytical needs associated with the 51 Hanford Site underground storage tanks classified on one or more of the four Watch Lists (ferrocyanide, organic, flammable gas, and high heat), and the safety screening of all 177 tanks have been identified through the DQO process. DQO's identify information needed by a program group in the Tank Waste Remediation System (TWRS) concerned with safety issues, regulatory requirements, or the transporting and processing of tank waste.

The *Tank Safety Screening Data Quality Objective* (Redus and Babad 1994) describes the sampling and analytical requirements that are used to screen waste tanks for unidentified safety issues. To meet the sampling requirements of this DQO effort, a vertical profile of the waste shall be obtained from at least two widely-spaced risers. This vertical profile may be realized using core, auger, or grab samples. The safety screening analyses shall be applied to all core samples, DST RCRA samples, and all auger samples, except auger samples taken exclusively to assess the flammable gas tank crust burn issue.

Both Watch List and non-Watch List tanks will be sampled and evaluated to classify the waste tanks into one of three categories: SAFE, CONDITIONALLY SAFE, or UNSAFE following safety parameters related to the four Watch-List and other safety issues. The Watch List DQO's identify the requirements used to determine which classification to place a tank, based on analyses that indicate if certain measures are above or below established thresholds. A tank can be removed from a Watch List if it is classified as SAFE. As indicated from the historical information on the tank (Section 3.1), the Watch List DQO applicable to tank T-111 is: *Data Quality Objective to Support Resolution of the Organic Fuel Rich Tank Safety Issue* (Babad et al. 1994).

DQO's concerned with fugitive vapor emissions from tank T-111 are: *Data Quality Objectives for Generic In-Tank Health and Safety Vapor Issue Resolution* (Osborne et al. 1994); and *Rotary Sampling Core Vapor Sampling Data Quality Objective* (Price 1994). Characterization of the tank headspace is needed to: 1) identify those tanks which can safely be sampled with intrusive equipment without risk of gas ignition; 2) identify and estimate concentrations of toxicologically significant compounds present in the tank headspace to establish worker safety precautions; and 3) support the startup and operation of the portable exhauster used during rotary mode core sampling.

2.2 RELEVANT SAFETY INFORMATION

The organic safety issue arises due to wastes added to SST's containing quantities of complexants used in waste management operations, as well as degradation products of these complexants and solvents used in fuel reprocessing and metal recovery operations. These waste tanks also contain a presumed stoichiometric excess of sodium nitrite/nitrate oxidizers that are sufficient to exothermally oxidize organic compounds.

Resolution of tank vapor safety issues involve the identification of potential flammable and fugitive vapor emissions from tanks which could become worker health and safety hazards.

3.0 TANK T-111 HISTORICAL INFORMATION

This section summarizes the available information on tank T-111. Discussions of the fill history, the age of tank, its process history, and general information are included. The number of potential layers and expected recoveries will also be discussed.

3.1 AGE AND PROCESS HISTORY

Single-shell tank T-111, with a capacity of 2,010 kL (530 kgal), was constructed in the 200 West area during 1943 and 1944 and was placed into service in 1945. It is the second tank of a cascade comprised of tanks 241-T-110 and 241-T-112 and, therefore, received mostly clarified liquids. A cascade is a system in which tanks were connected in series by pipes. Waste added to the first tank overflowed to the secondary tanks after the primary tank became full.

The fill history of tank T-111, described below and shown in Firure 1, is taken from *A History of the 200 Area Tank Farms* (Anderson 1990) and the *Historical Tank Content Estimate for the Northwest Quadrant of the Hanford 200 West Area* (Brevick 1994). From 1945 to 1952, tank T-111 received and stored second-cycle (2C) decontamination waste from the bismuth phosphate process. From 1953 to 1955, it was used to cascade 2C waste and lanthanum fluoride waste (244) from the LaF_3 finishing process in T Plant to a crib. The 224 waste was generated from the plutonium purification/concentration processes performed in the 224-T building. The 2C waste remained the major waste type received and transferred out of tank T-111 through the third quarter of 1956. In the 1960's, the tank received miscellaneous decontamination chemicals from T-plant operations. Anecdotal evidence exists that the cascade overflow line between tank T-110 and T-111 was plugged and that a direct discharge line from T Plant was used to dispose of waste directly to T-111. Between 1964 and 1974, records show solid volumes fluctuating widely. Several recorded numbers are not credible and are considered to be the result of a transcription error. In the second quarter of 1974, two small transfers out of tank T-111 were made, and in the third quarter the tank was removed from service. In 1976, two additional small transfers were made and saltwell pumping commenced in the third quarter. Tank T-111 was declared an assumed leaker in 1984 and an assumed re-leaker in 1994. It was added to the Organics Watch List on February 1994 (Hanlon 1994).

The most recent surveillance data include a total waste inventory estimate of 1,710 kL (453 kgal) of non-complexed waste (NCPLX) with approximately 197 kL (52 kgal) of drainable liquids (Hanlon 1994). These figures translate to a waste depth of 406 cm (160 in) underneath the riser or 437 cm (172 in) at the tank centerline. Recent readings (December, 1994) obtained from Tank Farm Surveillance and the Surveillance Analysis Computer System database indicate a waste depth of 402.1 cm (158.3 in) below riser 4. From this, the total waste volume is calculated to be 1,700 kL (448 kgal). The recent waste temperature in tank T-111, taken from a thermocouple tree in riser 5, is approximately 16 °C (60.5 °F).

3.2 EXPECTED TANK CONTENTS

In-tank photographs showing a moist pliant waste surface, suggest that the waste in tank T-111 is a relatively soft sludge. Since there were no mixing equipment in tank T-111, evidence of layering is expected to be observed in the segment-level analytical results. The waste layers are expected to follow the chronological order of waste types received: 2C waste in the bottom layer, 224 waste in the middle layer, and T-Plant decontamination and 224 wastes in the top layer. Tank T-111 was never subjected to waste volume reduction or in-tank solidification processes; consequently, there is no formation of hard salt cake on top of the sludge. The solids from the neutralized solution have settled out in the tank and the supernatant has been disposed to cribs. Table 2 summarizes the core-composite analytical results obtained from the October-November 1991 core sampling event. Three cores, each with nine segments were extruded. However, samples from one of the three cores did not correspond to the observed conditions in the tank and were considered non-representative. Therefore, the results presented in Table 2 are average concentration values from four composites (two for each core). The full data package (McKinney et al. 1993) containing all of the results is available from the Hanford-Site Central Files.

Figure 1. Fill history of Tank 241-T-111.

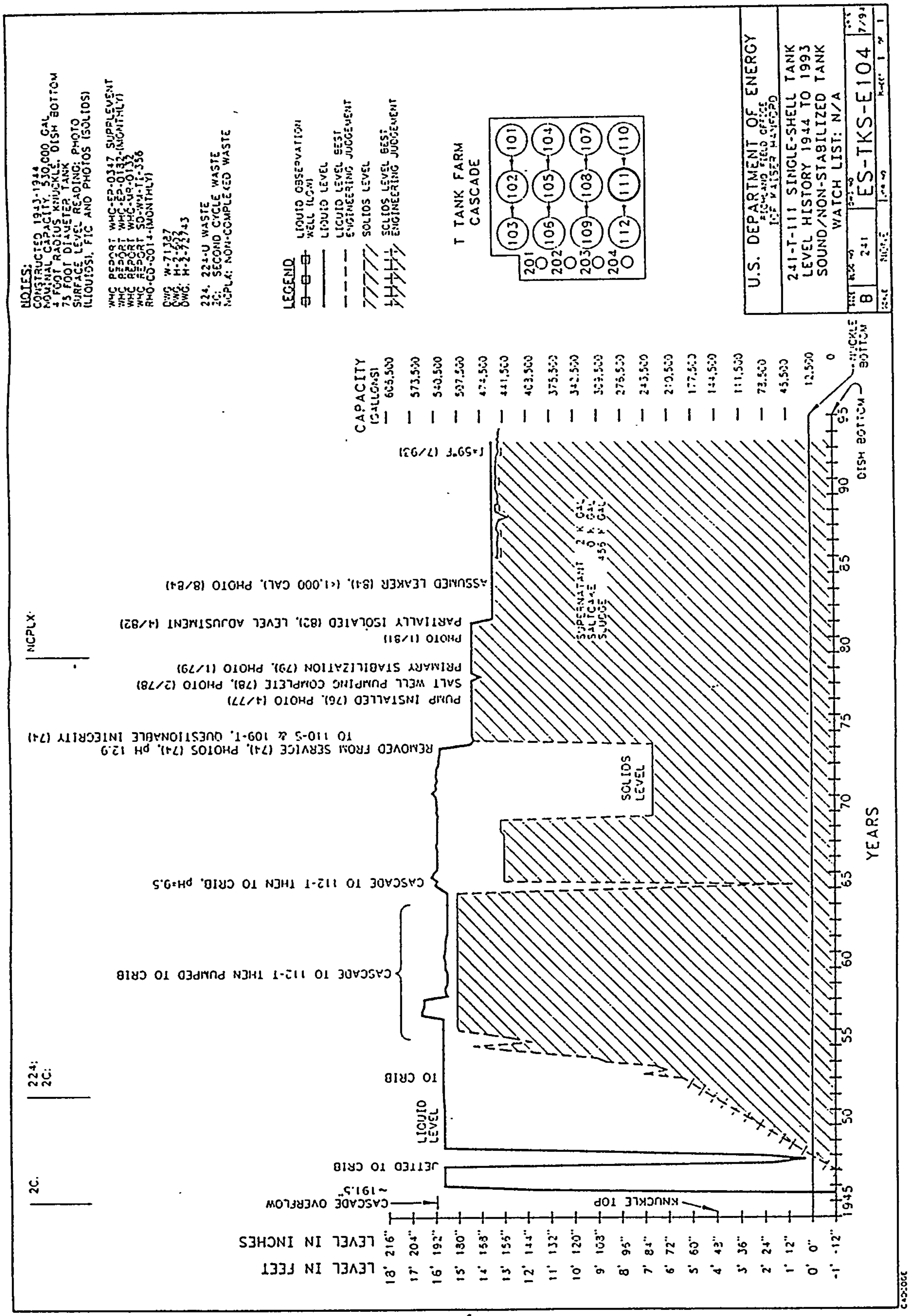

Table 1: Tank T-111 Analytical Results from the 1991 Core Sampling Event*

Physical Properties			
pH	11.65	TIC	812 μg/g
Temperature	16 °C	TOC	3,120 μg/g
Density	1.16-1.28 g/mL	Heat Load	81 W (24 BTU/hr)
Metals	Concentration (μg/g)	Metals	Concentration (μg/g)
Aluminum (Al)	570	Manganese (Mn)	6,330
Antimony (Sb)	93.6	Mercury (Hg)	1.43
Arsenic (As)	15.0	Nickel (Ni)	132
Barium (Ba)	69.0	Phosphorus (P)	10,400
Beryllium (Be)	0.5	Potassium (K)	1,140
Bismuth (Bi)	26,000	Selenium (Se)	38.0
Boron (B)	28.0	Silicon (Si)	5,670
Cadmium (Cd)	8.14	Silver (Ag)	128
Calcium (Ca)	2,420	Sodium (Na)	37,000
Cerium (Ce)	50.5	Strontium (Sr)	300
Chromium (Cr)	1,980	Sulfur (S)	1,230
Cobalt (Co)	11.5	Tin (Sn)	7.99
Copper (Cu)	33.6	Titanium (Ti)	47.9
Iron (Fe)	18,500	Vanadium (V)	14.7
Lanthanum (La)	4,220	Zinc (Zn)	106
Lead (Pb)	365	Zirconium (Zr)	4.00
Magnesium (Mg)	377		
Ions	Concentration (μg/g)	Ions	Concentration (μg/g)
Chloride (Cl^-)	573	Nitrite (NO_2^-)	793
Fluoride (F^-)	2,310	Phosphate (PO_4^{3-})	15,600
Nitrate (NO_3^-)	41,300	Sulfate (SO_4^{2-})	3,550
Radionuclides	Concentration (μCi/g)	Radionuclides	Concentration (μCi/g)
Americium-241	0.00425	Plutonium-239/240	0.304
Cesium-137	0.166	Strontium-90	5.42
Europium-154	0.00216	Technecium-99	0.00792
Europium-155	0.00307	Total Alpha	0.368
		Total Beta	15.1

*(Simpson 1994)

4.0 SAMPLING EVENTS

4.1 TANK T-111 SAMPLING IN FISCAL YEAR 1995

Two sampling events of tank T-111 are scheduled for the 1995 fiscal year: a vapor sampling in January and a push-mode core sampling in April. The first sampling event shall be performed in accordance with the two DQO's dealing with fugitive vapor emissions: *Data Quality Objectives for Generic In-Tank Health and Safety Vapor Issue Resolution* (Osborne et al. 1994) and *Rotary Sampling Core Vapor Sampling Data Quality Objective* (Price 1994). The second sampling event shall be performed in accordance with the *Tank Safety Screening Data Quality Objective* (Redus and Babad 1994) and the *Data Quality Objective to Support Resolution of the Organic Fuel Rich Tank Safety Issue* (Babad et al. 1994).

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APPENDIX A

TANK T-111 VAPOR SAMPLING AND ANALYSIS PLAN FOR FISCAL YEAR 1995

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LIST OF ACRONYMS FOR APPENDIX A

T-111	Tank 241-T-111
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act of 1980
CGM	Combustible Gas Meter
DOT	Department of Transportation
DQO	Data Quality Objective
ECN	Engineering Change Notice
EPA	Environmental Protection Agency
ESH&QA	Environmental Safety, Health, and Quality Assurance
FAS	Field Analytical Services
GC/MS	Gas Chromatography/Mass Spectrometry
IC	Ion Chromatography
IDLH	Immediately Dangerous to Life and Health
LFL	Lower Flammability Limit
OGIST	Oregon Graduate Institute of Science and Technology
ORNL	Oak Ridge National Laboratory
PNL	Pacific Northwest Laboratory
ppbv	parts per billion by volume
ppmv	parts per million by volume
QAPP	Quality Assurance Project Plan
RCRA	Resource Conservation and Recovery Act
SAP	Sampling and Analysis Plan
SML	Sampling and Mobile Laboratories
SUMMA®	registered trademark for passivated stainless steel canister
TCP	Tank Characterization Plan
TNMHC	Total Non-Methane Hydrocarbons
TRP	Toxicology Review Panel
TO-12	EPA task order protocol 12
TO-14	EPA task order protocol 14
TOC	Total Organic Carbon
TST	Triple Sorbent Trap
TWAP	Tank Waste Analysis Plan
TWRS	Tank Waste Remediation System
VSS	Vapor Sampling System
WHC	Westinghouse Hanford Company

A1.0 INTRODUCTION

This Sampling and Analysis Plan (SAP) will identify characterization objectives for tank 241-T-111 (T-111) pertaining to sample collection, preparation, and analysis, and laboratory analytical evaluation and reporting requirements in accordance with the *Tank Waste Remediation System Tank Waste Analysis Plan* (Haller 1994) and the following applicable Data Quality Objectives (DQO's): *Data Quality Objectives for Generic In-Tank Health and Safety Vapor Issue Resolution* (Osborne et al. 1994) and *Rotary Sampling Core Vapor Sampling Data Quality Objective* (Price 1994).

Vapor samples are used to identify potential flammable and fugitive vapor emissions from the tanks which could become worker health and safety issues. Sampling and analysis of the vapor space can identify: 1) volatile compounds above the surface of the waste; and 2) the amount of gases generated by chemical or radiolytic reactions within the waste.

A2.0 SCHEDULED SAMPLING EVENT

The following information provides the methodology and procedures to be used in the preparation, retrieval, transport, analysis, and reporting of results for vapor space samples retrieved from tank T-111. The requirements for the vapor sampling of tank T-111 in the 1995 fiscal year, contained within this SAP of the Tank Characterization Plan (TCP), are within the scope of work specified in the appropriate laboratory financial plans. Any decisions, observations, or deviations to this SAP made during sample receipt, preparation, and analysis shall be documented and justified in the deliverable report.

A2.1 PREPARATION OF SAMPLE MEDIA CONTAINERS

The laboratory performing the contracted analytical work shall supply prepared and labeled sample containers (SUMMA® canisters and/or selective sorbent sampling media) to Field Analytical Services (FAS) at least 48 hours in advance of the scheduled sampling date. Each sample media container shall be certified as clean and prepared according to procedures called out in Table A-1. FAS shall provide sample identification numbers to the laboratories as requested following the quality assurance/quality control format given in Section A3.1.

A2.2 FLAMMABILITY OF VAPOR SPACE GASES

Prior to performing intrusive work on a tank, an assessment of the flammability of the tank vapor space gases is required by standard WHC safety practices. The flammability test procedure is given in the sampling event work package (ES-94-1191) and performed by Industrial Hygiene Field Services personnel using a combustible gas meter (CGM). Under present guidelines no operational or sampling activity is permitted if a single sample of the tank vapor fuel content is greater than 20% of the lower flammability limit (LFL). If the CGM sample has a total fuel content between 10% and 20% of the LFL, a vapor sampling activity may continue under CGM monitoring to better identify the hazard level. Under 10% of the LFL the tank is not considered a flammability problem and all scheduled work can proceed (Osborne et al. 1994).

A2.3 SAMPLE COLLECTION

In fiscal year 1995, the tank T-111 vapor space shall be sampled through a heated probe in an available riser using the vapor sampling system (VSS) in accordance with laboratory operating procedure LO-080-450 "Collection of SUMMA® Canisters & Sorbent Tube Samples Using the Vapor Sampling System (VSS)". Table A-1 specifies the sample type, the type of collection media to be used, and the number of samples requested. Table A-2 provides a sequence of sampling activities and specifies the sample collection time and the flow rate through the sample collection tubes.

A cleanliness check shall be performed in accordance with procedure LO-080-450, Appendix C. Cleanliness of the VSS shall also be addressed by collecting ambient air SUMMA® samples prior to sampling the tanks using the following conditions: 1) with the VSS manifold and transfer lines fully heated; and 2) without the VSS, upwind of T-111.

The GC/FID shall be used to monitor organic vapors during the sampling event. The GC/FID shall be operated in accordance with LO-080-450, Appendix D and Bellus (1993).

Table A-1: General Sampling Information.

Sample Container	Prepared By	Preparation Procedure	Sample Type	Number of Samples
SUMMA®	PNL	PNL-TVP-02	Tank Air	6
SUMMA®	PNL	PNL-TVP-02	Ambient Air[1]	2
Triple Sorbent Traps	ORNL	AC-OP-300-0907 CASD-AM-300-WP01[2]	Tank Air	12
	ORNL	AC-OP-300-0907	Field Blank	2
	ORNL	AC-OP-300-0907	Trip Blank	2
Sorbent Trap System for NH_3, NO_2, NO, H_2O	PNL	PNL-TVP-09	Tank Air	6
	PNL	PNL-TVP-09	Trip Blank	3
Tritium Trap	WHC	LA-548-111	Tank Air	1
HEPA Filters	WHC	N/A	Tank Air	4

[1]One sample taken through the VSS, one sample taken upwind of the tank.
[2]Preparation procedure for samples spiked with surrogate(s).

Table A-2: List of Samples and Activities

SAMPLE CODE	SAMPLE/ACTIVITY DESCRIPTION	SAMPLER POSITION DURING COLLECTION	GAS FLOW RATE	SAMPLE DURATION
--	Adjust VSS temperature setpoint to 50°C	N/A	N/A	N/A
--	Purge VSS with ambient air[1]	N/A	5,450 mL/min	30 min.
01	Collect ambient air sample SUMMA #1	Upwind of T-111		1 min.
--	Perform cleanliness check			
02	Collect ambient air sample SUMMA #2	Port 15		1 min.
--	Leak test	N/A		
--	Purge VSS with tank air	N/A	5,450 mL/min	30 min.
--	Measure tank pressure	N/A	N/A	N/A
03	Collect Tritium Trap	Sorbent line 8	200 mL/min	5 min.
--	Collect GC sample and initiate GC run[2]			
04	Collect SUMMA #3	Port 11		1 min.
05	Collect SUMMA #4	Port 13		1 min.
06	Collect SUMMA #5	Port 15		1 min.
07	Collect SUMMA #6	Port 12		1 min.
08	Collect SUMMA #7	Port 14		1 min.
09	Collect SUMMA #8	Port 16		1 min.
10	Collect Triple Sorbent Trap (TST) sample #1	Sorbent line 9	50 mL/min	4 min.
11	Collect TST sample #2	Sorbent line 10	50 mL/min	4 min.
12	Collect TST sample #3	Sorbent line 8	50 mL/min	4 min.
13	Open, close, & store TST Field Blank #1	In VSS truck	0 mL/min	
14	Collect TST sample #4	Sorbent line 10	50 mL/min	4 min.
15	Collect TST sample #5	Sorbent line 9	200 mL/min	5 min.
16	Collect TST sample #6	Sorbent line 10	200 mL/min	5 min.
17	Collect TST sample #7	Sorbent line 8	200 mL/min	5 min.
18	Collect TST sample #8	Sorbent line 10	200 mL/min	5 min.
19	Collect TST sample #9	Sorbent line 9	200 mL/min	20 min.
20	Open, close, & store TST Field Blank #2	In VSS truck	0 mL/min	
21	Collect TST sample #10	Sorbent line 10	200 mL/min	20 min.
22	Collect TST sample #11	Sorbent line 8	200 mL/min	20 min.
23	Collect TST sample #12	Sorbent line 10	200 mL/min	20 min.
24,25	Store TST Trip Blanks #1 & #2	None	None	None
26	Collect NH3/NOx/H2O Sorbent Trap #1	Sorbent line 9	200 mL/min	15 min.
27	Collect NH3/NOx/H2O Sorbent Trap #2	Sorbent line 10	200 mL/min	15 min.
28	Collect NH3/NOx/H2O Sorbent Trap #3	Sorbent line 8	200 mL/min	15 min.
29	Collect NH3/NOx/H2O Sorbent Trap #4	Sorbent line 10	200 mL/min	15 min.
30	Collect NH3/NOx/H2O Sorbent Trap #5	Sorbent line 9	200 mL/min	15 min.
31	Collect NH3/NOx/H2O Sorbent Trap #6	Sorbent line 10	200 mL/min	15 min.
32,33,34	Store NH3/NOx/H2O Trap Trip Blanks #1, #2, & #3	None	None	None
35	Remove upstream HEPA Filter from HEPA transfer box	Upstream of box	Continuous	
36	Remove downstream HEPA Filter from HEPA transfer box	Downstream of box	Continuous	
37	Remove upstream HEPA Filter from VSS	Upstream of VSS	Continuous	
38	Remove downstream HEPA Filter from VSS	Downstream of VSS	Continuous	

[1]Not required if ambient air purge incorporated in VSS setup.
[2]Additional GC runs may be performed to obtain organic data and to assure cleanliness of system at the discretion of the sampling scientist and shall be identified in the deliverable report. Organic data obtained from the on-line GC is developmental.

A2.4 RADIATION SCREENING AND SAMPLE TRANSPORT

All vapor samples shall be stored under chain-of-custody requirements by Field Analytical Services while a radiological survey of certain items used during sampling is performed by the 222-S Laboratory. Surveys are conducted to assure compliance with Department of Transportation (DOT) shipping regulations and offsite laboratory acceptance criteria. Items surveyed include four HEPA filters and one tritium trap and shall be analyzed following procedures specified in a Letter of Instruction (Bratzel 1994). These procedures are reproduced in Table A-4.

The results from the radiation screening are submitted to and shall be evaluated by Sampling and Mobile Laboratories (SML) to ensure the samples meet the analytical criteria specified in Table A-3. SML shall provide a report to each analytical laboratory to identify the number of picocuries per sample (pCi/sample) for each sample that is submitted for analysis.

Table A-3: Limits For Acceptable Radionuclide Activity Levels

Organization	Total α	Total β/γ	Units
PNL Analytical Chemistry Laboratory	$\leq$ 100	$\leq$ 400	pCi/g
Oak Ridge National Laboratory	$\leq$ 135	$\leq$ 450	pCi/g
WHC-CM-2-14[1]	$\leq$ 60	$\leq$ 200	pCi/g

[1] Samples above these limits may be shipped as Limited Quantity of Radioactive Material.

Trip blanks and field blanks are to accompany the waste samples to the laboratory. For specific information concerning sample and blank handling, custody, and transport refer to quality assurance/quality control requirements in Section A3.1.

A2.5 TANK-SPECIFIC ANALYTICAL PROCEDURES

A flowchart and narrative showing the sample collection, isolation, and analysis scheme is presented as Figure A-1. All samples are to be prepared and analyzed in accordance with this scheme. Sample receipt, custody, preparation, and analysis shall be performed in accordance with approved procedures.

Sample material retrieved from the tank T-111 vapor space and contained within the SUMMA® canisters shall be analyzed for total non-methane hydrocarbons (TNMHC) following modified EPA procedure TO-14 and the permanent gases CO_2, CO, CH_4, H_2, and N_2O using gas chromatography. The sorbent traps contain analyte-specific sorbent media and shall be analyzed for these specific analytes. The triple sorbent traps contain sorbent media designed to allow a broad range of organic species to be retained. Table A-4 identifies the appropriate laboratory procedures used in each analysis.

Any analyses prescribed by this document, but not performed, shall be identified and justification for non-performance written in the appropriate data report. If there are insufficient samples to perform all requested analyses, a partial listing of the analyses in Table A-4 that could be performed with available samples will be developed by Tank Vapor Issue Resolution Program personnel. The laboratory shall proceed with these analyses.

Figure A-1. Test Plan Outline and Flowchart for Tank Vapor Space Characterization.

- **Step 1** Labs: Prepare sample and blank containers at contract laboratories. Label containers using sample identification numbers and sampling data provided by Field Analytical Services.
- **Step 2** Labs: Ship containers to Field Analytical Services at least 48 hours in advance of scheduled sampling event. Shipping, receiving, and control of containers shall be guided by procedures LO-080-450 and either PNL-TVP-07 or CASD-AM-300-WP02 (ORNL).
- **Step 3** SML: If tank is safe with regard to flammability, set up vapor sampling system (VSS) and collect samples following procedure LO-080-450 and guidelines in Table A-2.
- **Step 4** SML: Move the vapor sample containers to custody locked storage. Submit the HEPA filters and Tritium Trap to the 222-S Laboratory for radiological survey.
- **Step 5** SML: Using radiological survey report results, determine if samples are acceptable to ship offsite (see Section A3.4).
- **Step 6** SML: If determined to be acceptable by offsite laboratory requirements and WHC-CM-2-14, ship samples and blanks following DOT requirements. If not acceptable to ship, maintain samples in storage and contact J. W. Osborne of Vapor Issue Resolution Program for further direction.
- **Step 7** Labs: Perform laboratory analyses.

  A. SUMMA® Canisters (PNL): Perform modified full scan EPA-TO-14. Perform permanent gas analysis for the following: H_2, CO, N_2O, CH_4, CO_2.

  B. Sorbent Traps (PNL): Perform gravimetric analysis for moisture. Perform selective electrode analysis for NH_3 Analyze NO and NO_2 Traps.

  C. Triple Sorbent Traps (ORNL): Perform organic vapor analysis.
- **Step 8** Labs and SML: Following the Section A7.0 reporting requirements, deliver a Format VI Report to the Vapor Issue Resolution Safety Program.

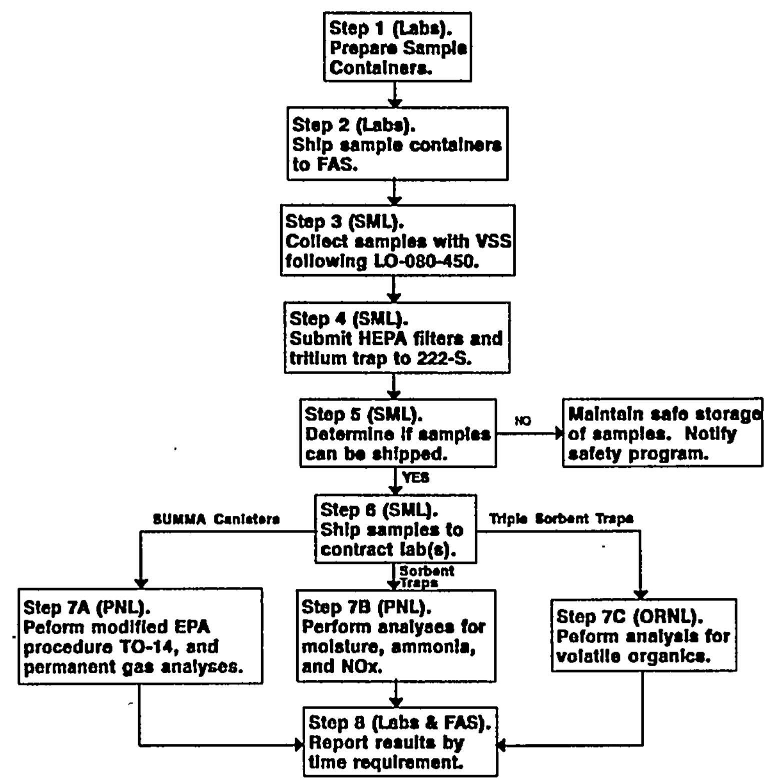

Table A-4. T-107 Sample Chemical, Physical, and Radiological Analytical Requirements

PROJECT	T-107 VAPOR
Plan Number	WHC-SD-WM-TP-200
Tank	241-T-111
Program Contact	J. W. Osborne
TWRS Contact	R. D. Schreiber B. C. Carpenter C. S. Homi
Lab Project Coordinator	S. C. Goheen (PNL) R. A. Jenkins (ORNL)

COMMENTS
Type 3 vapor sampling system (VSS) using heated vapor probes.

REPORT FORMATS	
I	Early Notify
II	Process Control
III	Safety Screen
IV	Waste Management
V	RCRA Compliance
VI	Special

NO. OF SAMPLE/BLANK CONTAINERS PROCESSED				
Organization	WHC	PNL	ORNL	TOTAL
SUMMA® Canister		6[a]/2		8
Sorbent Trap System[b]		6/3		9
Triple Sorbent Trap			12/4	16
HEPA Filter	4			4
Tritium Trap	1			1

PRIMARY ANALYSES						QUALITY CONTROL[c]			CRITERIA				REPORT FORMAT
ANALYSIS METHOD	PRIMARY ANALYTE	PROCEDURE	LAB	SAMPLE PREP	SAMPLE CONTAINER	NO. OF SAMPLES	SURR SPIKE[d]	NO OF BLANKS	NOTIFICATION LIMIT (NL)[e]	EXPECTED RANGE	PRECN @NL	ACCURACY @NL	
GCM	Flammability	CGIMX251 CGITMX410	N/A	N/A	N/A	1	N/A	N/A	>20% LFL	<10% LFL	N/A	N/A	I
EPA TO-14 GC/MS	Organic* Speciation	PNL-TVP-01 PNL-TVP-02 PNL-TVP-03	PNL	Direct	SUMMA®	3	none	2	≥ 4000 ppmv n-Butanol 50% IDLH for all others*	not available	±25%	70-130%	I, VI
GC/TCD	CO_2 CO CH_4 H_2 N_2O	PNL-TVP-05 PNL-TVP-02	PNL	Direct	SUMMA®	3	none	2	N/A ≥ 20% LFL ≥ 20% LFL ≥ 20% LFL not available	not available	±25% ±25% ±25% ±25% ±25%	70-130%	VI I, VI I, VI I, VI I, VI
IC	NO NO_2	PNL-TVP-09 PNL-ALO-212	PNL	H_2O Extraction	Sorbent Trap	6	none	3	≥ 50 ppmv ≥ 25 ppmv	≥ 2 ppmv ≥ 0.1 ppmv	±25% ±25%	70-130%	I, VI I, VI
Gravimetric	H_2O	PNL-TVP-09	PNL	Direct	Sorbent Trap	6	none	3	N/A	≥ 3 mg/L	±25%	70-130%	VI
Selective Electrode	NH_3	PNL-ALO-226 PNL-TVP-09	PNL	H_2O Extraction	Sorbent Trap	6	none	3	≥ 250 ppmv	≥ 2 ppmv	±25%	70-130%	I, VI
GC/MS	Organics**	AC-MM-1-003153 CASD-OP-300-WP03 CASD-OP-300-WP04 CASD-OP-300-WP05 CASD-OP-300-WP06	ORNL	Thermal Desorption	Triple Sorbent Trap	12	all	4[f]	≥ 4000 ppmv n-Butanol 50% IDLH for all others**	not available	±25%	70-130%	I, VI
Total α Total β Total γ	Radon Daughters	LA-508-110 LA-508-111 LA-508-162	WHC	Direct	HEPA Filter	4	N/A	N/A	≥60 pCi/g α ≥200 pCi/g β ≥200 pCi/g γ	<60 pCi/g α <200 pCi/g β <200 pCi/g γ	±25% ±25% ±25%	70-130%	I, II
Liq. Scin.	Tritium	LA-548-111	WHC	Direct	Tritium Trap	1	N/A	N/A	N/A	not available	±25%	N/A	II
GC/FID	Organics	LO-080-450	FAS	Direct	On-line	N/A	N/A	N/A	N/A	N/A	N/A	N/A	II, VI

N/A: Not Applicable
a Three canisters will be archived at PNL until arrangements can be made for transport and analytical work at the OGIST laboratory.
b System contains individual sorbent media sections for NO_x, NH_3, & H_2O.
c Multiple samples and blanks are taken.
d Samples spiked with surrogates.
e Action required if any compound exceed 50% IDLH.
f Includes two trip and two field blanks.

*Acetone, acetonitrile, benzene, 1,3- butadiene, butanal, n-butanol, n-hexane, methane, propane nitrile. Other organic species detected at levels deemed sufficient by the laboratory scientist to be of potential toxicological concern shall be reported following Format I.

**Acetone, acetonitrile, benzene, butanol, n-dodecane, n-hexane, propane nitrile, tributyl phosphate, n-tridecane. Other organic species detected at level deemed sufficient by the laboratory scientist to be of potential toxicological concern shall be reported following Format I.

A3.0 QUALITY ASSURANCE/QUALITY CONTROL

This SAP and analytical laboratory operations are approved by the WHC Environmental Safety, Health, and Quality Assurance (ESH&QA) Program provided the following conditions are met.

1) Each laboratory has a quality assurance program that meets the applicable requirements of DOE order 5700.6C or United States 10 CFR 830.120. In addition, it must also meet the requirements of the vapor QAPP (Keller 1994).

2) Each analysis and media preparation procedure given in Tables A-1 and A-4 is documented by the laboratory and available to ESH&QA.

3) Any modifications made to, or deviations from, the prescribed procedures are documented and justified in the deliverable report.

The PNL tank vapor program has an impact level II Laboratory Quality Assurance Plan (Barnes 1995) written to comply with 5700.6C. ESH&QA will qualify laboratories for continued use by the TWRS Characterization program after receipt of the Laboratory quality assurance plans, followed by an audit and corrective action phase.

A3.1 SAMPLING OPERATIONS

The laboratory supplying the sample collection media shall initiate the chain-of-custody form in accordance with the laboratory operating procedure LO-090-443, "Chain-of-Custody for RCRA and CERCLA Protocol Samples" using unique sample label and identification numbers provided by FAS. Each sample identification number shall have the following format:

SXXXX-WYY-LLL, where:

XXXX = unique number assigned to the sampling event,
W = a letter code indicating the day of a multi-day sampling event,
YY = a 2-digit sample code found in Table A-2, List of Sample and Activities, column one.
LLL = a special lab assigned code.

Once the sample collection media has been received by FAS from the laboratory, it shall remain in the physical control of the custodian, locked in a secure area, or prepared for shipping with tamper evident tape. The sample collection media shall also remain in a controlled area under conditions specified on the chain-of-custody form.

Applicable operating procedures for the tank T-111 vapor space sampling activities are contained in work package ES-94-1191. Vapor samples, trip blanks, and field blanks are to be collected in accordance with Tables A-1 and A-2 and laboratory operating procedure LO-080-450 "Collection of SUMMA® Canisters & Sorbent Tube Samples Using the Vapor Sampling System (VSS)" and shipped to the analytical laboratories in accordance with Hazardous Material Packaging and Shipping, WHC-CM-2-14.

All sampling activities shall be documented in controlled field logbooks maintained by sampling personnel (Sampling and Mobile Laboratories) and shall contain, but are not limited to:

1) identification of tank and riser number and photographs of the sample location in which the sampling is conducted,
2) if any anomalies are observed, corresponding sample identification numbers, flow rates, pressures, temperatures, and other operational parameters affecting the sample,
3) any conditions that the sampler may observe during the sampling event (i. e., odors, nearby machinery in operation, etc.),
4) names and titles of personnel involved in the field activity and their responsibilities,
5) instrument calibration dates.

Sampling and Mobile Laboratories is responsible for documenting any problems and procedural changes affecting the validity of the sample in a controlled field notebook and shall enter this information in the comment section of the chain-of-custody form for addition to the data reports.

A3.2 LABORATORY OPERATIONS

Prepared and labeled sample collection containers, trip blanks, and field blanks are supplied by the performing laboratories to FAS. The SUMMA® canisters and Sorbent Trap Systems are prepared and certified following the laboratory quality control procedures identified in Table A-1. The laboratory supplying the sample collection media shall initiate the chain-of-custody form in accordance with the laboratory operating procedure LO-090-443, "Chain-of-Custody for RCRA and CERCLA Protocol Samples" using sample label and identification numbers provided by FAS.

The sample receipt and control steps used in the PNL laboratories are identified in procedure PNL-TVP-07. Oak Ridge National Laboratory shipping and receiving is done by procedure CASD-OP-300-WP02. Analyses will be performed according to the procedures in Table A-4.

Method specific quality control such as calibrations and blanks are also found in the analytical procedures. Sample quality control (duplicates, spikes, standards) are identified in Table A-4. If no criteria are provided in Table A-4, the performing laboratory shall perform to its Quality Assurance Plan(s).

Due to the developmental work being done with the analysis procedures and potential sample differences (between tanks), changes in procedures may be needed. These changes must be done following laboratory QA plan procedures, documented in controlled notebooks, and referenced in the deliverable reports to ensure traceability.

All laboratories performing work shall comply with the Analytical Services Quality Assurance Plan, when implemented in August 1995.

A4.0 ORGANIZATION

The organization and responsibility of key personnel involved in this tank T-111 vapor sampling project are listed in Table A-5.

Table A-5: Tank T-111 Project Key Personnel List.

Individual(s)	Organization	Responsibility
S. C. Goheen	Pacific Northwest Laboratory	Project Manager for Vapor Sample Characterization
R. A. Jenkins	Oak Ridge National Laboratory	Project Manager for Vapor Sample Characterization
J. G. Kristofzski	WHC 222-S Laboratory	Project Manager for Sample Radiological Survey
B. C. Carpenter C. S. Homi	TWRS Characterization Support	T-111 Tank Characterization Plan Engineers
J. W. Osborne	TWRS Tank Vapor Issue Resolution Program	Vapor Issue Resolution Program Manager
H. Babad	TWRS Characterization Program	Tank Safety Screening Scientist
R. S. Viswanath	Field Analytical Services	Special Analytical Studies Vapor Sampling Technical Support
R. D. Mahon	Field Analytical Services	Sampling and Mobile Laboratories Vapor Sampling Program Lead
E. H. Neilsen	Waste Tank Safety Engineering	Vapor Sampling Cognizant Engineer
D. R. Carls	Industrial Hygiene and Safety Program	Industrial Hygiene Point of Contact if Notification Limit is Exceeded (FAX 372-3522)
West Area Shift Operations Manager	Tank Farm Operations	West Tank Farm Point of Contact if Notification Limit is Exceeded (373-3475)

A5.0 EXCEPTIONS, CLARIFICATIONS, AND ASSUMPTIONS

Trip Blanks and Field Blanks

Trip Blanks are sampling devices prepared and handled in the same manner as samples, except that they are never opened in the field. Field Blanks are sampling devices prepared and handled in the same manner as the samples, but no tank gases are drawn through them. Laboratories supplying blanks may opt to analyze only one trip blank unless it is determined to be contaminated, in which case all trip blanks are to be analyzed.

Sample Custodian

The sample custodian is the designated FAS cognizant scientist or assisting scientific technician, lead sampler, or laboratory scientist or technician who signs the *received by* block on the chain-of-custody form. Transfer of custodianship occurs when the custodian signs the *relinquished by* block on the chain-of-custody from and releases the sample(s) to the new custodian signator.

Physical Control

Physical control of a sample includes being in the sight of the custodian, in a room which shall signal an alarm when entered, or locked in a cabinet.

A6.0 DELIVERABLES

The Pacific Northwest Laboratory, Oak Ridge National Laboratory, and Sampling and Mobile Laboratories VSS sampling and analyses of tank T-111 vapors shall be reported as Format VI (Section A6.3). In addition, the analytical laboratories shall receive Format II reports from Sampling and Mobile Laboratories as described in Section A6.2. Any analyte exceeding the notification limit prescribed in Table A-4 shall be reported as Format I (Section A6.1). Other organic species detected at levels deemed sufficient by the laboratory scientist to be of potential toxicological concern shall also be reported following Format I. Additional information regarding reporting formats and organization point of contact is given in Schreiber (1994a, 1994b, 1994c).

A6.1 FORMAT I REPORTING

Table A-4 contains the notification limits for specific analytes. Analytes that exceed notification limits defined in the DQO processes shall be reported by the Project Manager, delegate, or Health Physics Management by calling the West Area Shift Manager of Tank Farm Operations at 373-3475 immediately. This verbal communication must be followed within 3 working days by written communication to the Tank Vapor Issue Resolution Program, the Industrial Hygiene and Safety Program, and the Characterization Program, documenting the observation(s). A further review of the data, including quality control results and additional analyses for verification of the exceeded analyte, may be contracted between the performing laboratory and the contacts above.

A6.2 FORMAT II REPORTING

Results of the 222-S Laboratory's radiological survey shall be reported by Sampling and Mobile Laboratories as Format II to the vapor analytical laboratories listing the picocuries per sample (pCi/sample) for each sample submitted for analysis. This Format II report should also provide the sample collection sequence and volumes, verification of trip and field blank use, and any anomalous sampling conditions to accompany, if possible, the shipment of samples. Alternatively, this sampling report may be transmitted by FAX to the analytical laboratories within 48 hours after the samples have been shipped.

A6.3 FORMAT VI REPORTING

All Format VI reports shall be delivered to the Tank Vapor Safety Resolution Program, the Field Analytical Services representative, the Characterization Program Office, Analytical Services, and the Tank Characterization Resource Center.

Each analytical laboratory and SML shall deliver three reports. Sampling and analytical data are requested within 5 weeks after receipt of both the samples and supporting data and shall consist of, at a minimum, data tables reporting sample collection data, industrial hygiene tank monitoring data, and radiation screening results obtained by SML, or the results of each analysis performed by the analytical laboratories. A final report shall be delivered within a nine week period after receipt of both the samples and supporting data. A cleared final report shall be delivered after it has completed the proper clearance. Final reports shall be submitted to clearance in parallel to being submitted to the WHC customers identified above.

The final sampling report from Sampling and Mobile Laboratories shall be a WHC supporting document, with sponsor-limited release. It should include:

1) a description of sampling equipment used;
2) a description of sampling quality controls applied (e.g., leak and cleanliness tests of the sampling manifold, system temperature and pressure monitoring/alarms, instrument calibration details);
3) sampling event chronology and sample collection schedule (complete list of samples, by ID#, time collected, flow rates, etc.);
4) any industrial hygiene tank monitoring data collected before or during sampling event;
5) an evaluation of sources of sampling errors;
6) sample radiation screening results;
7) sample storage and shipment details; and
8) copies of all chain-of-custody forms.

The cleared final report from the analytical laboratories shall be acceptable for distribution to the public. To the extent possible, the final reports should include:

1) A summary of analytical results;
2) a description of sample device preparation (and manufacture if appropriate), citing procedures and logbooks used;
3) references providing traceability of sample device cleanliness;
4) a brief description of analytical methods, with procedures cited;
5) a brief explanation of how analytical systems control was demonstratably maintained;
6) a brief description of sample storage and shipment conditions, citing procedures and logbooks used;
7) a listing of analytes of quantitation (target analytes), with analytical method detection limit, range for which instrumentation is calibrated, number of calibration points used, and statistical data on linearity of calibration;
8) quantitative analytical results, expressed as dimensionless (ppmv or ppbv) concentration, and mass concentration ($\mu g/m^3$, mg/L, etc., calculated at 0 °C and 1 atm) of target analytes (identified by name and Chemical Abstract Service number) in each tank air sample;

9) tentative identification and semi-quantitative analytical results, expressed in both mass and dimensionless concentrations (if possible) of non-target organic analytes (identified by name and Chemical Abstract Service number) in each organic vapor sample;
10) a statistical summary (i.e., mean, standard deviation) for multiple analyses and/or multiple samples for all analytes (positively and tentatively identified compounds) in both mass and dimensionless concentrations (if possible);
11) a summary of all exceptional conditions, such as deviations from procedure or protocol, results obtained outside of instrument calibration range, sorbent trap breakthrough of analytes, or poor surrogate recoveries; and
12) copies of chain-of-custody forms attached.

A7.0 CHANGE CONTROL

Under certain circumstances, it may become necessary for the performing laboratory to make decisions concerning a sample without review of the data by the customer or the Characterization Program. These changes shall be brought to the attention of the project manager and the Characterization Program as quickly as possible and documented accordingly. Changes must be justified in their documentation. Changes may be documented through the use of internal change notices or analytical deviation reports for minor, low-impact changes. All significant changes (such as changes in scope) shall be documented by Characterization Support via an Engineering Change Notice to this Tank Characterization Plan. All changes shall also be clearly documented in the final data package.

Additional analysis of sample material from this vapor space characterization project at the request of the Characterization Program shall be performed according to a revision of this Tank Characterization Plan.

A8.0 REFERENCES

Barnes, B. O., 1995, *Quality Assurance Plan for PNL TWRS Tank Vapor Program*, MCS-046 Rev. 0, Pacific Northwest Laboratory, Richland, Washington.

Bellus, T. H., 1993, *Configuration of Hewlett Packard (HP) 5890 Series II Gas Chromatograph (GC) for DML1*, (internal memo 12240-SAA93-039 to L. L. Lockrem, July 10), Westinghouse Hanford Company, Richland, Washington.

Bratzel, D. R., 1994, *Letter or Instruction for Radiological Analyses to Support Fiscal Year 1995 Tank Vapor Sampling*, (internal memo 74310-94-32 to J. G. Kristofzski, November 30), Westinghouse Hanford Company, Richland, Washington.

Haller, C. S., 1994, *Fiscal Year 1995 Tank Waste Remediation System Tank Waste Analysis Plan*, WHC-SD-WM-PNL-091, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

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