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12800 Middlebrook Road
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J. A. Poppitti	X

Oak Ridge National Laboratory
Post Office Box 2009
Oak Ridge, TN 37831-8088

R. A. Jenkins	X
A. D. Dindal	X

Los Alamos Technical Associates
750 Swift, Suite 14
Richland, WA 99352

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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-107.		

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WHC-SD-WM-TP-295
Revision 0

Tank 241-T-107 Tank Characterization Plan

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

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LIST OF ACRONYMS

T-107	Tank 241-T-107
DQO	data quality objective
EPA	Environmental Protection Agency
ppm	parts per million
RCRA	Resource Conservation and Recovery Act
TBP	tributyl phosphate
TCP	Tank Characterization Plan
TOC	total organic carbon
TWRS	Tank Waste Remediation System
WHC	Westinghouse Hanford Company

TANK 241-T-107 TANK CHARACTERIZATION PLAN

1.0 INTRODUCTION

The Defense Nuclear Facilities Safety Board has advised the Department of Energy to concentrate the near-term sampling and analysis activities on identification and resolution of safety issues (Conway 1993). The data quality objective (DQO) 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-107 (T-107) sampling activities.

2.0 APPLICABLE DATA QUALITY OBJECTIVES

The sampling and analytical needs associated with the 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 Data Quality Objective (DQO) process. DQO's identify information needed by a program group in the Tank Waste Remediation System concerned with safety issues, regulatory requirements, or the transporting and processing of tank waste. As of December 1994 the following DQOs apply to tank T-107. Refer to section 4.0 for the applicable sampling event DQO discussion.

2.1 Vapor Sampling Data Quality Objectives

A portable modular exhaustor has been developed to exhaust the tank atmosphere during a rotary drill sampling operation. Characterization of the tank headspace is needed to support exhaustor start-up and define operational monitoring parameters. The *Rotary Sampling Core Vapor Sampling Data Quality Objective* (Price et al. 1994) defines requirements needed to identify the potential for release of regulated pollutants, confirm that the exhaustor can be safely started, and establish alarm setpoints for total organic carbon (TOC) and ammonia release to maintain safe exhaustor operation. To start the exhaustor, the flammability and concentration of toxic gases in the tank vapor space is needed.

Waste tank vapor characterization generic to all 177 underground storage tanks on the Hanford Site are addressed in the DQO entitled *Data Quality Objectives for Generic In-Tank Health and Safety Vapor Issue Resolution* (Osborne 1994b). Data are needed to identify and quantify constituents of the tank headspaces to address potential vapor flammability and toxicity. Resolution of these two issues involves a sequence of sampling events. The first step is a qualitative assessment of a tank's headspace vapor flammability. Further samples may be taken to determine the composition and concentration of any flammable constituents. Following resolution of the flammability issue, tank headspace samples will be taken to assess vapor toxicity. Samples are removed from a single location at or near the midpoint of the tank's headspace. Tanks that are actively ventilated will have samples removed at the exhaust header.

2.2 Ferrocyanide Safety Issue Data Quality Objective

This DQO effort is used as a guide for characterizing tanks on the Ferrocyanide Watch List. It concluded that the most reliable information is obtained from core samples and that two core samples taken from risers separated by maximum distances would provide characterization data of sufficient quality to enable decision makers to confidently resolve the safety issues associated with these tanks. The most important output from the characterization of ferrocyanide tanks through the DQO planning process is the safety classification of the tanks. These classifications will dictate the future operation of those tanks. Two primary parameters, sodium nickel ferrocyanide concentration and moisture content, determine whether a tank is safe, conditionally safe, or unsafe. For further information on this DQO effort refer to *Data Requirements for the Ferrocyanide Safety Issue Developed through the Data Quality Objectives Process* (Meacham et al. 1994).

2.3 Safety Screening Data Quality Objective

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. Both Watch List and non-Watch List tanks will be sampled and evaluated to identify safety conditions related to the ferrocyanide, organic, flammable gas, vapor, and criticality safety issues.

The analytical requirements for the safety screening of a tank are concerned with identifying a common set of primary analytes and characteristics of the waste. These analytes are energetics, total alpha activity, moisture and flammable gas concentrations. If a specific criteria level on one of these items is exceeded, further analysis of a secondary set of analytes and a possible Watch-List tank classification would be warranted.

3.0 TANK T-107 HISTORICAL INFORMATION

Included in this section are a physical description of tank T-107, its process history, and recorded sampling events.

3.1 December 1994 Tank Status

Single-shell tank T-107 is classified as a Ferrocyanide Watch List tank. The tank was declared an assumed leaker in 1984 and is in partially isolated status (Hanlon 1994).

Tank T-107 is estimated to contain 647,200 liters (171,000 gal.) of sludge and with 34,065 liters (9,000 gal.) of pumpable liquid for a total of 681,300 liters (180,000 gal.). The median temperature of the waste in tank T-107 is 20°C, as measured in July 1994. Its contents are categorized as non-complexed waste (Hanlon 1994).

Recent readings (October, 1994) obtained from Tank Farm Surveillance and the Surveillance Analysis Computer System database indicate a waste depth of 61.54 inches below riser #1, which is located on the north side of the tank. From this, the total waste volume is calculated at 688,900 liters (182,000 gal.).

3.2 Tank Configuration and Monitoring Activities

Tank T-107 is one of 16 single-shell tanks in the 200 West area T Farm constructed during 1944-47. It is 23 meters (75 ft.) in diameter with a concave-shaped base and has a 2.01 million liter (530,000 gal.) tank capacity. The tank is the first of a three cascade series ending with tank T-109.

Waste level measurements are taken on a quarterly basis through riser 1 using a manual tape. Three active dry wells monitor radiation in the surrounding soil (Hanlon 1994).

3.3 Process History

Tank T-107 was filled by September 1945 with first-cycle decontamination waste from the T-Plant BiPO_4 process which cascaded to and filled tank T-108 by March 1946. In 1952, most of the supernate was pumped from tank T-107 to make room for tributyl phosphate (TBP) waste from the TBP uranium-extraction process at U Plant which filled the tank by the end of 1952. In 1953, supernatant was sent to tank TX-118. Unconcentrated scavenged TBP waste and flushes from tank T-101 were received in 1953 and again in 1954. In 1966, supernatant was again transferred to tank TX-118. PUREX cladding waste from tank C-102 was received in 1967 and a transfer to tank TY-103 was made in 1969. During 1973, ion-exchange waste from the cesium recovery process was transferred from tank BX-104, and the supernatant was transferred to tanks T-108 and T-105. Most of the liquids were pumped to tank T-101 in 1976 and the tank was removed from service and labeled inactive in 1977. The fill history of tank T-107 is illustrated in Figure 1.

3.4 Historical Sampling Events

Three sets of core samples were taken from tank T-107 in November 1992, February 1993, and March 1993. Results for select analytes for both the water and fusion digestions are shown in Table 1 (Valenzuela, 1994).

Table 1. Results for Select Analytes for Tank T-107.

ANALYTES	Average Result (Water Digestion)	Average Result (Fusion Digestion)
RADIONUCLIDES		
Sr-89/90 $\mu\text{Ci/g}$	NR	108
Cs-137 $\mu\text{Ci/g}$	9.25	12.0
Pu-239/240 $\mu\text{Ci/g}$	NR	0.18
CHEMICAL COMPONENTS		
Na $\mu\text{g/g}$	107,900	117,250
Ca $\mu\text{g/g}$	270	760
Cr $\mu\text{g/g}$	210	360
Fe $\mu\text{g/g}$	355	29,175
Mn $\mu\text{g/g}$	2.1	213
Bi $\mu\text{g/g}$	243	11,997
Si $\mu\text{g/g}$	3,945	6,057
U $\mu\text{g/g}$	Not Measured	25,425
Zr $\mu\text{g/g}$	5.4	93.2
Total Organic Carbon g/g		
F $\mu\text{g/g}$	11,400	NR
NO3 $\mu\text{g/g}$	74,550	NR
SO4 $\mu\text{g/g}$	3,540	3,275
PO4 $\mu\text{g/g}$	23,725	32,075

NR = Not reported

3.5 Expected Tank Contents

Segment trending of the cores show evidence of 1C, TBP, and CW wastes with 1C waste at the bottom. The waste shows definite layering within the tank. The tank received ferrocyanide scavenged TBP waste during 1953-54 and because of this is considered a Ferrocyanide Watch List tank. Inventory estimates are shown in Table 2 (Valenzuela 1994).

Combustible gas meter measurements made in October 1992 indicated combustible gases were less than 1% of the lower flammability limit in tank T-107. Organic vapor monitor tests taken at the same time indicate approximately 40 ppm organics present in the vapor. Drager tube measurements show about 20 ppm ammonia. Hydrazine (<0.2 ppm) and oxides of nitrogen (NO_x , NO, NO_2 , all <0.5 ppm) were not detected in the vapor (Pingel 1992).

Table 2. Single-Shell Tank T-107 Inventory Estimate.

Physical Properties		
Total Waste Mass	1.028+06 kg	
Heat Load	0.8 kW (2720 BTU/hr)	
Bulk Density	1.51 g/cc	
Chemical Constituents	Average Concentration (wt%)	Bulk Inventory (kg)
Na ⁺	13.04	134,000
Ca ²⁺	0.076	780
Fe ³⁺ (total Fe)	2.84	30,000
Bi ³⁺	1.20	12,350
Cr ³⁺	0.036	370
Mn ³⁺	0.023	230
U (Total)	2.62	27,000
NO ₃ ⁻	7.49	77,000
NO ₂ ⁻	1.17	12,000
PO ₄ ³⁻	10.6	109,000
SO ₄ ²⁻	1.0	10,300
Si (as SiO ₃ ²⁻)	0.6	6,200
F ⁻	1.16	12,000
Total Organic Carbon	0.15	1,600
CN ⁻	0.0069	71
Radionuclides	μCi/g	Ci
Pu (Total)	0.144	148
Am-241	0.0141	14.5
Cs-137	12.0	12,300
Sr-90	108	111,000

4.0 SPECIFIC SAMPLING EVENTS

4.1 Sampling of Tank T-107 in Fiscal Year 1995

In fiscal year 1995 tank T-107 will be vapor sampled 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.

The relevant safety issues with tanks on the Ferrocyanide Watch List concern 1) the potential for a propagating reaction between complexes of ferrocyanide and nitrate and nitrite that could result in a release of radioactive material, and 2) the possibility that other, as yet unidentified, safety issues exist for the tank.

DQO's concerned with fugitive vapor emissions from tank T-107 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.

A tank characterization report (TCR) for tank T-107 was issued on September 29, 1994 (Valenzuela, 1994) which included the results on fiscal year 1993 core sample analyses.

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APPENDICES

TANK 241-T-107 SAMPLING AND ANALYSIS PLAN

SAMPLE EVENT A

**VAPOR SAMPLING
IN FISCAL YEAR 1995**

SAMPLE EVENT A: VAPOR SAMPLING IN FISCAL YEAR 1995

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LIST OF ACRONYMS

T-107	Tank 241-T-107
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
RCRA	Resource Conservation and Recovery Act
SML	Sampling and Mobile Laboratories
SUMMA®	registered trademark for passivated stainless steel canister
TCP	Tank Characterization Plan
TNMHC	Total Non-Methane Hydrocarbons
TO-14	EPA task order protocol 14
TOC	total organic carbon
TWRS	Tank Waste Remediation System
VSS	vapor sampling system
WHC	Westinghouse Hanford Company

TANK 241-T-107 VAPOR SPACE SAMPLING AND ANALYSIS PLAN

1.0 INTRODUCTION

This sampling and analysis plan will identify characterization objectives for tank T-107 pertaining to sample collection, sample 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 applicable Data Quality Objectives identified in Section 4.0 (page 6) of the main report body.

2.0 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-107. The requirements for sample event A, contained within this appendix of the TCP, are within the scope of work specified in the appropriate laboratory financial plans. Any decisions, observations, or deviations to this TCP made during sample receipt, preparation, and analysis shall be documented and justified in the deliverable report.

2.1 Preparation of Sample Media Containers

The laboratories 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 following the quality assurance/quality control format given in Section 4.1.

2.2 Flammability of Vapor Space Gases

Prior to this sampling event and performing any 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 is identified in the sampling event work package 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 measures a total fuel content between 10% and 20% of the LFL, a vapor sampling activity may continue under concurrent 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).

2.3 Sample Collection

In fiscal year 1995, the tank T-107 vapor space shall be sampled through a heated probe in riser 1 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

A.1

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-107.

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 ₂ O	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

¹One sample taken through the VSS, one sample taken upwind of the tank.

²Preparation procedure for samples spiked with surrogate(s).

2.4 Radiation Screening and Sample Transport

All vapor samples shall be stored at the 222-S Laboratory Annex while performing a radiological survey of certain items used during sampling. 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 to ensure the samples meet the criteria specified in Table A.3. Sampling and Mobile Laboratories 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.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			
--	Purge VSS with ambient air ³	N/A	5,450 mL/min	30 min.
01	Collect ambient air sample SUMMA #1	Upwind of T-107		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 ⁴			
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 10	100 mL/min	2 min.
11	Collect TST sample #2	Sorbent line 10	100 mL/min	2 min.
12	Collect TST sample #3	Sorbent line 8	100 mL/min	2 min.
13	Open, close, & store TST Field Blank #1	In VSS truck	0 mL/min	
14	Collect TST sample #4	Sorbent line 10	100 mL/min	2 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	

³Not required if ambient air purge incorporated in VSS setup.

⁴Additional 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.

Table A.3. Limits For Acceptable Radionuclide Activity Levels.

Organization	Total α	Total B/y	Units
PNL Analytical Chemistry Laboratory	≤ 100	≤ 400	pCi/g
Oak Ridge National Laboratory	≤ 135	≤ 450	pCi/g
WHC-CM-2-14 ⁴	≤ 60	≤ 200	pCi/g

⁵ 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 4.1.

2.5 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-107 vapor space and contained within the SUMMA® canisters shall be analyzed for total non-methane hydrocarbons following modified EPA procedure TO-14 and the permanent gases CO₂, CO, CH₄, H₂, and N₂O 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. Receipt and control of containers shall be guided by procedures PNL-TVP-07 and 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 to the 222-S Laboratory, the vapor sample containers for locked storage, and the HEPA filters and Tritium Trap for radiological survey.
- Step 5 SML: Using radiological survey report results, determine if samples are acceptable to ship offsite (see Section 3.4).
- 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 7.0 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		COMMENTS		REPORT FORMATS			NO. OF SAMPLE/BLANK CONTAINERS PROCESSED				
Plan Number		WHC-SD-WM-TP-281		Type 3 vapor sampling system (VSS) using heated vapor probes.		I	Early Notify	Organization		WHC	PNL	ORNL	TOTAL
Tank		T-107				II	Process Control	SUMMA® Canister			6 ^a /2		8
Program Contact		J. W. Osborne				III	Safety Screen	Sorbent Trap System ^b			6/3		9
TWRS Contact		B. C. Carpenter C. S. Homi				IV	Waste Management	Triple Sorbent Trap				12/4	16
Lab Project Coordinator		S. C. Goheen (PNL) R. A. Jenkins (ORNL)				V	RCRA Compliance	HEPA Filter		4			4
				VI	Special	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*	<100 ppbv	±25%	70-130%	I, VI
GC/TCD	CO ₂ CO CH ₄ H ₂ N ₂ O	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%	70-130%	VI I, VI I, VI I, VI I, VI
IC	NO NO ₂	PNL-TVP-09 PNL-ALO-212	PNL	H ₂ O 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 ₂ O	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 ₂ O 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**	< 100 ppbv	±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, NH₃, & H₂O.

c Multiple samples and blanks are taken.

d Samples are 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.

3.0 QUALITY ASSURANCE/QUALITY CONTROL

This Tank Characterization Plan 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, NQA-1, QAMS-005/80 or 10 CFR 830.120. They also must meet the requirements of the Characterization Program QAPP (Whelan 1994), the TWAP (Haller 1994), and the Vapor QAPJP (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 Quality Assurance Plan (Barnes 1994) written to comply with 5700.6C. ESH&QA will qualify laboratories for continued use by the TWRS Characterization program after receipt of a QA plan, followed by an audit and corrective action phase.

3.1 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-107 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.

3.2 Laboratory Operations

Prepared and labeled sample collection containers, trip blanks, and field blanks are supplied by the performing laboratories to Field Analytical Services. 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 Field Analytical Services.

The sample receipt and control steps used by 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. The analytical procedures used are identified 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 documented in controlled notebooks and referenced in the deliverable reports to ensure traceability.

4.0 ORGANIZATION

The organization and responsibility of key personnel involved in this tank T-107 vapor sampling project are listed in Table A.5.

Table A.5. Tank T-107 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-107 Tank Characterization Plan Engineers
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)
East Area Shift Operations Manager	Tank Farm Operations	East Tank Farm Point of Contact if Notification Limit is Exceeded (373-2689)

5.0 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 1 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 form 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.

6.0 DELIVERABLES

The Pacific Northwest Laboratory, Oak Ridge National Laboratory, and Sampling and Mobile Laboratories VSS sampling and analyses of tank T-107 vapors shall be reported as Format VI (Section 7.3). In addition, the analytical laboratories shall receive Format II reports from Sampling and Mobile Laboratories as described in Section 7.2. Any analyte exceeding the notification limit prescribed in Table A.4 shall be reported as Format I (Section 7.1). 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 is given in Schreiber (1994a, 1994b, 1994c).

6.1 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 East Area Shift Manager of Tank Farm Operations at (509) 373-2689 immediately. This verbal communication must be followed within 3 working days by written communication to J. W. Osborne of the Tank Vapor Issue Resolution Program, D. R. Carls in the Industrial Hygiene and Safety Program, and D. R. Bratzel of 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.

6.2 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.

6.3 Format VI Reporting

All Format VI reports shall be delivered to J. W. Osborne of the Tank Vapor Safety Resolution Program, R. S. Viswaneth of Field Analytical Services, 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 demonstrably 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 ($\mu\text{g}/\text{m}^3$, 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.

7.0 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.

8.0 REFERENCES

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