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1. EDT 609588

2. To: (Receiving Organization) CHARACTERIZATION PROGRAM	3. From: (Originating Organization) TWRS/CHARACTERIZATION SUPPORT	4. Related EDT No.: N/A
5. Proj./Prog./Dept./Div.: TWRS ENG/CHAR SUPPORT	6. Cog. Engr.: C. S. HOMI	7. Purchase Order No.: N/A
8. Originator Remarks: N/A		9. Equip./Component No.: N/A
		10. System/Bldg./Facility: 2750E/200E
11. Receiver Remarks:		12. Major Assm. Dwg. No.: N/A
		13. Permit/Permit Application No.: N/A
		14. Required Response Date: 11/2/94

15. DATA TRANSMITTED

(A) Item No.	(B) Document/Drawing No.	(C) Sheet No.	(D) Rev. No.	(E) Title or Description of Data Transmitted	(F) Approval Designator	(G) Reason for Transmittal	(H) Originator Disposition	(I) Receiver Disposition
1	WHC-SD-WM-TP-280		0	TANK 241-BY-111 TANK CHARACTERIZATION PLAN	Q	1	1	

16. KEY

Approval Designator (F)	Reason for Transmittal (G)		Disposition (H) & (I)	
E, S, Q, D or N/A (see WHC-CM-3-5, Sec.12.7)	1. Approval 2. Release 3. Information	4. Review 5. Post-Review 6. Dist. (Receipt Acknow. Required)	1. Approved 2. Approved w/comment 3. Disapproved w/comment	4. Reviewed no/comment 5. Reviewed w/comment 6. Receipt acknowledged

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BD-7400-172-2 (04/94) GEF097

BD-7400-172-1

RELEASE AUTHORIZATION

Document Number:	WHC-SD-WM-TP-280, REV.0
Document Title:	TANK 241-BY-111 TANK CHARACTERIZATION PLAN
Release Date:	November 3, 1994

This document was reviewed following the procedures described in WHC-CM-3-4 and is:

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SUPPORTING DOCUMENT

1. Total Pages 28

2. Title

TANK 241-BY-111 TANK CHARACTERIZATION PLAN

3. Number

WHC-SD-WM-TP-280

4. Rev No.

0

5. Key Words

CHARACTERIZATION, DQO, HEALTH AND SAFETY VAPOR ISSUE, FERROCYANIDE, QUALITY CONTROL, SINGLE-SHELL TANK, VAPOR SAMPLING, ANALYSIS, TANK CHARACTERIZATION PLAN

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7. Abstract

This document is a plan which serves as the contractual agreement between the Characterization Program, Sampling Operations, WHC 222-S Laboratory, Oak Ridge National Laboratory, and PNL 329 Laboratory. The scope of this plan is to provide guidance for the sampling and analysis of vapor samples from tank 241-BY-111.

8. RELEASE STAMP

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Sta 4

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A-6400-073 (08/94) WEF124

WHC-SD-WM-TP-280
Revision 0

Tank 241-BY-111 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

BY-111	Tank 241-BY-111
DQO	data quality objective
EPA	Environmental Protection Agency
GC/MS	gas chromatography/mass spectrometry
HEPA	high efficiency particulate air
ISS	in-situ sampling
ppbv	parts per billion by volume
ppmv	parts per million by volume
RCRA	Resource Conservation and Recovery Act
SUMMA®	registered trademark for passivated stainless steel canister
TBP	Tributyl phosphate
TCP	Tank Characterization Plan
TNMHC	Total Non-Methane Hydrocarbons
TO-12	EPA task order protocol 12
TO-14	EPA task order protocol 14
TOC	total organic carbon
WHC	Westinghouse Hanford Company

TANK 241-BY-111 TANK CHARACTERIZATION PLAN

1.0 SPECIFIC TANK CHARACTERIZATION 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 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.

This Tank Characterization Plan will identify characterization objectives for tank BY-111 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 the following sections. In addition, an estimate of the current contents and status of the tank is given.

1.1 Tank Safety Screening Data Quality Objectives

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 tank safety conditions related to the four Watch-List safety issues and classify the waste tanks into one of three categories: SAFE, CONDITIONALLY SAFE, or UNSAFE. A tank can be removed from the a Watch List if it is classified as SAFE. 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.

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 analytical requirements are concerned with measuring four primary analytes: energetics, total alpha activity, moisture level, and flammable gas concentration. If a specific criteria level on one of these items is exceeded, further analysis of a secondary set of analytes and a possible CONDITIONALLY SAFE or UNSAFE tank classification would be warranted.

1.2 Health and Safety Vapor Issue Resolution Data Quality Objectives

The *Data Quality Objectives for Generic In-Tank Health and Safety Vapor Issue Resolution* (Osborne et al. 1994a) concerns fugitive vapor emissions from tanks on the current "Suspect Tank List" and describes the methodology used to: 1) identify those tanks which can safely be sampled with intrusive equipment without risk of gas ignition; and 2) identify and estimate concentrations of toxicologically significant compounds present in the tank headspace and compare to published (if available) exposure limits.

1.3 Vapor Sampling Data Quality Objectives to Support Rotary Core Sampling

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

1.4 Ferrocyanide Safety Issue Data Quality Objectives

The *Data Requirements for the Ferrocyanide Safety Issue Developed through the Data Quality Objective Process* (Meacham et al. 1994) identifies the requirements needed to determine which classification to place a tank, based on analyses that establish if total fuel and moisture content are above or below an established threshold.

2.0 RELEVANT SAFETY INFORMATION

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.

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.

2.1 Tank Status

Single-shell tank BY-111 is classified as a Ferrocyanide Watch List tank. The tank is categorized as sound; interim stabilized was completed in January 1985. To prevent further waste addition, intrusion prevention was completed (Hanlon 1994).

Tank BY-111 is estimated to contain 79,500 liters (21,000 gal.) of sludge and 1,658,000 liters (438,000 gal.) of saltcake with no pumpable or drainable liquid for a total of 1,737,000 liters (459,000 gal). The median temperature of the waste in tank BY-111 is 28°C; the maximum temperature is 33°C (Brevick et al. 1994). The saltcake is estimated to contain no interstitial liquid. 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 162.5 inches below riser 5, which is located on the east side approximately 1/3 of the radius from the center of the tank. From this, the total waste volume is calculated at 1,614,000 liters (426,000 gal.).

2.2 Tank Monitoring Activities

Waste level measurements are taken on a quarterly basis through riser 5 using a manual tape. Internal tank temperature is automatically recorded from 13 thermocouples on a tree in riser 1. Four active dry wells monitor radiation in the surrounding soil (Hanlon 1994).

3.0 SUMMARY OF HISTORICAL INFORMATION FOR TANK BY-111

Included in this section are a physical description of tank BY-111, its process history, and recorded sampling events.

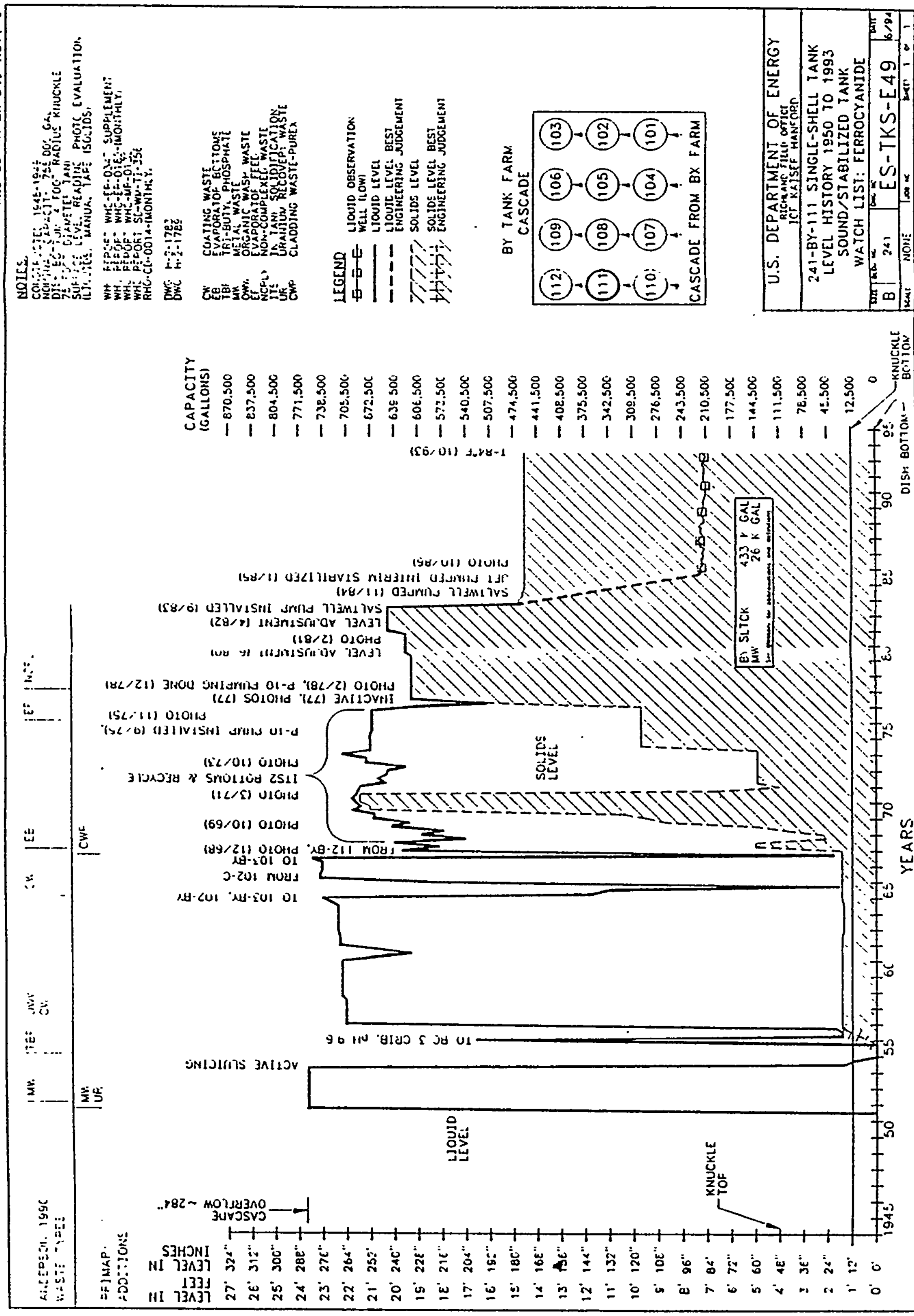
3.1 Configuration

Tank BY-111 is one of 12 single-shell tanks in the 200 East area BY Farm constructed during 1948-49. It is 23 meters (75 ft.) in diameter with a concave-shaped base and has a 2.87 million liter (758,000 gal.) tank capacity. The tank is equipped to cascade to BY-112 and is the second tank in the three tank cascade series.

3.2 Process History

Tank BY-111 was filled to capacity with metal waste in 1952 and sluiced out during the fourth quarter of 1954. Tributyl phosphate (TBP) process waste was added in early 1956 and transferred to number 3 crib and ditch 38C during the third quarter of 1956. Organic wash and coating waste was added during the second quarter of 1957. The supernate was pumped to a ditch in the third quarter of 1954 and the tank received TBP process waste in the fourth quarter of 1954. Transfers were made to BY-103 and BY-102 during late 1965 and early 1966. The tank was filled to near capacity with cladding waste from C-102 in early 1966 and later transferred to BY-103, BY-108, and BY-112 in early 1968. During the second quarter of 1968 evaporator bottoms waste was added and recycled. The tank, installed with a saltwell pump in September 1983, was pumped during November 1984. The tank was jet pumped and interim stabilized in January 1985.

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



3.3 Historical Sampling Events

No historical analytical data was found in the Tank Characterization Resource Center for the solid and liquid waste in tank BY-111. However, a type 2 vapor insitu sampling (ISS) event collected vapor space samples from tank BY-111 on May 11, 1994. Three SUMMA® canister samples were collected from the tank headspace and shipped to the Oregon Graduate Institute for analysis following Letter of Instruction guidelines (Osborne 1994b). Modified EPA TO-12 and TO-14 methods were applied to analyze the organic vapor. Analyses for nitrous oxide, hydrogen, and carbon monoxide were also performed. A data letter report, submitted to the TWRS Tank Vapor Issue Resolution Program, was produced as screening data and is not qualified data. These results and 9 of the 42 EPA TO-14 compounds detected are given in Table 1.

Results of an ambient air SUMMA® canister sample (field blank) collected upwind of BY-111 are 0 $\mu g/m^3$ of volatile organics following procedure EPA TO-12. Nitrous oxide, hydrogen, and carbon monoxide were not detected.

Table 1. Vapor Space Characterization Data for Tank BY-110.

Compound	Sample Identification Number		
	101	102	103
TNMHC[1] by procedure TO-12, $\mu g/m^3$	9,648	9,699	9,402
Nitrous Oxide, ppmv	98.2	99.3	99.2
Hydrogen, ppmv	68.4	68.5	64.7
Carbon Monoxide, ppmv	< 1	< 1	< 1
EPA TO-14 Analytes, ppbv			
1,3-Butadiene	3.8	5.3	4.6
Freon 11	254.9	288.8	292.8
Vinylidenechloride	0.7	0.5	1.0
Freon 113	0.4	0.3	0.5
Toluene	5.7	5.7	7.1
Ethyl Benzene	2.4	2.4	3.0
m&p-Xylene	5.4	5.4	6.7
1,1,2,2-Tetrachloroethane	--	0.1	0.1
o-Xylene	3.2	3.4	4.4

[1]Total Non-Methane Hydrocarbons

3.4 Expected Tank Contents

Tank BY-111 is expected to have two primary layers of waste. The bottom layer should be ferrocyanide sludge generated from in-plant scavenging of waste from uranium recovery. This waste type has high concentrations of sodium and nitrate, and a very low concentration of plutonium. The upper layer is expected to be saltcake formed from in-tank solidification of slurry product from the evaporator. Table 1 gives modeling estimates for the waste composition and inventory from a tank layering model developed at Los Alamos National Laboratory (Brevick et al. 1994).

Table 1. Single-Shell Tank BY-111 Solids Composite Inventory Estimate.

Physical Properties		
Total Solid Waste	2.62E+06 kg (459 kgal)	
Heat Load	3.11 kW (1.06+04 BTU/hr)	
Bulk Density	1.51 g/cc	
Void Fraction	0.67	
Water Wt%	34.31	
TOC Wt% C (wet)	0.05	
Chemical Constituents	**μg/g**	**kg**
Na^{+}	1.73E+05	4.53E+05
Al^{3+}	6.36E+03	1.67E+04
Fe^{3+} (total Fe)	--	--
Bi^{3+}	--	--
Ni^{2+}	--	--
K^{+}	64.13	1.68E+02
OH^{-}	1.55E+04	4.06E+04
NO_3^{-}	3.22E+05	8.44E+05
NO_2^{-}	7.78E+03	2.04E+04
CO_3^{2-}	2.07E+04	5.43E+04
PO_4^{3-}	1.84E+04	4.83E+04
SO_4^{2-}	2.71E+04	7.10E+04
Si (as SiO_3^{2-})	--	--
F^{-}	6.52E+03	1.71E+04
Cl^{-}	3.63E+02	9.52E+02
acetate^{-}	--	--
$Fe(CN)_6^{4-}$		-- (g-mol)
Radionuclides	**μg/g or μCi/g**	**Kg or Ci**
Pu	7.89E-03 μCi/g	0.34 kg
U	1.03E+04 μg/g	2.69E+04 kg
Cs	2.35E+02 μCi/g	6.17E+05 Ci
Sr	12.17 μCi/g	3.19E+04 Ci

3.4.1 Expected Tank Dome Space Vapor Composition

Combustible gas meter measurements made in March 1993 showed no combustible gases present in tank BY-111. Organic vapor monitor tests taken at the same time indicate approximately 6 ppm organics present in the vapor. Drager tube measurements show about 10 ppm NH_3. Other vapors of concern expected to be present in the vapor space are methane, nitric oxide, and nitrogen dioxide.

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APPENDICES

TANK 241-BY-111
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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BY-111	Tank 241-BY-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
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
TRP	Toxicology Review Panel
TO-12	EPA task order protocol 12
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-BY-111 VAPOR SPACE SAMPLING AND ANALYSIS PLAN

1.0 INTRODUCTION

Vapor samples are used to identify potential flammable and fugitive vapor emissions from the tanks which could become worker health and safety issues. Sampling 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.

2.0 SCHEDULED SAMPLING EVENT

The following information provides the methodology and procedures to be used in the preparation, sample retrieval, transport, analysis, and reporting of results for vapor space samples retrieved from tank BY-111. 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 characterization plan made during sample receipt, preparation, and analysis shall be documented and justified in the deliverable report.

2.1 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 3. FAS shall provide sample identification numbers following the quality assurance/quality control format given in Section 3.1 and other label information to the laboratories as requested.

2.2 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. Under present guidelines no operational or sampling activity is permitted if a single sample of the tank vapor fuel content, as measured with a combustible gas meter (CGM), 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 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 BY-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 BY-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-002	Tank Air	3
SUMMA®	OGI	EPA TO-14	Tank Air	3
SUMMA®	PNL	PNL-TVP-002	Ambient Air[1]	2
Triple Sorbent Traps	ORNL	AC-OP-300-0907 CASD-AM-300-WP01[2]	Tank Air	4
	ORNL	AC-OP-300-0907	Field Blank	1
	ORNL	AC-OP-300-0907	Trip Blank	1
Sorbent Trap System for NH_3, NO_2, NO, H_2O	PNL	PNL-TVP-002	Tank Air	6
	PNL	PNL-TVP-002	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).

2.4 Radiation Screening and Sample Transport

All samples shall be stored at the 222-S Laboratory Annex while performing a radiological survey of the HEPA filters used in the VSS and the tritium trap sampler. This is necessary to comply with Department of Transportation (DOT) shipping regulations and offsite laboratory acceptance criteria.

The HEPA filters used in the VSS shall be received by the 222-S Laboratory and analyzed for the acceptable specific (alpha, beta, gamma) activity levels given in Table A.3. The Tritium Trap shall be analyzed at the 222-S Laboratory for tritium using liquid scintillation counting to determine tritium activity.

The results from the radiation screening shall be submitted to and evaluated by Sampling and Mobile Laboratories to ensure the samples meet the analytical laboratory's acceptance criteria. 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
--	Purge VSS with ambient air[3]	N/A	5,450 mL/min	30 min.
01	Collect ambient air sample SUMMA #1	Upwind of BY-103		1 min.
--	Collect GC sample and initiate GC run			
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			
04	Collect SUMMA #3 OGI	Port 11		1 min.
05	Collect SUMMA #4 OGI	Port 13		1 min.
06	Collect SUMMA #5 OGI	Port 15		1 min.
07	Collect SUMMA #6 PNL	Port 12		1 min.
08	Collect SUMMA #7 PNL	Port 14		1 min.
09	Collect SUMMA #8 PNL	Port 16		1 min.
10	Collect Triple Sorbent Trap (TST) sample #1	Sorbent line 9	200 mL/min	10 min.
11	Collect TST sample #2	Sorbent line 10	200 mL/min	10 min.
12	Open, close, & store TST Field Blank #1	In VSS truck	0 mL/min	
13	Collect TST sample #3	Sorbent line 8	200 mL/min	10 min.
14	Collect TST sample #4	Sorbent line 10	200 mL/min	10 min.
15	Store TST Trip Blank #1	None	None	None
16	Collect NH3/NOx/H2O Sorbent Trap #1	Sorbent line 9	200 mL/min	15 min.
17	Collect NH3/NOx/H2O Sorbent Trap #2	Sorbent line 10	200 mL/min	15 min.
18	Collect NH3/NOx/H2O Sorbent Trap #3	Sorbent line 8	200 mL/min	15 min.
19	Collect NH3/NOx/H2O Sorbent Trap #4	Sorbent line 10	200 mL/min	15 min.
20	Collect NH3/NOx/H2O Sorbent Trap #5	Sorbent line 9	200 mL/min	15 min.
21	Collect NH3/NOx/H2O Sorbent Trap #6	Sorbent line 10	200 mL/min	15 min.
22, 23, 24	Store NH3/NOx/H2O Trap Trip Blanks #1, #2, & #3	None	None	None
25	Remove upstream HEPA Filter from HEPA transfer box	Upstream of box	Continuous	
26	Remove downstream HEPA Filter from HEPA transfer box	Downstream of box	Continuous	
27	Remove upstream HEPA Filter from VSS	Upstream of VSS	Continuous	
28	Remove downstream HEPA Filter from VSS	Downstream of VSS	Continuous	

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

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

Organization	Total α	Total β/γ	Tritium	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

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

Shipment of samples destined to the PNL laboratory shall occur within 24 hours after the 222-S radiation screening. 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 3.1.

2.5 Tank-Specific Analytical Procedures

2.5.1 Sampling, Isolation, and Analysis Scheme

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.

Following a time period for evaluation of the laboratory report by the Toxicology Review Panel (TRP), and if deemed necessary by the TRP, requirements for further quantification and speciation shall be conveyed through a Letter of Instruction by the Characterization Program and/or revision to this Tank Characterization Plan.

2.5.2 Analytical Methods

Sample material retrieved from the tank BY-111 vapor space and contained within the SUMMA® canisters shall be analyzed for total non-methane hydrocarbons following modified EPA procedure TO-12. 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, Tank Vapor Issue Resolution Program personnel shall be contacted.

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

- **Step 1** — Prepare sample and blank containers at contract laboratories. Label containers using sample identification numbers and sampling data provided by Field Analytical Services.
- **Step 2** — Ship containers to Field Analytical Services at least 4 days 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** — 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** — Perform radiological field survey of HEPA filters. Ship to the 222-S Laboratory the vapor sample containers for locker storage, and the HEPA filters and Tritium Trap for radiological survey.
- **Step 5** — Using radiological survey report results, determine if samples are acceptable to ship offsite (see Section 2.4).
- **Step 6** — 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 the J. W. Osborne of Vapor Issue Resolution Program for further direction.
- **Step 7** — A. SUMMA® Canisters (PNL): Perform EPA-TO-12. Perform full scan EPA-TO-14. Perform analyte-specific analysis for the following: H_2, CO, N_2O, CH_4, CO_2. 3 SUMMA® canisters for OGI will be archived by SML until OGI meets WHC QA requirements.

  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** — Following the Section 6.0 reporting requirements, deliver a Format VI Report to the Vapor Issue Resolution Safety Program according to the contractual agreements .

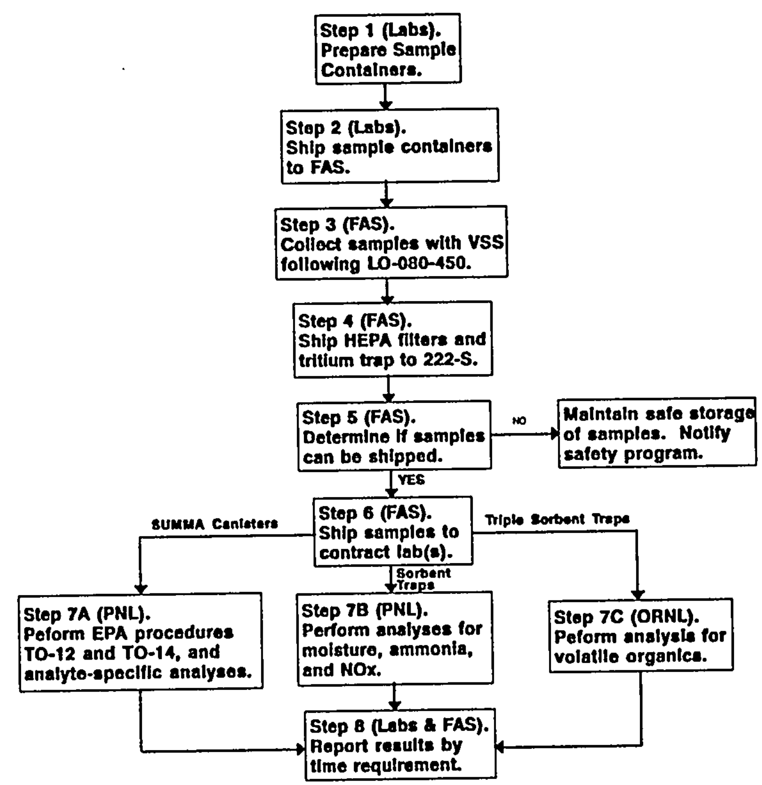

Table A.4. BY-111 Sample Chemical, Physical, and Radiological Analytical Requirements

PROJECT	BY-111 VAPOR	COMMENTS	REPORT FORMATS		NUMBER OF SAMPLE/BLANK CONTAINERS PROCESSED				
Plan Number	WHC-SD-WM-TP-280	Type 3 vapor sampling system (VSS) using heated vapor probes.	I	Early Notify	Organization	WHC/OGI	PNL	ORNL	TOTAL
Tank	BY-111		II	Process Control	SUMMA® Canister	3	3/2		8[a]
Program Contact	J. W. Osborne J. L. Huckaby		III	Safety Screen	Sorbent Trap System[b]		6/3		9
TWRS Contact	B. C. Carpenter C. S. Homi		IV	Waste Management	Triple Sorbent Trap			4/2	6
			V	RCRA Compliance	HEPA Filter	4			4
Lab Project Coordinator	S. C. Goheen (PNL) R. A. Jenkins (ORNL)		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 SAMPLE	SURR SPIKE[d]	BLANK	ACTION LIMIT[e]	EXPECTED RANGE	PRECN	ACCURACY	
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-12	TNMHC	PNL-TVP-004	PNL	Direct	SUMMA®	3	none	2	N/A	100-200 mg/m^3	±30%	50-150%	VI
EPA TO-14 GC/MS	Organic* Speciation	PNL-TVP-003 PNL-TVP-001	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_2O	PNL-TVP-006	PNL	Direct	SUMMA®	3	none	2	N/A ≥ 20% LFL ≥ 20% LFL ≥ 20% LFL not available	not available < 5 ppmv not available 600-800 ppmv 700-900 ppmv	±25% ±25% ±25% ±25% ±25%	70-130%	VI I, VI I, VI I, VI I, VI
IC	NO NO_2	PNL-ALO-009	PNL	H_2O Extraction	Sorbent Trap	4	none	1	≥ 50 ppmv ≥ 25 ppmv	not available not available	±25% ±25%	70-130%	I, VI I, VI
Gravimetric	H_2O	PNL-ALO-009	PNL	Direct	Sorbent Trap	4	none	1	N/A	not available	±25%	70-130%	VI
Selective Electrode	NH_3	PNL-ALO-266	PNL	H_2O Extraction	Sorbent Trap	4	none	1	≥ 250 ppmv	not available	±25%	70-130%	I, VI
GC/MS	Organics**	AC-MM-1-003153 AC-MM-1-003157	ORNL	Thermal Desorption	Triple Sorbent Trap	4	all	2[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	±10% ±10% ±10%	90-110%	I, II
Liq. Scin.	Tritium	LA-548-111 LA-218-111	WHC	Direct	Tritium Trap	1	N/A	N/A	N/A	not available	±10%	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 are spiked with surrogates.
- e Action required if any compound exceed 50% IDLH.
- f Includes one trip and one 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 resultant laboratory analysis data has been 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, QAMMS/005, and 10 CFR Part 830.120.

2) Each analysis and media preparation procedure given in Tables A.1 and A.3 are 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.

ESH&QA will qualify laboratories for continued use by the program after receipt of the Laboratory quality assurance plans, and an audit and corrective action phase.

3.1 Sampling Operations

The laboratory supplying the sample collection media shall initiate the chain of custody 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 by the sample collection media supplier. TO-14 certified rental SUMMA® canisters from OGI shall have chain of custody initiated by FAS.

Applicable operating procedures for the tank BY-111 vapor space sampling activities are contained in work package ES-94-1179. 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 laboratory in accordance with Hazardous Material Packaging and Shipping, WHC-CM-2-14.

All sampling activities shall be documented in a controlled field notebook 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 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 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 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 procedures used in the Pacific Northwest Laboratory 326 Laboratory are reported by procedure PNL-TVP-07. Oak Ridge National Laboratory shipping and receiving is done by procedure CASD-AM-300-WP02. Analyses performed at a laboratory shall be guided by a quality assurance program that meets the applicable requirements of DOE order 5700.6C, NQA-1, QAMMS/005, and 10 CFR Part 830.120. The PNL 326 laboratory has an impact level II Laboratory Quality Assurance Plan (Barnes 1994).

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 BY-111 vapor sampling project are listed in Table A.5.

Table A.5. Tank BY-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	BY-111 Tank Characterization Plan Engineers
J. L. Huckaby	TWRS Tank Vapor Issue Resolution Program	Vapor Issue Resolution Engineer
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 Action Limit is Exceeded (FAX 372-3522)
East Area Shift Operations Manager	Tank Farm Operations	East Tank Farm Point of Contact if Action Limit is Exceeded (373-2689)

5.0 EXCEPTIONS, CLARIFICATIONS, AND ASSUMPTIONS

5.1 Exceptions to DQO Requirements

The determination of the flammability of tank vapor space gases will not be made during this sampling event. This determination is performed and reported prior to the sampling event periodically by industrial hygiene personnel and during probe installation. Once determined to be safe in regard to flammability, the tank is regarded as safe for a period of 6 months.

During this period normal tank operations and sampling is permitted, following which a new flammability test may be performed.

5.2 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. Transfer of custodianship occurs when the custodian signs the *relinquished by* block on the chain of custody 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 BY-111 vapors shall reported as Format VI (Section 6.3). All reports shall be submitted to J. W. Osborne of the Tank Vapor Safety Resolution Program and R. S. Viswanath of Field Analytical Services. In addition, the analytical laboratories shall receive Format II reports from Sampling and Mobile Laboratories as described in Section 6.2. Table A.4 identifies the primary analytes of concern expected to be present in the vapor space of tank BY-111. Any analyte exceeding the notification limit prescribed in Table A.4 shall be reported as Format I (Section 6.1). 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. Other report recipients are identified in the following sections. Additional information regarding reporting formats is given in Schreiber (1994).

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 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

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.

Each analytical laboratory shall deliver two reports. An interim report shall be delivered within the 5 week period after receipt of sample. A final report shall be delivered within a 9 week period after receipt of sample, in accordance with the following guidelines.

The final report from the analytical laboratories shall be suitable for public distribution. To the extent applicable, the 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) chain-of-custody forms attached.

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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