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Document Number:	WHC-SD-WM-TP-289, REV.0
Document Title:	TANK 241-U-105 TANK CHARACTERIZATION PLAN
Release Date:	February 7, 1995

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

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6. Author	Name: C. S. HOMI Signature: [signature] 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-U-105.

8. RELEASE STAMP

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WHC-SD-WM-TP-289
Revision 0

Tank 241-U-105
Tank Characterization Plan

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

MASTER

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U-105	Tank 241-U-105
DQO	data quality objective
EPA	Environmental Protection Agency
ppm	parts per million by volume
RCRA	Resource Conservation and Recovery Act
TBP	tributyl phosphate
TCP	Tank Characterization Plan
TLM	Tank Layer Model
TPA	Federal Facility Agreement and Consent Order (Tri-Party Agreement)
TOC	total organic carbon
TWRS	Tank Waste Remediation System
WHC	Westinghouse Hanford Company

TANK 241-U-105 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 analytical needs for the resolution of safety issues. As a result, a revision in the Federal Facility Agreement and Consent Order (Tri-Party Agreement or TPA) 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-U-105 (U-105) sampling activities.

2.0 DATA QUALITY OBJECTIVES APPLICABLE TO TANK 241-U-105

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 February 1995 the following DQOs apply to tank U-105. Refer to section 4.0 for the applicable sampling event DQO discussion.

2.1 Vapor Sampling Data Quality Objectives

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 et al. 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.

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 et al. 1994a). 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 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. 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 primary analytical requirements for the safety screening of a tank are energetics, total alpha activity, moisture and flammable gas concentrations. 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.

2.3 Organic Fuel-Rich Tank Data Quality Objective

This DQO effort focuses on SSTs that contain or may contain, based on safety screening, organic compounds above the established decision thresholds. It identifies the information needed to determine if tanks should be removed, not removed, or added to the Organic Watch List. As with the several other DQO efforts, the sampling and analyses prescribed by this DQO effort will allow tanks to be classified as safe, conditionally safe, or unsafe. The sampling requirements of this DQO effort are for a minimum of two cores samples separated radially to the maximum extent possible by existing risers. For further information on this DQO effort refer to *Data Quality Objective to Support Resolution of the Organic Fuel Rich Tank Safety Issue* (Babad et al. 1994).

2.4 Flammable Gas Safety Issue Data Quality Objective

This DQO effort focuses on DSTs that contain or may contain, based on safety screening, flammable gases above the established decision thresholds. It concluded that the most reliable information is obtained from one complete core and summarizes the analytical needs for the core sampling activities of the Flammable Gas Watch List tanks. Data from these core samples are needed to provide an understanding of the tank contents so that (1) insight may be obtained on the mechanisms for gas generation, retention and release, (2) models of the waste behavior can be developed to support safety analysis and development of mitigation methods, and (3) modeling of the flow of gases, and potential for ignition, can be done to support hazard analyses. For further information on this DQO effort refer to *Flammable Gas Safety Program: Data Requirements for Core Sample Analysis Developed through the Data Quality Objectives (DQO) Process* (McDuffie 1994).

2.5 Waste Compatibility Data Quality Objectives

The *Data Quality Objectives for the Waste Compatibility Program* (Carothers 1994) identified four safety-related decision elements, criticality, flammable gas accumulation, energetics, and corrosivity, needed to determine potential incompatibility of wastes that may occur from routine waste transfers into and within a DST. A routine transfer has the appropriate historical data necessary to determine the acceptability of the transfer from an engineering process control perspective. Four operations-related decision elements have been identified for a non-routine transfer: separation of transuranic from non-transuranic waste, limits on heat generation, segregation of complexant waste, and ensuring pumping system capabilities. A non-routine transfer includes waste that has unique chemical and/or physical properties for which no historical data exist to judge compatibility with safety and operations decision rules.

3.0 TANK U-105 HISTORICAL INFORMATION

Included in this section are a physical description of tank U-105, its process history, and recorded sampling events. Single-shell tank U-105 is classified as a Hydrogen and Organic Watch List tank. The tank is categorized as sound and is in partially isolated status (Hanlon 1994).

3.1 January 1995 Tank Status

Tank U-105 is estimated to contain 1,321,200 liters (349,000 gal.) of saltcake, 121,000 liters (32,000 gal.) of sludge and 140,000 liters (37,000 gal.) of supernatante liquid for a total of 1,582,000 liters (418,000 gal). Tank U-105 has approximately 594,000 liters (157,000 gal.) of pumpable liquid remaining. The median temperature of the waste in tank U-105 is 32°C, as measured in September 1994. Its contents are categorized as non-complexed waste (Hanlon 1994). Figure 1 summarizes activity history of tank U-105.

Recent readings (January, 1995) obtained from Tank Farm Surveillance and the Surveillance Analysis Computer System database indicate a waste depth of 150.0 inches below riser #19, which is located on the northwest side edge of the tank. From this, the total waste volume is calculated at 1,608,600 liters (425,000 gal.). The latest photograph shows approximately 50% of the tank surface covered with a light yellow colored salt cake. The remaining surface is covered with a dark supernatant liquid. A salt ring appears on the tank wall which may be residue left from lowering the tank level.

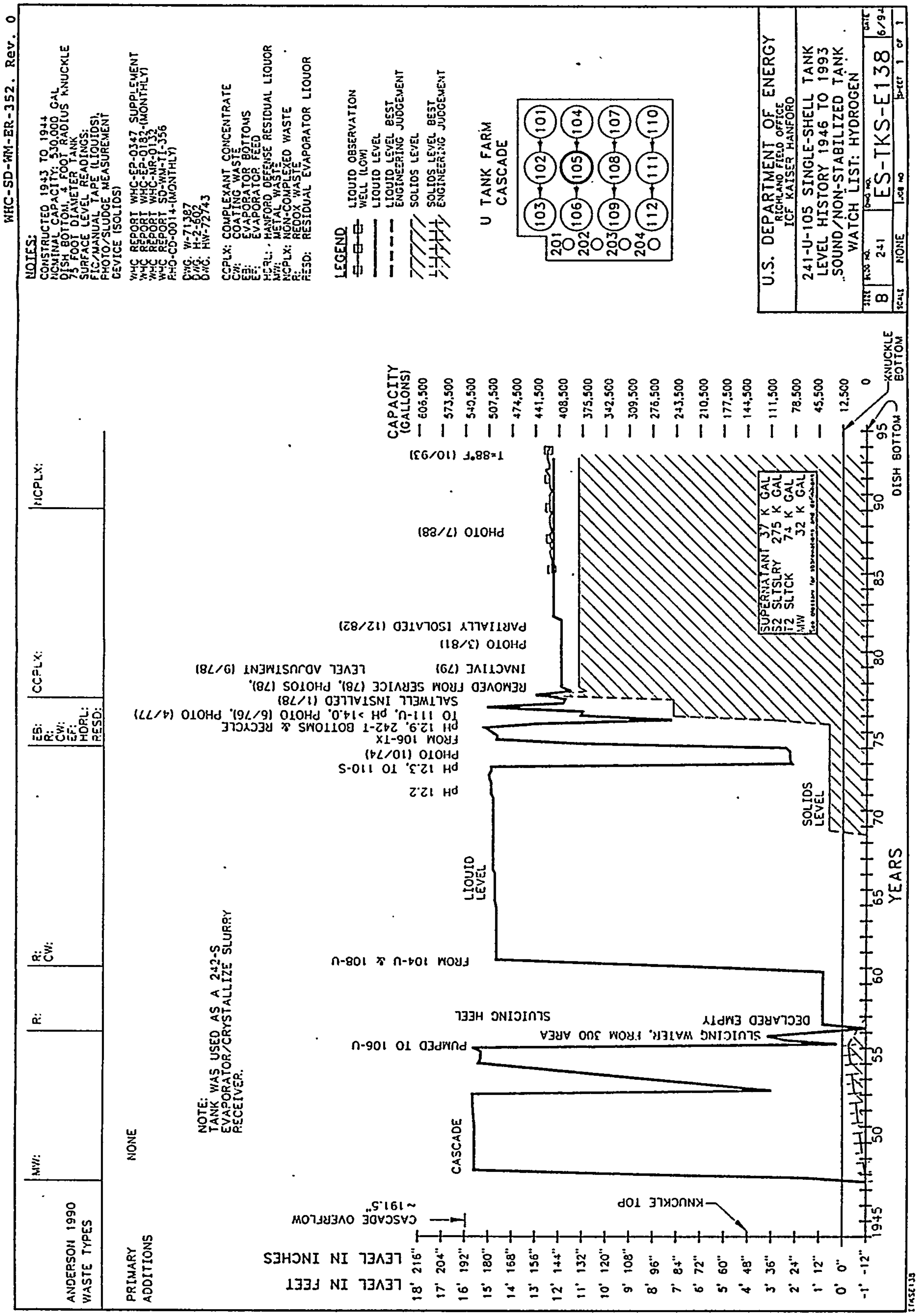
3.2 Tank Configuration and Monitoring Activities

Tank U-105 is one of 12 single-shell tanks in the 200 West area U Farm constructed during 1943-44. 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 second of a three cascade series ending with tank U-106. 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 241-U-105 was filled with metal waste from the fourth quarter of 1947 until the second quarter of 1956 when the supernatant was pumped to tank U-106. During the fourth quarter of 1956 uranium waste from the 300 Area was added and all contents removed by the second quarter of 1957 when the tank was declared empty. Redox and coating wastes from tanks U-104 and U-108 were transferred to tank U-105 in early 1961. Tank U-105 contents were pumped to tank S-110 during the first quarter of 1974. Evaporator bottoms were received from tank TX-106 during the second quarter of 1975 and bottoms from 242-T recycled to tank U-111 until the end of 1976. The tank was removed from service in 1978 and declared inactive in 1979. The tank was partially isolated in 1982.

Figure 1. Fill history of Tank 241-U-105.



3.4 Historical Sampling Events

Salts from tank U-105 were analyzed in December of 1978. Results for select analytes for both the water and fusion digestions are shown in Table 1 (Horton 1978). A average concentration and inventory estimate of the tank U-105 waste is shown in Table 2 (Brevick 1994).

3.5 Expected Tank Contents

The Tank Layer Model (TLM), which is the basis of the Brevick 1994 estimates, predicts a layer of metal waste sludge (approximately 17 inches) is located at the bottom of the tank beneath a layer of saltcake (approximately 132 inches), all covered by a top layer of approximatey 19 inches of supernatant. The TLM is in early stages of development and may not reflect the true stratification of the waste. In addition, the uncertainty of the TLM analyte estimates is unknown.

Table 1. Results for Select Analytes for Tank U-105.

ANALYTES	Average Result (Water Digestion)	Average Result (Fusion Digestion)
RADIONUCLIDES		
Sr-89/90 µCi/g	27.7	201.3
Cs-137 µCi/g	223.2	29.0
Pu-239/240 g/g	--	1.4 X 10E-6
Uranium g/g	2.46 X 10E-6	1.66 X 10E-4
CHEMICAL COMPONENTS		
Al %	1.2	--
CO_3 %	5.4	--
La %	0.06	--
NO_2 %	4.2	--
NO_3 %	18.4	--
Na %	37.0	--
OH %	1.2	--
PO_4 %	0.3	--
SO_4 %	1.5	--
SiO2 %	0.03	2.1
TOC %	2.8	--
Water Solubility %	95.0	NA
Bulk Density g/cc	1.62	NA
Percent Water %	20.8	NA

Table 2. Single-Shell Tank U-105 Inventory Estimate.

Solids Composite Inventory Estimate*		
Physical Properties		
Total Waste Mass	2.24+06 kg (381 kgal)	
Heat Load	3.02 kW (1.03E+04 BTU/hr)	
Bulk Density	1.55 (g/cc)	
Void Fraction	0.827	
Water wt%	43.4 11.52	
TOC wt% C	0.248	
Chemical Constituents	**ppm**	**kg**
Na^{1+}	1.53E+05	3.43E+05
Al^{3+}	2.93E+04	6.56E+04
Fe^{3+} (total Fe)	1.18E+03	2.65E+03
Cr^{3+}	1.80E+03	4.02E+03
Bi^{3+}	88.1	197
Zr (as $ZrO(OH)_2$)	77.0	172
Pb^{2+}	3.58E-02	8.01E-02
Ni^{2+}	273	612
Mn^{4+}	241	540
Ca^{2+}	1.21E+03	2.72E+03
K^{1+}	1.21E+03	2.70E+03
OH^{1-}	8.80E+04	1.91E+05
NO_3^-	1.93E+05	4.20E+05
NO_2^-	5.63E+04	1.22E+05
CO_3^{2-}	1.52E+04	3.30E+04
PO_4^{3-}	7.48E+03	1.62E+04
SO_4^{2-}	1.78E+04	3.87E+04
Si (as SiO_3^{2-})	823	1.79E+03
F^{1-}	1.10E+03	2.39E+03
Cl^{1-}	2.59E+03	5.63E+03
$C_6H_5O_7^{3-}$	4.37E+03	9.50E+03
HEDTA	8.49	18.4
glycolate^{1-}	1.99E+03	4.32E+03
DBP	567	1.23E+03
Radionuclides	**µCi/g**	**kg**
Pu	3.38E-02	2.16
U	1.49E+04(µg/g)	3.33E+04
Cs-137	2.72E+02	6.08E+05(Ci)
Sr-90	11.5	2.58E+04(Ci)

*Composite inventory excludes supernatent, diatomaceous earth, and cement.

4.0 STRATEGY FOR WASTE CHARACTERIZATION AND SAFETY ISSUE RESOLUTION

The DQO requirements for sampling and analyses are integrated and compared with scheduled sampling and analyses activities in this section.

4.1 Sampling of Tank U-105 in the Near Term

The characterization objectives in fiscal year 1995 involve sampling of tanks to identify and resolve safety issues. Head space vapor sampling in March 1995 and grab sampling in April 1995 are scheduled for tank U-105. The head space vapor sampling shall be conducted following *Data Quality Objectives for Generic In-Tank Health and Safety Vapor Issue Resolution* (Osborne et al. 1994a). Vapor sampling will satisfy part of the requirement specified in TPA Milestone M-40-08 to complete the vapor sampling of all organic Watch List tanks (Osborne and Huckaby 1994b).

Grab sampling shall be conducted following *Data Quality Objectives for the Waste Compatibility Program* (Carothers 1994). The Safety Screening and Organic DQO needs will be met by the planned FY 1996 rotary mode core sampling event. These sampling and analysis events, if successful, will satisfy the February 1995 applicable DQO requirements. These requirements are summarized in Table 3. A more complete list of analytical requirements are given, as an appended revision, in the appropriate sampling and analysis plan.

Table 3: Integrated DQO Requirements

Sampling Event	Applicable DQO	Sampling Requirements	Analytical Requirements
Vapor	▪Generic Health & Safety Vapor Issue Resolution	6 SUMMA® Cannisters 12 Triple Sorbent Traps 6 Sorbent Trap Systems	Flammability Toxicity
Rotary Sampling	▪ Safety Screening DQO ▪ Organic DQO ▪ Flammable Gas DQO	2 cores from risers separated radially to the maximum extent possible	Energetics, TOC, Total Alpha, Moisture, Gas Composition, Major Anions & Cations, Radionuclides, Primary Organics & Organic Products, Physical Properties
Grab Sampling	▪ Compatability DQO	3 grab samples	Energetics, Moisture, Major Anions, Cations & Radionuclides, SpG & pH, Separable Organics

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APPENDICES

TANK 241-U-105
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

U-105	Tank 241-U-105
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
GC/MS	gas chromatography/mass spectrometry
IC	ion chromatography
IDLH	immediately dangerous to life and health
LFL	lower flammability limit
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
QA	quality assurance
TCP	Tank Characterization Plan
TO-14	EPA Toxic Organics Protocol 14
TOC	total organic carbon
TWRS	Tank Waste Remediation System
VSS	vapor sampling system
WHC	Westinghouse Hanford Company

A1.0 INTRODUCTION

The Tank Vapor Issue Resolution Program was initiated in 1992 to resolve the health and safety issues associated with the high level waste tanks at the Hanford Site. The primary characterization efforts applicable to this Sampling and Analysis Plan (SAP) are focused on two areas: 1) determining the LFL and 2) the potential human toxicity of any compounds in the tank head space vapor. After resolution of the flammable issue of the tank head space vapor, safe operating procedures will be established to allow sampling of the head space vapor for characterization of potential human health toxicity. The industrial hygiene group will be advised of the presence of toxicological compounds at levels of concern in the head space vapor. The industrial hygiene group will then establish health and safety procedures to provide for worker protection during subsequent sampling or operational activities.

This SAP identifies objectives for tank 241-U-105 (U-105) following the *Fiscal Year 1995 Tank Waste Remediation System Tank Waste Analysis Plan* (Haller 1994) and *Data Quality Objectives for Generic In-Tank Health and Safety Vapor Issue Resolution* (Osborne et al. 1994).

Present vapor sampling systems include Type 2 (In Situ Sampling, or ISS) and Type 3 (the Vapor Sampling System, or VSS). These two sampling systems are operated by Sampling and Mobile Laboratories (SML). The ISS is a hand cart used to collect permanent (non-condensible) gas samples. The VSS is a more elaborate mobile truck sampling system which employs a heated sampling tube to collect condensible gases (i.e., moisture and organics).

A2.0 SCHEDULED SAMPLING EVENT

The following information provides the methods and procedures to be followed in the preparation, retrieval, transport, analysis, and reporting of results for head space vapor samples retrieved from tank U-105. The requirements for the vapor sampling of U-105 in the 1995 fiscal year, contained within this SAP, 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 in controlled notebooks and justified in the deliverable report.

A2.1 PREPARATION OF SAMPLE MEDIA CONTAINERS

The laboratories performing the contracted analytical work shall supply prepared and labeled sample containers (SUMMA® canisters and selective sorbent sampling media) to SML 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. SML shall provide sample identification numbers to the laboratories for the sample media as requested following the quality assurance format given in Section A3.1.

A2.2 FLAMMABILITY OF VAPOR SPACE GASES

Before performing intrusive work on a tank, an assessment of the flammable level of the tank head space vapor is required by standard WHC safety practices. The flammable test procedure is included in the sampling event work package (ES-95-00005) 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 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 flammable problem and all scheduled work can proceed (Osborne et al. 1994).

A2.3 SAMPLE COLLECTION

In fiscal year 1995, the tank U-105 head space vapor shall be sampled through a heated probe in an available riser using the 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 before sampling the tanks using the following conditions: 1) with the VSS manifold and transfer lines fully heated; and 2) without the VSS, upwind of U-105.

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	3
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 for Tank U-105

SAMPLE CODE	SAMPLE/ACTIVITY DESCRIPTION	SAMPLER POSITION DURING COLLECTION	GAS FLOW RATE	SAMPLE DURATION
--	Adjust VSS temperature setpoint to 50°C[1]	N/A	N/A	N/A
--	Purge VSS with ambient air[2]	N/A	5,450 mL/min	30 min
01	Collect ambient air sample SUMMA #1	Upwind of U-105		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[3]			
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 Triple Sorbent Trap (TST) sample #1	Sorbent line 9	50 mL/min	4 min
08	Collect TST sample #2	Sorbent line 10	50 mL/min	4 min
09	Collect TST sample #3	Sorbent line 8	50 mL/min	4 min
10	Open, close, & store TST Field Blank #1	In VSS truck	0 mL/min	
11	Collect TST sample #4	Sorbent line 10	50 mL/min	4 min
12	Collect TST sample #5	Sorbent line 9	200 mL/min	5 min
13	Collect TST sample #6	Sorbent line 10	200 mL/min	5 min
14	Collect TST sample #7	Sorbent line 8	200 mL/min	5 min
15	Collect TST sample #8	Sorbent line 10	200 mL/min	5 min
16	Collect TST sample #9	Sorbent line 9	200 mL/min	20 min
17	Open, close, & store TST Field Blank #2	In VSS truck	0 mL/min	
18	Collect TST sample #10	Sorbent line 10	200 mL/min	20 min
19	Collect TST sample #11	Sorbent line 8	200 mL/min	20 min
20	Collect TST sample #12	Sorbent line 10	200 mL/min	20 min
21,22	Store TST Trip Blanks #1 & #2	None	None	None
23	Collect NH3/NOx/H2O Sorbent Trap #1	Sorbent line 9	200 mL/min	15 min
24	Collect NH3/NOx/H2O Sorbent Trap #2	Sorbent line 10	200 mL/min	15 min
25	Collect NH3/NOx/H2O Sorbent Trap #3	Sorbent line 8	200 mL/min	15 min
26	Collect NH3/NOx/H2O Sorbent Trap #4	Sorbent line 10	200 mL/min	15 min
27	Collect NH3/NOx/H2O Sorbent Trap #5	Sorbent line 9	200 mL/min	15 min
28	Collect NH3/NOx/H2O Sorbent Trap #6	Sorbent line 10	200 mL/min	15 min
29,30,31	Store NH3/NOx/H2O Trap Trip Blanks #1, #2, & #3	None	None	None
32	Remove upstream HEPA Filter from HEPA transfer box	Upstream of box	Continuous	
33	Remove downstream HEPA Filter from HEPA transfer box	Downstream of box	Continuous	
34	Remove upstream HEPA Filter from VSS	Upstream of VSS	Continuous	
35	Remove downstream HEPA Filter from VSS	Downstream of VSS	Continuous	

[1]The historical vapor space temperature has a seasonal variation from the mid 20's°C to the low 30's°C

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

[3]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 by SML 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 in Table A-4 (Bratzel 1994).

The results from the radiation screening shall be submitted to and evaluated by SML to ensure the samples meet the analytical criteria specified in Table A-3. SML shall provide a Format II report to each analytical laboratory to specify survey results (refer to Section A6.2).

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 analytical laboratories. 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 flow chart 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 U-105 head space and contained within the SUMMA® canisters shall be analyzed for organic compounds following modified EPA procedure TO-14 and for permanent gases CO_2, CO, CH_4, H_2, and N_2O using gas chromatography. The sorbent traps, which contain analyte-specific sorbent media, 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.

One SUMMA® canister shall be archived at the PNL Laboratory following receipt and control procedure PNL-TVP-07 for six months or until instructed by the Tank Vapor Program to clean the canister for reuse. If necessary, 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.

Any analyses prescribed by this document, but not performed, or other deviations, shall be identified and include documented justification in the appropriate data report. Unlike a solid sample which may have full or partial recovery, vapor sample media contain either good, bad, or no sample. A sample that is bad or empty may not have a proper seal. Partial recovery of a vapor sample is not an issue, however, the number of good samples may be an issue. All good samples, except the SUMMA® canister archive, shall be analyzed. If there are insufficient good samples to perform all requested analyses, the Characterization Program Office and the Tank Vapor Issue Resolution Program shall be notified. The SUMMA® canister archive shall be used if one or more of the SUMMA® canister samples is compromised.

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

•Step 1	Contract Labs: Prepare sample and blank containers with sample identification numbers and sampling data provided by SML.
•Step 2	Labs: Ship Containers to SML at least 48 hours in advance of scheduled sampling event. Shipping, receiving, and control of containers shall be guided by procedures LO-090-443 (for SML), and either PNL-TVP-07 (for PNL) or CASD-AM-300-WP02 (for 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 A2.4).
•Step 6	SML: If determined to be acceptable according to offsite laboratory requirements and WHC-CM-2-14, ship samples and blanks. If not acceptable to ship, maintain samples in storage and contact the Tank Vapor Issue Resolution Program for further direction.
•Step 7	Labs: Perform laboratory analyses (see Table A-4 for procedure numbers). A. SUMMA® Canisters (PNL): Perform organic vapor analysis modified 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 A6.0 reporting requirements, deliver a Format VI report.

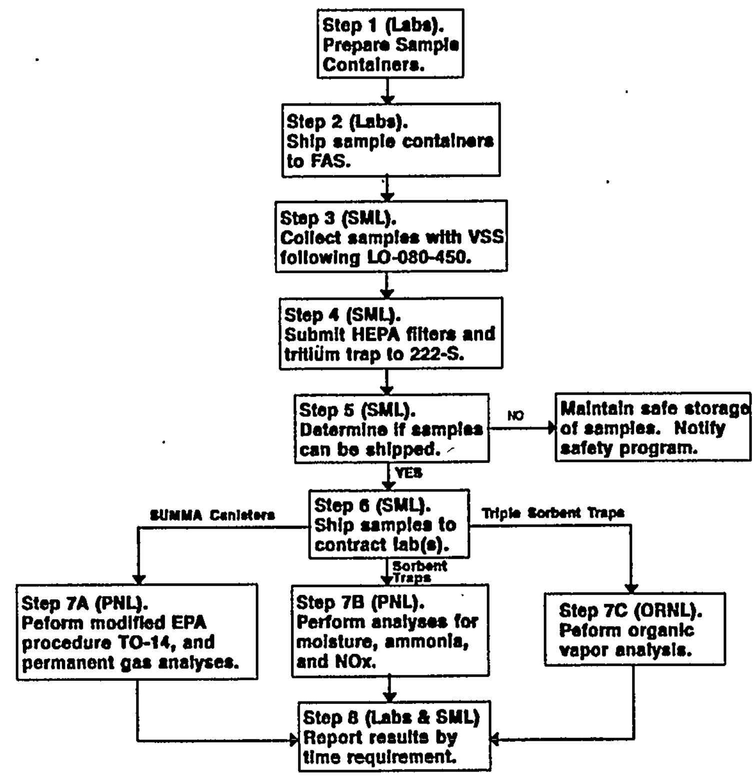

Table A-4. U-105 Sample Chemical, Physical, and Radiological Analytical Requirements

PROJECT	U-105 VAPOR	COMMENTS	REPORT FORMATS		NO. OF SAMPLE/BLANK CONTAINERS PROCESSED				
Plan Number	WHC-SD-WM-TP-250	Type 3 vapor sampling system (VSS) using heated vapor probes.	I	Early Notify	Organization	WHC	PNL	ORNL	TOTAL
Tank	U-105		II	Process Control	SUMMA® Canister		3[a]/2		5
Program Contact	J. W. Osborne		III	Safety Screen	Sorbent Trap System[b]		6/3		9
TWRS Contact	R. D. Schreiber B. C. Carpenter C. S. Homi		IV	Waste Management	Triple Sorbent Trap			12/4	16
			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 SAMPLES	SURR SPIKE[d]	NO OF BLANKS	NOTIFICATION LIMIT (NL)[e]	EXPECTED RANGE	PRECN @NL	ACCURACY @NL	
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[g]	LA-548-111	WHC	Direct	Tritium Trap	1	N/A	N/A	N/A	not availabl	N/A	N/A	II
GC/FID	Organics	LO-080-450	SML	Direct	On-line	N/A	N/A	N/A	N/A	N/A	N/A	N/A	II, VI

N/A: Not Applicable
a No extra canisters, except archive, will be stored by PNL.
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 two trip and two field blanks.
g Survey purposes only.

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

A3.0 QUALITY ASSURANCE

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 the DOE order 5700.6C or the United States 10 CFR 830.120. In addition, it must also meet the requirements of the vapor QAPP (Keller 1994) and when implemented in August 1995, the *Hanford Analytical Services Quality Assurance Plan* (DOE 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 in controlled notebooks and justified in the deliverable report.

The PNL tank vapor program is governed by an impact level II QA 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 a QA Plan, followed by an audit and corrective action phase.

A3.1 SAMPLING OPERATIONS

SML shall provide unique sample label and identification numbers to the laboratories. 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 SML 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 U-105 vapor space sampling activities are contained in work package WS-95-00005. 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 (SML) 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.

SML 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 SML. 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 SML.

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 QA Plan.

Due to the developmental work being done with the analysis procedures and potential sample differences (between tanks), changes in procedures may be needed.

A4.0 ORGANIZATION

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

Table A-5: Tank U-105 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	U-105 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	Special Analytical Studies	Vapor Program Technical Lead
R. D. Mahon	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

Toxicology Review Panel

The Toxicology Review Panel (TRP) is a group of toxicologists, industrial hygienists, and occupational medicine physicians that convene to review quantitative vapor sample data, identify compounds of toxicological concern, and make recommendations to the WHC Tank Vapor Program Manager concerning potential impacts to worker health and safety.

Toxicological Concern

From a list of 160 analytes found in tank C-103, the TRP identified 19 analytes of toxicological interest. These analytes and others may be identified during TRP review of qualitative GC vapor data as being of toxicological concern if they exceed recommended levels inside the tank headspace. Established guidelines these analytes are base on Consensus Exposure Standards (CES).

Consensus Exposure Standards

A CES is generally defined as the most stringent of known regulatory or recommended toxicological values for the occupational setting including the threshold limit value (TLV), permissible exposure limit (PEL), recommended exposure limit (REL), and biological exposure limit (BEL). For those constituents with unknown toxicological values, the TRP will be responsible for development of a CES.

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 SML 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.

A6.0 DELIVERABLES

The Pacific Northwest Laboratory, Oak Ridge National Laboratory, and Sampling and Mobile Laboratories VSS sampling and analyses of tank U-105 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). Additional information regarding reporting formats 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 East Area Shift Manager of Tank Farm Operations at 373-2689 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 SML 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, R. S. Viswanath of Special Analytical Studies, 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 for 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 will 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) 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) 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 all chain-of-custody forms.

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 (no change in scope). 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

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