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Tank 241-B-103 Tank Characterization Plan (WHC-SD-WM-TP-250)		ECN No.

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Document Number:	WHC-SD-WM-TP-250, REV.0
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Release Date:	January 23, 1995

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5. Key Words

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

6. Author

Name: B. C. CARPENTER

Brad Carpenter
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-B-103.

8. RELEASE STAMP

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WHC-SD-WM-TP-250
Revision 0

Tank 241-B-103
Tank Characterization Plan

Prepared for the U.S. Department of Energy

Office of Environmental Restoration
and Waste Management

by

Los Alamos Technical Associates
8633 Gage Boulevard
Kennewick, Washington 99336

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LIST OF ABBREVIATIONS

B-103	Tank 241-B-103
DOE	U.S. Department of Energy
DNFSB	Defense Nuclear Facilities Safety Board
DQO	Data Quality Objective
DST	Double-Shell Tank
HEPA	High-Efficiency Particulates Air Filter
HTCE	Historical Tank Content Estimates
RCRA	Resource Conservation and Recovery Act of 1976
SST	Single-Shell Tank
TCP	Tank Characterization Plan
TLM	Tank Layering Model
TPA	Federal Facility Agreement and Consent Order (Tri-Party Agreement)
TOC	Total Organic Carbon
TWRS	Tank Waste Remediation System
WHC	Westinghouse Hanford Company

1.0 INTRODUCTION

The Defense Nuclear Facilities Safety Board (DNFSB) has advised the U.S. Department of Energy (DOE) to concentrate the near-term sampling and analysis activities on identification and resolution of safety issues (Conway 1993). The data quality objective (DQO) process was chosen as a tool to be used to identify sampling and analytical needs for the resolution of safety issues. As a result, a revision in the Federal Facility Agreement and Consent Order (Tri-Party Agreement 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-B-103 (B-103) sampling activites.

2.0 DATA QUALITY OBJECTIVES APPLICABLE TO TANK 241-B-103

The sampling and analytical needs associated with the Hanford Site underground storage tanks on one or more of the four Watch Lists (ferrocyanide, organic, flammable gas, and high heat) and the safety screening of all 177 tanks have been identified through the DQO process. A DQO indentifies the information needed by a program group in the Tank Waste Remediation System (TWRS) concerned with safety issues, regulatory requirements, tank waste processing, or the transport of tank waste. As of January 1995, the DQOs that have been completed and apply to tank B-103 are discussed in the following paragraphs.

2.1 SAFETY ISSUE DATA QUALITY OBJECTIVES

Both Watch List and non Watch List tanks will be sampled and evaluated to classify waste tanks in one of three categories (SAFE, CONDITIONALLY SAFE, or UNSAFE). The Watch List and other safety issue DQO's identify the guidelines to determine to which classification a tank belongs based on analyses that indicate if certain measurements are within established parameters. If a specified parameter is exceeded, further analyses may be required to classify a tank. A tank can be removed from a Watch List if it is classified as SAFE. As indicated from the historical information for tank B-103, the *Data Quality Objective to Support Resolution of the Organic Fuel Rich Tank Safety Issue* (Babad et al. 1994) DQO is applicable. The sampling and analytical requirements for this DQO includes two widely spaced cores and primary analyses for organic carbon, moisture, tank temperature, and presence of a free organic liquid.

2.2 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. This DQO requires that a vertical profile of the tank waste be obtained from at least two widely spaced risers. This vertical profile may be obtained 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 concentration. The safety screening analyses shall be applied to all core samples, DST Resource Conservation and

Recovery Act (RCRA) samples, and auger samples, except those taken exclusively to assess the flammable gas crust burn issue.

2.3 FUGITIVE VAPOR EMISSION DATA QUALITY OBJECTIVES

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 two main issues related to this program are 1) an insufficient understanding of reported exposures of tank farm personnel to unacceptable levels of noxious vapors and 2) the risks to worker health and safety can not be determined until the vapors in the waste tanks are well characterized. Tank B-103 is one of the 36 tanks on the "Suspect Tank List" (Osborne and Huckaby 1994b). This list is composed of 20 Ferrocyanide Watch List tanks, 9 Organic Watch List tanks (one of which is also on the Ferrocyanide Watch List), and 8 tanks with a history of vapor incidents associated with them. Westinghouse Hanford Company (WHC) standard safety practices dictate that any flammable components in the headspace of any Watch List tank must be determined and quantified before intrusive work can be conducted on these tanks. The DQO applicable to head space vapor sampling is *Data Quality Objectives for Generic In-Tank Health and Safety Vapor Issue Resolution* (Osborne et al. 1994a).

A nitrogen gas purge will be used to clear and cool the drill bit during rotary core sampling. This purge gas exhausts into the waste tank head space and over the operating period could potentially pressurize the head space resulting in an uncontrolled release of pollutants. A portable modular unit has been developed to exhaust the tank head space during rotary core sampling. This modular unit will remove airborne particulates through high efficiency particulate (HEPA) filters, but is not designed or equipped to treat or remove toxic vapors. It is equipped with instruments to monitor and alarm for total organic carbon (TOC) and ammonia vapors. The tank head space must be characterized to confirm that the modular unit can be safely started and to establish acceptable TOC and ammonia levels for safe operation. The applicable DQO for rotary core sampling is *Rotary Core Vapor Sampling Data Quality Objective* (Price 1994).

3.0 TANK HISTORICAL INFORMATION

This section summarizes the available information for tank B-103. Included are the age of the tank, process history, and the expected contents of the tank based on historical information. The fill history information is available in *A History of the 200 Area Tank Farms* (Anderson 1990) and *Historical Tank Content Estimate for the Northeast Quadrant of the Hanford 200 West Areas* (Brevick et al. 1994).

3.1 JANUARY 1995 TANK STATUS

The organic safety issue arises due to wastes added to the tank containing quantities of complexants and solvents used in fuel reprocessing and metal recovery operations. The waste tank also contains a presumed stoichiometric excess of sodium nitrite or nitrate oxidizers to exothermally oxidize organic compounds.

Tank B-103 was placed on the Organic Watch List in January 1991 due to review of TRAC (Jungfleisch 1984) data that predicts a TOC content of 3.3 dry weight percent (Fisher 1990). The tank was classified as an assumed leaker of approximately 30,280 liters (8,000 gallons) in 1978 and declared inactive. Tank B-103 is passively ventilated with interim stabilization and intrusion prevention measures completed in 1985. From September 1974 to the present, the median temperature has been 17°C (62°F) with a minimum of 4°C (40°F) and a maximum of 28°C (83°F). The surface level is monitored through riser 1 with a Food Instrument Corporation gauge. Approximately 223,340 liters (59,000 gallons) of non complexed waste about 30.5 centimeters (1 foot) in depth are contained in the tank. The latest photograph shows a black sludge surface with little pools of supernate.

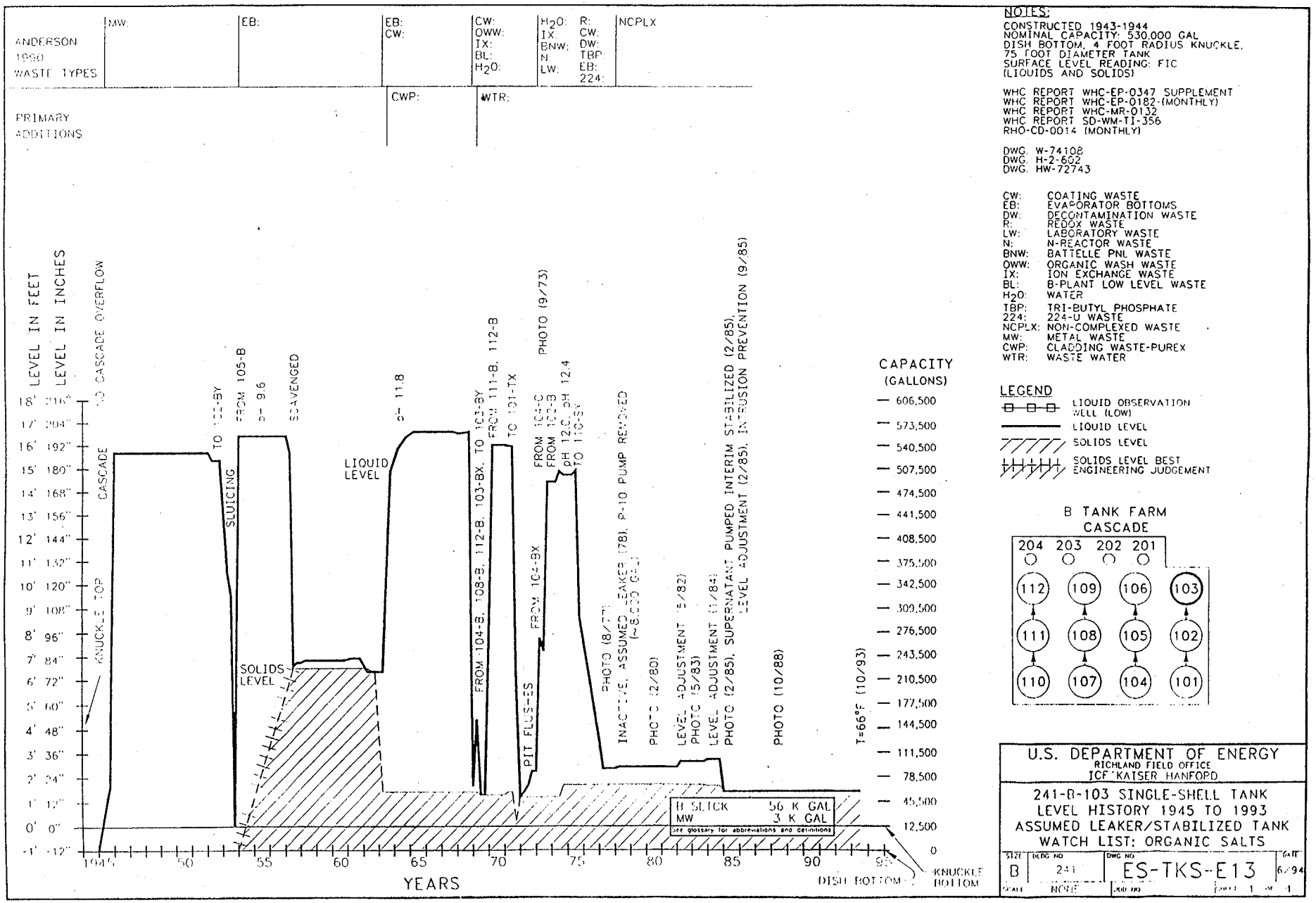
3.2 TANK CONFIGURATION

Single-shell tank B-103 was constructed between 1943 and 1944 as a first generation type II tank and is located in the 200 East Area. Tank B-103 is 23 meters (75 feet) in diameter and has a capacity of 2,010,000 liters (530,000 gallons). The tank is third in a cascade flow series consisting of tanks 241-B-101, 241-B-102, and B-103 (B-103 is not equipped to cascade to another tank). A cascade system consists of tanks connected in series by pipes. When the primary tank in the system became full, the waste would then flow to the secondary tanks in the system.

3.3 TANK HISTORY

Tank B-103 began to receive waste between December 1945 and March 1946. The 241-B tank farm received waste from B Plant, first and second cycle waste, and evaporator bottoms waste. Numerous waste transfers to and from B-103, many of which are unaccountable (Anderson 1980 and Agnew 1994), involved other tanks in the 241-B, -BX, -BY, -C, -SX, and -TX tank farms. The waste was sluiced from B-103 in 1953 as part of Uranium recovery operations and sent to the 244-BXR process vault. Tank B-103 was scavenged in 1957 with ferrocyanide to reclaim Cesium-137. Figure 1 summarizes the influx and effluent history of tank B-103.

Figure 1: Fill History of Tank 241-B-103



NOTES:
CONSTRUCTED 1943-1944
NOMINAL CAPACITY: 530,000 GAL
DISH BOTTOM, 4 FOOT RADIUS KNUCKLE,
75 FOOT DIAMETER TANK
SURFACE LEVEL READING: FIC
(LIQUIDS AND SOLIDS)

WHC REPORT WHC-EP-0347 SUPPLEMENT
WHC REPORT WHC-EP-0182-(MONTHLY)
WHC REPORT WHC-MR-0132
WHC REPORT SD-WM-TI-356
RHO-CD-0014 (MONTHLY)

DWG. W-74108
DWG. H-2-602
DWG. HW-72743

CW: COATING WASTE
EB: EVAPORATOR BOTTOMS
DW: DECONTAMINATION WASTE
R: REDOX WASTE
LW: LABORATORY WASTE
N: N-REACTOR WASTE
BNW: BATTELLE PNL WASTE
OWW: ORGANIC WASH WASTE
IX: ION EXCHANGE WASTE
BL: B-PLANT LOW LEVEL WASTE
H_2O: WATER
TBP: TRI-BUTYL PHOSPHATE
224: 224-U WASTE
NCPLX: NON-COMPLEXED WASTE
MW: METAL WASTE
CWP: CLADDING WASTE-PUREX
WTR: WASTE WATER

LEGEND
LIQUID OBSERVATION WELL (LOW)
LIQUID LEVEL
SOLIDS LEVEL
SOLIDS LEVEL BEST ENGINEERING JUDGEMENT

B TANK FARM CASCADE

U.S. DEPARTMENT OF ENERGY
RICHLAND FIELD OFFICE
ICF KAISER HANFORD

241-B-103 SINGLE-SHELL TANK
LEVEL HISTORY 1945 TO 1993
ASSUMED LEAKER/STABILIZED TANK
WATCH LIST: ORGANIC SALTS

SIZE	BLDG NO	DWG NO	DATE
B	241	ES-TKS-E13	6/94
SCALE: NONE	JOB NO	SHEET 1 OF 1	

3.4 EXPECTED TANK CONTENTS

The contents of B-103 are expected to consist of sludge and salt cake with no liquid capable of being pumped remaining in the tank. The current waste volume is 223,000 liters (59,000 gallons) of which 11,000 liters (3,000 gallons) are metal waste sludge and 212,000 liters (56,000 gallons) are salt cake (Brevick 1994). This conflicts with the Hanlon document that states there is 223,000 liters (59,000 gallons) of sludge and no salt cake. The TOC content from the *Historical Tank Characterization Estimates* (HTCE, Brevick 1994) is inconsistent with the TRAC prediction of 3.3 dry weight percent. Development and refinement of the Tank Layering Model (TLM) which is the basis of the HTCE is continuing. At this point, the uncertainty of the TLM estimates is unknown. Likewise, the TRAC model has in some instances been in error by more than ten times the predicted amount. Table 2 summarizes the expected tank contents.

Table 1: Tank B-103 Solids Composite Inventory Estimate[1]

Physical Property	Value	
Total Solid Waste	334,000 kg (59,000 gallons)	
Heat Load	32.8 W (112 BTU/hour)	
Bulk Density	1.49 g/ml	
Void Fraction	0.57	
Water	33.09 Weight Percent	
Total Organic Carbon	0 Wet Weight Percent	
Analytes	**µg/g**	**µg/ml**
Na^{+}	147,000	219,000
Al^{+3}	1,060	1,580
OH^{-}	4,260	6,350
NO_3^{-}	126,000	188,000
NO_2^{-}	1,490	2,220
CO_3^{-2}	28,000	41,700
PO_4^{-3}	75,500	112,000
SO_4^{-2}	52,100	77,600
F^{-}	808	1,200
Cl^{-}	274	410
U	10,500	15,600
Radionuclides	**µCi/g**	**µCi/ml**
Pu	0.00715	0.0107
Cs	5.08	7.60
Sr	11.04	16.45

[1](Brevick 1994)

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 B-103 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 January 1995 and auger sampling in February 1995 are scheduled for tank B-103. No other sampling is scheduled through fiscal year 1997 (Stanton 1994). 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). Auger sampling shall be conducted following *Data Quality Objective to Support Resolution of the Organic Fuel Rich Tank Safety Issue* (Babad et al. 1994) and *Tank Safety Screening Data Quality Objective* (Redus and Babad 1994). These two sampling and analysis events, if successful, will also satisfy the January 1995 applicable DQO requirements. These requirements are summarized in Table 2. A more complete list of analytical requirements are given, as an appended revision, in the appropriate sampling and analysis plan.

Table 2: 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
Auger	▪ Organic Fuel Rich Tank Safety Issue Resolution ▪ Tank Safety Screening	2 samples from risers separated radially to the maximum extent possible	Energetics,TOC, Moisture, Temperature, Total Alpha, Gas Composition, Major Anions & Cations, Radionuclides, Primary Organics & Organic Products, Physical Properties

5.0 REFERENCES

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APPENDIX A

TANK B-103

VAPOR SAMPLING AND ANALYSIS PLAN

FOR FISCAL YEAR 1995

TABLE OF CONTENTS FOR APPENDIX A

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B-103	Tank 241-B-103
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
HEPA	High-Efficiency Particulates Air Filters
IC	Ion Chromatography
IDLH	Immediately Dangerous to Life and Health
ISS	In Situ Sampling
LFL	Lower Flammability Limit
OGIST	Oregon Graduate Institute of Science and Technology
ORNL	Oak Ridge National Laboratory
PNL	Pacific Northwest Laboratory
ppbv	parts per billion by volume
ppmv	parts per million by volume
QAPP	Quality Assurance Project Plan
RCRA	Resource Conservation and Recovery Act of 1976
SAP	Sampling and Analysis Plan
SML	Sampling and Mobile Laboratories
SUMMA®	registered trademark for passivated stainless steel canister
TCP	Tank Characterization Plan
TNMHC	Total Non-Methane Hydrocarbons
TRP	Toxicology Review Panel
TO-12	EPA task order protocol 12
TOC	Total Organic Carbon
TST	Triple Sorbent Trap
TWAP	Tank Waste Analysis Plan
TWRS	Tank Waste Remediation System
VSS	Vapor Sampling System
WHC	Westinghouse Hanford Company

A1.0 INTRODUCTION

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-B-103 (B-103) 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).

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 B-103. The requirements for the vapor sampling of B-103 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 laboratory performing the contracted analytical work shall supply prepared and labeled sample containers (SUMMA® canisters and selective sorbent sampling media) to Field Analytical Services (FAS) at least 48 hours in advance of the scheduled sampling date. Each sample media container shall be certified as clean and prepared according to procedures called out in Table A-1. FAS shall provide sample identification numbers to the laboratories as requested following the quality assurance format given in Section A3.1.

A2.2 FLAMMABLE LEVEL 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 contained in the sampling event work package (ES-94-1294) 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, B-103 head space vapor 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 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 B-103.

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

Table A-1: General Sampling Information

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

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

Table A-2: List of Samples and Activities

SAMPLE CODE	SAMPLE/ACTIVITY DESCRIPTION	SAMPLER POSITION DURING COLLECTION	GAS FLOW RATE	SAMPLE DURATION
--	Adjust VSS temperature setpoint to 50°C	N/A	N/A	N/A
--	Purge VSS with ambient air[1]	N/A	5,450 mL/min	30 min
01	Collect ambient air sample SUMMA #1	Upwind of B-103		1 min
--	Perform Cleanliness Check			
02	Collect ambient air sample SUMMA #2	Port 15		1 min
--	Leak test	N/A		
--	Purge VSS with tank air	N/A	5,450 mL/min	30 min
--	Measure tank pressure	N/A	N/A	N/A
03	Collect Tritium Trap	Sorbent line 8	200 mL/min	5 min
--	Collect GC sample and initiate GC run[2]			
04	Collect SUMMA #3	Port 11		1 min
05	Collect SUMMA #4	Port 13		1 min
06	Collect SUMMA #5	Port 15		1 min
07	Collect SUMMA #6	Port 12		1 min
08	Collect SUMMA #7	Port 14		1 min
09	Collect SUMMA #8	Port 16		1 min
10	Collect Triple Sorbent Trap (TST) sample #1	Sorbent line 9	50 mL/min	4 min
11	Collect TST sample #2	Sorbent line 10	50 mL/min	4 min
12	Collect TST sample #3	Sorbent line 8	50 mL/min	4 min
13	Open, close, & store TST Field Blank #1	In VSS truck	0 mL/min	
14	Collect TST sample #4	Sorbent line 10	50 mL/min	4 min
15	Collect TST sample #5	Sorbent line 9	200 mL/min	5 min
16	Collect TST sample #6	Sorbent line 10	200 mL/min	5 min
17	Collect TST sample #7	Sorbent line 8	200 mL/min	5 min
18	Collect TST sample #8	Sorbent line 10	200 mL/min	5 min
19	Collect TST sample #9	Sorbent line 9	200 mL/min	20 min
20	Open, close, & store TST Field Blank #2	In VSS truck	0 mL/min	
21	Collect TST sample #10	Sorbent line 10	200 mL/min	20 min
22	Collect TST sample #11	Sorbent line 8	200 mL/min	20 min
23	Collect TST sample #12	Sorbent line 10	200 mL/min	20 min
24,25	Store TST Trip Blanks #1 & #2	None	None	None
26	Collect NH3/NOx/H2O Sorbent Trap #1	Sorbent line 9	200 mL/min	15 min
27	Collect NH3/NOx/H2O Sorbent Trap #2	Sorbent line 10	200 mL/min	15 min
28	Collect NH3/NOx/H2O Sorbent Trap #3	Sorbent line 8	200 mL/min	15 min
29	Collect NH3/NOx/H2O Sorbent Trap #4	Sorbent line 10	200 mL/min	15 min
30	Collect NH3/NOx/H2O Sorbent Trap #5	Sorbent line 9	200 mL/min	15 min
31	Collect NH3/NOx/H2O Sorbent Trap #6	Sorbent line 10	200 mL/min	15 min
32,33,34	Store NH3/NOx/H2O Trap Trip Blanks #1, #2, & #3	None	None	None
35	Remove upstream HEPA Filter from HEPA transfer box	Upstream of box	Continuous	
36	Remove downstream HEPA Filter from HEPA transfer box	Downstream of box	Continuous	
37	Remove upstream HEPA Filter from VSS	Upstream of VSS	Continuous	
38	Remove downstream HEPA Filter from VSS	Downstream of VSS	Continuous	

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

A2.4 RADIATION SCREENING AND SAMPLE TRANSPORT

All vapor samples shall be stored under Chain-of-Custody by Field Analytical Services (FAS) while performing a radiological survey of certain items used during sampling. Surveys are conducted to assure compliance with Department of Transportation (DOT) shipping regulations and offsite laboratory acceptance criteria. Items surveyed include four HEPA filters and one tritium trap and shall be analyzed following procedures specified by Internal Memo 74310-94-32 to J. G. Kristofzski, November 30 (Bratzel 1994). These procedures are reproduced in Table A-4.

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

Table A-3: Limits For Acceptable Radionuclide Activity Levels

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

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

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

A2.5 TANK SPECIFIC ANALYTICAL PROCEDURES

A 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 B-103 head space vapor and contained within the SUMMA® canisters shall be analyzed for total non methane hydrocarbons (TNMHC) following modified EPA procedure TO-14 and the permanent gases CO_2, CO, CH_4, H_2, and N_2O using gas chromatography. The sorbent traps contain analyte-specific sorbent media and shall be analyzed for these specific analytes. The triple sorbent traps contain sorbent media designed to allow a broad range of organic species to be retained. Table A-4 identifies the appropriate laboratory procedures used in each analysis.

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, shall be identified and justification for non performance noted in the appropriate data report. If there are insufficient samples to perform all requested analyses, a partial listing of the analyses in Table A-4 that could be performed with available samples will be developed by Tank Vapor Issue Resolution Program personnel. The laboratory shall proceed with these analyses.

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

- •Step 1 Labs: Prepare sample and blank containers at contract laboratories. Label containers using sample identification numbers and sampling data provided by Field Analytical Services.
- •Step 2 Labs: Ship containers to Field Analytical Services at least 48 hours in advance of scheduled sampling event. Receipt and control of containers shall be guided by WHC procedure LO-080-450 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 by offsite laboratory requirements and WHC-CM-2-14, ship samples and blanks following DOT requirements. If not acceptable to ship, maintain samples in storage and contact J. W. Osborne of Vapor Issue Resolution Program for further direction.
- •Step 7 Labs: Perform laboratory analyses.

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

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

  C. Triple Sorbent Traps (ORNL): Perform organic vapor analysis.
- •Step 8 Labs and SML: Following the Section A6.0 reporting requirements, deliver a Format VI Report to the Vapor Issue Resolution Safety Program.

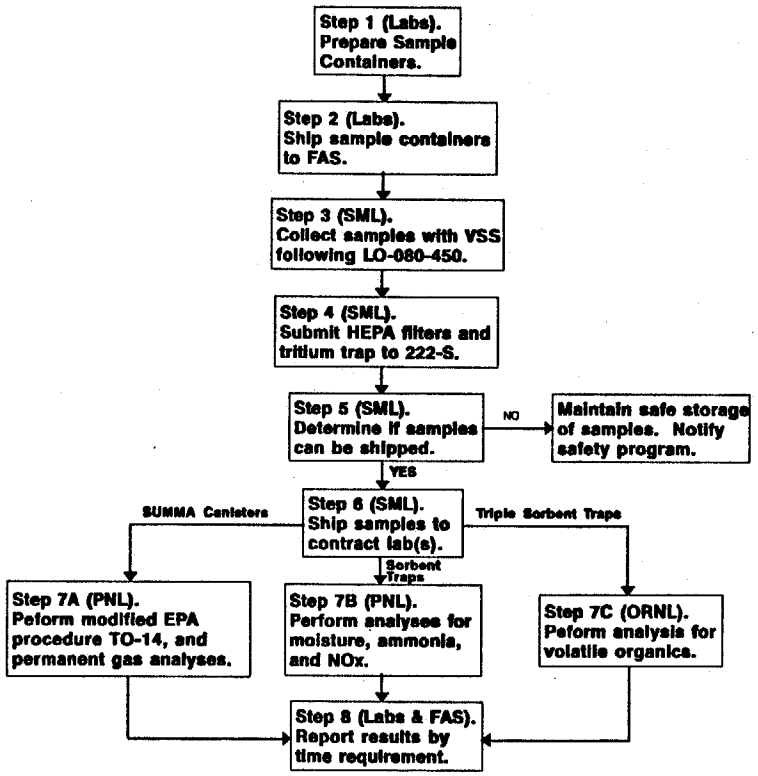

Table A-4. B-103 Sample Chemical, Physical, and Radiological Analytical Requirements

PROJECT	B-103 VAPOR
Plan Number	WHC-SD-WM-TP-250
Tank	B-103
Program Contact	J. W. Osborne
TWRS Contact	R. D. Schreiber B. C. Carpenter C. S. Homi
Lab Project Coordinator	S. C. Goheen (PNL) R. A. Jenkins (ORNL)

COMMENTS

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

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

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

PRIMARY ANALYSES						QUALITY CONTROL[c]			CRITERIA				
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	REPORT FORMAT
GCM	Flammability	CGIMX251 CGITMX410	N/A	N/A	N/A	1	N/A	N/A	>20% LFL	<10% LFL	N/A	±10%	I
EPA TO-14 GC/MS	Organic* Speciation	PNL-TVP-01 PNL-TVP-02 PNL-TVP-03	PNL	Direct	SUMMA®	3	none	2	≥ 4000 ppmv n-Butanol 50% IDLH for all others*	not available	±25%	70-130%	I, VI
GC/TCD	CO_2 CO CH_4 H_2 N_2O	PNL-TVP-05 PNL-TVP-02	PNL	Direct	SUMMA®	3	none	2	N/A ≥ 20% LFL ≥ 20% LFL ≥ 20% LFL not available	not available	±25% ±25% ±25% ±25% ±25%	70-130%	VI I, VI I, VI I, VI I, VI
IC	NO NO_2	PNL-TVP-09 PNL-ALO-212	PNL	H_2O Extraction	Sorbent Trap	6	none	3	≥ 50 ppmv ≥ 25 ppmv	≥ 2 ppmv ≥ 0.1 ppmv	±25% ±25%	70-130%	I, VI I, VI
Gravimetric	H_2O	PNL-TVP-09	PNL	Direct	Sorbent Trap	6	none	3	N/A	≥ 3 mg/L	±25%	70-130%	VI
Selective Electrode	NH_3	PNL-ALO-226 PNL-TVP-09	PNL	H_2O Extraction	Sorbent Trap	6	none	3	≥ 250 ppmv	≥ 2 ppmv	±25%	70-130%	I, VI
GC/MS	Organics**	AC-MM-1-003153 CASD-OP-300-WP03 CASD-OP-300-WP04 CASD-OP-300-WP05 CASD-OP-300-WP06	ORNL	Thermal Desorption	Triple Sorbent Trap	12	all	4[f]	≥ 4000 ppmv n-Butanol 50% IDLH for all others**	not available	±25%	70-130%	I, VI
Total α Total β Total γ	Radon Daughters	LA-508-110 LA-508-111 LA-508-162	WHC	Direct	HEPA Filter	4	N/A	N/A	≥60 pCi/g α ≥200 pCi/g β ≥200 pCi/g γ	<60 pCi/g α <200 pCi/g β <200 pCi/g γ	±25% ±25% ±25%	70-130%	I, II
Liq. Scin.	Tritium[g]	LA-548-111	WHC	Direct	Tritium Trap	1	N/A	N/A	N/A	not available	N/A	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 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 QA Plan shall be used for quality assurance guidance.
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 a Quality Assurance Plan (Barnes 1995) written to comply with 5700.6C. ESH&QA will qualify laboratories for continued use by the TWRS Characterization program after receipt of the Laboratory quality assurance plans, followed by an audit and corrective action phase.

A3.1 SAMPLING OPERATIONS

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

SXXXX-WYY-LLL, where:

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

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

Applicable operating procedures for the B-103 vapor space sampling activities are contained in work package ES-94-1294. Vapor samples, trip blanks, and field blanks are to be collected in accordance with Tables A-1 and A-2 and laboratory operating procedure LO-080-450 "Collection of SUMMA® Canisters & Sorbent Tube Samples Using the Vapor Sampling System (VSS)" and shipped to the analytical laboratories in accordance with Hazardous Material Packaging and Shipping, WHC-CM-2-14.

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

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

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

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

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

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

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 B-103 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	B-103 Tank Characterization Plan Engineers
J. W. Osborne	TWRS Tank Vapor Issue Resolution Program	Vapor Issue Resolution Program Manager
H. Babad	TWRS Characterization Program	Tank Safety Screening Scientist
R. S. Viswanath	Field Analytical Services	Special Analytical Studies Vapor Sampling Technical Support
R. D. Mahon	Field Analytical Services	Sampling and Mobile Laboratories Vapor Sampling Program Lead
E. H. Neilsen	Waste Tank Safety Engineering	Vapor Sampling Cognizant Engineer
D. R. Carls	Industrial Hygiene and Safety Program	Industrial Hygiene Point of Contact if Notification Limit is Exceeded (FAX 372-3522)
East Area Shift Operations Manager	Tank Farm Operations	East Tank Farm Point of Contact if Notification Limit is Exceeded (373-2689)

A5.0 EXCEPTIONS, CLARIFICATIONS, AND ASSUMPTIONS

Toxicology Review Panel

The Toxicology Review Panel (TRP) is a group of toxicologists, industrial hygenists, 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 FAS cognizant scientist or assisting scientific technician, lead sampler, or laboratory scientist or technician who signs the *received by* block on the chain-of-custody form. Transfer of custodianship occurs when the custodian signs the *relinquished by* block on the chain-of-custody form and releases the sample(s) to the new custodian signator.

Physical Control

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

A6.0 DELIVERABLES

The Pacific Northwest Laboratory, Oak Ridge National Laboratory, and Sampling and Mobile Laboratories VSS sampling and analyses of tank B-103 vapors shall be reported as Format VI (Section A6.3). In addition, the analytical laboratories shall receive Format II reports from Sampling and Mobile Laboratories as described in Section A6.2. Any analyte exceeding the notification limit prescribed in Table A-4 shall be reported

as Format I (Section A6.1). Other organic species detected at levels deemed sufficient by the laboratory scientist to be of potential toxicological concern shall also be reported following Format I. Additional information regarding reporting formats 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, the Field Analytical Services representative, the Characterization Program Office, Analytical Services, and the Tank Characterization Resource Center.

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

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

6) sample radiation screening results;
7) sample storage and shipment details; and
8) copies of all chain-of-custody forms.

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

1) A summary of analytical results;
2) a description of sample device preparation (and manufacture if appropriate), citing procedures and logbooks used;
3) references providing traceability of sample device cleanliness;
4) a brief description of analytical methods, with procedures cited;
5) a brief explanation of how analytical systems control was demonstratably maintained;
6) a brief description of sample storage and shipment conditions, citing procedures and logbooks used;
7) a listing of analytes of quantitation (target analytes), with analytical method detection limit, range for which instrumentation is calibrated, number of calibration points used, and statistical data on linearity of calibration;
8) quantitative analytical results, expressed as dimensionless (ppmv or ppbv) concentration, and mass concentration ($\mu g/m^3$, mg/L, etc., calculated at 0 °C and 1 atm) of target analytes (identified by name and Chemical Abstract Service number) in each tank air sample;
9) tentative identification and semi-quantitative analytical results, expressed in both mass and dimensionless concentrations (if possible) of non-target organic analytes (identified by name and Chemical Abstract Service number) in each organic vapor sample;
10) 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 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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United States Code of Federal Regulations, 10 CFR, Part 830, *Nuclear Safety Management*; Section 120, *Quality Assurance Requirements*.

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