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1. ECN No 617845

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2. ECN Category (mark one) Supplemental ☐ Direct Revision ☒ Change ECN ☐ Temporary ☐ Standby ☐ Supersedure ☐ Cancel/Void ☐	3. Originator's Name, Organization, MSIN, and Telephone No. R. D. SCHREIBER, 71520, R2-12, 373-5589		3a. USQ Required? ☐ Yes ☒ No	4. Date 02-24-95
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13b. Justification Details Appendix B of this document provides sampling and analytical requirements for the auger sampling event pertaining to tank 241-BY-103. Earlier revisions of this document were released prior to the recent change in format, so a complete revision was performed to align the format of this document with other Tank Characterization Plans.				
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7. Abstract This document is a plan which serves as the contractual agreement between the Characterization Program, Sampling Operations, and WHC 222-S Laboratory. The scope of this plan is to provide guidance for the sampling and analysis of samples for tank 241-BY-103.		
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Tank 241-BY-103 Tank Characterization Plan

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Office of Environmental Restoration
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LIST OF ABBREVIATIONS

BY-103	Tank 241-BY-103	MW	Metal Waste
CW	Coating Waste	NCPLX	Noncomplexed Waste
DNFSB	Defense Nuclear Facilities	P	Purex Waste
	Safety Board	TBP	Tributyl Phosphate
DOE	Department of Energy	TBP	Tributyl Phosphate
DQO	Data Quality Objective	TCP	Tank Characterization Plan
DST	Double Shell Tank	WHC	Westinghouse Hanford Company

1.0 INTRODUCTION

The Defense Nuclear Facilities Safety Board has advised the 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 the analytical and sampling needs for the resolution of safety issues. As a result, a revision in the Federal Facility Agreement and Consent Order (Tri-Party Agreement) milestone M-44 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" (Ecology et al. 1994). This document satisfies that requirement for the tank 241-BY-103 (BY-103) sampling activities.

2.0 DATA QUALITY OBJECTIVES APPLICABLE TO TANK 241-BY-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 identifies the information needed by a program group concerned with safety issues, regulatory requirements, tank waste processing, or the transport of tank waste. As of January 1995, tank BY-103 is classified as a Ferrocyanide Watch List tank. The DQOs applicable to this tank are discussed below.

2.1 SAFETY SCREENING DATA QUALITY OBJECTIVES

The *Tank Safety Screening Data Quality Objective* (Babad and Redus 1994) describes the sampling and analytical requirements that are used to screen waste tanks for unidentified safety issues. Both Watch List and non Watch List tanks will be sampled and evaluated to classify waste tanks in one of three categories (SAFE, CONDITIONALLY SAFE, or UNSAFE). The safety screening DQO identifies the guidelines to determine to which classification a tank belongs based on analyses that indicate if certain measurements are within established parameters. The primary analytical requirements for the safety screening of a tank are energetics, total alpha activity, moisture, and flammable gas concentration. 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.

The safety screening 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 safety screening analyses shall be applied to all core samples, Double Shell Tank (DST) Resource Conservation and Recovery Act (RCRA) samples, and auger samples, except those taken exclusively to assess the flammable gas crust burn issue.

2.2 FERROCYANIDE DATA QUALITY OBJECTIVES

Data Requirements for the Ferrocyanide Safety Issue Development through the Data Quality Objectives Process (Meacham et al. 1994) describes the sampling and

analytical requirements for tanks on the Ferrocyanide Watch List, including tank BY-103. It concluded that two core samples taken from risers separated by maximum distances would provide characterization data of sufficient quality to enable decision makers to confidently resolve the safety issues associated with these tanks. The most important output from the characterization of ferrocyanide tanks through the DQO planning process is the safety classification of the tanks. These classifications will dictate the future operation of those tanks. Two primary parameters, sodium nickel ferrocyanide concentration and moisture content, determine whether a tank is safe, conditionally safe, or unsafe.

2.3 WASTE COMPATIBILITY DATA QUALITY OBJECTIVES

The *Data Quality Objectives for the Waste Compatibility Program* (Carothers 1994) identifies four safety-related decisions 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 for the Waste Compatibility Program 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 waste 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 exists to judge compatibility with safety and operations decision rules.

2.4 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. 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. 1994).

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 particles 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 BY-103 HISTORICAL INFORMATION

3.1 AGE AND PROCESS HISTORY

Single Shell Tank BY-103 is one of 16 single-shell tanks in the 200 East Area BY Farm and was constructed between 1948 and 1949. The tank is 23 meters (75 ft.) in diameter with a concave-shaped base and has a 2,870 kL (758 Kgal) tank capacity. Tank BY-103 began to receive waste in October 1950 from the BiPO₄ process at B Plant and T Plant, as the third tank in a three tank cascade series with tanks 241-BY-101 and 241-BY-102. In March 1951, the cascade was full and the tank continued to store this waste until 1954. In 1954 the tank was emptied in three transfers to tanks C-104, C-105, and BY-109. In 1955, the tank received tributyl phosphate (TBP) waste in a transfer from tank BY-110. Process records indicate that ferrocyanide was introduced into tank BY-103 in 1956 due to the implementation of an in-tank scavenging program. In 1957 and 1958, Plutonium-Uranium Extraction (PUREX) Plant high activity neutralized acid waste was transferred from tank C-106. In mid-1965, the supernate was pumped to tank BY-101.

From 1965 to 1970, waste was transferred to tanks BY-101, BY-102, and BY-109. During this time cladding waste, evaporator bottoms, and organic wash waste were received from the following tanks: B-101, B-103, BX-102, BX-106, BY-102, BY-105, BY-106, BY-111, and C-102.

In 1971, the in-tank solidification process began and continued through 1973. In mid-1973, the tank was found to leak. Consequently, from 1973 to mid-1976, in eight separate transfers to tank BY-109 all the remaining supernate was removed from the tank.

In 1977, the tank was declared a stabilized leaker. The tank is currently an assumed leaker and is partially isolated. On April 3, 1990 the last recorded tank volume was 1,510 kL (400 kgal); 18,900 L (5,000 gal) was sludge and 1,500 kL (395 kgal) was saltcake (Sathyanarayana 1993).

Table 1 and Figure 1 summarize the fill history from when tank BY-103 was first placed on active status to the present time.

3.2 EXPECTED TANK CONTENTS

Tank BY-103 is expected to have two layers of waste. The bottom layer consists of a sludge composed primarily of uranium recovery process waste (TBP). TBP waste has a high concentration of sodium, nitrate, aluminum, and a very low concentration of plutonium. Ferrocyanide is also expected to be present in the sludge layer. The upper layer is expected to be saltcake formed from the precipitation of the slurry product (evaporator bottoms) from the In-Tank Solidification Process. Evaporator bottom waste is mainly sodium nitrate (73.8%) and water (12.8%) (Hill 1991).

Analyses of liquid samples acquired from tank BY-103 were conducted in the first quarter of 1991. A summary of the analytical data from those analyses is reported in Table 2 (Edrington 1991).

A type 2 vapor insitu sampling (ISS) event collected vapor space samples from tank BY-103 on May 5, 1994. Three SUMMA® canister samples were collected from the tank headspace and shipped to the Oregon Graduate Institute of Science and

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Technology for analysis following Letter of Instruction guidelines (Osborne 1994b). Modified EPA TO-12 and TO-14 methods were applied to analyze the organic vapor. Analyses for nitrous oxide, hydrogen, and carbon monoxide were also performed. A data letter report, submitted to the TWRS Tank Vapor Issue Resolution Program, was produced as screening data and is not qualified data. These results and 9 of the 42 EPA TO-14 compounds detected are given in Table 3.

Results of an ambient air SUMMA® canister sample (field blank) collected upwind of BY-103 for volatile organics following procedure EPA TO-12 were not reported. Nitrous oxide was found at 0.8 ppmv. Hydrogen and carbon monoxide were not detected.

The quantification of the total non-methane hydrocarbons by the EPA TO-12 procedure indicates a low level of organic vapors in the tank BY-103 vapor space. Other vapors of concern which may be present in the vapor space are ammonia, methane, nitric oxide, and nitrogen dioxide.

Table 1: Fill History of Tank BY-103 (Anderson 1992; Hanlon 1994; Jungfleisch 1984a)

Qtr:Year	Transfers In	Transfers Out
4:1950 to 1:1954	Tank on active status. Tank was filled with 7,100 kL (1,880 kgal) metal waste from BiPO_4 . 90% of fission product, all of Uranium, 1% of Plutonium.	Transfer to 104-C, 105-C, 109-BY: 3,790 kL (1,000 kgal), with an unknown loss of 303 kL (80 kgal).
2:1954 to 4:1954		Tank empty ¹ .
1:1955 to 2:1965	Tank was filled with 5,640 kL (1,490 kgal) of Tri-Butyl Phosphate waste from solvent based Uranium Recovery Operation. 79.5 kL (21 kgal) solids.	Scavenged: 2,680 kL (707 kgal) Transfer to BY-101: 541 kL (143 kgal) Unknown : 163 kL (43 kgal)
3:1965 to 4:1970	BY-103 contained Cladding Waste mixed with Organic Wash Waste and Evaporator Bottoms, There were several transfers into the tank from PUREX, and the B,BX,BY,and C tanks.	Tank became part of the In-Tank Solidification Program (ITS) as a decant tank. There were several transfers of supernate out to other BY tanks.
1:1971 to 1:1973	In-Tank Solidification program began in tank BY-103. Tank was found to be leaking.	Several transfers of remaining supernate to tank BY-109.
1:1977	Leaker Stabilized	
Present	Tank BY-103 currently contains: 1,510 kL (400 kgal) of NCPLX waste. This is divided as follows: 1,500 kL (395 kgal) saltcake, 18.9 kL (5 kgal) sludge, and 519 kL (137 kgal) of pumpable interstitial liquid.	

¹A discrepancy exists between gains and losses of 3,010 kL (1,080 kgal).

Table 2. Liquid Results for Tank BY-103

Physical Property			
Analyte	Result	Analyte	Result
Density	1.45 g/mL	pH	13.5
Percent Water	52 %	TOC	2.7 g/L of C
Radiochemistry			
Analyte	Result	Analyte	Result
Americium-241	< DL ¹	GEA Liquid (¹³⁷ Cs)	2.00E+05 µCi/L
Plutonium-239/240	< DL ¹	Total Alpha	0.68 µCi/L
Strontium-89/90	233 µCi/L	Total Beta	3.65E+05 µCi/L
Technetium-99	117 µCi/L		
Anion			
Analyte	Result	Analyte	Result
CO ₃ ²⁻	20,400 µg/mL	NO ₂ ⁻	91,400 µg/mL
OH ⁻	44,200 µg/mL	PO ₄ ³⁻	< 3,050 µg/mL
NO ₃ ⁻	2.76E+05 µg/mL	SO ₄ ²⁻	10,400 µg/mL
CN ⁻	9.7 µg/mL		

Cation			
Analyte	Result	Analyte	Result
Aluminum	55,700 µg/mL	Manganese	1.45 µg/mL
Arsenic	1.8 µg/mL	Mercury	< DL ¹
Barium	1.45 µg/mL	Molybdenum	76.9 µg/mL
Bismuth	21.8 µg/mL	Potassium	8,560 µg/mL
Cadmium	2.90 µg/mL	Selenium	7.60 µg/mL
Calcium	4.35 µg/mL	Silicon	79.8 µg/mL
Chromium	787 µg/mL	Sodium	2.89E+05 µg/mL
Iron	119 µg/mL	Strontium	1.45 µg/mL
Lead	219 µg/mL	Tin	69.6 µg/mL
Magnesium	4.35 µg/mL		

¹ Less than Detection Limit

Table 3. Vapor Space Characterization Data for Tank BY-103.

Compound	Sample Identification Numbers		
	106	107	108
TNMHC ¹ by procedure T0-12, $\mu\text{g}/\text{m}^3$	5,190 (± 14)	4,764 (± 60)	5,513 (± 5)
Nitrous Oxide, ppmv	49.2	49.2	49.2
Hydrogen, ppmv	21.8	21.2	21.2
Carbon Monoxide, ppmv	< 1	< 1	< 1
Non-Methane VOC by procedure EPA T0-14, ppbv			
Freon 12	1	1	1
Methylchloride	1	1	1
1,3-Butadiene	2	1	--
Freon 11	95	67	60
Benzene	2	1	1
Toluene	33	25	23
Perchloroethylene	1	1	1
m&p-Xylene	1	1	1
o-Xylene	1	1	--

¹Total Non-Methane Hydrocarbons

4.0 TANK BY-103 SCHEDULED SAMPLING EVENTS

Three sampling events of tank BY-103 are currently scheduled: a vapor sample in October 1994, an auger sample February 1995, and a rotary sample in April 1995. No other sampling events are scheduled through Fiscal Year 1997 (Stanton 1994). The vapor sample shall be conducted in accordance with the *Data Quality Objectives for Generic In-Tank Health and Safety Vapor Issue Resolution* (Osborne et al. 1994), and the *Rotary Core Vapor Sampling Data Quality Objective* (Price 1994). The auger sample shall be conducted in accordance with the *Data Requirements for the Ferrocyanide Safety Issue Development through the Data Quality Objectives Process* (Meacham et al. 1994), and the *Tank Safety Screening Data Quality Objective* (Babad and Redus 1994). The rotary sample shall be conducted in accordance with the *Data Requirements for the Ferrocyanide Safety Issue Development through the Data Quality Objectives Process* (Meacham et al. 1994), the *Tank Safety Screening Data Quality Objective* (Babad and Redus 1994), and the *Data Quality Objectives for the Waste Compatibility Program* (Carothers 1994). Sampling and analytical requirements from these DQOs are identified in Table 4. A more complete list of analytical requirements are given, as an appended revision, in the appropriate Sampling and Analysis Plan.

Table 4: Integrated DQO Requirements

Sampling Event	Applicable DQO	Sampling Requirements	Analytical Requirements
Vapor	<ul style="list-style-type: none"> Generic Health & Safety Vapor Issue Resolution 	<ul style="list-style-type: none"> 6 SUMMA® Canisters 12 Triple Sorbent Traps 6 Sorbent Trap Systems 	<ul style="list-style-type: none"> Flammability Toxicity
Auger	<ul style="list-style-type: none"> Tank Safety Screening Ferrocyanide 	Samples from 2 risers separated radially to the maximum extent possible	<ul style="list-style-type: none"> Energetics TOC Moisture Content Temperature Total Alpha Gas Composition Major Anions Major Cations Radionuclides Primary Organics Physical Properties
Rotary	<ul style="list-style-type: none"> Tank Safety Screening Ferrocyanide Compatibility 	Samples from 2 risers separated radially to the maximum extent possible	<ul style="list-style-type: none"> Energetics TOC Moisture Content Temperature Total Alpha Gas Composition Major Anions Major Cations Radionuclides Primary Organics Physical Properties

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APPENDIX A

SAMPLING AND ANALYSIS PLAN FOR VAPOR SAMPLING
IN FISCAL YEAR 1995

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LIST OF ACRONYMS

BY-103	Tank 241-BY-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
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
RCRA	Resource Conservation and Recovery Act
SACS	Surveillance Analysis Computer System
SML	Sampling and Mobile Laboratories
SUMMA®	registered trademark for passivated stainless steel canister
TCP	Tank Characterization Plan
TNMHC	Total Non-Methane Hydrocarbons
TRP	Toxicology Review Panel
TO-12	EPA task order protocol 12
TO-14	EPA task order protocol 14
TOC	total organic carbon
TWRS	Tank Waste Remediation System
VSS	vapor sampling system
WHC	Westinghouse Hanford Company

A1.0 SPECIFIC TANK VAPOR SPACE CHARACTERIZATION OBJECTIVES

The sampling and analytical needs associated with the 51 Hanford Site underground storage tanks classified on one or more of the four Watch Lists (ferrocyanide, organic, flammable gas, and high heat), and the safety screening of all tanks have been identified through the Data Quality Objective (DQO) process. Sampling of the vapor space will identify: 1) volatile compounds above the surface of the waste; and 2) the amount of gases generated by chemical or radiolytic reactions within the waste.

This Sampling and Analysis Plan will identify vapor space characterization objectives for tank BY-103 pertaining to sample collection, sample preparation and analysis, and laboratory analytical evaluation and reporting requirements in accordance with the *Tank Waste Remediation System Tank Waste Analysis Plan* (Haller 1994) and the applicable Data Quality Objectives identified in the following sections. In addition, an estimate of the current contents and status of the tank is given.

A1.1 Tank Status

Single-shell tank BY-103 is classified as a Ferrocyanide Watch List tank and was declared an assumed leaker in 1973.

Tank BY-103 is estimated to contain 34,000 liters (9,000 gal.) of sludge and 1,480,000 liters (391,000 gal.) of saltcake for a total of 400,000 gal. The saltcake is estimated to contain 520,000 liters (137,000 gal) of pumpable interstitial liquid. Its contents are categorized as non-complexed waste (NCPLX) (Hanlon 1994). The median temperature of the waste in tank BY-103 is 24.9°C; the maximum temperature is 58.3°C.

Recent readings (July, 1994) obtained from Tank Farm Surveillance and the Surveillance Analysis Computer System (SACS) database indicate a waste depth of 147.5 inches below riser 5, which is located on the east side approximately 1/4 of the radius from the center of the tank. From this, the total waste volume is calculated at 1,580,000 liters (418,000 gal.).

A1.2 Tank Monitoring Activities

Waste level measurements are taken through riser 4 using a manual tape. Internal tank temperature is automatically recorded from 15 thermocouples on a tree in riser 1. A liquid observation well is located in riser 7. Six active dry wells monitor radiation in the surrounding soil (Brevick et al. 1994).

A2.0 SCHEDULED SAMPLING EVENT

The following information provides the methodology and procedures to be used in the preparation, retrieval, transport, analysis, and reporting of results for vapor space samples retrieved from tank BY-103. The requirements for sample event A, contained within this TCP, are within the scope of work specified in the appropriate laboratory financial plans. Any decisions, observations, or deviations to this characterization plan made during sample receipt, preparation, and analysis shall be documented in the deliverable report.

A2.1 Preparation of Sample Media Containers

The laboratory performing the contracted analytical work shall supply prepared and labeled sample containers (SUMMA® canisters and/or selective sorbent sampling media) to Field Analytical Services (FAS) at least 48 hours in advance of the scheduled sampling date. Each sample media container is certified that preparation procedures were performed and it complies to cleanliness requirements. FAS shall provide sample identification numbers following the quality assurance/quality control format given in Section 5.1 and other label information to the laboratories as requested.

A2.2 Flammability of Vapor Space Gases

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

A2.3 Sample Collection

In fiscal year 1995, the tank BY-103 vapor space shall be sampled through a heated probe in riser 10B 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 3 specifies the sample type, the type of collection media to be used, and the number of samples requested. Table 4 provides a sequence of sampling activities and specifies the sample collection time and the flow rate through the sample collection tubes.

A cleanliness check shall be performed in accordance with procedure LO-080-450, Appendix C. Cleanliness of the VSS shall also be addressed by collecting ambient air SUMMA® samples prior to sampling the tanks using the following conditions: 1) with the VSS manifold and transfer lines fully heated; and 2) without the VSS, upwind of BY-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 ²	2
Triple Sorbent Traps	ORNL	AC-OP-300-0907 CASD-AM-300-WP01 ³	Tank Air	4
	ORNL	AC-OP-300-0907	Field Blank	1
	ORNL	AC-OP-300-0907	Trip Blank	1
Sorbent Trap System for NH ₃ , NO ₂ , NO, H ₂ O	PNL	PNL-TVP-09	Tank Air	6
	PNL	PNL-TVP-09	Trip Blank	3
Tritium Trap	WHC	LA-548-111	Tank Air	1
HEPA Filters	WHC	N/A	Tank Air	4

²One sample taken through the VSS, one sample taken upwind of the tank.

³Preparation procedure for samples spiked with surrogate(s).

A2.4 Radiation Screening and Sample Transport

All vapor samples shall be stored at the 222-S Laboratory Annex while performing a radiological survey of certain items used during sampling. Surveys are conducted to assure compliance with Department of Transportation (DOT) shipping regulations and offsite laboratory acceptance criteria. Items surveyed include four HEPA filters and one tritium trap and shall be analyzed following procedures specified in a Letter of Instruction (Bratzel 1994). These procedures are reproduced in Table 6.

The results from the radiation screening are submitted to and shall be evaluated by Sampling and Mobile Laboratories to ensure the samples meet the criteria specified in Table 5. Sampling and Mobile Laboratories shall provide a report to each analytical laboratory to identify the number of picocuries per sample (pCi/sample) for each sample that is submitted for analysis.

Table A-2. List of Samples and Activities.

SAMPLE CODE	SAMPLE/ACTIVITY DESCRIPTION	SAMPLER POSITION DURING COLLECTION	GAS FLOW RATE	SAMPLE DURATION
--	Purge VSS with ambient air ⁴	N/A	5,450 mL/min	30 min.
01	Collect ambient air sample SUMMA #1	Upwind of BY-103	N/A	1 min.
--	Collect GC sample and initiate GC run	N/A	N/A	N/A
02	Collect ambient air sample SUMMA #2	Port 15	N/A	1 min.
--	Leak test	N/A	N/A	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	N/A	N/A	N/A
04	Collect SUMMA #3	Port 11	N/A	1 min.
05	Collect SUMMA #4	Port 13	N/A	1 min.
06	Collect SUMMA #5	Port 15	N/A	1 min.
07	Collect SUMMA #6	Port 12	N/A	1 min.
08	Collect SUMMA #7	Port 14	N/A	1 min.
09	Collect SUMMA #8	Port 16	N/A	1 min.
10	Collect Triple Sorbent Trap (TST) sample #1	Sorbent line 9	200 mL/min	5 min.
11	Collect TST sample #2	Sorbent line 10	200 mL/min	5 min.
12	Open, close, & store TST Field Blank #1	In VSS truck	0 mL/min	N/A
13	Collect TST sample #3	Sorbent line 8	200 mL/min	5 min.
14	Collect TST sample #4	Sorbent line 10	200 mL/min	5 min.
15	Store TST Trip Blank #1	None	None	None
16	Collect NH ₃ /NO _x /H ₂ O Sorbent Trap #1	Sorbent line 9	200 mL/min	15 min.
17	Collect NH ₃ /NO _x /H ₂ O Sorbent Trap #2	Sorbent line 10	200 mL/min	15 min.
18	Collect NH ₃ /NO _x /H ₂ O Sorbent Trap #3	Sorbent line 8	200 mL/min	15 min.
19	Collect NH ₃ /NO _x /H ₂ O Sorbent Trap #4	Sorbent line 10	200 mL/min	15 min.
20	Collect NH ₃ /NO _x /H ₂ O Sorbent Trap #5	Sorbent line 9	200 mL/min	15 min.
21	Collect NH ₃ /NO _x /H ₂ O Sorbent Trap #6	Sorbent line 10	200 mL/min	15 min.
22, 23, 24	Store NH ₃ /NO _x /H ₂ O Trap Trip Blanks #1, #2, & #3	None	None	None
25	Remove upstream HEPA Filter from HEPA transfer box	Upstream of box	Continuous	
26	Remove downstream HEPA Filter from HEPA transfer box	Downstream of box	Continuous	
27	Remove upstream HEPA Filter from VSS	Upstream of VSS	Continuous	
28	Remove downstream HEPA Filter from VSS	Downstream of VSS	Continuous	

⁴Not required if ambient air purge incorporated in VSS setup.

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

Organization	Total α	Total β/γ	Tritium	Units
PNL Analytical Chemistry Laboratory	≤ 100	≤ 400	--	pCi/g
Oak Ridge National Laboratory	≤ 135	≤ 450	--	pCi/g
WHC-CM-2-14 ⁵	≤ 60	≤ 200	--	pCi/g

⁵Samples above DOT limits may be shipped as Limited Quantity of Radioactive Material in accordance with DOT approval.

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

A2.5 Tank-Specific Analytical Procedures

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

Sample material retrieved from the tank BY-103 vapor space and contained within the SUMMA® canisters shall be analyzed for total non-methane hydrocarbons following modified EPA procedure TO-14 and the permanent gases CO₂, CO, CH₄, H₂, and N₂O using gas chromatography. The sorbent traps contain analyte-specific sorbent media and shall be analyzed for these specific analytes. The triple sorbent traps contain sorbent media designed to allow a broad range of organic species to be retained. Table 6 identifies the appropriate laboratory procedures used in each analysis.

Any analyses prescribed by this document, but not performed, shall be identified and justification for non-performance written in the appropriate data report. If there are insufficient samples to perform all requested analyses, Tank Vapor Safety Resolution Program personnel shall be contacted.

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 procedure PNL-TVP-07 and CASD-AM-300-WP02 (ORNL).
- Step 3 SML: If tank is safe with regard to flammability, set up vapor sampling system (VSS) and collect samples following procedure LO-080-450 and guidelines in Table A-2.
- Step 4 SML: Move to the 222-S Laboratory the vapor sample containers for locked storage, and the HEPA filters and Tritium Trap for radiological survey.
- Step 5 SML: Using radiological survey report results, determine if samples are acceptable to ship offsite (see Section 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: H₂, CO, N₂O, CH₄, CO₂.
 - B. Sorbent Traps (PNL): Perform gravimetric analysis for moisture. Perform selective electrode analysis for NH₃. Analyze NO and NO₂ 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 according to the contractual agreements.

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

PROJECT		BY-103 VAPOR		COMMENTS		REPORT FORMATS			NUMBER OF SAMPLE/BLANK CONTAINERS PROCESSED					
Plan Number	WHC-SD-WM-TP-231		Type 3 vapor sampling system (VSS) using heated vapor probes.		I		Early Notify		Organization		WHC	PNL	ORNL	TOTAL
Tank	BY-103				II		Process Control		SUMMA® Canister		3*	3/2		8
Program Contact	J. W. Osborne J. L. Huckaby				III		Safety Screen		Sorbent Trap System ^b			6/3		9
TWRS Contact	B. C. Carpenter C. S. Homi				IV		Waste Management		Triple Sorbent Trap				4/2	6
					V		RCRA Compliance		HEPA Filter		4			4
Lab Project Coordinator	S. C. Goheen (PNL) R. A. Jenkins (ORNL)				VI		Special		Tritium Trap		1			1
PRIMARY ANALYSES						QUALITY CONTROL ^c			CRITERIA				REPORT FORMAT	
ANALYSIS METHOD	PRIMARY ANALYTE	PROCEDURE	LAB	SAMPLE PREP	SAMPLE CONTAINER	NO. OF SAMPLES	SURR SPIKE ^d	NO. OF BLANKS	NOTIFICATION LIMIT (NL) ^a	EXPECTED RANGE	PRECN σ NL	ACCURACY σ NL		
GCM	Flammability	CGIMX251 CGITMX410	N/A	N/A	N/A	1	N/A	N/A	>20% LFL	<10% LFL	N/A	N/A	I	
EPA TO-14 GC/MS	Organic* Speciation	PNL-TVP-01 PNL-TVP-02 PNL-TVP-03	PNL	Direct	SUMMA®	3	none	2	≥ 4000 ppmv n-Butanol 50% IDLH for all others*	<100 ppbv	± 25%	70-130%	I, VI	
GC/TCD	CO ₂ CO CH ₄ H ₂ N ₂ O	PNL-TVP-05	PNL	Direct	SUMMA®	3	none	2	N/A ≥ 20% LFL ≥ 20% LFL ≥ 20% LFL not available	not available < 5 ppmv not available 600-800 ppmv 700-900 ppmv	± 25% ± 25% ± 25% ± 25%	70-130%	VI I, VI I, VI I, VI I, VI	
IC	NO NO ₂	PNL-TVP-09 PNL-ALO-212	PNL	H ₂ O Extraction	Sorbent Trap	6	none	3	≥ 50 ppmv ≥ 25 ppmv	≥ 2ppmv ≥ 0.1 ppmv	± 25% ± 25%	70-130%	I, VI I, VI	
Gravimetric	H ₂ O	PNL-TVP-09	PNL	Direct	Sorbent Trap	6	none	3	N/A	≥ 3 mg/L	± 25%	70-130%	VI	
Selective Electrode	NH ₃	PNL-ALO-226 PNL-TVP-09	PNL	H ₂ O Extraction	Sorbent Trap	6	none	3	≥ 250 ppmv	≥ 2 ppmv	± 25%	70-130%	I, VI	
GC/MS	Organics**	AC-MM-1-003153 AC-MM-1-003157	ORNL	Thermal Desorption	Triple Sorbent Trap	4	all	2 ^f	≥ 4000 ppmv n-Butanol 50% IDLH for all others**	< 100 ppbv	± 25%	70-130%	I, VI	
Total α Total β Total γ	Radon Daughters	LA-508-110 LA-508-111 LA-508-162	WHC	Direct	HEPA Filter	4	N/A	N/A	≥ 60 pCi/g α ≥ 200 pCi/g β	<60 pCi/g α <200 pCi/g β <200 pCi/g γ	± 25% ± 25% ± 25%	70-130%	I, II	
Liq. Scin.	Tritium	LA-548-111 LA-218-111	WHC	Direct	Tritium Trap	1	N/A	N/A	≥ 200 pCi/g γ N/A	not available	± 25%	N/A	II	
GC/FID	Organics	LO-080-450	FAS	Direct	On-line	N/A	N/A	N/A	N/A	N/A	N/A	N/A	II, VI	

N/A: Not Applicable

a Three canisters will be archived at PNL until arrangements can be made for transport and analytical work at the OGIST laboratory.

b System contains individual sorbent media sections for NO_x, NH₃, & H₂O.

c Multiple samples and blanks are taken.

d Samples spiked with surrogates.

e Action required if any compound exceed 50% IDLH.

f Includes one trip and one field blanks.

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

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

A3.0 QUALITY ASSURANCE/QUALITY CONTROL

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

- 1) Each laboratory has a quality assurance program that meets the applicable requirements of DOE order 5700.6C, American Society of Mechanical Engineers NQA-1, EPA QAMS-005/80 or United States 10 CFR 830.120.
- 2) Each analysis and media preparation procedure given in Tables A-1 and A-4 are documented by the laboratory and available to ESH&QA.
- 3) Any modifications made to, or deviations from, the prescribed procedures are documented and justified in the deliverable report.

The PNL tank vapor program has an impact level II Laboratory Quality Assurance Plan (Barnes 1994) written to comply with 5700.6C. ESH&QA will qualify laboratories for continued use by the TWRS Characterization program after receipt of the Laboratory quality assurance plans, and an audit and corrective action phase.

A3.1 Sampling Operations

The laboratory supplying the sample collection media shall initiate the chain of custody in accordance with the laboratory operating procedure LO-090-443, "Chain-of-Custody for RCRA and CERCLA Protocol Samples" using unique sample label and identification numbers provided by Field Analytical Services. 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 4, List of Sample and Activities, column one.
LLL =	a special lab assigned code.

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

Applicable operating procedures for the tank BY-103 vapor space sampling activities are contained in work package ES-94-1159. Vapor samples, trip blanks, and field blanks are to be collected in accordance with Tables A-1 and A-2 and laboratory operating procedure LO-080-450 "Collection of SUMMA® Canisters & Sorbent Tube Samples Using the Vapor Sampling System (VSS)" and shipped to the laboratory by Field Analytical Services in accordance with Hazardous Material Packaging and Shipping, WHC-CM-2-14.

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

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

Sampling and Mobile Laboratories is responsible for documenting any problems and procedural changes affecting the validity of the sample in a 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 Field Analytical Services. The SUMMA® canisters and Sorbent Trap Systems are prepared and certified following the laboratory quality control procedures identified in Table A-1. The laboratory supplying the sample collection media shall initiate the chain of custody in accordance with the laboratory operating procedure LO-090-443, "Chain-of-Custody for RCRA and CERCLA Protocol Samples" using sample label and identification numbers provided by Field Analytical Services.

The sample receipt and control procedures used in the PNL laboratories is PNL-TVP-07. Oak Ridge National Laboratory shipping and receiving is done by procedure CASD-AM-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 documented in controlled notebooks referenced in the deliverable reports to ensure traceability.

A4.0 ORGANIZATION

The organization and responsibility of key personnel involved in this tank BY-103 vapor sampling project are listed in Table A-5.

Table A-5. Tank BY-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	BY-103 Tank Characterization Plan Engineers
J. L. Huckaby	TWRS Tank Vapor Issue Resolution Program	Vapor Issue Resolution Engineer
H. Babad	TWRS Characterization Program	Tank Safety Screening Scientist
R. S. Viswanath	Field Analytical Services	Special Analytical Studies Vapor Sampling Technical Support
R. D. Mahon	Field Analytical Services	Sampling and Mobile Laboratories Vapor Sampling Program Lead
E. H. Neilsen	Waste Tank Safety Engineering	Vapor Sampling Cognizant Engineer
D. R. Carls	Industrial Hygiene and Safety Program	Industrial Hygiene Point of Contact if 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**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 samples are collected with them. Laboratories supplying blanks may opt to analyze only 1 trip blank unless it is determined to be contaminated, in which case all trip blanks are to be analyzed.

Sample Custodian

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

Physical Control

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

A6.0 DELIVERABLES

The Pacific Northwest Laboratory, Oak Ridge National Laboratory, and Sampling and Mobile Laboratories VSS sampling and analyses of tank BY-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 (509) 373-2689 immediately. This verbal communication must be followed within 3 working days by written communication to J. W. Osborne of the Tank Vapor Issue Resolution Program, D. R. Carls in the Industrial Hygiene and Safety Program, and D. R. Bratzel of the Characterization Program, documenting the observation(s). A further review of the data, including quality control results and additional analyses for verification of the exceeded analyte, may be contracted between the performing laboratory and the contacts above.

A6.2 Format II Reporting

Results of the 222-S Laboratory's radiological survey shall be reported by Sampling and Mobile Laboratories as Format II to the analytical laboratories listing the picocuries per sample (pCi/g of 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 J. W. Osborne of the Tank Vapor Safety Resolution Program, R. S. Viswaneth of Field Analytical Services, the

Characterization Program Office, Analytical Services, and the Tank Characterization Resource Center.

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

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

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

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

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

- 10) a statistical summary (i.e., mean, standard deviation) for multiple analyses and/or multiple samples for all analytes (positively and tentatively identified compounds) in both mass and dimensionless concentrations (if possible);
- 11) a summary of all exceptional conditions, such as deviations from procedure or protocol, results obtained outside of instrument calibration range, sorbent trap breakthrough of analytes, or poor surrogate recoveries; and
- 12) chain-of-custody forms attached.

A7.0 CHANGE CONTROL

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

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

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APPENDIX B

**SAMPLING AND ANALYSIS PLAN FOR AUGER SAMPLING
IN FISCAL YEAR 1995**

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LIST OF ABBREVIATIONS

ACL	Analytical Chemistry Laboratory
DOE	Department of Energy
DQO	Data Quality Objective
DSC	Differential Scanning Calorimetry
DST	Double-Shell Tank
GEA	Gamma Energy Analysis
HPGE/MCA	High Purity Germanium-multi channel analysis
IC	Ion Chromatography
ICP	Inductively Coupled Plasma - atomic emission spectroscopy
PNL	Battelle Pacific Northwest Laboratory
PUREX	Plutonium-Uranium Extraction plant
QC	Quality Control
RSST	Reactive System Screening Tool-adiabatic calorimetry
SST	Single-Shell Tank
TCP	Tank Characterization Plan
TGA	Thermogravimetric Analysis
TOC	Total Organic Carbon
TWRS	Tank Waste Remediation System
WHC	Westinghouse Hanford Company

B1.0 SPECIFIC TANK CHARACTERIZATION OBJECTIVES

Process records indicate that the underground storage tank 241-BY-103 (BY-103) on the Hanford Site contains ferrocyanide from in-tank processing. Consequently, tank BY-103 is one of 18 tanks currently on the Ferrocyanide Watch List. The characterization effort described in this Sampling and Analysis Plan will aid in the resolution of the Ferrocyanide Safety Issue. Further, the results of the sampling activity prescribed by this Sampling and Analysis Plan shall help determine if there are any as yet unidentified safety issues associated with this tank.

B1.1 RELEVANT SAFETY ISSUES

The relevant safety issues with tanks on the Ferrocyanide Watch List are as follows:

- 1) The potential for an uncontrolled exothermic reaction occurring between complexes of ferrocyanide and nitrate or nitrite that could result in a release of radioactive material.
- 2) The possibility that other, as yet unidentified, safety issues exist for the tank.

B1.1.1 Tank BY-103 Characterization Objectives

This characterization effort of tank BY-103 is focused on the relevant safety issues above. Resolution of the Ferrocyanide Safety Issue is the ultimate goal of the Ferrocyanide Safety Program. That program has identified two key safety questions that should be answered from analytical data on tank waste (Postma et al. 1994):

- (1) "Is a significant exothermic reaction possible during interim storage?"
- (2) "Is a significant exothermic reaction possible under present conditions of waste moisture content?"

Each tank on the Ferrocyanide Watch List has been categorized as either Safe or Conditionally Safe by the Ferrocyanide Safety Program. The answers to the above questions will allow each tank's categorization to be revised.

To satisfy other objectives of this sampling and analysis effort, the tank contents shall be safety screened in order to identify any other potential safety issues associated with tank BY-103, and to ensure that the tank should not be placed on an additional Watch List.

B1.1.2 Ferrocyanide and Safety Screening Data Quality Objectives

As described below, the sampling and analytical needs associated with ferrocyanide tanks, as well as the safety screening of all tanks, have been identified through the Data Quality Objective (DQO) process. Additional data needs associated with tank BY-103 may be identified in subsequent DQO efforts, which may then be incorporated into future sampling and analysis plans.

Pertinent documents to this effort include the following:

- (1) *Data Requirements for the Ferrocyanide Safety Issue Developed through the Data Quality Objectives Process* (Meacham et al. 1994), which describes the sampling and analytical requirements for tanks on the Ferrocyanide Watch List, including tank BY-103.
- (2) *Tank Safety Screening Data Quality Objectives* (Babad and Redus 1994), which describes the sampling and analytical requirements for screening waste tanks for unidentified safety issues. The criteria for placing a tank on a particular Watch List are enumerated in that document.

B1.1.3 Data Quality Objectives Integration

The ferrocyanide and safety screening DQOs have compatible sampling and sample breakdown requirements. Two samples taken from risers located approximately 180° apart and near the outer edge of the tank are required for sampling. For this tank BY-103 sampling event two risers are available. From each riser, one auger sample shall be taken.

For sample breakdown the safety screening DQO requests primary and secondary analyses on a quarter and half segment levels.

Anticipating near-term approval of the new characterization strategy, the Ferrocyanide Safety Program has re-evaluated its need to sample all ferrocyanide tanks. A revised priority tank sampling list includes tanks with the highest initial ferrocyanide concentration, the least exposure to high caustic solutions, the lowest radionuclide inventory, and the lowest historic temperature profile. Assuming aging has occurred in these tanks, then it can be extrapolated that the other tanks have aged to the same or to a greater extent as well (Cash 1995). Tank BY-103 is not on the priority sampling list; however, as a precaution in the event that the new strategy is not approved, sample material will be archived. If analyses are necessary at a later time, the Ferrocyanide Program will contact the laboratory to run analysis on the archived samples (see Section B6.1).

B2.0 TANK STATUS AND SAMPLING INFORMATION

B2.1 TANK STATUS

The volume of solid waste in tank BY-103 is 1,510 kL (400 kgals), which equals approximately 389 cm (153 in.). However, the most current manual tape reading (taken in the first of October) corresponds to a waste height of 375 cm (147.5 in.). The waste consists of 18.9 kL (5 kgals) of ferrocyanide sludge, 1,500 kL (395 kgals) of saltcake, of which 606 kL (160 gal) is drainable interstitial liquids (Hanlon 1994). Tank BY-103 has been partially interim isolated and is classified as an assumed leaker with respect to tank integrity (Hanlon 1994).

B2.2 SAMPLING INFORMATION

Tank BY-103 is currently scheduled to be sampled by the auger sampling method. Samples shall be taken from risers 10B and 12A. Sampling shall be conducted according to procedures and documentation included in tank BY-103 work package ES-95-00079. If it becomes necessary to change the riser(s) for sampling, this change must satisfy the intent of the applicable DQOs and be made by the sampling cognizant engineer and kept in a controlled document such that traceability is preserved. Risers used may be recorded on permanent data sheets, or recorded directly in the work package. Although the applicable DQOs require a full vertical profile of the waste be obtained during sampling, for this sampling event only an auger sample from each riser is scheduled (see Section B6.2).

B3.0 SAMPLE EXTRUSION AND BREAKDOWN INSTRUCTIONS

It should be noted that in accordance with the Safety and Analysis Report Packaging (SARP), samples from tank BY-103 must be vented every 15 days from the time of cask sealing to allow any retained gas to escape.

B3.1 TANK-SPECIFIC ANALYTICAL PROCEDURES

A flowchart depicting the general sample breakdown and analysis scheme is presented in Figures B-2, B-3, B-4, and B-5. The steps are described in detail to provide the hot cell and laboratory chemists with guidance for the breakdown of the segments, and may be altered as appropriate by the performing laboratory. Several analyses listed in Table B-1 require a 45 day reporting time, as noted. The 45 day reporting format, Format III, is explained in Section B7.3.

Any decisions, observations, or deviations made to this work plan or the flowchart during the sample removal shall be documented in the writing, with appropriate justification. These decisions and observations shall also be reported in the data report. The reporting formats for analyses are contained in Table B-1.

- Step 1 Receive auger samples at the laboratory in accordance with approved procedures.
- Step 2 Conduct the following on the sample material from each isolated auger sample:
- Perform a visual examination of the sample(s).
 - Record observations. This shall include a sketch of the auger sample in addition to written documentation of pertinent descriptive information such as color, texture, homogeneity, and consistency.
 - Note the color and clarity of any drainable liquid.
 - Take color photographs and/or a videotape to visually document the auger samples.
 - Note sludge/saltcake interface.

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- Step 3A Does the sample contain drainable liquids?
- Yes: Proceed to Step 3B
No: Proceed to Step 4B
- Step 3B Is the sample 100% drainable liquid?
- Yes: Proceed to Step 17
No: Proceed to Step 4A
- Step 4A Separate any drainable liquid from the solids. Measure and record the volume. Retain drainable liquids for further processing.

SOLIDS PATH

- Step 4B Remove and store 50 grams of the uppermost section of the sample. It is important that this material represents the top layer of waste in the tank. If there is not enough sample to perform the requested analyses in Table B-1, plus retain a sufficient amount of sample for archive, this amount can be reduced to as low as 25 grams. If there is not enough material up store 25 grams, notify the Organic Safety Program, the Characterization Program, and Characterization Support so that alternate instructions may be given.
- Step 5A Is there a hard, dry layer on the top portion of the auger sample?
- YES: Proceed to Step 5B
No: Proceed to Step 6
- Step 5B Separate the hard, dry layer and retain for analysis.
- Step 6 Does the auger sample contain any saltcake?
- Yes: Proceed to Step 7A
No: Proceed to Step 8
- Step 7A Is there both sludge and saltcake in the sample?
- Yes: Proceed to Step 7B
No: Proceed to Step 7C
- Step 7B Separate sample at the sludge/saltcake interface and keep separate for all analyses. Retain sludge for further breakdown in Step 8. For remaining saltcake, proceed to step 7C.
- Step 7C Is there more than 20 g of saltcake?
- Yes: Proceed to Step 7D
No: Proceed to Step 7E
- Step 7D Divide the saltcake into two subsamples (i.e., half-segments).
- Step 7E Homogenize each saltcake subsample using the appropriate procedure.

- Step 7F Collect sufficient aliquots from each saltcake subsegment to perform the appropriate analyses listed in Table B-1 in duplicate.
- Step 7G Archive at least 10 mL and up to 20 mL of each homogenized saltcake subsample (Bratzel 1994). If insufficient material is available to perform the required analyses and meet archiving needs, notification should be given as directed in Section B3.2.
- Step 7H Was the auger sample entirely composed of saltcake?
- Yes: Proceed to Step 17 (Steps 8-16 are to be performed on the sludge material only.)
- No: Proceed to Step 8
- Step 8 Divide the remaining sludge material from the sample into four 12 cm quarter samples (segments). Figure B-1 illustrates how a typical segment sample will be extruded and divided into quarter segments. The first 12 cm segment extruded from the sampler originates from the lowest portion of the tank relative to the other segments and therefore shall be assigned to the fourth quarter segment and shall be uniquely identified as (Tank - Core No. - Segment No. - D). The following three 12 cm sections of the isolated auger sample shall be labeled as C, B, and A, respectively. An example of this labeling protocol for the third quarter segment from the first segment of the first core would be (BY-103 - Core 1 - Segment 1 - B). If the isolated auger sample is less than 48 cm long, then the same labeling convention shall still apply until no solid material is left to make a complete 12 cm quarter segment. The first 12 cm extruded (i.e., bottom portion of the core) shall still be assigned to the D quarter segment, etc.

Figure B-1: Tank BY-103 Sample Breakdown

- Step 9 Homogenize each quarter segment of sludge from Step 8 using the appropriate, approved procedure.
- Step 10 Will a homogenization test be performed?
- YES: Proceed to Step 11
- NO: Proceed to Step 12

NOTE: One sludge quarter segment per core, at a minimum, should be used if a homogenization test is performed.

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Additional tests may be performed at the laboratory's discretion.

- Step 11 Conduct the homogenization test by taking a 1 to 2 g subsample from widely separated locations of the homogenized quarter segment. Conduct the homogenization test in accordance with (Bell 1993).
- Step 12A Collect sufficient aliquots from each homogenized quarter segment to perform the appropriate preparations and analyses listed in Table A-1 in duplicate.
- Step 12B Remove 20 mL of each homogenized quarter segment for the Ferrocyanide Program archive sample (Bratzel 1994).
- Step 13 Combine the remainder of quarter segments A and B to create a half segment. Do the same with quarter segments C and D.
- Step 14 Homogenize each sludge half segment from Step 13 using the appropriate, approved procedure.
- Step 15 Collect sufficient aliquots from each homogenized half segment to perform the appropriate preparations and analyses listed in Table B-1 in duplicate.
- Step 16 Remove at least 10 mL and up to 20 mL of each homogenized half segment for archive sample (Bratzel 1994).

LIQUIDS PATH

- Step 17 Closely inspect the liquid sample obtained in Step 4A for the presence and approximate volume of any potential organic layers. Does the sample contain any immiscible (potential organic) layers?
 - YES: Proceed to Step 18A
 - NO: Proceed to Step 19
- Step 18A Report any visually observed immiscible (potential organic) layer immediately by the early notification system (see Section B7.2).
- Step 18B Separate and retain the potential organic layer for possible future analysis.
 - NOTE:** Steps 19 through 23 shall be performed on the remaining (probable aqueous) liquid layer only.
- Step 19 Filter the remaining liquid sample through a 0.45 micron filter.
- Step 20 Is there greater than 1 gram of solid on the filter?
 - YES: Proceed to Step 21
 - NO: Proceed to Step 22
- Step 21 Archive the solids for possible future analysis (Bratzel 1994).

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- Step 22 Remove sufficient aliquots from the segment-level liquid sample to perform the appropriate analyses listed in Table B-1 in duplicate.
- Step 23 Archive at least 10 mL and up to 20 mL of the segment-level drainable liquid as the segment-level liquid archive (Bratzel 1994).

PRIMARY ANALYSIS PATH

- Step 24 Perform primary analyses as listed in Table B-1.
- Step 25 Compare the primary analysis data with notification limits.
- Step 26A Do the results exceed the notification limits (Table B-1)?
YES: Proceed to step 26B.
NO: Proceed to Step 29.
- Step 26B Report results exceeding notification limits using Format I reporting deliverable requirements (Section B7.2).

SECONDARY ANALYSIS PATH

- Step 27 Perform secondary analyses according to Table B-1.
- Step 28A Do the results of secondary analyses exceed the notification limits?
YES: Proceed to Step 28B
NO: Proceed to Step 29
- Step 28B Report results for the secondary analyses which exceed the notification limits using Format I reporting requirements (Section B7.2).

REPORTING PATH

- Step 29 Report and deliver data obtained using reporting requirements (Section B7.0).

SAMPLE EXTRUSION AND BREAKDOWN

Figure B-2: Sample Extrusion and Breakdown Flow Chart

SLUDGE PATH

Figure B-3: Sludge Analysis Flow Chart

B-4: Liquid Analysis Flow Chart

ANALYSIS AND REPORTING PATH

Figure B-5: Sample Analysis and Reporting Flow Chart

B3.2 INSUFFICIENT SAMPLE RECOVERY

If the amount of material recovered from the auger samples taken from tank BY-103 is insufficient to perform the requested analyses and permit a minimum 20 gram archive per sample, the laboratory project coordinator or project manager shall notify the Tank Cognizant Engineer and the manager of Analytical Services, Program Management and Integration within one working day. A prioritization of the analyses requested in this document is given in Section B3.3. Any analyses prescribed by this document, but not performed, shall be identified in the appropriate data report, with justification for non-performance.

B3.3 PRIORITIES OF REQUESTED ANALYSES

Confirmation of prioritization levels or revision of sample breakdown procedures may be provided to the laboratory by the Characterization Program based upon the sample recovery, readily observable physical property distinctions within the sample, and the requested sample breakdown procedures as provided in Section B3.1. The priority of an analysis is specified by its designation as a primary or secondary analysis. Further prioritization may be determined by the program on a DQO basis.

B4.0 SPECIFIC ANALYTE, QUALITY CONTROL, AND DATA CRITERIA

B4.1 SPECIFIC METHODS AND ANALYSES

The analyses in Table B-1 to be performed on waste from tank BY-103 are based on the safety screening DQO referenced in Section B1.1.2. The laboratory procedure numbers, which shall be used for the analyses, are included in the table.

B4.2 QUALITY ASSURANCE/QUALITY CONTROL

B4.2.1 Laboratory Operations

The 222-S Laboratory has a quality assurance program plan (Meznarich 1994) and a quality assurance project plan (Taylor 1993) that shall provide the primary direction for the quality assurance of analyzing the waste tank core samples at the 222-S Laboratory. Additionally, the *Hanford Analytical Services Quality Assurance Plan* (DOE 1994), when implemented (August 31, 1995), shall be used as quality assurance guidance.

Method specific quality control such as calibrations and blanks are also found in the analytical procedures. Sample quality control (duplicates, spikes, and standards) are identified in Table B-1. If no criteria are provided in Table B-1, the performing laboratory shall perform to its quality assurance plan.

B4.2.2 Sample Collection

Two auger samples are to be taken and shipped to the performing laboratory by Sampling Operations in accordance with Work Package ES-95-00079. That work package shall also initiate the chain-of-custody for the samples. Approved work procedure TO-080-090 ("*Load/Transport Sample Cask(s)*") is to be used during the sampling event. Samples shall be identified by a unique number before being shipped to the performing laboratory. The sampling team is responsible for documenting any problems and procedural changes affecting the validity of the sample in a field notebook. Sampling Operations shall enter this information in the comment section of the chain-of-custody form for inclusion into the data reports.

Sampling Operations should transport each segment collected to the performing laboratory within 1 working day of removing the segment from the tank, but must transport each segment within 3 calendar days. Sampling Operations is responsible for verbally notifying the 222-S shift manager at the laboratory (373-2435) at least 24 hours in advance of an expected shipment.

B4.2.3 Sample Custody

The chain-of-custody form is initiated by the sampling team as described in Work Package ES-95-00079. Auger samples are shipped in a cask and sealed with the Waste Tank Sample Seal. All sample shipments are to be labeled with the following information:

WASTE TANK SAMPLE SEAL

Supervisor
Date of Sampling
Shipment No.

Sample No.
Time of Sampling
Serial No.

The sealed and labeled samples are shipped to the laboratory along with the chain-of-custody form. The receipt and control of samples at WHC 222-S Laboratory are described in procedure LO-090-101.

Table B-1: BY-103 Chemical, Radiological and Physical Analytical Requirements

SOLID ANALYSES																		
Project Name			BY-103 Auger Sample				COMMENTS								REPORTING LEVELS			
Plan Number			WHC-SD-WM-TP-231, REV. 1				Homogenization Test - Per Laboratory Discretion Field Blank - Not Required Hot Cell Blank - Per Laboratory Discretion								FORMAT I		Early Notify	
															FORMAT II		Process Control	
PROGRAM			PROGRAM CONTACTS												FORMAT III		Safety Screen	
A. Safety Screening			Safety Screening		M. A. Payne										FORMAT IV		Waste Management	
			TWRS		R. D. Schreiber										FORMAT V		RCRA Compliance	
			222-S Laboratory		J. G. Kristofzski										FORMAT VI		Special	
							TANK		#AUGERS									
							BY-103		2									
PROGRAM	PRIMARY ANALYSES			SAMPLE ¹			PREP ²	QUALITY CONTROL ³						CRITERIA			FOR-MAT	
	METHOD	ANAL.	WHC PROCEDURE	1/4 SEG SLDG	½ SEG SLDG	½ SEG SC		DUP	SPK/ MSD	BLK	CALIB STD	PR	AC	UNITS	NOTIFICATION LIMIT ⁴	EXPECTED RANGE ⁴		
A	DSC	Energy	LA-514-113	X		X	d	ea smpl	N/A	N/A	ea AB	±10	90-110	J/g ⁵	> 481	unknown	I, III	
A	TGA	% H ₂ O	LA-560-112	X		X	d	ea smpl	N/A	N/A	ea AB	±10	90-110	wt%	< 17	unknown	I, III	
A	Alpha	Total Alpha	LA-508-101		X		f or a	ea smpl	1/mtrx	ea PB	ea AB	±10	90-110	µCi/g	> 41	unknown	I, III	
PROGRAM	SECONDARY ANALYSES			SAMPLE ¹			PREP ²	QUALITY CONTROL ³						CRITERIA			FOR-MAT	
	METHOD	ANAL.	WHC PROCEDURE	1/4 SEG SLDG	½ SEG SLDG	½ SEG SC		DUP	SPK/ MSD	BLK	CALIB STD	PR	AC	UNITS	NOTIFICATION LIMIT ⁴	EXPECTED RANGE ⁴		
A	Distillation ⁷	CN	LA-695-102	X ⁷		X ⁷	d	ea smpl	1/mtrx	ea AB	ea AB	±10	90-110	µg/g	> 39,000	unknown	I, III	
A	Direct Persulfate ⁷	TOC	LA-342-100		X ⁷	X ⁷	d	ea smpl	1/mtrx	ea AB	ea AB	±10	90-110	µg C/g	> 30,000	unknown	I, III	
A	Sep. & α counting ¹¹	Pu-239/240	LA-503-156		X ¹¹		f	ea smpl	1/mtrx ⁸	ea PB	ea AB	±10	90-110	µCi/g	> 41	unknown	I, III	
A	ICP ¹¹	Fe Mn U	LA-505-151		X ¹¹		f or a	ea smpl	see ⁹	ea PB	ea AB	±10	90-110	µg/g	none none none	unknown unknown unknown	III	
A	RSST ¹⁰	Energy	see 10 below	X ¹⁰		X ¹⁰	d	N/A	N/A	N/A	ea AB	±10	90-110	J/g	> 481	unknown	I, III	

¹ 1/2 SEG SLDG-1/2 segment, sludge; 1/2 SEG SC-1/2 segment, saltcake² d-direct, f-fusion, a-acid, w-water³ PR-precision, AC-accuracy, ea-each, smpl-sample, DUP-duplicate, SPK/MSD-spike or matrix spike duplicate, AB-analytical batch, PB-preparation blank, N/A-not applicable, mtrx-matrix⁴ Units for notification limits and expected range are those listed in the "units" column.⁵ Dry weight basis⁶ Direct liquid samples may be diluted in acid or water to adjust to proper sample size and/or pH.⁷ Analyses performed if DSC exotherm exceeds notification limit.⁸ Tracer or carrier may be used in place of a spike and results corrected for recovery.⁹ Either serial dilutions or matrix spikes will be performed.¹⁰ This analysis required if DSC exceeds notification limits. The RSST method, yet to be proceduralized, may be found in WHC-SD-WM-TP-104.¹¹ Performed only if total alpha on half segment exceeds notification limit.

Table B-1: BY-103 Chemical, Radiological and Physical Analytical Requirements

LIQUID ANALYSES																
Project Name		BY-103 Auger Sample				COMMENTS						REPORTING LEVELS				
Plan Number		WHC-SD-WM-TP-231, REV. 1				Homogenization Test - Per Laboratory Discretion Field Blank - Not Required Hot Cell Blank - Not Required						FORMAT I		Early Notify		
												FORMAT II		Process Control		
PROGRAM		PROGRAM CONTACTS										FORMAT III		Safety Screen		
A. Safety Screening		Safety Screening		M. A. Payne								FORMAT IV		Waste Management		
		TWRS		R. D. Schreiber								FORMAT V		RCRA Compliance		
		222-S Laboratory		J. G. Kristofzski								FORMAT VI		Special		
						TANK		#AUGERS								
						BY-103		2								
PROGRAM	PRIMARY ANALYSES				PREP ²	QUALITY CONTROL ³						CRITERIA				FOR-MAT
	METHOD	ANAL.	WHC PROCEDURE	FB & S-LEV LIQ		DUP	SPK/MSD	BLK	CALIB STD	PR	AC	UNITS	NOTIFICATION LIMIT ⁴	EXPECTED RANGE ⁴		
A	DSC	Energy	LA-514-113	X	d	ea smpl	N/A	N/A	ea AB	±10	90-110	J/g ⁵	> 481	unknown	I, III	
A	TGA	% H ₂ O	LA-560-112	X	d	ea smpl	N/A	N/A	ea AB	±10	90-110	wt%	< 17	41.6-62.4	I, III	
A	Visual	Organic Layer	LA-519-151	X	d	N/A	N/A	N/A	N/A	N/A	N/A	none	presence	unknown	I, III	
PROGRAM	SECONDARY ANALYSES				PREP ²	QUALITY CONTROL ³						CRITERIA				FOR-MAT
	METHOD	ANAL.	WHC PROCEDURE	FB & S-LEV LIQ		DUP	SPK/MSD	BLK	CALIB STD	PR	AC	UNITS	NOTIFICATION LIMIT ⁴	EXPECTED RANGE ⁴		
A	RSST ¹²	Energy	see 12 below	X	d	N/A	N/A	N/A	ea AB	±10	90-110	J/g	> 481	unknown	I, III	
A	Furnace Oxidation ¹³	TOC	LA-344-105	X	d ⁶	ea smpl	1/mtrx	ea AB	ea AB	±10	90-110	µg C/mL	> 30,000 ⁷	2,160-3,140	I, III	
A	Distillation ¹³	CN	LA-695-102	X	d ⁶	ea smpl	1/mtrx	ea AB	ea AB	±10	90-110	µg/mL	> 39,000 ⁷	7.76-11.64	I, III	

¹S-LEV LIQ-liquid taken from the segment level, FB-field blank²d-direct, f-fusion, a-acid, w-water³PR-precision, AC-accuracy, ea-each, smpl-sample, DUP-duplicate, SPK/MSD-spike or matrix spike duplicate, AB-analytical batch, PB-preparation blank, N/A-not applicable, mtrx-matrix⁴Units for notification limits and expected range are those listed in the "units" column.⁵Dry weight basis.⁶Direct liquid samples may be diluted in acid or water to adjust to proper sample size and/or pH.⁷Action limit converted from a weight basis to a volumetric basis assuming a liquid density of 1.0 g/mL.⁸Tracer or carrier may be used in place of a spike and results corrected for recovery.⁹Either serial dilutions or matrix spikes will be performed.¹²RSST performed only if DSC exceeds notification limits. The RSST method, yet to be proceduralized, may be found in WHC-SD-WM-TP-104.¹³This analysis required if DSC exceeds notification limits.

B5.0 ORGANIZATION

The organization and responsibility of key personnel involved with this tank BY-103 characterization project are listed in Table B-2.

Table B-2: Tank BY-103 Project Key Personnel List

Individual	Organization	Responsibility
J. L. Deichman	WHC Analytical Services, Program Management & Integration	Manager, Analytical Services, Program Management & Integration
J. G. Kristofzski	222-S Analytical Operations	Program Support Manager of Analytical Operations
R. J. Cash	Ferrocyanide Safety Program	Manager, Ferrocyanide Safety Program
H. Babad	WHC Characterization Program	Point of Contact for Safety Screening DQO
R. D. Schreiber	TWRS Characterization Support	TWRS Tank BY-103 Cognizant Engineer
Tank Farms Operations Shift Manager	Tank Farms Operations	200 East Tank Farm Operations point of contact if notification limits are exceeded (373-2689)

B6.0 EXCEPTIONS, CLARIFICATIONS, AND ASSUMPTIONS**B6.1 EXCEPTIONS TO DQO REQUIREMENTS**

In the safety screening DQO, it is specified that the notification limit for the DSC analysis is 125 cal/g (523 J/g). However, the revised ferrocyanide DQO has changed the requirements such that the DSC notification limit is 115 cal/g (481 J/g dry weight basis). This change will be made to the safety screening DQO when it is revised (currently in progress). Therefore, although this Sampling and Analysis Plan uses the current safety screening DQO, it specifies that notification shall be made if the DSC value exceeds 481 J/g (115 cal/g dry weight basis).

The safety screening DQO specifies that if the DSC limit is exceeded for ferrocyanide tanks, total organic carbon analysis is to be performed using the furnace oxidation method. However, it is only possible to perform the total organic carbon analysis on liquid samples or solids that have been diluted. Diluting solid samples in water may not release all the organic carbon in the material, possibly yielding inaccurate results. Therefore, although the furnace oxidation method is identified for the liquid analyses, the alternate total organic carbon method, direct persulfate oxidation, is listed as the method to be used if total organic carbon analysis must be run on solid samples.

Anticipating near-term approval of the new characterization strategy, the Ferrocyanide Safety Program has re-evaluated its need to sample all ferrocyanide tanks. The Ferrocyanide Safety Program is also attempting to accelerate resolution

of the Ferrocyanide Safety Issue to mid Fiscal Year 1996 (approximately 1½ years earlier than previously planned). Experiments on waste simulants and waste tank sampling to date indicate that ferrocyanide (fuel) no longer exists in sufficient quantities because of radiolytic and chemical degradation (aging). The revised priority tank sampling list includes tanks with the highest initial ferrocyanide concentration, the least exposure to high caustic solutions, the lowest radionuclide inventory, and the lowest historic temperature profile. Assuming aging has occurred in these tanks, then it can be extrapolated that the other tanks have aged to the same or to a greater extent as well (Cash 1995, see Section B9.0). Tank BY-103 is not on the priority sampling list; however, as a precaution in the event that the new strategy is not approved, a sample will be archived. If analyses are necessary at a later time, the Ferrocyanide Program will contact the laboratory to run analyses on the archived samples.

B6.2 CLARIFICATIONS AND ASSUMPTIONS

A number of clarifications and assumptions relating to the notification limits or decision thresholds identified in the applicable DQO efforts needs to be made with respect to the analyses in Table B-1. Each of these issues are discussed below.

- Any exotherm determined by differential scanning calorimetry (DSC) must be reported on a dry weight basis as shown in equation (1), using the weight percent water determined from thermogravimetric analysis:

$$\text{Exotherm (dry wt)} = \frac{[\text{exotherm (wet wt)} \times 100]}{(100 - \% \text{ water})} \quad (1)$$

Note: A large error in the DSC value may result when converting samples containing greater than 90% water to a dry weight basis. However, this conversion is still required.

- The safety screening DQO does not sufficiently address the analyses of any drainable liquid present. To adequately characterize the tank, all analyses performed on solids for the safety screening DQO, with the exception of total alpha analyses, shall also be performed on any drainable liquids and the field blank.
- The safety screening DQO (Babad and Redus 1994) requires that additional analyses be performed if total alpha activity measures greater than 1 g/L. Total alpha is measured in $\mu\text{Ci/g}$ rather than g/L. To convert the notification limit for total alpha into a number more readily usable by the laboratory, it was assumed that all alpha decay originates from Pu-239. The notification limit may then be calculated as shown in equation (3):

$$\left(\frac{1 \text{ g}}{L}\right) \left(\frac{1 \text{ L}}{10^3 \text{ mL}}\right) \left(\frac{1}{\text{density}} \frac{\text{mL}}{\text{g}}\right) \left(\frac{0.0615 \text{ Ci}}{1 \text{ g}}\right) \left(\frac{10^6 \text{ } \mu\text{Ci}}{1 \text{ Ci}}\right) = \frac{61.5 \text{ } \mu\text{Ci}}{\text{density} \text{ g}}$$

(2)

NOTE: If a density of 1.5 g/mL is assumed for solid material, the notification limit becomes 41 $\mu\text{Ci/g}$.

The Organic Safety Program has requested that 50 g of material from the uppermost section of the uppermost sample be stored. Presently, the Organic Safety Program is writing a DQO that will specify the analytical requirements on the stored sample. If there is not enough sample to store 50 g and satisfy all requested analysis and archiving requirements, the amount of material stored for the Organic Safety Program may be reduced, provided a minimum of 25 g is saved. If this is not possible, notify the Organic Safety Program, the Characterization Program, and Characterization Support so that alternate instructions may be given.

In the safety screening DQO, it is stated that a vertical profile of the waste in the tank is to be obtained. Since tank BY-103 currently consists of approximately 389 cm (153 in.) of waste material, a core sample is necessary to achieve a vertical profile. A core sampling event for tank BY-103 is scheduled in fiscal year 1995, but for this sampling event auger samples are to be obtained.

B7.0 DELIVERABLES

All analyses of tank BY-103 waste material will be reported as Format I, or III as indicated in Table B-1. Additional information regarding reporting formats is given in (Schreiber 1994a).

B7.1 PROGRESS REPORTS

Each laboratory performing analyses on tank BY-103 waste material from this core sampling project shall provide monthly status reports to the Characterization Program. This report shall contain 1) a summary of the activities on the analysis of tank BY-103, 2) preliminary results of interest to the program, and 3) schedule and cost information on a DQO basis.

Monthly and accumulative costs will be compared to the base as part of the Progress report. Variances greater than 10% and \$10,000, or variances greater than \$50,000 from the estimated costs or schedule must be explained in the report. Cost reporting shall consist of the following:

1. budgeted cost of work scheduled
2. monthly cost (actual cost of work performed)
3. year-to-date costs (actual cost of work performed)

Schedule reporting shall consist of the following:

1. monthly schedule
2. year-to-date schedule

B7.2 FORMAT I REPORTING

Table B-1 contains the notification limits for each analyte. Any results exceeding their notification limits shall be reported by calling the East Tank Farm Operations Shift Manager at 373-2689 and the Characterization Program (Schreiber 1994b). This verbal notification must be followed within 1 working day by written communication to the Safety Screening Representative, Analytical Services, Characterization Support, Waste Tanks Process Engineering, and the Characterization Program Office documenting the observations (Schreiber 1994c). Additional analyses for verification purposes may be contracted between the performing laboratory and the contacts above by a revision to this document, or by a letter of instruction.

B7.3 FORMAT III REPORTING

A Format III report, reporting the results of the primary safety screen analyses, shall be issued to the Ferrocyanide Safety Program, the Safety Screening Representative, Characterization Support, Waste Tanks Process Engineering, the Characterization Program Office, and the Tank Characterization Resource Center (Schreiber 1994c) within 45 days of receipt of the last segment of the last core sample at the laboratory loading dock. The DSC and TGA scans have been requested due to the interpretive nature of the analysis. If analyses for the safety screening secondary analytes are required, these results shall be provided within 90 days of receipt of the last segment of the last core sample at the laboratory loading dock. No calibration data are requested for these reports. Detailed information regarding the contents of this reporting format are given in (Schreiber 1994a).

B8.0 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 documented accordingly. Changes may be documented through the use of internal characterization change notices or analytical deviation reports for minor, low-impact changes and documented in applicable laboratory notebooks. All significant changes (such as changes in scope) shall be documented by Characterization Support via an Engineering Change Notice to the Tank Characterization Plan. All changes shall also be clearly documented in the final data package.

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

B9.0 ATTACHMENTS

The following memorandum is intended to be used as interim guidance pertaining to the ferrocyanide analysis requests until the ferrocyanide DQO is revised (scheduled release date of April 1995).

Westinghouse
Hanford CompanyInternal
Memo

From: Ferrocyanide Safety Program
 Phone: 373-3132
 Date: November 29, 1994
 Subject: LIST OF FERROCYANIDE TANKS TO BE SAMPLED

74260-95-003

To: G. A. Stanton S7-31

cc: D. R. Bratzel S7-31*
 R. J. Cash S7-15*
 G. T. Dukelow S7-15*
 C. S. Haller ~~S7-15*~~ R2-12
 T. J. Kelley S0-06*
 *CC:Mail

J. E. Meacham S7-15*
 G. J. Miskho S7-12*
 M. A. Payne S7-15*
 R. H. Stubbs S7-12*
 D. A. Turner S7-15*

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DEC. 01 1994

C. S. HALLER

Anticipating near-term approval of the new characterization strategy, the Ferrocyanide Safety Program has re-evaluated its need for rotary core samples. In the current five-year plan, resolution of the Ferrocyanide Safety Issue is achieved in September 1997, after core sampling and analyses of all eighteen ferrocyanide tanks are completed. However, experiments on waste simulants and waste tank sampling to date indicate that ferrocyanide (fuel) no longer exists in sufficient quantities because of radiolytic and chemical degradation (aging). Therefore, it is not necessary to core sample every ferrocyanide tank.

Ferrocyanide waste aging studies were started in FY 1992 and will be completed in September 1995. Studies have shown that there are three parameters that play an important role in the rate of aging: integrated radiation dose, waste temperature, and exposure of the waste to caustic ($\text{pH} \geq 12$) solutions. Work remaining this year is examining these three parameters to determine the rate limiting conditions for aging. However, enough information is presently available to determine which tanks should be sampled to bound aging. That is, tanks which historically have conditions less conducive to aging should be sampled. This is an additional six tanks.

The revised sampling includes tanks with the highest initial ferrocyanide concentration, the least exposure to high caustic solutions, the lowest radionuclide inventory, and the lowest historic temperature profile. Assuming aging has occurred in these tanks, then it can be extrapolated that the other tanks have aged to the same or to a greater extent as well.

The list of tanks (in sequence) requested for sampling are:

- 241-BY-106: deep sludge tank; may not have been exposed to high pH solution.
- 241-BY-105: low integrated dose tank; lowest temperature ferrocyanide tank in BY Farm.
- 241-BY-104: highest inventory tank; take only 1 core sample.
- 241-BY-110: tank produces high ammonia concentration which is a product of ferrocyanide and/or organic aging.
- 241-BY-108: tank may contain organic solvent.
- 241-TY-103: low temperature tank; low pH tank (this could be the first rotary core taken using truck #3).

Mr. G. A. Stanton
Page 2
November 29, 1994

74260-95-003

The above order is critical in order to adhere to a U.S. Department of Energy (DOE) request to resolve the Ferrocyanide Safety Issue by the end of the fiscal year.

Tank 241-BY-103 would not need to be sampled per the proposed strategy to resolve the Ferrocyanide Safety Issue. This means the instrument tree can be installed after concurrence is received from the DOE. If the strategy is not approved, there will still be adequate time to core sample before the instrument tree is installed.

A handwritten signature in black ink, appearing to read 'R. J. Cash', with a large, stylized initial 'C'.

R. J. Cash
Manager

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B10.0 REFERENCES

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