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DISTRIBUTION SHEET

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		Date 03/23/95
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		ECN No.

Name	MSIN	Text With All Attach.	Text Only	Attach./Appendix Only	EDT/ECN Only
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Richland, WA 99352

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G. P. Westleigh	X

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Document Number: WHC-SD-WM-TP-310, REV.0

Document Title: Tank 241-U-203 Tank Characterization Plan

Release Date: March 28, 1995

**This document was reviewed following the
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APPROVED FOR PUBLIC RELEASE

WHC Information Release Administration Specialist:

Vicky Birkland

March 28, 1995

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Tank 241-U-203

Tank Characterization Plan

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

by

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LIST OF ABBREVIATIONS

DOE	U.S. Department of Energy
DNFSB	Defense Nuclear Facilities Safety Board
DQO	Data Quality Objective
DST	Double-Shell Tank
HEPA	High-Efficiency Particulate Air Filter
RCRA	Resource Conservation and Recovery Act of 1976
SST	Single-Shell Tank
TCP	Tank Characterization Plan
TOC	Total Organic Carbon
TPA	Federal Facility Agreement and Consent Order (Tri-Party Agreement)
TWRS	Tank Waste Remediation System
U-203	Tank 241-U-203
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 has been made, which states that "A Tank Characterization Plan (TCP) will 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 tank 241-U-203 (U-203) sampling activities.

2.0 DATA QUALITY OBJECTIVES APPLICABLE TO TANK 241-U-203

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. The DQOs that have been completed and apply to tank U-203 as of January 1995 are discussed in the following paragraphs.

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. If a specified parameter is exceeded, further analyses may be required to classify a tank. The primary analytical requirements for the safety screening of a tank are energetics, total alpha activity, moisture, and flammable gas concentration. A tank can be removed from a Watch List if it is classified as SAFE.

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 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.

2.2 ORGANIC DATA QUALITY OBJECTIVES

As indicated by the present status of the tank, the Watch List DQO applicable to tank U-203 is the *Data Quality Objective to Support Resolution of the Organic*

Fuel Rich Tank Safety Issue (Babad et al. 1994). The organic safety issue arises due to wastes added to SSTs containing quantities of complexants used in waste management operations, as well as degradation products of the complexants and solvents used in fuel reprocessing and metal recovery operations. These waste tanks also contain a presumed stoichiometric excess of sodium nitrite and sodium nitrate that are sufficient to exothermally oxidize the organic compounds in the tank. The relevant safety issues that are of concern for tanks on the Organic Watch List are as follows:

- The potential for an exothermic reaction occurring from the flammable mixture of organic materials and nitrate/nitrite salts that could result in a release of radioactive material.
- The possibility that other safety issues may exist for the tank.

Sampling and analytical requirements for the Organic Fuel Rich Tank Safety Issue DQO includes two widely spaced core samples and primary analyses for organic carbon, moisture content, tank temperature, and presence of a free organic liquid.

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 U-203 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. 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 HISTORICAL INFORMATION

This section summarizes the available historical information for tank U-203. 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).

3.1 JANUARY 1995 TANK STATUS

Tank U-203 is on the Organic Watch List and is passively ventilated with interim stabilization completed in 1978. The tank is classified as sound and intrusion prevention measures were completed in 1982. Approximately 11,400 liters (3,000 gallons) of material, consisting of 7,600 liters (2,000 gallons) of sludge and 3,800 liters (1,000 gallons) of supernatant, are contained in the tank. The surface level is monitored manually each day through riser 1 and the waste measures about 48 centimeters (18 inches) in depth. The latest photograph was taken in June 1989 and shows a dark yellow supernatant surface surrounded by a light yellow sludge peppered with dark material. The highest temperature reading is 68°F (20°C) (Hanlon 1994).

3.2 TANK CONFIGURATION

Single shell tank U-203 was constructed as a type I tank between 1943 and 1944 and is located in the 200 West Area. Tank U-203 is 6 meters (20 feet) in diameter and has a capacity of 208,000 liters (55,000 gallons). The tank is not in a cascade flow system but does cascade to a junction box. 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. Tank U-203 has 8 risers; two 31 centimeters (12 inch) risers (#2 and #6) are available for use.

3.3 TANK HISTORY

During 1956, tank U-203 was filled with REDOX supernatant waste transferred from tank U-111. This waste was pumped to an unknown destination in 1977. Tank U-203 was removed from service in 1977 and placed on the Organic Watch List in May 1994 due to an estimated Total Organic Carbon (TOC) content greater than 3 dry weight percent. The fill history information is available in *A History of the 200 Area Tank Farms* (Anderson 1990). Figure 1 summarizes the influx and effluent history of tank U-203.

3.4 EXPECTED TANK CONTENTS

Tank U-203 contents are expected to consist of supernatant and sludge layers with no liquid capable of being pumped remaining in the sludge. The organic content reported in *Historical Tank Characterization Estimates for the SW Quadrant of the Hanford 200 West Area* (Brevick 1994) is inconsistent with the predicted 3.01 weight percent from a Pacific Northwest Laboratory study (Toth et al. 1994). Table 1 summarizes the expected tank contents.

Table 1: Tank U-203 Composite Inventory Estimate¹

Physical Data	Value	
Total Solid Waste	11,700 kg (2,000 gallons)	
Heat Load	0 (0 B1U/hr)	
Density	1.54 g/ml	
Void Fraction	0.65	
Weight % Water	55.61	
TOC (Wet Weight %)	0	
Analytes	$\mu\text{g/g}$	$\mu\text{g/ml}$
Na ⁺	17,300	26,600
Al ⁺³	101,000	156,000
NO ₃ ⁻	21,200	32,600
NO ₂ ⁻	5,510	8,490
CO ₃ ⁻²	2,570	3,960
OH ⁻	195,000	300,000
Radionuclides	$\mu\text{Ci/g}$	$\mu\text{Ci/ml}$
Pu	2.53	3.90

¹(Brevick 1994)

4.0 TANK U-203 SCHEDULED SAMPLING EVENTS

Head space vapor sampling and core sampling in fiscal year 1995 are currently scheduled for tank U-203. No other sampling is scheduled through fiscal year 1997 (Stanton 1994). The head space vapor sampling shall be conducted in accordance with *Data Quality Objectives for Generic In-Tank Health and Safety Vapor Issue Resolution* (Osborne et al. 1994). Vapor sampling will satisfy part of the requirement specified in TPA Milestone M-40-08 to complete the vapor sampling of all Watch List tanks (Osborne and Huckaby 1994b).

Core sampling shall be conducted following the *Tank Safety Screening Data Quality Objective* (Babad and Redus 1994) and the *Data Quality Objective to Support Resolution of the Organic Fuel Rich Tank Safety Issue* (Babad et al. 1994). The recommended method of sampling for tank U-203 is the push mode sampling system. This tank is expected to contain approximately 18 inches of waste, although this depth should be verified prior to sampling. The most recent photographs of tank U-203 show a liquid pool in the center, although this pool does not extend to the edges of the tank. The risers to be used during sampling are near the outer diameter of the tank and are therefore expected to have solid material beneath the opening.

The sampling and analytical requirements from these DQOs 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	Primary 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
Core	<ul style="list-style-type: none"> Tank Safety Screening Organic Fuel Rich Tank Safety Issue 	Samples from a minimum of 2 risers separated radially to the maximum extent possible	<ul style="list-style-type: none"> Energetics TOC Moisture Content Total Alpha

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APPENDIX A
SAMPLING AND ANALYSIS PLAN
FOR CORE SAMPLING IN FISCAL YEAR 1995

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SAMPLING EVENT A: CORE SAMPLING IN FISCAL YEAR 1995

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LIST OF ABBREVIATIONS FOR APPENDIX A

ACL	Analytical Chemistry Laboratory
U-203	Tank 241-U-203
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
LIMS	Laboratory Information Management Systems
RCRA	<i>Resource Conservation and Recovery Act of 1976</i>
RSST	Reactive System Screening Tool
SARP	Safety and Analysis Report for Packaging
SAP	Sampling and Analysis Plan
SST	Single-Shell Tank
TCP	Tank Characterization Plan
TGA	Thermogravimetric Analysis
TOC	Total Organic Carbon
TWRS	Tank Waste Remediation System
USQ	Unreviewed Safety Question
WHC	Westinghouse Hanford Company

A1.0 SPECIFIC TANK OBJECTIVES

There are four Watch List tank classifications (ferrocyanide, organic, hydrogen/flammable gas, and high heat load). These classifications cover the six safety issues related to public and worker health that have been associated with the Hanford Site underground storage tanks. These safety issues are as follows: ferrocyanide, flammable gas, organic, criticality, high heat, and vapor safety issues (Babad 1992). Tank 241-U-203 is one of 20 tanks on the Organic Salts Watch List. This Sampling and Analysis Plan (SAP) will identify characterization objectives pertaining to sample collection, hot cell sample breakdown, and laboratory analytical evaluation and reporting requirements in accordance with the appropriate DQO documents.

A1.1 RELEVANT SAFETY ISSUES

The organic safety issue arises due to wastes added to SSTs containing quantities of complexants used in waste management operations, as well as degradation products of the complexants and solvents used in fuel reprocessing and metal recovery operations. These waste tanks also contain a presumed stoichiometric excess of sodium nitrite and sodium nitrate that are sufficient to exothermally oxidize the organic compounds in the tank.

The relevant safety issues that are of concern for tanks on the Organic Watch List are as follows:

- The potential for an exothermic reaction occurring from the flammable mixture of organic materials and nitrate/nitrite salts that could result in a release of radioactive material.
- The possibility that other safety issues may exist for the tank.

A1.1.1 Tank U-203 Characterization Objectives

The characterization efforts applicable to this Sampling and Analysis Plan are focused on the relevant safety issues listed above. The Organic Safety Program has identified two key safety questions that should be answered from analytical data on tank U-203 waste are as follows:

- Is the tank SAFE and or does it belong on the Organic Salts Watch List?
- Is the tank CONDITIONALLY SAFE OR UNSAFE?

Based on the answers to these two questions, actions will be identified and implemented to mitigate or remediate the conditions that resulted in classifying the tank as UNSAFE (Babad et al. 1994).

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 U-203, and to ensure that the tank should not be placed on additional Watch Lists.

A1.1.2 Safety Screening and Organic Data Quality Objectives

The sampling and analytical needs associated with organic salts 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 U-203 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) *Tank Safety Screening Data Quality Objective* (Babad and Redus 1994) 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.
- (2) *Data Quality Objective to Support Resolution of the Organic Fuel Rich Tank Safety Issue* (Babad et al. 1994), which describes the sampling and analytical requirements for tanks on the Organics Salts Watch List, including tank U-203.

A1.1.3 Data Quality Objectives Integration

The organic and the safety screening DQO efforts have compatible sampling requirements. At a minimum, two cores samples from widely spaced risers located approximately 180° apart and near the outer edge of the tank must be taken.

The analytical requirements for the safety screening of a tank specify sample analyses to be performed on half-segments, as does the organic DQO. Since the organic DQO specifies homogenized half-segments, the aliquots for safety screening will be also be homogenized.

The analytes identified in the safety screening DQO for the various safety issues are a subset of the suite of the analyses identified in the organic DQO with the exception of analytes measured for the criticality safety issue. If notification limits for immediately reporting of analytes identified in the DQO efforts were conflicting, the most stringent limits of the DQO efforts were used in this Sampling and Analysis Plan.

A2.0 TANK STATUS AND SAMPLING INFORMATION

A2.1 TANK STATUS

Tank U-203 currently contains 11,400 liters (3,000 gallons) of material, consisting of 7,600 liters (2,000 gallons) of sludge and 3,800 liters (1,000 gallons) of supernatant. This volume of waste corresponds to approximately 46 centimeters (18 inches) of waste. Tank U-203 is presently on the Organic Watch List and is passively ventilated with interim stabilization completed in 1978. The tank is classified as sound and intrusion prevention measures were completed in 1982. The latest photograph was taken in June 1989 and shows a dark yellow supernatant surface surrounded by a light yellow sludge peppered with dark material. The highest temperature reading is 68°F (20°C) as of October 1994 (Hanlon 1994).

A2.2 SAMPLING INFORMATION

Tank U-203 is scheduled to be sampled by the core sampling method. One core sample shall be taken from Riser 2 and one core sample shall be taken from Riser 6. If a different riser is necessary to meet the sampling and analysis requirements, this change must be recorded and approved by the cognizant engineer before sampling. The risers used may be recorded on a permanent data sheet or recorded directly in a work package. Based on current records, one segment is expected from each core, and is expected to contain approximately 46 cm (18 inches) of waste material. It should be noted that the sampling objective is to obtain a vertical profile of the waste; therefore, more or less segments may need to be taken depending on the accuracy of the volume estimates. For detailed information regarding the sampling activities, refer to work package WS-95-0035. This document contains operating procedures and the chain of custody records for this sampling event.

Hydrostatic head fluid (HHF) with lithium bromide (LiBr) as a tracer may be used to aid in the collection of core samples. If so, this must be recorded on the chain of custody form and an HHF blank must be prepared as part of the sampling procedure. The blank shall consist of a container filled with HHF (with LiBr tracer) from the same batch of HHF used during the core sampling. It shall be analyzed for Li (and Br, if the Li notification limit is exceeded) in order to determine the concentration of the tracer at the time the core was taken. If HHF is used during the sampling event, only one HHF blank per tank would be required. This blank is required in addition to the field/trip blank (sampler filled with water). For specific information concerning sample handling, custody, and transport, refer to the quality assurance/quality control requirements in Section A4.2.

A3.0 SAMPLE EXTRUSION AND BREAKDOWN INSTRUCTIONS

It should be noted that, in accordance with the Safety and Analysis Report for Packaging (SARP), core samples from tank U-203 must be vented every 47 days from the time of the cask sealing to allow any retained gas to escape.

A3.1 TANK-SPECIFIC ANALYTICAL PROCEDURES

A flowchart depicting the sample breakdown and analysis scheme is presented in Figures A-1, A-2, and A-3. These steps are described in detail to provide the hot cell and laboratory chemists with guidance for the breakdown of the samples and may be altered as appropriate by the performing laboratory. Several analyses listed in Table A-1 require a 45 day reporting time, as noted. The 45-day reporting format, Format III, is explained in Section A7.3.

Any decisions, observations, or deviations and justifications made to this work plan or during the sample breakdown shall be documented in writing. These decisions and observations shall also be reported in the data report. The reporting formats for analyses are contained in Table A-1. If the steps in this flowchart cannot be performed due to insufficient sample, the Characterization Program, Characterization Support, and the Organic Safety Program shall be notified for further direction.

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- Step 1 Receive core segments at the laboratory in accordance with approved procedures.
- Step 2 Conduct the following on the material from each segment:
- Perform a visual examination of the segment(s)
 - Record observations. This may include a sketch of the sample in addition to written documentation of pertinent descriptive information such as color, texture, homogeneity, consistency.
 - Note color and clarity of any drainable liquid.
 - Report sample recovery results to the Organic Safety Program within one working day of sample breakdown.
 - Take color photographs and/or a videotape to visually document the sample.
- Step 3A Does the sample contain any drainable liquid?
- Yes: Proceed to Step 3B
No: Proceed to Step 5
- Step 3B Is the sample 100% drainable liquid?
- Yes: Proceed to Step 11
No: Proceed to Step 4
- Step 4 Separate any drainable liquid from the solids. Measure and record the volume. Retain drainable liquids for further processing.

SOLIDS PATH

- Step 5 Divide each core sample into two subsegments (i.e., half segments).
- Step 6 Homogenize each subsample using the appropriate approved procedure.
- Step 7 Will a homogenization test be performed?
- Yes: Proceed to Step 8
No: Proceed to Step 9
- NOTE:** One subsample per core, at a minimum, should be used if a homogenization test is to be performed. Additional tests may be performed at the laboratory's discretion.
- Step 8 Conduct the homogenization test by taking 1 to 2 g aliquot from widely separated locations of the homogenized subsample. Conduct the homogenization test in accordance with Bell (1993).
- Step 9 Collect sufficient aliquots from each homogenized subsample to perform the appropriate preparations and analyses listed in Table A-1.

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- Step 10 Remove at least 20 mL and up to 40 mL of each homogenized subsample for the archive sample (Bratzel 1994).

LIQUIDS PATH

- Step 11 Closely inspect the liquid sample for the presence and approximate volume of any potential organic layers. Does the sample contain any immiscible (potentially organic) layers?

Yes: Proceed to Step 12A
No: Proceed to Step 13

- Step 12A Report any visually observed immiscible (potential organic) layer immediately by the early notification system (see Section A7.2).

- Step 12B Separate and retain the potential organic layer for possible future analysis.

NOTE: Steps 13 through 17 shall be performed on the remaining (probable aqueous) liquid layer only.

- Step 13 Filter the remaining liquid sample through a 0.45 micron filter.

- Step 14 Is there greater than 1 gram of solid on the filter?

Yes: Proceed to Step 15
No: Proceed to Step 16

- Step 15 Archive the solids for possible future analysis (Bratzel 1994).

- Step 16 Remove sufficient aliquots from the liquid sample to perform the appropriate analyses listed in Table A-1 in duplicate.

- Step 17 Archive at least 20 mL and up to 40 mL of the drainable liquid as the liquid archive (Bratzel 1994).

PRIMARY ANALYSIS PATH

- Step 18 Perform primary analyses as listed in Table A-1.
- Step 19 Compare the primary analysis data with notification limits.
- Step 20A Do the results exceed the notification limits (Table A-1)?
- Yes: Proceed to Step 20B.
No: Proceed to Step 23.
- Step 20B Report results exceeding the notification limits using Format I reporting deliverable requirements as listed in Section A7.2.

SECONDARY ANALYSIS PATH

- Step 21 Perform secondary analyses as listed in Table A-1.
- Step 22A Do the secondary analyses exceed the notification limits?
- Yes: Proceed to Step 22B
No: Proceed to Step 23
- Step 22B Report results exceeding the notification limits using Format I reporting deliverable requirements as listed in Section A7.2.
- Step 23 Report results as listed in Section A7.

A3.2 INSUFFICIENT SAMPLE RECOVERY

If the amount of material recovered from samples taken from tank U-203 is insufficient to perform the analyses requested and to permit a minimum 10 mL archive per sample, the laboratory shall notify the Tank Cognizant Engineer, the Characterization Program Office, and the Organic Safety Program within one working day (See Table A-2). A prioritization of the analyses requested in this document is given in Section A3.3. Any analyses prescribed by this document, but not performed, shall be identified in the appropriate data report, with justification for non-performance.

A3.3 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 A3.1. The priority of an analysis is specified by its designation as a primary or secondary analysis. Further prioritization will be determined by the program on a DQO basis.

Figure A-1: Solid Analysis Flow Chart

LIQUID PATH

Figure A-2: Liquid Analysis Flow Chart

ANALYSIS AND REPORTING PATH

Figure A-3: Sample Analysis and Reporting Flow Chart

A4.0 SPECIFIC ANALYTE, QUALITY ASSURANCE, AND DATA CRITERIA

A4.1 SPECIFIC METHODS AND ANALYSES

The analyses in Table A-1 to be performed on the tank U-203 samples are based on the safety screening and organic DQOs referenced in Section A1.0. The laboratory procedure numbers, which shall be used for the analyses, are included in this table.

A4.2 QUALITY ASSURANCE

A4.2.1 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 samples at the 222-S Laboratory. Additionally, the *Hanford Analytical Services Quality Assurance Plan* (DOE 1994), when implemented (scheduled for August 1995), shall be used as quality assurance requirements.

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-1. If no criteria are provided in Table A-1, the performing laboratory shall perform to its quality assurance plan(s).

A4.2.2 Sample Collection

Two core samples, with an expected one segment each, are to be taken from tank U-203 and shipped to the performing laboratory by Sampling Operations in accordance with work package WS-95-0035. That work package shall also initiate the chain-of-custody for the samples. Approved work procedure T0-080-090 ("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 addition to the data reports.

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

A4.2.3 Sample Custody

The chain-of-custody form is initiated by the sampling team as described in work package WS-95-0035. Samples are shipped in a cask and sealed with a Waste Tank Sample Seal.

WASTE TANK SAMPLE

Supervisor:

Sample No.:

Date of Sampling:

Time of Sampling:

Shipment No.:

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 in the WHC 222-S Laboratory are described in laboratory procedure LO-090-101.

Table A-1: U-203 Chemical, Radiological and Physical Analytical Requirements

SOLID ANALYSES																
Project Name		U-203 Push Core Sample				COMMENTS				REPORTING LEVELS						
Plan Number		WHC-SD-WM-TP-310, REV. 0				Homogenization Test - Per Laboratory Discretion				FORMAT I		Early Notify				
						Field Blank - Required				FORMAT II		Process Control				
PROGRAM		PROGRAM CONTACTS				Hot Cell Blank - Per Laboratory Discretion				FORMAT III		Safety Screen				
A. Safety Screening		Safety Screening								FORMAT IV		Waste Management				
C. Organic		Organic								FORMAT V		RCRA Compliance				
		TWRS				TANK				# CORES		FORMAT VI				
						U-203				2						

¹1/2 SEG SOLID-1/2 segment, solids

²d-direct, f-fusion dissolution, a-acid dissolution, w-water dissolution

³PR-precision, AC-accuracy, ea-each, smpl-sample, DUP-duplicate, SPK/MSD-spike and matrix spike duplicate, AB-analytical batch, PB-preparation blank, N/A-not applicable, mtr-matrix

⁴Units for notification limits and expected range are those listed in the "units" column.

⁵Dry weight basis.

Table A-1: U-203 Chemical, Radiological and Physical Analytical Requirements

- ⁷Tracer or carrier may be used in place of a spike and results corrected for recovery.
- ⁸Either serial dilutions or matrix spikes will be performed.
- ⁹This analysis required if DSC exceeds notification limits. The RSST method, yet to be proceduralized, may be found in WHC-SD-WM-TP-104.
- ¹⁰Performed only if total alpha exceeds notification limit.
- ¹¹These analyses are primary analyses for the organic DQO, but also are secondary analyses for the safety screening DQO. Therefore, if the DSC limit is exceeded, these analyses must be performed and reported within 90 days of receipt of the last sample at the laboratory dock.
- ¹²This analysis required if the energy equivalent of the TOC by hot persulfate is < 75% of the DSC value.
- ¹³This analysis is required if moisture analysis by TGA exceeds the notification limit.
- ¹⁴This analysis is required if the energy equivalent of the TOC assay by hot persulfate is > 125% of the DSC value.
- ¹⁵This analysis is required if the energy equivalent of the TOC assay by furnace combustion is < 75% of the DSC value.
- ¹⁶This analyses is required if the Li exceeds notification limits.
- ¹⁷This analysis to be performed if the chain of custody form indicates that Li was used during sampling.

Table A-1: U-203 Chemical, Radiological and Physical Analytical Requirements

LIQUID ANALYSES																
Project Name				U-203 Push Core Sample				COMMENTS				REPORTING LEVELS				
Plan Number				WHC-SD-WM-TP-310, REV. 0				Homogenization Test - Per Laboratory Discretion				FORMAT I				
				PROGRAM CONTACTS				Field Blank - Required				FORMAT II				
PROGRAM				Safety Screening				E. J. Lipke				FORMAT III				
A. Safety Screening				Organic				D. A. Turner				FORMAT IV				
C. Organic				TWRS				P. Sathyanarayana				FORMAT V				
								TANK				# CORES				
								U-203				2				

Table A-1: U-203 Chemical, Radiological and Physical Analytical Requirements

- 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 weight basis assuming 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.
- ¹⁰RSST performed only if DSC exceeds notification limits. The RSST method, yet to be proceduralized, may be found in WHC-SD-WM-TP-104.
- ¹¹This analysis required if DSC exceeds notification.
- ¹²These analyses are primary analyses for the organic DQO, but also are secondary analyses for the safety screening DQO. Therefore, if the DSC limit is exceeded, these analyses must be performed and reported within 90 days of receipt of the last sample at the laboratory dock.
- ¹³This analysis is required if the energy equivalent of the TOC assay by hot persulfate is > 125% of the DSC value.
- ¹⁴This analysis is required if the energy equivalent of the TOC by hot persulfate is < 75% of the DSC value.
- ¹⁵This analysis is required if the energy equivalent of the TOC assay by furnace oxidation is < 75% of the DSC value.
- ¹⁶This analysis is required if moisture analysis by TGA exceeds the notification limit.
- ¹⁷This analysis is required if the Li exceeds notification limits.
- ¹⁸This analysis is to be performed if the chain of custody form indicates that Li was used during sampling.

A5.0 ORGANIZATION

The organization and responsibility of key personnel involved with this tank U-203 characterization project are listed in Table A-2.

Table A-2: Tank U-203 Project Key Personnel List

Individual	Organization	Responsibility
P. Sathyanarayana	TWRS Characterization Plans and Reports	TWRS Tank U-203 Tank Characterization Plan Cognizant Engineer
E. J. Lipke	WHC Safety Program	Safety Screening Point of Contact
D. A. Turner	Organic Safety Program	Organic Safety Program Manager
West Tank Farm Operations Shift Manager	Tank Farm Operations	200 West Tank Farm Point of Contact if Action Limit is Exceeded (373-3475)

A6.0 EXCEPTIONS, CLARIFICATIONS, AND ASSUMPTIONS**A6.1 EXCEPTIONS TO DQO REQUIREMENTS**

In the safety screening DQO, it is specified that cyanide analyses are to be run on a quarter-sample level and that the notification limit for the DSC analysis is 523 J/g (125 cal/g). However, the revised ferrocyanide DQO has changed the requirements such that the cyanide analysis is now to be run on a half-segment level and the DSC notification limit is 115 cal/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 cyanide is to be run on a half-segment basis and that notification shall be made if the DSC value exceeds 481 J/g (115 cal/g dry weight basis).

In the organic DQO (Babad et al. 1994), ^{137}Cs and ^{90}Sr on half-segments are requested as secondary analyses. However, there are no primary analyses that would require ^{137}Cs or ^{90}Sr to be conducted should a notification limit be exceeded. Therefore, it has been decided by both the Organic Safety Program and the Characterization Program that ^{137}Cs and ^{90}Sr on a half-segment level should not be analyzed.

In the organic DQO, the method of analyses for principal organic species, equilibrium moisture content, and Cr and Mn oxidation states has not been developed at this point. Therefore, if it is necessary to analyze these secondary constituents, archived samples will be used for analyses at a later date.

A6.2 CLARIFICATIONS AND ASSUMPTIONS

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

- Any exotherm (in cal/g or J/g) determined by 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: If there is greater than 90 percent water in a sample, converting to a dry weight basis may lead to a large error in the DSC value. However, the conversion is still required.

- The safety screening DQO (Babad and Redus 1994) requires that additional analyses be performed if total alpha activity measures greater than 1 g/L. However, total alpha is measured in $\mu\text{Ci/g}$ by the laboratory 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 (2):

$$\left(\frac{1 \text{ g}}{\text{L}} \right) \left(\frac{1 \text{ L}}{10^3 \text{ mL}} \right) \left(\frac{1}{\text{density}} \frac{\text{mL}}{\text{g}} \right) \left(\frac{0.0615 \text{ Ci}}{1 \text{ g}} \right) \left(\frac{10^6 \mu\text{Ci}}{1 \text{ Ci}} \right) = \frac{61.5}{\text{density}} \frac{\mu\text{Ci}}{\text{g}} \quad (2)$$

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

- Neither the safety screening nor the organic DQOs, upon which the analyses in Table A-1 are based, sufficiently addresses the analyses of any drainable liquid present. In order to characterize the tank waste adequately, all analyses performed on the solids for the safety screening and organic DQOs, with the exception of total alpha analyses, shall also be performed on any drainable liquids and the field blank.
- None of the DQOs, upon which the analyses in Table A-1 are based, address the analyses performed on the field blank. To adequately determine if contamination of the sample material has occurred, the field blank shall be analyzed for those analyses done on the segment level liquid samples.

- In the organic DQO it is unclear as to when secondary analyses are to be run. Whether or not a secondary DQO is run depends on the comparison between the value of the energy equivalent for TOC, "X", and the DSC energetics value. The energy equivalent of TOC is given in equation (3).

$$X = (\text{wt\% TOC dry weight basis}) * \frac{151 \text{ cal/g}}{5} \quad (3)$$

NOTE: 151 cal/g represents the energy equivalent of 5 wt% TOC (based on sodium acetate average energetics standard).

Secondary analyses for the Organic Safety Program are run on half-segments based on this equation. Therefore the following rules apply:

- ▶ If X by hot persulfate is $\leq$ 75% of the DSC value, run TOC by furnace combustion on the half-segment.
- ▶ If X by hot persulfate is $\geq$ 125% of the DSC value, run nitrite, nitrate, and hydroxide analyses on the half-segment.
- ▶ If X by furnace combustion is $\leq$ 75% of the DSC, analyze for the presence of Mn and Cr on the half-segment.

A7.0 DELIVERABLES

All analyses of tank U-203 waste material shall be reported as Formats I, III or IV as indicated in Table A-1. Additional information regarding reporting formats is given in Schreiber (1994a).

A7.1 PROGRESS REPORTS

Each laboratory performing analyses on tank U-203 waste material from this 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 U-203, 2) preliminary results 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. Monthly variances greater than 10% and \$10,000, and accumulative 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

A7.2 FORMAT I REPORTING

Table A-1 contains the notification limits for each analyte. Any results exceeding their notification limits shall be reported by calling the West Tank Farm Operations Shift Manager at 373-3475 and the Characterization Program Office (Schreiber 1994b). This verbal notification must be followed within 1 working day by written communication, documenting the observations, to the Organic Safety Program, Characterization Plans and Reports, the Characterization Program Office, Safety Screening Representative, and Process Control. Points of contact within each program/project are defined by Schreiber (1995). 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 memorandum of understanding.

A7.3 FORMAT III REPORTING

A Format III report, reporting the results of the primary safety screen analyses shall be issued to the Safety Screening Representative, Characterization Program Office, Los Alamos Technical Associates (LATA), Tank Characterization Resource Center, Process Control, Characterization Plans and Reports, and the Tank Characterization Database representative 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 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).

A7.3 FORMAT IV REPORTING

Analytical results requested for the characterization project of tank U-203 shall be compiled into a Format IV type data package. The data package shall be provided to Analytical Services, Organic Safety Program, Los Alamos Technical Associates, the Tank Characterization Resource Center, and the Characterization Program within 216 days of the sampling event. Detailed information regarding the contents of this reporting format are given in (Schreiber 1994a).

In addition to this data package, an electronic version of the analytical results shall be provided to the Tank Characterization Database representative. The data must be available to the Washington State Department of Ecology within 216 days of the sampling event, so this electronic copy must be sent at the time of data package delivery or within 209 days of the sampling event, whichever is earlier, to allow time for data entry. The electronic version shall be in the standard electronic format specified in (Bobrowski 1994).

A8.0 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 through the use of internal characterization change notices or analytical deviation reports for minor low-impact changes and documented in applicable laboratory reports. 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 report.

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

A9.0 REFERENCES

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Figure 1 shows 12 resolution test charts arranged in a 4x3 grid. Each chart consists of a 5x5 grid of horizontal and vertical lines. The top-left chart is labeled '1.0' and has a resolution of 1.0 mm. The top-right chart is labeled '2.8' and has a resolution of 2.8 mm. The middle-left chart is labeled '1.1' and has a resolution of 1.1 mm. The middle-right chart is labeled '4.0' and has a resolution of 4.0 mm. The bottom-left chart is labeled '1.25' and has a resolution of 1.25 mm. The bottom-right chart is labeled '1.6' and has a resolution of 1.6 mm. The charts are labeled with their resolution values in mm and their corresponding line widths in mm.

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