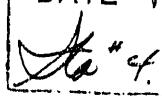


1 of 1

SUPPORTING DOCUMENT		1. Total Pages 72
2. Title Fiscal Year 1995 Tank Waste Remediation System Tank Waste Analysis Plan	3. Number WHC-SD-WM-PLN-091	4. Rev No. CA
5. Key Words CHARACTERIZATION, DQO, SAFETY, TANK CHARACTERIZATION PLAN, TANK CHARACTERIZATION REPORT, SAMPLING, ANALYSIS, TRI-PARTY AGREEMENT	6. Author Name: T. H. Dove <u>T. H. Dove 11/01/99</u> Signature	
7. Abstract This change clarifies the references required to prepare process development Tank Characterization Plans and to comply with reporting format requirements.	Organization/Charge Code 7E720/N4169	
DISCLAIMER		
<p>This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.</p>		
8. RELEASE STAMP <div style="border: 1px solid black; padding: 5px; text-align: center;"> OFFICIAL RELEASE (2) BY WHC DATE NOV 01 1994  </div>		

an analysis for percent water on a core sample at the segment level with a 20% accuracy while another relevant DQO may specify that the same analyte be measured on quarter segments with 10% accuracy. The TCP must then direct that percent water be measured on quarter segments with 10% accuracy.

5.3 TANK CHARACTERIZATION PLAN OUTLINE

The following is an outline of the TCP along with a brief description of each major section.

1. **Specific Tank Objectives.** This section shall identify the specific processes and safety or regulatory issues that relate to the characterization data to be gathered from this tank. This information should be available in the applicable DQO documents. The specific reasons for analyzing the tank waste shall be described, the appropriate DQO efforts shall be referenced, and how these DQO efforts were integrated into the TCP shall be explained. When preparing TCPs for process development sampling and analysis, the objectives may be provided through process memos and/or test plans in lieu of DQO efforts. The recommended outline for preparing a process development TCP is illustrated in *Tank 241-AN-107 Tank Characterization Plan* (Schreiber 1994a). The TCP should clearly identify the safety criteria, regulatory compliance, and process criteria that are important to decisions to be made from the data.
2. **Tank, Waste, and Sampling Information.** A summary of information describing the tank being analyzed is provided here. Information about the age, expected contents of the tank based on the tank's fill history, and the risers used for sampling shall be described or referenced. Note that the information about the age and expected tank contents exists in the respective tank characterization report, if it has been prepared. The amount and type (hardness and chemical composition) of waste in the tank shall be described or referenced. The number of cores, segments, potential layers, and expected recoveries shall be discussed. The sampling procedure(s) and/or work package, and the use of any hydrostatic head fluid or tracer shall be identified. The requirements for transporting samples to the laboratory shall also be specified.
3. **Sample Extrusion/Removal or Receiving Instructions.** The TCP shall describe the sample extrusion/removal and breakdown instructions to be used. The following items shall be identified or provided. Except for the fourth and last items, this information should be available in the applicable DQO documents.
 - Special observations (such as potential organic layers or solids) that are important during sample extrusion or removal
 - Samples to be taken before storage or homogenization

7. **Deliverables.** The deliverables resulting from the characterization shall be specified in this section. The TCP shall clearly identify the notification limits for each analyte, whom shall be notified, the method of notification, and any other follow-up activities that may be required. Reporting format guidance is provided in Revised Interim Tank Characterization Plan Guidance (Schreiber 1994b).
8. **References.** The TCP shall have a reference section that identifies all the appropriate program and laboratory documents that are used to support the characterization of the tank.

5.4 TANK CHARACTERIZATION PLAN EXEMPTIONS

All sampling and analysis of tank waste shall be supported by approved TCPs with the exceptions described below. Sampling and analysis activities not supported by TCPs shall be supported by letters of instruction or test plans.

5.4.1 Emergency Sampling Events

Emergency sampling events are defined at the discretion of the Characterization Program Manager, Field Sampling and Equipment. Normally, emergencies are based on tank conditions that exceed or may exceed the boundaries specified in operational safety requirements. These sampling events shall be placed at the top of the Sampling Schedule. Letters of instruction or TCPs shall be used to direct laboratory work.

5.4.2 Prior Agreements

Agreements may be made in advance to perform certain sampling and analysis activities without a TCP. Examples may include sampling and analysis contracted in a pre-existing Statement of Work.

5.5 TANK CHARACTERIZATION PLANS ISSUED IN FISCAL YEAR 1995

The FY 1995 Integrated Sampling Schedule details the tanks for which TCPs will be prepared and the required date of approval for FY 1995. It includes sampling from the 149 SSTs and 28 DSTs. Because of the commitment to comply with Recommendation 93-5, the majority of tanks to be core sampled in FY 1995 are Watch List tanks. The following assumptions were made in the preparation of the TCP schedule (1) The Sampling Schedule will be followed. (2) Writing and approval of each TCP will be accomplished in thirty calendar days. (3) There will exist adequate staff and funding to support TCP preparation.

WHC-SD-WM-PLN-091, REV. 0A
FY 1995 Tank Waste Analysis Plan

McDuffie, N. G., G. D. Johnson, 1994, *Flammable Gas Safety Program: Data Requirements for the Flammable Gas Safety Issue Developed through the Data Quality Objectives (DQO) Process*, WHC-SD-WM-DQO-004, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Meacham, J. E., R. J. Cash, G. T. Dukelow, and H. Babad, 1994, *Data Requirements for the Ferrocyanide Safety Issue Developed through the Data Quality Objectives Process*, WHC-SD-WM-DQO-007, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Osborne, J. W., 1994a, Vapor Sampling Program Plan (in preparation).

Osborne, J. W.; J. L. Huckaby, and E. R. Hewitt, 1994, *Data Quality Objectives for Generic In-Tank Health and Safety Vapor Issue Resolution*, WHC-SD-WM-DQO-002, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Price, D. N., 1994, *Rotary Core Vapor Sampling Data Quality Objective*, WHC-SD-WM-SP-003, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Resource Conservation and Recovery Act of 1976, 42 U.S.C. 6901, et seq.

Schreiber, R. D., 1994a, *Tank 241-AN-107 Tank Characterization Plan*, WHC-SD-WM-TP-215 REV 0, Westinghouse Hanford Company, Richland, Washington.

Schreiber, R. D., 1994b, Letter to C. S. Haller, "Revised Interim Tank Characterization Plan Guidance," 7E720-94-121, dated May 13, 1994.

Suydam, C. D., 1993, *Quality Assurance Project Plan for Waste Tank Vapor Characterization*, WHC-EP-0708, Westinghouse Hanford Company, Richland, Washington.

Wang, O. S., K. E. Bell, C. M. Anderson, M. S. Peffers, B. A. Pulsipher, J. L. Scott, 1994, *Tank 241-C-106 Sampling Data Requirements Developed Through the Data Quality Objectives (DQO) Process*, WHC-EP-0723, Westinghouse Hanford Company, Richland, Washington.

WHC, 1994, *TWRS Characterization Sample and Analysis Scheduling Procedure*, WHC-IP-0842, Rev. 0, Section 10.9, Westinghouse Hanford Company, Richland, Washington.

Whelan, T. E., 1994, *TWRS Characterization Program Quality Assurance Plan*, WHC-SD-WM-QAPP-025, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Wood, T. W., C. E. Willingham, and J. A. Campbell, 1993, *Organic Layer Sampling for SST 241-C-103 Background, and Data Quality Objectives, and Analytical Plan*, PNL-8871, UC-510, Battelle Memorial Institute, Richland, Washington.

AUG 30 1994

ENGINEERING DATA TRANSMITTAL

Original Destroyed New Original

Page 1 of 1
608057

2. To: (Receiving Organization) TWRS PROGRAM OFFICE	3. From: (Originating Organization) TWRS/CHARACTERIZATION SUPPORT	4. Related EDT No.: N/A
5. Proj./Prog./Dept./Div.: TWRS ENG/CHAR SUPPORT	6. Cog. Engr.: T. H. DOVE	7. Purchase Order No.: N/A
8. Originator Remarks: N/A		9. Equip./Component No.: N/A
		10. System/Bldg./Facility: 2750E/200E
11. Receiver Remarks: —		12. Major Assm. Dwg. No.: N/A
		13. Permit/Permit Application No.: N/A
		14. Required Response Date: 08/31/94

DATA TRANSMITTED					(F)	(G)	(H)	(I)
(A) Item No.	(B) Document/Drawing No.	(C) Sheet No.	(D) Rev. No.	(E) Title or Description of Data Transmitted	Approval Design- ator	Reason for Trans- mittal	Origin- ator Dispo- sition	Receiv- er Dispo- sition
1	WHC-SD-WM-PLN-091		0	FISCAL YEAR 1995 TANK WASTE REMEDIATION SYSTEM TANK WASTE ANALYSIS PLAN	N/A	1	1	

16.

KEY

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

SIGNATURE/DISTRIBUTION (See Approval Designator for required signatures)												
(G)	(H)	17.	(J) Name	(K) Signature	(L) Date	(M) MSIN	(J) Name	(K) Signature	(L) Date	(M) MSIN	(G)	(H)
Reason	Disp.										Reason	Disp.
1	1	Cog. Eng.	T. H. DOVE	<i>T. H. DOVE 8/30/94</i>	R2-12		Central Files			L8-04	3	
1	1	Cog. Mgr.	C. S. HALLER	<i>C. S. HALLER</i>	R2-12		OSTI (2)			L8-07	3	
		QA										
		Safety										
		Env.										

18. <i>T. H. DOVE</i> T. H. DOVE Signature of EDT Originator	19. <i>S. J. EBERLEIN</i> S. J. EBERLEIN Authorized Representative for Receiving Organization	20. <i>C. S. HALLER</i> C. S. HALLER Cognizant Manager	21. DOE APPROVAL (if required) Ctrl. No. <input type="checkbox"/> Approved <input type="checkbox"/> Approved w/comments <input type="checkbox"/> Disapproved w/comments
--	---	---	---

RELEASE AUTHORIZATION

Document Number: WHC-SD-WM-PLN-091 Revision 0

Document Title: Fiscal Year 1995 Tank Waste Remediation System Tank Waste Analysis Plan

Release Date: 08-30-94

* * * * *

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

APPROVED FOR PUBLIC RELEASE

* * * * *

WHC Information Release Administration Specialist:



Kara Broz

(Signature)

08-30-94

(Date)

SUPPORTING DOCUMENT		1. Total Pages 72
2. Title Fiscal Year 1995 Tank Waste Remediation System Tank Waste Analysis Plan	3. Number WHC-SD-WM-PLN-091	4. Rev No. 0
5. Key Words CHARACTERIZATION, DQO, SAFETY, TANK CHARACTERIZATION PLAN, TANK CHARACTERIZATION REPORT, SAMPLING, ANALYSIS, TRI-PARTY AGREEMENT <i>KMB 8/30/94</i>	6. Author Name: C. S. HALLER <i>C. Haller</i> 8/30/94 Signature	
7. Abstract This document lays the groundwork for preparing and implementing the TWRS tank waste analysis planning and reporting for Fiscal Year 1995. This Tank Waste Characterization Plan meets the requirements specified in the Hanford Federal Facility Agreement and Consent Order, better known as the Tri-Party Agreement.		
8. PURPOSE AND USE OF DOCUMENT - This document was prepared for use within the U.S. Department of Energy and its contractors. It is to be used only to perform, direct, or integrate work under U.S. Department of Energy contracts. This document is not approved for public release until reviewed. PATENT STATUS - This document copy, since it is transmitted in advance of patent clearance, is made available in confidence solely for use in performance of work under contracts with the U.S. Department of Energy. This document is not to be published nor its contents otherwise disseminated or used for purposes other than specified above before patent approval for such release or use has been secured, upon request, from the Patent Counsel, U.S. Department of Energy Field Office, Richland, WA.	10. RELEASE STAMP <div style="border: 1px solid black; padding: 5px; text-align: center;">OFFICIAL RELEASE BY WHC DATE AUG 30 1994 <i>data 4</i></div>	
9. Impact Level NA		

**Fiscal Year 1995
Tank Waste
Remediation System
Tank Waste
Analysis Plan**

**C. S. Haller,
Westinghouse Hanford Company**

CONTENTS

1.0	INTRODUCTION	1-1
1.1	PURPOSE	1-1
1.2	SCOPE	1-1
1.2.1	Regulatory Concerns	1-2
1.3	OBJECTIVES	1-2
1.4	TWRS PROGRAMMATIC NEEDS	1-3
1.4.1	Waste Tank Safety Program	1-5
1.4.2	Low-Level Waste Disposal	1-5
1.4.3	High-Level Waste Disposal	1-5
1.4.4	Waste Pretreatment	1-5
1.4.5	Waste Retrieval	1-6
1.4.6	Tank Farm Operations and Maintenance	1-6
1.4.7	Tank Farm Upgrades Program	1-7
1.5	CHARACTERIZATION PLANNING DOCUMENT HIERARCHY	1-7
1.6	ASSUMPTIONS	1-9
1.7	CHARACTERIZATION DRIVERS	1-9
2.0	TWRS SAMPLING METHODS	2-1
2.1	SAMPLING WORK PACKAGES	2-1
2.2	SAMPLING METHODOLOGIES	2-1
2.2.1	Core Samples	2-1
2.2.2	Auger Samples	2-1
2.2.3	Supernate and Soft Slurry Grab Samples	2-2
2.2.4	Vapor Sampling	2-2
3.0	FISCAL YEAR 1995 SAMPLING SCHEDULE	3-1
3.1	SAMPLING PRIORITY LIST	3-1
3.2	SAMPLING SCHEDULE	3-1
3.2.1	Scheduling Constraints	3-1
4.0	DQO-BASED CHARACTERIZATION REQUIREMENTS	4-1
4.1	DQO EFFORTS AND TYPES	4-1
4.2	MODULAR APPROACH TO SAMPLING AND ANALYSIS	4-1
4.2.1	Accuracy and Precision Requirements	4-4
4.3	DQO-BASED SAMPLING AND ANALYTICAL REQUIREMENTS	4-4
4.3.1	Ferrocyanide Safety Issue DQO Effort	4-4
4.3.2	High-Heat Safety Issue DQO Effort	4-5
4.3.3	Tank Safety Screening Data Quality Objectives	4-5
4.3.4	Waste Compatibility Data Quality Objectives	4-6
4.3.5	Flammable Gas Tanks Crust Burn Issue Data Quality Objectives	4-6
4.3.6	Data Quality Objectives for Organic Layer Sampling of Tank C-103	4-6
4.3.7	Rotary Core Vapor Sampling Data Quality Objective	4-7
4.3.8	Organic Fuel-Rich Tank Data Quality Objective	4-7
4.3.9	Tank C-103 Vapor and Gas Sampling Data Quality Objectives	4-7
4.3.10	Generic Tank Vapor Issue Resolution Data Quality Objectives	4-8

WHC-SD-WM-PLN-091, REV. 0
FY 1995 Tank Waste Analysis Plan

4.3.11	Flammable Gas Safety Issue Data Quality Objectives	4-8
4.3.12	Waste Tank Retrieval Data Quality Objectives	4-8
4.3.13	RCRA Part B Permit Application Data Quality Objectives	4-9
4.3.14	Evaporator Operations Data Quality Objectives	4-9
4.3.15	Waste Tank Pretreatment Data Quality Objectives	4-9
4.3.16	High-Level and Low-Level Waste Feed Data Quality Objectives	4-9
4.3.17	Solid, Low-Level Waste Disposal Data Quality Objectives	4-9
4.3.18	Process Control Data Quality Objectives	4-9
5.0	TANK CHARACTERIZATION PLANS	5-1
5.1	TANK CHARACTERIZATION PLAN REQUIREMENTS	5-1
5.2	TANK CHARACTERIZATION PLAN PREPARATION	5-1
5.3	TANK CHARACTERIZATION PLAN OUTLINE	5-2
5.4	TANK CHARACTERIZATION PLAN EXEMPTIONS	5-4
5.4.1	Emergency Sampling Events	5-4
5.4.2	Prior Agreements	5-4
5.5	TANK CHARACTERIZATION PLANS ISSUED IN FISCAL YEAR 1995	5-4
6.0	TANK CHARACTERIZATION REPORT DELIVERABLES	6-1
6.1	INTRODUCTION	6-1
6.2	GENERAL TANK CHARACTERIZATION REPORT OUTLINE	6-1
6.2.1	Executive Summary	6-2
6.2.2	Introduction	6-2
6.2.3	Historical Tank Information	6-2
6.2.4	Sampling	6-4
6.2.5	Description of Sample Handling and Analytical Scheme	6-4
6.2.6	Sample Extrusion/Removal and Preparation	6-5
6.2.7	Interpretation of Analytical Results	6-6
6.2.8	Statiscal Interpretation of the Data	6-7
6.2.9	Conclusions and Recommendations	6-8
6.2.10	References	6-8
6.3	TRI-PARTY AGREEMENT REQUIREMENTS	6-9
6.4	TANK CHARACTERIZATION REPORT DELIVERY CONSTRAINTS	6-10
7.0	REFERENCES	7-1

LIST OF FIGURES

Figure 1.	TWRS FY 1995 Work Breakdown Structure	1-4
Figure 2.	TWRS Characterization Document Hierarchy	1-8

WHC-SD-WM-PLN-091, REV. 0
FY 1995 Tank Waste Analysis Plan

LIST OF TABLES

3-1	FY 1995 Forecasted Sampling-Related Activities	3-2
4-1	TWRS DQO Efforts	4-3
4-2	DQO-Based Analytical Requirements for Ferrocyanide Watch List Tanks	4-11
4-3	DQO-Based Analytical Requirements for Tank C-106	4-12
4-4	DQO-Based Analytical Requirements for Tank Safety Screening	4-15
4-5	DQO-Based Analytical Requirements for Waste Compatibility	4-17
4-6	DQO-Based Analytical Requirements for the Flammable Gas Tank Curst Burn Safety Issue	4-20
4-7	Rotary Core Vapor Sampling DQO-Based Analytical Requirements	4-22
4-8	DQO-Based Analytical Requirements for Organic Fuel Rich Tanks	4-24
4-9	DQO-Based Analytical Requirements for Generic Tank Vapor Sampling	4-27
4-10	DQO-Based Analytical Requirements for Flammable Gas Tanks	4-28
6-1	Tank Characterization Report-Related Tri-Party Agreement Milestones	6-9
6-2	Specific Tank Characterization Report Deliverables by Tank for FY 1995	6-10
6-3	Data Analysis Schedule	6-10

LIST OF TERMS

Acc	accuracy
ACL	Analytical Chemistry Laboratory
AEA	Alpha Energy Analysis
DNFSB	Defense Nuclear Facilities Safety Board
DOE	U.S. Department of Energy
DQO	Data Quality Objective
DSC	Differential Scanning Calorimetry
DST	Double-Shell Tank
EPA	U.S. Environmental Protection Agency
FY	Fiscal Year
GC/MS	Gas Chromatography/Mass Spectroscopy
GEA	Gamma Energy Analysis
HPLC	High-Performance Liquid Chromatography
IC	Ion Chromatography
ICP	Inductively Coupled Plasma
LFL	Lower Flammability Limit
NEPA	National Environmental Policy Act
OES	Optical Emission Spectroscopy
PNL	Pacific Northwest Laboratory
Pre	Precision
PQL	Practical Quantitation Limit
QA	Quality Assurance
QC	Quality Control
RCRA	Resource Conservation and Recovery Act
RPD	Relative Percent Difference
RSST	Reactive System Screening Tool
SST	Single-Shell Tank
TBD	To Be Determined

WHC-SD-WM-PLN-091, REV. 0
FY 1995 Tank Waste Analysis Plan

TCP Tank Characterization Plan
TGA Thermalgravimetric Analysis
TIC Total Inorganic Carbon
TRAC Track Radioactive Constituents (computer program)
TWRS Tank Waste Remediation System
WHC Westinghouse Hanford Company

1.0 INTRODUCTION

This fiscal year (FY) 1995 *Tank Waste Analysis Plan* is the guidance document that lays the groundwork for preparing and implementing the documentation that provides for efficient characterization planning. It meets the requirements specified in the *Hanford Federal Facility Agreement and Consent Order* (Ecology et al. 1994), better known as the Tri-Party Agreement. The Tri-Party Agreement requires that the *Tank Waste Analysis Plan*

- establish the framework and process for conducting characterization of all tank waste
- covers safety, retrieval, pretreatment, and other processing needs
- identify sampling and analysis activities projected for the following fiscal year
- describe the Tank Characterization Plans (TCPs) to be issued for the year
- identify the following year's Tank Characterization Reports to be submitted
- specify the contents of the Tank Characterization Reports.

1.1 PURPOSE

The primary purpose of this document is to direct the integrated, DQO-based sampling and analysis of waste tank samples through TCPs. It provides guidance to the authors of the TCPs on content and format; furnishing a template for the common elements found in all TCPs and providing for the incorporation of tank-specific information derived from the DQO process. It also provides an orderly and cost-effective means of generating the large number of these planning documents, which define the characterization activities necessary for safely storing, maintaining, treating, and disposing onsite, or packaging for offsite disposal, all tank waste.

This *Tank Waste Analysis Plan* is not intended to fulfill all the regulatory requirements of the *Hanford Resource Conservation and Recovery Act (RCRA) Part B* permitting process for waste sampling and analysis plans. When such plans are required, they will be generated in a manner consistent with the *Tank Waste Analysis Plan*, TCPs, and supplemented with any necessary additional information.

1.2 SCOPE

This FY 1995 *Tank Waste Analysis Plan* details sampling and analysis activities performed in FY 1995 and is updated at least annually as required by the Tri-Party Agreement. Significant programmatic changes will result in controlled revisions of this document.

No distinctions are made between the characterization planning demands for single-shell tanks (SSTs), double-shell tanks (DSTs), or the various waste tank sample types. Sampling and analysis activities are prioritized into three groups: safety, compliance, and waste treatment/disposal. The highest near-term priority for the Tank Waste Remediation System (TWRS) Characterization Program is the sampling and analysis of those tanks with unreviewed safety questions and other safety issues.

The current waste tank sampling and analysis strategy employs waste tank safety screening. The purpose of the safety screening is to screen the 177 DSTs and SSTs for imminent safety concerns in accordance with the *Defense Nuclear Facilities Safety Board (DNFSB) Recommendation 93-5* (Conway 1993). Other sampling and analysis activities covered under the tank safety category are waste compatibility assessments with respect to SST stabilization activities and other tank farm activities such as tank 241-SY-101 mixer pump operation, monitoring equipment maintenance or installation, or water addition to tank 241-C-106. The compliance category covers activities such as 242-A Evaporator feed tank sampling and analysis, emergency pumping of SSTs, DST RCRA sampling and analysis, certain vapor sampling activities, (See Section 2.2.4.) or Tri-Party Agreement compliance. Waste Treatment/Disposal covers those sampling and analysis activities associated with retrieval, pretreatment, and the low-level or high-level vitrification of the tank waste.

1.2.1 Regulatory Concerns

The regulatory issues associated with evaporator feed samples, DST RCRA samples, and SST emergency pumping supernate samples are discussed in each respective Waste Analysis Plan or DQO document. Each TCP will identify the regulatory issues as they relate to laboratory analyses.

The decision, adopted by TWRS, to retrieve all tank wastes has eliminated the need for analyses that support leaving the tank wastes in place. The emphasis of tank waste analysis is on mitigation/resolution of the waste tank safety issues and technology development to support retrieval, pretreatment, and final disposal of the tank wastes, as described in Section 1.3. Thus, most waste tank analytical data is collected in support of these activities.

There are significant technical and logistical challenges involved in obtaining and analyzing waste tank samples, which make strict adherence to regulatory analytical methods difficult or unsafe. These regulatory methods are often inappropriate for the tank waste matrices and therefore must be modified. To protect worker health, to comply with the many regulations regarding the handling and storage of mixed-waste materials, and to recognize the constraints of time and analytical resources, sampling and analysis limitations must be accommodated.

1.3 OBJECTIVES

The objectives of this *Tank Waste Analysis Plan* are to:

- Integrate and centralize in one document, the waste tank sampling and analytical requirements of all the TWRS program elements. The DQO planning process is the principle means for identifying these requirements.
- Standardize the procurement of tank samples and analytical services (provide a standard logistics path).
- Establish or describe waste tank sample prioritization.
- Provide the basis for a primary interface document (the TCP) between the Characterization Program and the laboratories.
- Be consistent with the systems engineering functions and requirements process.

This document only covers sampling and analysis of waste tank samples for the purposes identified in this document, and does not cover sampling or analysis of wastes generated from any waste tank sampling or analysis activity, or from leaks, spills, or releases from the waste tanks.

The first objective above is maintained as the TWRS program elements update and revise their respective DQO efforts. This document mandates that each TCP address all DQO efforts applicable to that tank sampling event, and that all DQO efforts identified are referenced. This is compliant with the Tri-Party Agreement requirement to use the DQO planning process for identifying sampling and analysis activities. This compels the TWRS program elements to formally identify their needs to ensure that they will be met.

Following is a brief description of this document, which when implemented, will meet the objectives and requirements cited above. Section 1.0 describes the characterization document hierarchy followed by a brief description of the various TWRS programmatic needs. Sampling methods are described in Section 2.0, after which the tank scheduling and prioritization process is discussed in Section 3.0. Section 4.0 summarizes the DQO-based characterization requirements and Section 5.0 describes how each TCP is a tank-specific sampling and analysis plan that melds these DQO requirements into a single document that the performing laboratories use to perform all necessary analyses. Section 6.0 provides guidance as to Tank Characterization Report content and summarizes the Tank Characterization Report deliverables as required by the Tri-Party Agreement.

1.4 TWRS PROGRAMMATIC NEEDS

The TWRS program is divided into eleven program elements as shown in Figure 1. Presently, only seven of these program elements have data needs that are addressed in this plan. In order to fulfill their data needs, these program elements must establish, or have established, their sampling and

TWRS PROGRAM FY 1995 WORK BREAKDOWN STRUCTURE

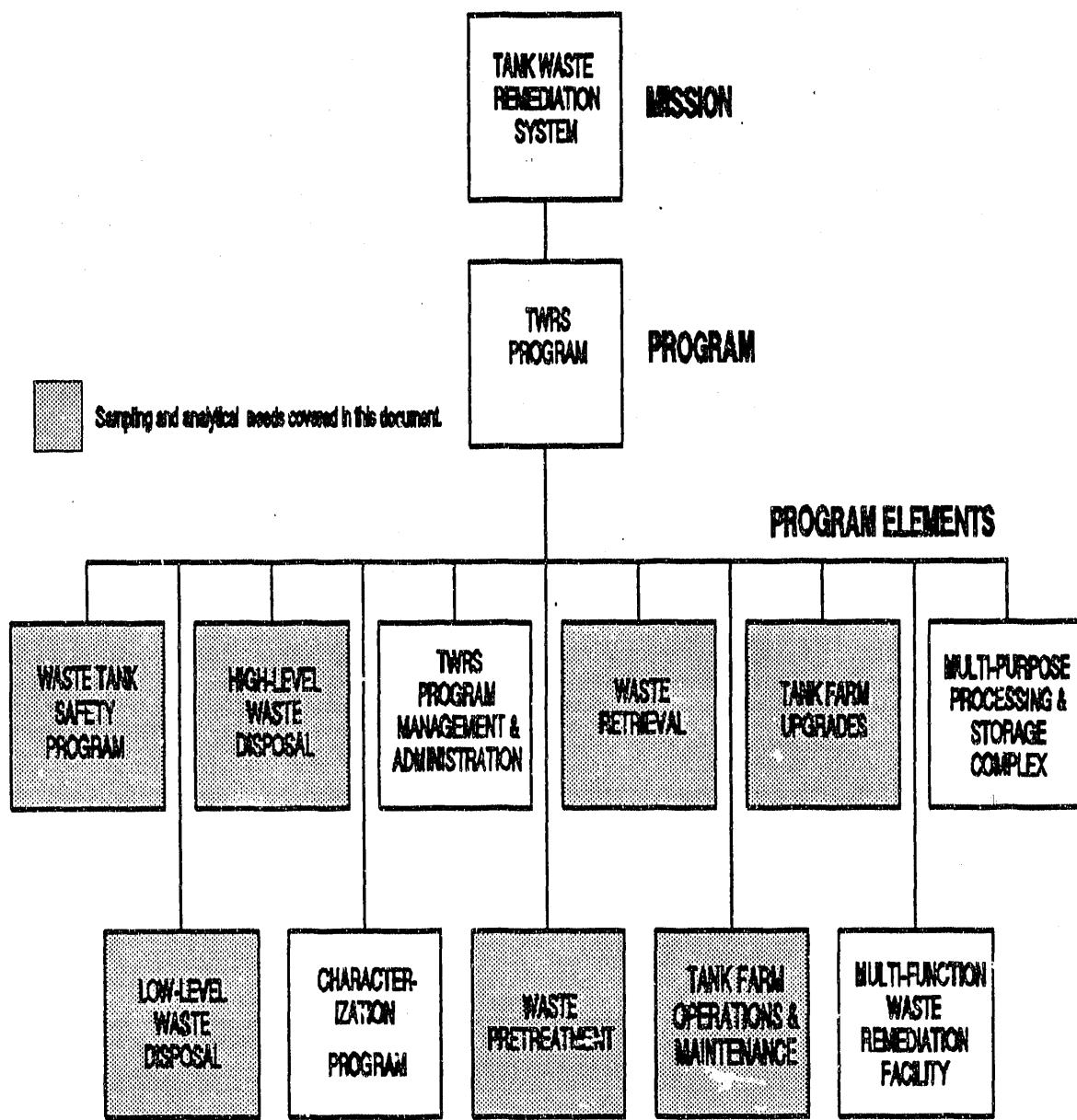


Figure 1. TWRS FY 1995 Work Breakdown Structure

analytical requirements in a DQO document or waste analysis plan. This section provides a brief description of these TWRS program elements and the types of characterization information required to support their activities.

1.4.1 Waste Tank Safety Program

This program element requires characterization data to address unreviewed safety questions or other tank safety issues including flammable gas, ferrocyanide, criticality, organics, high-heat, and noxious vapors. This program element includes safety issues associated with other underground storage tanks in addition to the 177 SSTs and DSTs. The sampling needs for Safety include core, auger, vapor space, and grab sampling.

1.4.2 Low-Level Waste Disposal

This program element was formed as a replacement for the eliminated grout disposal option. The planned replacement is a low-level waste vitrification plant. The characterization needs of this program element are being defined, although it is anticipated that their needs will include tank waste samples necessary to develop proper low-level feed formulation for product qualification and for waste compatibility evaluation of waste transfer to a feed tank. It is expected that safety screening and other sampling efforts will contribute data of useable value to this program element.

1.4.3 High-Level Waste Disposal

The needs of this program element include characterization requirements for process development, process control, and regulatory compliance of high-level waste disposal systems. The process development effort uses waste samples from tanks to provide bounding design criteria. Further process development testing will be performed on pretreated waste materials that are candidates for Hanford Waste Vitrification Plant feed to determine their suitability for vitrification or if further pretreatment is necessary. The laboratory will analyze process control samples of vitrified waste in its final disposal form to optimize certain glass properties and the glass manufacturing process. The vitrified waste will also be analyzed to ensure its compliance with applicable environmental regulations.

1.4.4 Waste Pretreatment

This program element has characterization requirements primarily for technology development. Separation processes are being developed to divide the waste into high-level, low-level, and transuranic fractions. The high-level and transuranic fractions are to be vitrified in the high-level waste vitrification plant, and the low-level waste is to be vitrified in the low-level vitrification facility. The pretreatment process must be able to produce feed streams that satisfy the operating requirements of both facilities. Optimization of the separation process is also necessary to reduce the amount of vitrified waste and, ultimately, the cost of final

disposal. The technology development effort requires comprehensive physical and chemical information from waste tank samples.

1.4.5 Waste Retrieval

Technology development, process control, and equipment design activities determine the characterization requirements of this program element. Several different retrieval methods, including development of the long reach manipulator system, are being considered to remove the waste from the tanks safely and with minimal intrusion/disruption to the tank environment. For process control purposes, Waste Retrieval needs extensive physical and rheological data from core samples on the wastes' mechanical behavior. These data are also important for equipment design to support planned retrieval by sluicing. In situ measurement systems are the preferred route, but sampling and laboratory analysis is currently used.

1.4.6 Tank Farm Operations and Maintenance

This program element includes characterization requirements for evaporator feed characterization, waste compatibility, regulatory compliance, and solid, low-level waste disposal.

- Characterization is performed on grab samples from evaporator candidate feed tanks to determine their suitability for treatment. Evaporator process control samples such as concentrated waste, ventilation samples, process condensate, steam condensate, and cooling water are characterized to ensure optimal operation of the evaporator; however, the characterization of these samples is not covered in this plan. The only evaporator samples covered in this plan are candidate evaporator feed tank samples.
- Waste analyses are conducted on liquid and/or sludge process samples obtained from SSTs and DSTs to support waste transfers and emergency pumping preparations. A DST must be designated as the receiving tank of SST liquid should the SST be declared an assumed leaker. The program requests that these samples be taken and analyzed in advance to reduce pumping delays. Process samples are also analyzed to support in-tank operations.
- RCRA samples are characterized to ensure that Westinghouse Hanford Company (WHC) is operating in compliance with applicable state requirements as well as those requirements deemed necessary to manage the waste safely. This regulatory compliance supports WHC's application of a RCRA Part B Permit.
- Solid, low-level wastes such as transfer lines or sampling equipment generated from tank farm activities must be characterized before disposal in accordance with *Radioactive Waste Management* (DOE 1994d). Waste tank characterization data with respect to radionuclide content allows this program element to model the origin and activity of any radionuclides present on the equipment being disposed of.

1.4.7 Tank Farm Upgrades Program

The Tank Farm Upgrades program element has characterization requirements to support tank farm ventilation system and transfer line upgrades. Characterization of vapors, airborne particles, and heat loads is required to properly select filtration for the ventilation systems. Transfer line upgrades require characterization of tank waste to validate construction material selection, which is based, in part, on waste compatibility and erosion properties.

1.5 CHARACTERIZATION PLANNING DOCUMENT HIERARCHY

The characterization planning document hierarchy for sampling and analysis activities is presented in Figure 2 and described in this section. Some FY 1995 sampling and analysis activities may not follow this documentation scheme as described in Section 5.3. These exempted, sampling and analysis activities shall be documented by TCPs, letters of instruction, and test plans. The documentation scheme below was developed through the System Engineering process described in *Tank Waste Remediation System Functions and Requirements* (DOE 1994b).

This characterization planning documentation leads to efficient characterization planning. The ultimate goal of this planning is to secure DQO-supported sampling and laboratory services as accurately and as quickly as possible, while maintaining documentation traceability throughout. The Tank Waste Analysis Plan/Hanford Analytical Services Quality Assurance Plan/TCP documentation integrated with the TWRS program elements' requirements allows TCPs, letters of instruction, or test plans to serve as guides to the laboratory for all analytical activities.

The Sampling Priority List and the Sampling Schedule are described in Section 3.0. Each TWRS program element that has waste tank data needs has at least one DQO document defining those needs. The sampling and analytical needs identified in those DQO efforts help determine each program element's sample priorities. At the same time, the program elements' needs influence the timing of the DQO activity.

Quality assurance program plans identify the respective program's requirements and provide implementation guidance for all activities of that program. It must satisfy the requirements of control manual WHC-CM-4-2 for a Quality Assurance Program Plan and provide a Quality Assurance Program Index. WHC-CM-4-2 requires each TWRS program to have a Quality Assurance Program Plan. The *TWRS Characterization Program Quality Assurance Program Plan* (Whelan 1994) is the quality assurance program plan specific to the Characterization Program. This plan provides implementation guidance for the data customers and provides an unambiguous source document to establish levels of quality requirements.

The Waste Tank Operations and Maintenance program element has several data users, e.g., 242-A Evaporator, DST RCRA compliance, and SST waste compatibility, who must specify their data needs in a waste analysis plan. Each of these data users has also identified their data needs in respective

WHC-SD-WM-PLN-091, REV. 0
FY 1995 Tank Waste Analysis Plan

DQO efforts. Those DQO efforts are being used to update the respective waste analysis plan so they meet the regulatory requirements of a waste analysis

CHARACTERIZATION DOCUMENT HIERARCHY

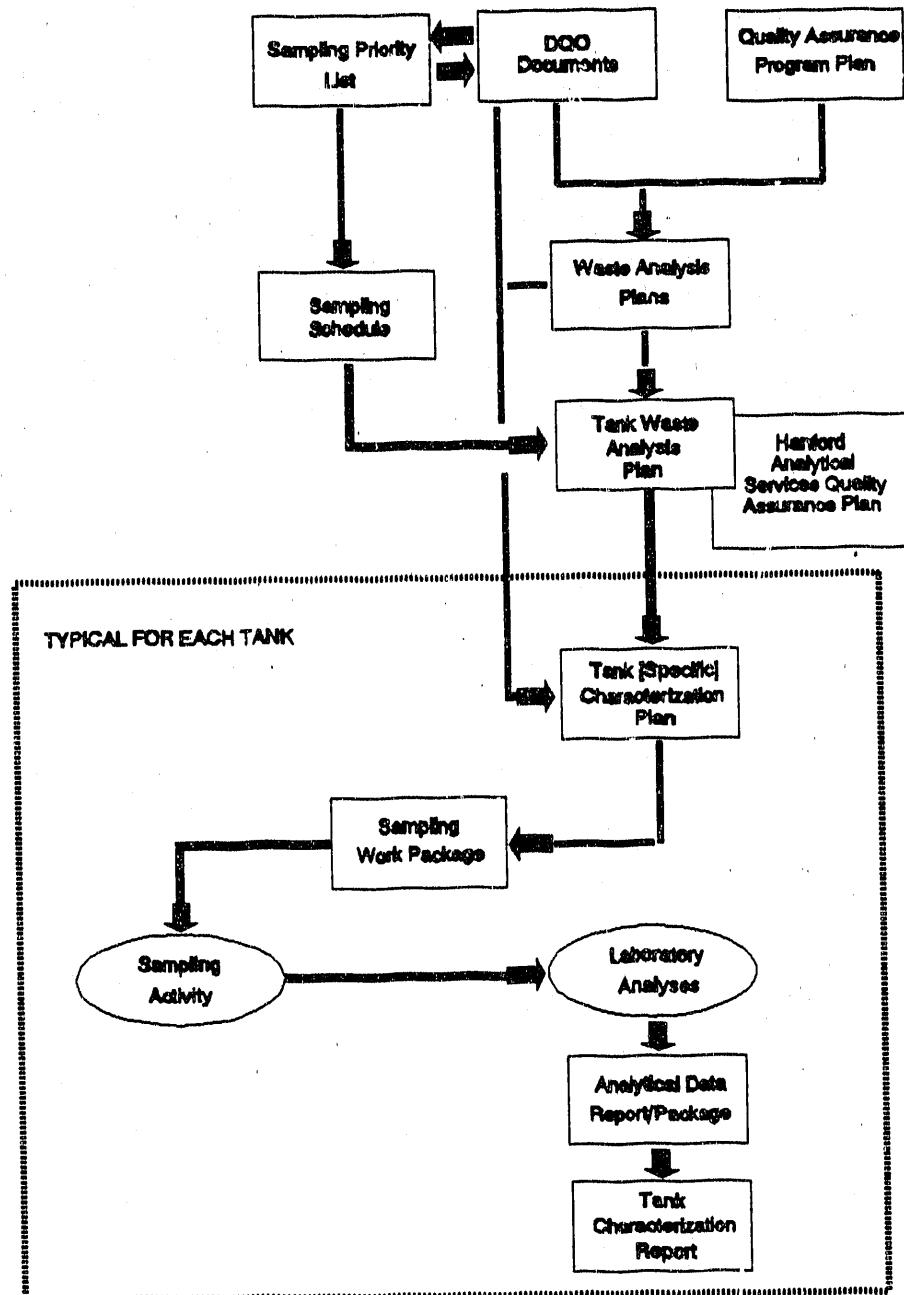


Figure 2. TWRS Characterization Document Hierarchy

plan and reflect the data needs identified through the DQO process. Until the Waste Analysis Plans are completed, the respective DQO documents shall be used as the source for the sampling and analytical requirements to be specified in the TCPs for tanks where the DST RCRA, 242-A Evaporator, or Waste Compatibility programs have data needs.

As the governing document providing the framework for securing laboratory services, this document is influenced by the tank Sampling Schedule, DQO documents, Waste Analysis Plans, and the TWRS Characterization Program Quality Assurance Program Plan (Whelan 1994). The Hanford Analytical Services Quality Assurance Plan allows the analytical quality assurance requirements identified in TCPs for all the TWRS program elements to be treated uniformly. The portion of Figure 2 within the dashed line indicates documents or activities associated with each tank sampled. The TCPs integrate the results of the various issue- and process-based DQO efforts or the appropriate Waste Analysis Plan (if applicable) into a tank-specific sampling and analytical plan. Based on the number, location, and type of sample(s) required by the TCP, a Work Package is prepared to allow the field sampling activity to occur. Both the sampling activity and the TCP lead to the laboratory analysis activity. The laboratory analyzes the sample material and issues a data report and/or package as directed by the TCP. The final output of the document hierarchy is the Tank Characterization Report, which includes historical information, sampling history, analytical data, and data evaluation for a particular tank.

1.6 ASSUMPTIONS

The success of the Tank Waste Analysis Plan strategy is based on a number of assumptions.

- Resolving the unreviewed safety questions, and other safety issues associated with the waste tanks, are the highest priority with respect to sampling and analytical resources.
- Adequate laboratory capacity will exist to perform all requested analyses. Capacity maintenance includes (1) availability of additional hot cells at the 222-S Laboratory in FY 1995; (2) conducting multiple-shift laboratory operation; (3) procuring offsite laboratory capacity coupled with availability of shipping casks; and (4) funding to administer and support a continuing program of laboratory staff and equipment upgrades.
- There will be funding of laboratory and Characterization Program support staff sufficient to support the activities described herein.

1.7 CHARACTERIZATION DRIVERS

Following is a list of the drivers for characterizing the Hanford Site waste tanks. While the first task at hand is to safely manage the tank waste, waste characterization is also conducted to (1) satisfy the various TWRS program element data needs; (2) respond to the DNFSB Recommendation 93-5; and (3) satisfy any relevant Tri-Party Agreement commitments.

WHC-SD-WM-PLN-091, REV. 0
FY 1995 Tank Waste Analysis Plan

- Resolve unreviewed safety questions and other safety issues associated with Watch List tanks.
- Identify any safety issues associated with current non-Watch List tanks.
- Furnish safety-related characterization data necessary for the safe operation of the tank farms.
- Provide characterization data required to ensure waste compatibility for the SST stabilization program.
- Provide characterization data required to support continued operations of the 242-A Evaporator.
- Provide characterization data required to maintain the permit status and support continued operations of the DST Storage Facility.
- Provide characterization data required for development of retrieval, pretreatment, and vitrification technologies.
- Comply with Tri-Party Agreement Milestone M-44-00, which requires the issuance of 177 *Tank Characterization Reports* based on process knowledge, previous characterization data, and validated empirical data.

2.0 TWRS SAMPLING METHODS

2.1 SAMPLING WORK PACKAGES

Each sampling event has an associated work package. A work package may cover the sampling of more than one tank and describes the scope of the sampling event(s). Furthermore, a work package contains or references the work plans, work procedures, and plant operating procedures necessary to perform the tank sampling. Preparing the work package is the joint responsibility of the assigned cognizant engineer from Waste Tank Sampling Engineering and the assigned planner from the Production Control, Zone Six organization.

2.2 SAMPLING METHODOLOGIES

The types of sampling efforts that support the various TWRS activities include push-mode and rotary-mode core sampling, grab sampling, auger sampling, and various types of vapor sampling. A brief, introductory description of each type of sample and sampling procedure is provided.

2.2.1 Core Samples

Two types of core sampling methodologies, push mode and rotary mode, are used to obtain solid and/or supernatant liquid samples of the high-level waste materials remaining in the waste tanks. The waste tanks contain three general waste types; sludge, salt cake, and liquid. These are obtained from the tanks using specially designed core-sampling trucks and sampling devices. The sampler bit is either pushed or rotated through the waste to obtain a cylindrical cross section of the tank contents below the riser used for sampling. Each sampler measures approximately 2.5 cm x 48 cm. The waste approximately 2 cm from the bottom during push-mode sampling, and approximately 2.5 cm from the bottom during rotary-mode sampling, can not be sampled with these systems. Push-mode sampling is performed on tanks containing supernatant liquid or soft sludge. Rotary-mode sampling is primarily used to sample hard salt cake, although it may also be used to sample the other waste types.

2.2.2 Auger Samples

Auger samples are limited to approximately the first 20 cm of solids on the tank waste surface and are not planned for all tanks. Auger samples are used to screen the surface of ferrocyanide and gas-generating Watch List tanks, and may also substitute for core samples in tanks containing less than 20 cm to 30 cm of waste. Auger samples are taken using a stainless steel, hand-turned auger bit contained in a sleeve in a method similar to wood boring or ice auguring.

2.2.3 Supernate and Soft Slurry Grab Samples

Liquid or soft slurry samples of the waste remaining in the DSTs and SSTs are taken from various depths in the liquid using a special sampling bottle contained in a cage. The bottle is stoppered and lowered to the desired level. Once that level is reached, the bottle is unstoppered, fills with liquid, and is retrieved from the tank.

2.2.4 Vapor Sampling

Flammable and/or noxious vapors and gases are generated and released from the high-level radioactive waste within the 200 Area tank farms. Vapor sampling is performed by (1) Health and Safety Technical Services or the Tank Vapor Issue Resolution Program, which involves taking samples of the airspace in the tanks to address the potential for build-up of these unsafe vapors; or (2) the Flammable Gas Tank Safety Program, which is in the process of installing standard hydrogen monitoring systems on each of the 25 flammable gas Watch List tanks by April 1995 as required in Commitment 3.14 of DNFSB Recommendation 93-5 (DOE 1994c). There are several different measuring devices, procedures, and instruments for vapor sampling that are described in Section 2.2.4.1. The tank vapor sampling currently being conducted may be classified by purpose into three general types; ferrocyanide tank flammability and health hazards vapor sampling; heated-tube vapor sampling; and exhaust air permit vapor sampling.

2.2.4.1 Waste Tank Vapor Sample Types

Ferrocyanide tank flammability and health hazards vapor sampling is required before any work inside the ferrocyanide Watch List tanks can be performed. A safety assessment specifically outlines the requirements for this sampling, which involves a check of the flammability of the headspace using a combustible gas meter and a check of the organic vapor concentration using an organic vapor monitor within the tank. Sorbant tubes are used to measure certain hazardous compounds, including hydrazine, ammonia, hydrogen cyanide, and nitrogen oxides in the tank dome space.

Heated-tube vapor sampling to resolve health and safety issues uses the vapor sampling system developed by the Tank Vapor Issue Resolution Program, and employs a heated sampling probe, heated sample transfer lines, and a heated manifold to eliminate the condensation of vapors. Presently, all Ferrocyanide and Organic Watch List tanks are scheduled to be sampled by this method.

Exhaust air permit vapor sampling is used to support exhaust use during rotary-mode core drilling. To acquire a state air permit to operate an exhaust in a tank, the vapors in a waste tank must be sampled and analyzed before using the exhaust. This also identifies gases and vapors that are of interest to the Tank Vapor Issue Resolution Program.

2.2.4.2 Vapor Sampling Methods

Generally, there are three processes used for obtaining vapor samples. The sample may be passed through a device that traps or concentrates targeted

vapors and gases, a sample may be collected in an appropriate container, or the vapor may be analyzed *in situ*. The four samplers used for vapor sampling include sorbent tubes, Tedlar or Saran grab bag samplers, SUMMA canisters, and Hoke cylinders.

Sorbent tubes are small tubes filled with a sorbent material that traps specific vapors and/or gases from sample vapor drawn through the tube. This vapor can then be extracted and analyzed at a remote laboratory.

Grab bags made of Tedlar or Saran, highly impermeable plastics that do not off-gas significantly, are used to collect samples for analysis. A small pump is used to fill the bag. However, grab bags are not an ideal sampling device for certain vapors, because of the ability of the vapor to be adsorbed by the plastic.

SUMMA canisters or SUMMA bottles are stainless steel containers that collect samples in the same fashion as grab bags. To collect a sample, the canister is first evacuated and placed in the vapor to be sampled. Then a valve on the canister is opened, allowing the sample vapor to surge in. SUMMA canisters are passivated to reduce adsorption of constituents of interest.

The Hoke cylinder is a metal bottle typically constructed of stainless steel with either one or two valved openings. In the case of the single opening, the cylinder is evacuated before sample collection and filled with the vapor sample by opening the valve. If the Hoke cylinder has two valves, the valves are positioned at opposite ends of the bottle. This arrangement allows the sample vapor to be drawn through the cylinder with a pump before actual sample collection, thereby purging any non-sample vapors that may have been present from the system.

In situ analysis presently consists of standard hydrogen monitoring systems on flammable gas Watch List tanks that are designed to continuously measure hydrogen levels in a tank's dome space. These systems also allow gas samples to be retrieved for detailed laboratory analyses (Atencio 1992). The principal components of the monitor are a main flow loop, grab sample loop, and a calibration system. Two electrochemical cells in the main flow loop measure hydrogen in the respective ranges of 0 to 1 and 0 to 10 volume percent.

Toxilog use an electrochemical cell detector designed to respond to specific gases or to general types of gases and vapors. These devices provide a readout of contaminant level, and include a visual and audible alarm to provide a warning when a preset limit is exceeded. Therefore, toxilog may be used as both a monitoring instrument and as a personal alarm device. Further, these instruments use a datalogger to continuously record the contaminant levels observed for later downloading to a computer.

WHC-SD-WM-PLN-091, REV. 0
FY 1995 Tank Waste Analysis Plan

This page intentionally left blank.

3.0 FISCAL YEAR 1995 SAMPLING SCHEDULE

A procedure for prioritizing and scheduling TWRS sampling and analysis activities may be found in *TWRS Characterization Sample and Analysis Scheduling Procedure* (WHC 1994). Waste tank core, auger, grab, and vapor sampling activities are integrated into a schedule covering all TWRS sampling activities. The Hanford Site analytical resources are coordinated with the sampling capabilities and commitments made in *Recommendation 93-5 Implementation Plan* (DOE 1994c) and any applicable DQO documents.

3.1 SAMPLING PRIORITY LIST

The Sampling Priority List is a list of all tanks to be sampled for a given FY in order of priority. As required in *TWRS Characterization Sample and Analysis Scheduling Procedure* (WHC 1994), it is developed by the Characterization Program, with input by the TWRS program elements, by assessing programmatic needs and priorities. From the Sampling Priority List, a Sampling Schedule is generated that reflects the priorities of the Sampling Priority List to the extent possible given a number of scheduling constraints.

Compliance with the DNFSB Recommendation 93-5 requires that the Watch List tanks, and others with identified safety problems, receive the highest priority in the Sampling Schedule. Prioritization of the non Watch List tank samples is performed by considering the priority assigned by each program element and the remaining sampling capacity. The various TWRS program elements have specific waste tank characterization requirements to fulfill their individual programmatic responsibilities and they are responsible for identifying their respective sample priorities.

3.2 SAMPLING SCHEDULE

The FY 1995 Integrated Sampling Schedule details the sampling activities (core, auger, grab, and vapor) for FY 1995. It includes samples from the 149 SSTs, 28 DSTs, and other miscellaneous underground storage tanks. Because of the commitment to comply with Recommendation 93-5, the majority of tanks to be core sampled in FY 1995 are Watch List tanks. The forecasted sampling activities associated with the Sampling Schedule are shown in Table 3-1.

3.2.1 Scheduling Constraints

3.2.1.1 Operational Constraints

The FY 1995 Sampling Schedule does not mirror the Sampling Priority List because of the various operational and laboratory constraints. The following is a list of operational constraints that affected the scheduling of tanks for sampling in FY 1995.

- Allowance must be made for preparing significant documentation, including safety analysis reports, environmental assessments, National Environmental Policy Act (NEPA) documentation, and

readiness reviews, necessary before initiating any core sampling events in Watch List tanks.

- Allowance must be made for worker health and safety vapor sampling of Watch List tanks before further sampling activities.
- The accessibility of tank risers must be evaluated before sampling.
- Tanks identified as potential flammable gas generators must have monitoring instrumentation installed and safety evaluations conducted before entering these types of tanks.

At times, the geographical location of the tanks to be sampled may be taken into consideration. For example, the Sampling Priority List may show that consecutive tanks to be core sampled are in tank farms separated by a large distance. A slight reorganization of the Sampling Priority List, reflected in the Sampling Schedule, could allow one or more additional high priority tanks in the same or a nearby tank farm to be sampled before moving the sampling truck over the distance.

To ensure optimal use of sampling teams while the core sampling truck is repositioned, auger and vapor samples were interspersed in the Sampling Schedule. Also interspersed in the schedule are grab samples requested by the Double-Shell Tanks and Stabilization and Isolation organizations.

Table 3-1 FY 1995 Forecasted Sampling-Related Activities

Sampling Activity
Sample 3 DSTs Using the Push-Mode Core Sampling Method
Sample 22 SSTs Using the Push-Mode Core Sampling Method
Sample 13 SSTs Using the Rotary-Mode Core Sampling Method
Provide Flammability and Toxic Gas Vapor Sampling of 34 Tanks
Sample 27 Tanks using the Auger Sampling Method
Sample 33 Tanks using the Grab Sample Method

3.2.1.2 Laboratory Capacity Constraints

The current projection shows that the laboratory capacity dedicated to TWRS should be able to support known TWRS needs with current planned onsite laboratory upgrades. Several factors listed below pertaining to the laboratory had to be considered when developing the Sampling Schedule because of their capability of influencing laboratory capacity.

WHC-SD-WM-PLN-091, REV. 0
FY 1995 Tank Waste Analysis Plan

- There is no surge capacity, or peak-loading or back-up capability.
- Future needs of the Waste Tank Safety, Waste Pretreatment, Low-Level Waste Disposal, and High-Level Waste Disposal program elements may impose additional characterization requirements.
- Revisions of current DQO documents may identify the need for additional waste tank samples or analyses.

The laboratory constraints include uncertainty in the present TWRS laboratory capacity projection and sample analytical requirements. The key question is whether the analytical laboratories' capacity is consistent with the sampling capacity. The laboratory analytical burden is described in terms of the analytical equivalency unit that considers sample receiving, extruding, homogenizing, analyzing, and preparing data reports/packages. These factors are integrated by Analytical Services into a single laboratory sample schedule for both onsite laboratories that presents a time-phased outline showing when different types of samples from the different TWRS program elements can be received and analyzed.

4.0 DQO-BASED CHARACTERIZATION REQUIREMENTS

The DQO process is invaluable for determining the current characterization data requirements needed for the continued safe storage, retrieval, and disposal of the Hanford Site DST and SST wastes. In addition, the DQO process can help cost planning and scheduling activities, tank sample scheduling, and laboratory scheduling because it helps identify what resources are needed and when they are needed to satisfy the characterization objectives. The strategy for the phased implementation of the DQO planning process that supports all TWRS tank characterization needs is presented in *The TWRS DQO Strategy* (Babad et al. 1994a).

The DQO efforts described in and implemented through this document only pertain to characterization of waste tank samples. Other activities such as enhanced monitoring or mitigation associated with the waste tanks may be addressed via the DQO process, but they are not covered or discussed here.

4.1 DQO EFFORTS AND TYPES

The overall strategy for implementing DQO efforts in the TWRS is to divide the universe of relevant data needs into a finite number of DQO efforts with focused data needs. Thus, the various DQO efforts have been divided into issue- and process-based activities. Issue-based DQO efforts are focused on a unique safety or regulatory issue such as ferrocyanide tanks or DST RCRA sampling. The process-based DQO efforts address specific waste handling processes such as tank retrieval. Table 4-1 lists the completed DQO efforts and the DQOs in preparation to be completed in 1995 by type that apply to the waste tank characterization effort described herein.

Each DQO effort results in a corresponding document. These DQO documents provide the necessary information to identify (1) the types of samples needed; (2) the number of samples needed; (3) the (riser) location of the samples; and (4) the appropriate time for sample collection.

4.2 MODULAR APPROACH TO SAMPLING AND ANALYSIS

Because all the characterization activities directed by this document are DQO-based, differences between programmatic sampling and analytical requirements may be accounted for using a modular design in developing the various waste tank characterization scenarios. A summary of the sampling and analytical requirements for each DQO effort in Table 4-1 is presented in the following Section. Normally, more than one DQO effort applies to a given tank, and several of the DQO efforts have overlapping analytical requirements. This modular approach facilitates preparation of the TCPs once the DQO efforts applicable to each tank on the FY 1995 Sampling Schedule have been identified. This is done in Section 5.2.

As described in Section 1.5, DQO efforts performed for SST stabilization/compatibility, DST RCRA compliance, or the evaporator are being used to update the respective waste analysis plans. Once a waste analysis plan has been

WHC-SD-WM-PLN-091, REV. 0
FY 1995 Tank Waste Analysis Plan

updated according to its respective DQO effort, it will once again serve as the basis for any applicable TCP, letter of instruction, or test plan.

WHC-SD-WM-PLN-091, REV. 0
FY 1995 Tank Waste Analysis Plan

Table 4-1 TWRS DQO Efforts

DQO Title	Document #	DQO Type
<i>Data Requirements for the Ferrocyanide Safety Issue Developed Through the Data Quality Objectives Process</i>	WHC-SD-WM-DQO-007	Issue
<i>Tank 241-C-103 Vapor and Gas Sampling Data Quality Objectives</i>	WHC-EP-0774	Issue
<i>Organic Layer Sampling for SST 241-C-103 Background, and Data Quality Objectives, and Analytical Plan</i>	PNL-8871 UC-510	Issue
<i>Tank 241-C-106 Sampling Data Requirements Developed Through the Data Quality Objectives (DQO) Process</i>	WHC-EP-0723	Issue
<i>Data Requirements Required Through the Data Quality Objectives Process for the Crust Burn Issue Associated with Flammable Gas Tanks</i>	WHC-SD-WM-DQO-003	Issue
<i>Data Quality Objectives for Waste Compatibility Program</i>	WHC-SD-WM-DQO-001	Issue
<i>Rotary Core Vapor Sampling Data Quality Objective</i>	WHC-SD-WM-SP-003	Issue
<i>Data Quality Objectives for Generic In-Tank Health and Safety Vapor Issue Resolution</i>	WHC-SD-WM-DQO-002	Issue
<i>Tank Safety Screening Data Quality Objective</i>	WHC-SD-WM-DQO-012	Issue
<i>Flammable Gas Safety Program: Data Requirements for the Flammable Gas Safety Issue Developed through the Data Quality Objectives (DQO) Process</i>	WHC-SD-WM-DQO-004	Issue
<i>Data Quality Objective to Support Resolution of the Organic Fuel Rich Tank Safety Issue</i>	WHC-SD-WM-DQO-006	Issue
<i>Characterization Data Needs for Development of Retrieval Equipment and Processes for SSTs and DSTs, Developed through the DQO Process</i>	WHC-SD-WM-DQO-008	Process
<i>RCRA Permit B Application DQO (in preparation)</i>	TBD	Issue
<i>Evaporator Operations DQO (in preparation)</i>	TBD	Process
<i>Pretreatment Interim Data Quality Objectives</i>	WHC-SD-WM-DQO-011	Process
<i>Pretreatment Data Quality Objectives in Support of High-Level and Low-Level Waste Feed</i>	WHC-SD-WM-DQO-010	Process
<i>Solid, Low-Level Waste Disposal DQO (in preparation)</i>	TBD	Process
<i>Process Control DQO (TBD)</i>	TBD	Process

The tables below summarizing the analytical requirements from each DQO effort were taken directly from the documented DQO efforts listed in Table 4-1. The analytical measurements or the desired accuracy and precision were not interpreted or altered. The TCP, letter of instruction, or test plan shall address any differences between what the analytical laboratories can provide and the requirements of each DQO effort.

4.2.1 Accuracy and Precision Requirements

The accuracy and precision requirements specified in the various DQO efforts are based on what each respective program determined was necessary to meet their needs. A number of issues with respect to when the performing laboratory can reasonably be expected to achieve the DQO-based accuracy and precision requirements are addressed below.

- Physical methods may not have representative standards on which to base accuracy and precision performance.
- Heterogeneity in samples may affect spike recoveries and precision of duplicate determinations.
- Accuracy and precision is a function of analyte concentration - the nearer to the detection limit, the greater the error.
- Spike recoveries are a function of the ratio of the spike concentration to the sample analyte concentration and may exceed the acceptance criteria if this ratio falls below 0.25.
- Sample matrices may impact method performance.

4.3 DQO-BASED SAMPLING AND ANALYTICAL REQUIREMENTS

The sampling and analytical requirements for all DQO efforts are summarized in this section. This aids in the preparation of TCPs because there is one source document for all sampling and analytical requirements. The individual modules presented here will be used to prepare each TCP, which provides specific technical guidance on the individual treatment of the samples.

4.3.1 Ferrocyanide Safety Issue DQO Effort

This DQO effort is used as a guide for characterizing tanks on the Ferrocyanide Watch List. It concluded that the most reliable information is obtained from core samples and 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 classification of the tanks as safe, conditionally safe, or unsafe. 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. Table 4-2 summarizes the analytical requirements determined by the Ferrocyanide Safety Program's application of the DQO process. For further information on this DQO effort refer to *Data Requirements for the Ferrocyanide Safety Issue Developed through the Data Quality Objectives Process* (Meacham et al. 1994).

4.3.2 High-Heat Safety Issue DQO Effort

The sampling and analytical requirements necessary for resolving the high-heat safety issue associated with tank 241-C-106, the only tank on the high-heat Watch List, are covered in this DQO effort. The DQO has identified the need for two rotary-mode core samples from tank C-106 taken from opposite sides of the tank. The Waste Tank Safety Program is primarily concerned about obtaining data on strontium-90 layering, thermal conductivity, and waste permeability, which is the ability of the waste to reabsorb water once dried. Waste Retrieval requires physical and chemical characterization to support design of the tank C-106 retrieval systems and to meet regulatory requirements. Based on the limited amount of data with respect to spatial variability that exists for the key measures of interest, the DQO effort recommends that these key measurements be performed on duplicate samples to allow for the estimation and detectability of spatial, sampling, and analytical uncertainties. Accuracy and precision requirements were not explicitly defined by the Waste Tank Safety Program. The DQO document describes that it is not necessary to measure these key analytes with extreme accuracy because the parameters of the model affected by the analytical results may be adjusted to ensure tank safety. *Tank 241-C-106 Sampling Data Requirements Developed Through the Data Quality Objectives (DQO) Process* (Wang et al. 1994) states that the precision and accuracy provided by the laboratory would meet the program's needs. Table 4-3 summarizes the analytical requirements determined by the high-heat safety issue DQO effort.

4.3.3 Tank Safety Screening Data Quality Objectives

This DQO effort defines the sampling and analytical requirements and decision logic necessary to determine if each of the 177 SSTs and DSTs, and other miscellaneous, high-activity underground storage tanks, is appropriately categorized with respect to four safety issues: ferrocyanide, organic, criticality, and flammable gas. To meet the sampling requirements of this DQO effort, a vertical profile of the waste shall be obtained from at least two widely-spaced risers. This vertical profile may be realized using core, auger, or grab samples. The safety screening DQO effort is comprised of four primary analytes measured for safety screening classification. Secondary analyses are performed if a non-Watch List tank exceeds the notification limit for total fuel content or total alpha. The safety screening analyses shall be applied to all core samples, DST RCRA samples, and all auger samples, except auger samples taken by the Flammable Gas Tank Safety Program to assess the flammable gas tank crust burn issue (Section 4.3.5). The analytical requirements identified in the safety screening DQO effort are summarized in Table 4-4. For further information on this DQO effort refer to *Tank Safety Screening Data Quality Objective* (Babad and Redus 1994).

4.3.4 Waste Compatibility Data Quality Objectives

The generic sampling and analysis program related to the potential incompatibility of wastes that may occur from waste transfers into and within the DST system is the subject of this DQO effort. This 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, and applies primarily to liquid samples from SSTs to be salt well pumped in the near term. It also applies to tanks scheduled as receiver tanks from waste retrieval activities. The sampling of SST liquid wastes is limited to liquid in salt wells or surface liquid located below available risers. Until a generic sampling plan is developed, the number of liquid samples to be taken will be determined using a best engineering judgement approach by the Waste Compatibility Program based on criteria that were established in the DQO effort. Table 4-5 presents the analytes to be measured on liquid samples taken for waste compatibility evaluation. For some analytes, two alternative analytical methods are given. Alternative analytical methods for which no precision or accuracies were given are not included. The measurements of pump velocity, pipe diameter, and tank temperature are not measured in the laboratory or hot cell and were not included in Table 4-5. For further information on this DQO effort refer to *Data Quality Objectives for the Waste Compatibility Program* (Carothers 1994).

4.3.5 Flammable Gas Tanks Crust Burn Issue Data Quality Objectives

This DQO effort addresses an issue associated with flammable gas Watch List tanks: the potential for an exothermic reaction between organic carbon and nitrate or nitrite in the crust, initiated by the burning of flammable gases, or by a mechanical in-tank energy source, i.e., core sampling. Data is needed to determine (1) if water addition to the crust, if present, is necessary before core sampling; and (2) to further evaluate the crust burn safety issue. The DQO process determined that auger samples from three widely-spaced risers would provide the necessary information to satisfy items (1) and (2). A summary of the analytical requirements associated with this DQO effort are presented in Table 4-6. For further information on this DQO effort refer to *Data Requirements Developed Through the Data Quality Objectives Process for the Crust Burn Issue Associated with Flammable Gas Tanks* (Johnson 1994).

4.3.6 Data Quality Objectives for Organic Layer Sampling of Tank C-103

This DQO effort was undertaken specifically to cover the collection and analysis of organic layer grab samples from tank C-103 in order to address safety issues related to the potential flammability of the floating organic layer. The sampling events addressed by this DQO effort were performed in FY 1994, therefore the intent of this DQO effort has been fulfilled, and a summary of the analytical requirements is not necessary. For further information on this DQO effort refer to *Organic Layer Sampling for SST 241-C-103 Background, and Data Quality Objectives, and Analytical Plan* (Wood 1993) and *Data Quality Objectives to Support Resolution of the Organic Fuel Rich Tank Safety Issue* (Babad et al. 1994b).

4.3.7 Rotary Core Vapor Sampling Data Quality Objective

This DQO effort addresses (1) the required vapor sampling and analysis of a tank's headspace before operation of the rotary-mode core sampling exhauster; and (2) monitoring of the exhauster during rotary-mode core sampling. Because the monitoring activity is associated with operations and not tank characterization, only the tank headspace sampling and analysis activities prior to exhauster start-up are discussed here. The spatial boundaries and configurations for vapor sampling to allow exhauster start-up are as follows: (1) Sample the interior of the tank at the approximate center of the volume of the tank head space using a single heated vapor sampling assembly; or (2) Sample the vent header of the tank if it is actively vented. One set of vapor samples will be taken per tank consisting of the following items.

- Six 6L SUMMA canisters
- 12 sorbant tubes
- 6 nitric oxide/nitrogen dioxide sorbent tubes
- 6 ammonia sorbant tubes
- QC samples as specified in *Quality Assurance Project Plan for Waste Tank Vapor Characterization* (Suydam 1993)

The analytical requirements associated with exhauster start-up vapor sampling are given in Table 4-7. For further information on this DQO effort refer to *Rotary Core Vapor Sampling Data Quality Objective* (Price 1994).

4.3.8 Organic Fuel-Rich Tank Data Quality Objective

This DQO effort focuses on SSTs that contain or may contain, based on safety screening (Section 4.3.3), organic compounds above the established decision thresholds. It identifies the information needed to determine if tanks should be removed, not removed, or added to the Organic Watch List. As with the ferrocyanide DQO effort, the sampling and analyses prescribed by this DQO effort will allow tanks to be classified as safe, conditionally safe, or unsafe. The sampling requirements of this DQO effort are for a minimum of two cores samples separated radially to the maximum extent possible by existing risers. Each 48 cm segment of each core shall be analyzed at the half segment level. Table 4-8 identifies the analyses required by this DQO effort. The tank temperature and identification of a floating organic layer are not measured in the laboratory or hot cell and were not included in Table 4-8. Quantification of several of the analytes specified in the DQO document will be obtained from safety screening analyses. These are noted in the table. For further information on this DQO effort refer to *Data Quality Objective to Support Resolution of the Organic Fuel Rich Tank Safety Issue* (Babad et al. 1994b).

4.3.9 Tank C-103 Vapor and Gas Sampling Data Quality Objectives

Resolution of the potential flammability and worker health and safety hazards associated with the presence of gases, vapors, or aerosols in tank C-103 is the focus of this DQO effort. It covers the sampling events required to resolve these issues. The number, type, and riser location of samples, and

the sampling methods were determined before initiation of this DQO effort. Therefore, this DQO effort was performed to define decision rules and document criteria that will enable users of the analytical data to determine the data's adequacy and limitations. The TCP addressing vapor sampling of tank C-103 will obtain sampling and analytical requirements from Osborne (1994).

4.3.10 Generic Tank Vapor Issue Resolution Data Quality Objectives

This DQO effort is a generic version of the tank C-103 DQO effort described in Section 4.3.9. Waste tank vapor characterization generic to all 177 underground storage tanks on the Hanford Site are addressed in this DQO exercise. Data are needed to identify and quantify constituents of the tank headspaces to address potential vapor flammability and toxicity. Resolution of these two issues involves a sequence of sampling events. The first step is a qualitative assessment of a tank's headspace vapor flammability. Further samples may be taken to determine the composition and concentration of any flammable constituents. Following resolution of the flammability issue, tank headspace samples will be taken to assess vapor toxicity. The spatial boundaries of vapor sampling events are defined by the waste surface and the walls and dome of the waste tank. Samples are removed from a single location at or near the midpoint of the tank's headspace. Tanks that are actively ventilated will have samples removed at the exhaust header. Analytical requirements of generic tank vapor samples are provided in Table 4-9. For further information on this DQO effort refer to *Data Quality Objectives for Generic In-Tank Health and Safety Vapor Issue Resolution* (Osborne 1994b).

4.3.11 Flammable Gas Safety Issue Data Quality Objectives

This DQO effort focuses on DSTs that contain or may contain, based on safety screening (Section 4.3.3), flammable gases above the established decision thresholds. It concluded that the most reliable information is obtained from one complete core and summarizes the analytical needs for the core sampling activities of the Flammable Gas Watch List tanks. Data from these core samples are needed to provide an understanding of the tank contents so that (1) insight may be obtained on the mechanisms for gas generation, retention and release, (2) models of the waste behavior can be developed to support safety analysis and development of mitigation methods, and (3) modeling of the flow of gases, and potential for ignition, can be done to support hazard analyses. A summary of the analytical requirements associated with this DQO effort are presented in Table 4-10. For further information on this DQO effort refer to *Flammable Gas Safety Program: Data Requirements for the Flammable Gas Safety Issue Developed through the Data Quality Objectives (DQO) Process* (McDuffie and Johnson 1994).

4.3.12 Waste Tank Retrieval Data Quality Objectives

This DQO effort, currently in preparation, will detail the various retrieval methods being considered to remove the waste from the tanks safely and with minimal intrusion or disruption to the tank environment. For process control purposes, Waste Retrieval will need extensive physical and rheological data from core samples on the mechanical behavior of the wastes. Data is also important for the designing of equipment to support planned retrieval by sluicing.

4.3.13 RCRA Part B Permit Application Data Quality Objectives

This DQO effort, currently in preparation, will provide the sampling requirements for Resource Conservation and Recovery Act (RCRA) purposes. These samples will be characterized to ensure that WHC is operating in compliance with applicable state requirements as well as those requirements deemed necessary to manage the waste safely. These samples will also be for regulatory compliance purposes to support WHC's application for a RCRA Part B Permit.

4.3.14 Evaporator Operations Data Quality Objectives

This DQO effort, currently in preparation, will include characterization requirements for evaporator feed characterization. Characterization will be performed on grab samples from evaporator candidate feed tanks to determine their suitability for treatment.

4.3.15 Waste Tank Pretreatment Data Quality Objectives

This DQO effort, currently in preparation, gives the characterization requirements primarily for technology development. This technology development effort will require comprehensive physical and chemical information from waste tank samples. The pretreatment process must be able to produce feed streams that satisfy the operating requirements for the low-level and high-level vitrification facilities.

4.3.16 High-Level and Low-Level Waste Feed Data Quality Objectives

This DQO effort, currently in preparation, is in support of the high-level vitrification process and the low-level waste vitrification process to be used as a replacement for the eliminated grout disposal option. It is anticipated that tank waste samples will be necessary to develop proper formulation for product qualification and will include the characterization requirements for process development, process control, and regulatory compliance of high-level and low-level waste disposal systems.

4.3.17 Solid, Low-Level Waste Disposal Data Quality Objectives

This DQO effort, currently in preparation, will support the characterization of the solid, low-level wastes such as transfer lines or sampling equipment generated from tank farm activities before disposal. Waste characterization data with respect to radionuclide content will allow the modeling of the origin and activity of any radionuclides present on the equipment being disposed of.

4.3.18 Process Control Data Quality Objectives

This DQO effort, currently in preparation, will identify the characterization requirements to support tank farm ventilation system and transfer line upgrades. Characterization of vapors, airborne particles, and heat loads are required to properly select filtration for the ventilation

WHC-SD-WM-PLN-091, REV. 0
FY 1995 Tank Waste Analysis Plan

systems. Transfer line upgrades require characterization of tank waste to validate construction material selection.

WHC-SD-MM-PLN-091, REV. 0
FY 1995 Tank Waste Analysis Plan

Table 4-2 DQO-Based Analytical Requirements for Ferrocyanide Watch List Tanks

Analyte or Measurement	Analytical method	Notification Limit	Sample	Desired Accuracy & Precision
Nickel concentration	Inductively Coupled Plasma	> 1000 $\mu\text{g/g}$	Acid and fusion dissolution of homogenized quarter segments	Acc: $\pm 10\%$ Pre: $\pm 10\%$
Total fuel content	Differential Scanning Calorimetry/Adiabatic Calorimetry	> 8 wt% (0.48 MJ/kg or 115 cal/g)	Direct measurement on homogenized quarter segments	Acc: $\pm 10\%$ Pre: $\pm 10\%$
Total cyanide	Direct Assay (method is PNL-ALO-285)	> 3.9 wt%	Direct measurement on homogenized quarter segments	Acc: $\pm 10\%$ Pre: $\pm 10\%$
Moisture content	Thermogravimetric Analysis	> [(0.0932*DSC exotherm) - 10.7] weight %	Direct measurement on homogenized quarter segments	Acc: $\pm 10\%$ Pre: $\pm 10\%$
Total Organic Carbon	Direct Persulfate Oxidation	>3 weight % (based on zero free water)	Direct measurement on homogenized quarter segments	Acc: $\pm 10\%$ Pre: $\pm 10\%$
Cesium-137	Gamma Energy Analysis	None specified	Water and fusion dissolution of homogenized quarter segments/supernate	Acc: $\pm 10\%$ Pre: $\pm 10\%$
Strontium-90	Beta radiochemistry	None specified	Acid and fusion dissolution of homogenized quarter segments/supernate	Acc: $\pm 10\%$ Pre: $\pm 10\%$

WHC-SD-WH-PLN-091, REV. 0
FY 1995 Tank Waste Analysis Plan

Table 4-3 DQO-Based Analytical Requirements for Tank C-106

Analyte or Measurement	Analytical method	Notification Limit	Sample	Desired Accuracy & precision
Thermal conductivity	Thermal conductivity	None specified	On as-sampled and dried waste from each unhomogenized stratum	Acc.: $\pm 50\%$ Pre.: $\pm 20\%$ RPD
Permeability	Permeability	None specified	Each unhomogenized stratum	Acc.: TBD Pre.: TBD
Strontium-90	β Radiochemistry	None specified	Unhomogenized quarter segments and liquid, core, and hardpan composites	Acc.: $\pm 15\%$ Pre.: $\pm 20\%$ RPD
Bulk density	Bulk density	None specified	On as-sampled, 1:1, 3:1, 5:1 supernate:sludge dilutions from core and hardpan composites	Acc.: $\pm 15\%$ Pre.: $\pm 20\%$ RPD
Bulk viscosity and shear strength	Shear stress vs. shear rate rheogram	None specified	On as-sampled, 1:1, 3:1, 5:1 supernate:sludge dilutions from each unhomogenized stratum at ambient temperature and 50° C	Acc.: $\pm 15\%$ Pre.: $\pm 20\%$ RPD
Bulk F ⁻ , Cl ⁻ concentration	Ion Chromatography	None specified	On as-sampled, 1:1, 3:1, 5:1 supernate:sludge dilutions from liquid composite, and water leach of core and hardpan composites	Acc.: $\pm 15\%$ Pre.: $\pm 20\%$ RPD
Aluminate, bicarbonate, carbonate, and hydroxide concentrations	Not specified for aluminate, TIC and pH for bicarbonate and carbonate. Titration and pH for hydroxide.	None specified	On as-sampled, 1:1, 3:1, 5:1 supernate:sludge dilutions from liquid, core, and hardpan composites	Acc.: $\pm 15\%$ Pre.: $\pm 20\%$ RPD

WHC-SD-WH-PLN-091, REV. 0
FY 1995 Tank Waste Analysis Plan

Table 4-3 DQO-Based Analytical Requirements for Tank C-106

Analyte or Measurement	Analytical method	Notification Limit	Sample	Desired Accuracy & Precision
Organic species identification and concentrations	GC for chelators and organic acids. T0C, VOA, semi-VOA	None specified	On as-sampled, 1:1, 3:1, 5:1 supernate:sludge dilutions from liquid, core, and hardpan composites	Acc.: $\pm 15\%$ Pre.: $\pm 20\%$ RPD
Hard sludge and hard salt cake characteristics	Penetrometer and photography	None specified	Unhomogenized crust and hardpan material	Acc.: $\pm 10\%$ Pre.: $\pm 15\%$ RPD
Static and dynamic settling velocities	Settling velocity	None specified	On as-sampled, 1:1, 3:1, 5:1 supernate:sludge dilutions from core and hardpan composites	Acc.: $\pm 10\%$ Pre.: $\pm 15\%$ RPD
Particle size distribution	No current method of analysis	None specified	None specified	N/A
Erosion test	Abrasiveness	None specified	Core and hardpan composites	Acc.: $\pm 15\%$ Pre.: $\pm 20\%$ RPD
Radionuclides	Total α , β , γ , and U; U and Pu isotopes by ICP/MS; I-129 by ICP/MS; Pu-239/40; GEA for Sb-125, Ru/Rh-106, and Sn-113; H-3 by liquid scintillation	Total α > 40 $\mu\text{Ci/g}$	Total α , β , and γ on liquid, core and hardpan composites; total U, Ru/Rh-106, H-3, Sn-113, Sb-125, U and Pu isotopes, I-129, and Pu-239/40 on core and hardpan composites	Acc.: $\pm 10\%$ Pre.: $\pm 15\%$ RPD

WHC-SD-WH-PLN-091, REV. 0
FY 1995 Tank Waste Analysis Plan

Table 4-3 DQO-Based Analytical Requirements for Tank C-106

Analyte or Measurement	Analytical method	Notification Limit	Sample	Desired Accuracy & Precision
Air toxics	VOA, semi-VOA, ICP/AA for As, Hg	None specified	VOA and semi-VOA on unhomogenized segments immediately after extrusion; ICP and AA on liquid composite and acid and fusion preparation of core and hardpan composites	VOA Acc. and Pre.: 60-140% spike recovery and $\pm 30\%$ RPD. Semi-VOA Acc. and Pre.: 30-120% spike recovery and $\pm 50\%$ RPD. ICP and AA Acc. and Pre.: 75-125% spike recovery and $\pm 20\%$ RPD.
Flammable gasses/vapor	No method available for this request	None specified	Gasses or vapors trapped in waste in tank	None specified

WHC-SD-WM-PLN-091, REV. 0
FY 1995 Tank Waste Analysis Plan

Table 4-4 DQO-Based Analytical Requirements for Tank Safety Screening

Analyte or Measurement	Analytical method	Notification Limit	Sample	Desired Accuracy and Precision
Total Fuel Content (dry weight basis) ¹	Differential Scanning Calorimetry/Adiabatic Calorimetry	> 125 cal/g	Every half segment for salt cake and sludge waste types; Every quarter segment on Ferrocyanide Watch List tanks	Acc: $\pm 10\%$ Pre: $\pm 10\%$
Percent Moisture ¹	Thermogravimetric Analysis	> [(0.0932*DSC exotherm)- 10.7] weight% ² or < 17 weight % ³	Every half segment for salt cake and sludge waste types.	Acc: $\pm 10\%$ Pre: $\pm 10\%$
Total Alpha ¹	Alpha counting	> 1 g/L (> 41 μ Ci/g)	Every half segment for sludge waste types; no analysis on saltcake waste types	Acc: $\pm 10\%$ Pre: $\pm 10\%$
Gas Composition ¹	Gas-specific monitoring gauges; GC/MS	>25% of LFL for any flammable gas present	Tank dome space sampling or monitoring	Acc: $\pm 10\%$ Pre: $\pm 10\%$
Fe, Mn, U ⁴	Inductively Coupled Plasma	None specified	Every half segment for sludge waste types; no analysis on saltcake waste types	Acc: $\pm 10\%$ Pre: $\pm 10\%$
Pu-239/240 ⁴	Separation and α counting	> 1 g/L (> 41 μ Ci/g)	Every half segment for sludge waste types; no analysis on saltcake waste types	Acc: $\pm 10\%$ Pre: $\pm 10\%$
Total organic carbon	Persulfate oxidation; furnace oxidation on Ferrocyanide Watch List tanks	> 3 wt%	Every half segment for salt cake and sludge waste types	Acc: $\pm 20\%$ Pre: $\pm 10\%$

WHC-SD-WW-PLN-091, REV. 0
FY 1995 Tank Waste Analysis Plan

Table 4-4 DQO-Based Analytical Requirements for Tank Safety Screening

Analyte or Measurement	Analytical method	Notification Limit	Sample	Desired Accuracy and Precision
Total cyanide ⁴	Micro distillation	> 3.1 wt%	Every quarter segment for sludge waste types; every half segment for salt cake waste types	Acc: ±20 % Pre: ±10 %

¹ Primary safety screening analyte.

² Applies if the tank is on the Ferrocyanide Watch List.

³ Applies to tanks not on the Ferrocyanide Watch List.

⁴ Secondary safety screening analyte. Analysis is performed if the total alpha notification limit is exceeded, or if a non-Watch List tank exceeds the Total Fuel notification limit.

Table 4-5 D00-Based Analytical Requirements for Waste Compatibility

Analyte or Measurement	Analytical method	Notification Limit	Sample	Desired Accuracy and Precision
Pu-239/240	Separation/ α counting	> 0.8 μ Ci/mL	Filtered liquid grab sample	Acc: ± 20 % Pre: ± 20 %
Am-241	Separation/ α counting	> 0.1 μ Ci/mL	Filtered liquid grab sample	Acc: ± 20 % Pre: ± 20 %
Cs-137	Gamma Energy Analysis	None specified	Filtered liquid grab sample	Acc: ± 20 % Pre: ± 20 %
Sr-90	Separation/ β counting	None specified	Filtered liquid grab sample	Acc: ± 20 % Pre: ± 20 %
Hydroxide	Titration	$\geq 8M$ or $\leq 0.01M$	Filtered liquid grab sample	Acc: ± 20 % Pre: ± 20 %
Carbonate	Total Inorganic Carbon	None specified	Filtered liquid grab sample	Acc: ± 20 % Pre: ± 20 %
Sulfate	Ion Chromatography	None specified	Filtered liquid grab sample	Acc: ± 20 % Pre: ± 20 %
Nitrate	Ion Chromatography	$\geq 62,000 \mu$ g/mL	Filtered liquid grab sample	Acc: ± 20 % Pre: ± 20 %
Nitrite	Ion Chromatography; Spectrophotometric	$\geq 253,000 \mu$ g/mL or $\leq 500 \mu$ g/mL	Filtered liquid grab sample	Acc: ± 20 % Pre: ± 20 %
Chloride	Ion Chromatography	None specified	Filtered liquid grab sample	Acc: ± 20 % Pre: ± 20 %
Fluoride	Ion Chromatography	None specified	Filtered liquid grab sample	Acc: ± 20 % Pre: ± 20 %

WMC-SD-WM-PLN-091, REV. 0
FY 1995 Tank Waste Analysis Plan

Table 4-5 DQO-Based Analytical Requirements for Waste Compatibility

Analyte or Measurement	Analytical method	Notification Limit	Sample	Desired Accuracy and Precision
Phosphate	Ion Chromatography; Inductively Coupled Plasma	None specified	Filtered liquid grab sample	Acc: $\pm 20\%$ Pre: $\pm 20\%$
Sodium	Inductively Coupled Plasma	None specified	Filtered liquid grab sample	Acc: $\pm 20\%$ Pre: $\pm 20\%$
Aluminum	Inductively Coupled Plasma	None specified	Filtered liquid grab sample	Acc: $\pm 20\%$ Pre: $\pm 20\%$
Iron	Inductively Coupled Plasma	None specified	Filtered liquid grab sample	Acc: $\pm 20\%$ Pre: $\pm 20\%$
TOC	Furnace Oxidation	> 10,000 $\mu\text{g}/\text{mL}$	Filtered liquid grab sample	Acc: $\pm 20\%$ Pre: $\pm 20\%$
Energetics	Differential Scanning Calorimetry/Thermogravimetric Analysis; Adiabatic Calorimetry	net exothermic energy > 0	Filtered liquid grab sample	Acc: $\pm 20\%$ Pre: $\pm 20\%$
Weight percent water	Gravimetry; Thermogravimetric Analysis	None specified	Filtered liquid grab sample	Acc: $\pm 20\%$ Pre: $\pm 20\%$
pH	Glass electrode	None specified	Filtered liquid grab sample	Acc: $\pm 20\%$ Pre: $\pm 20\%$
Specific gravity	Liquid Density	> 1.3 g/mL	Unfiltered liquid grab sample	Acc: $\pm 20\%$ Pre: $\pm 20\%$

WHC-SD-WM-PLN-091, REV. 0
FY 1995 Tank Waste Analysis Plan

Table 4-5 DQO-Based Analytical Requirements for Waste Compatibility

Analyte or Measurement	Analytical method	Notification Limit	Sample	Desired Accuracy and Precision
Volume percent solids	Centrifugation	None specified	Unfiltered liquid grab sample	Acc: ± 20 % Pre: ± 20 %
Separable organic layer	Visual	separable layer present	Unfiltered liquid grab sample	N/A
Viscosity	None specified	None specified	Unfiltered liquid grab sample	Not specified
Cooling curve	None specified	None specified	N/A	Not specified

¹ Assumes all phosphorus is present as phosphate. ² Performed only if the exotherm/endotherm ratio > 1.0.

WHC-SD-MM-PLN-091, REV. 0
FY 1995 Tank Waste Analysis Plan

Table 4-6 DQO-Based Analytical Requirements for the Flammable Gas Tank Curst Burn Safety Issue

Analyte or Measurement	Analytical method	Notification Limit	Sample	Desired Accuracy and Precision
Total organic Carbon	Direct Persulfate Oxidation	None specified	Unhomogenized auger sample	Acc: $\pm 20\%$ Pre: $\pm 20\%$
Percent moisture	Thermogravimetric Analysis	None specified	Unhomogenized auger sample	Acc: $\pm 20\%$ Pre: $\pm 20\%$
Net exothermic energy	Differential Scanning Calorimetry	net exo. > 0	Unhomogenized auger sample	Acc: $\pm 20\%$ Pre: $\pm 20\%$
Total exothermic energy	Adiabatic Calorimetry	> 140 cal/g	Unhomogenized auger sample	Acc: $\pm 20\%$ Pre: $\pm 20\%$
Pu-239/240 ¹	Separation/α counting	None specified	Unhomogenized auger sample	Acc: $\pm 20\%$ Pre: $\pm 20\%$
Cs-137 ¹	Gamma Energy Analysis	None specified	Unhomogenized auger sample	Acc: $\pm 20\%$ Pre: $\pm 20\%$
Sr-90 ¹	Separation/β counting	None specified	Unhomogenized auger sample	Acc: $\pm 20\%$ Pre: $\pm 20\%$
I-129 ¹	Gamma Energy Analysis	None specified	Unhomogenized auger sample	Acc: $\pm 20\%$ Pre: $\pm 20\%$
Np-237 ¹	Separation/α counting	None specified	Unhomogenized auger sample	Acc: $\pm 20\%$ Pre: $\pm 20\%$
Am-241 ¹	Gamma Energy Analysis	None specified	Unhomogenized auger sample	Acc: $\pm 20\%$ Pre: $\pm 20\%$
Tc-99 ¹	Liquid Scintillation	None specified	Unhomogenized auger sample	Acc: $\pm 20\%$ Pre: $\pm 20\%$

WHC-SD-WM-PLN-091, REV. 0
FY 1995 Tank Waste Analysis Plan

¹ Performed only if the DSC measurement indicates an energy content greater than 140 cal/g, or an in-tank camera indicates the presence of a dry crust ring.

MHC-SD-~~HM~~-PLN-091, REV. 0
FY 1995 Tank Waste Analysis Plan

Table 4-7 Rotary Core Vapor Sampling DQO-Based Analytical Requirements

Analyte or Measurement	Analytical method	Notification Limit	Sample	Desired Accuracy and Precision
Dodecane	GC or GC/MS	None specified	Vapor sample in SUMMA container	±40% of true value with 95% confidence
Tridecane	GC or GC/MS	None specified	Vapor sample in SUMMA container	±40% of true value with 95% confidence
Hexane	GC or GC/MS	None specified	Vapor sample in SUMMA container	±40% of true value with 95% confidence
Vinyl acetate	GC or GC/MS	None specified	Vapor sample in SUMMA container	±40% of true value with 95% confidence
Methylene chloride	GC or GC/MS	None specified	Vapor sample in SUMMA container	±40% of true value with 95% confidence
1,1-Dichloro-ethane	GC or GC/MS	None specified	Vapor sample in SUMMA container	±40% of true value with 95% confidence
Tributyl phosphate	GC or GC/MS	None specified	Vapor sample in SUMMA container	±40% of true value with 95% confidence
Toluene	GC or GC/MS	None specified	Vapor sample in SUMMA container	±40% of true value with 95% confidence
Benzene	GC or GC/MS	None specified	Vapor sample in SUMMA container	±40% of true value with 95% confidence
Acetone	GC or GC/MS	None specified	Vapor sample in SUMMA container	±40% of true value with 95% confidence

WHC-SD-WM-PLN-091, REV. 0
FY 1995 Tank Waste Analysis Plan

Table 4-7 Rotary Ccore Vapor Sampling D00-Based Analytical Requirements

Analyte or Measurement	Analytical method	Notification Limit	Sample	Desired Accuracy and Precision
1-Butanol	GC or GC/MS	None specified	Vapor sample in SUMMA container	±40% of true value with 95% confidence
Aliphatic nitriles	GC or GC/MS	None specified	Vapor sample in SUMMA container	±40% of true value with 95% confidence
Carbon tetrachloride	GC or GC/MS	None specified	Vapor sample in SUMMA container	±40% of true value with 95% confidence
Ammonia	SIE or IC	None specified	Vapor sample in midget bubbler	±40% of true value with 95% confidence
Nitric oxide	Not specified	None specified	Vapor sample in sorbant tube	±40% of true value with 95% confidence
Nitrous oxide	Not specified	None specified	Not specified	±40% of true value with 95% confidence
Nitrogen dioxide	Not specified	None specified	Vapor sample in sorbant tube	±40% of true value with 95% confidence
Water	Gravimetry	None specified	Vapor sample in sorbant tube	±40% of true value with 95% confidence
Hydrogen cyanide	SIE or IC	None specified	Vapor sample in midget bubbler	±40% of true value with 95% confidence
Hydrogen	Not specified	None specified	Not specified	±40% of true value with 95% confidence
Tritium	Liquid scintillation	None specified	Vapor sample in sorbant tube	±40% of true value with 95% confidence

Table 4-8 DQO-Based Analytical Requirements for Organic Fuel Rich Tanks

Analyte or Measurement	Analytical method	Notification Limit	Sample*	Desired Accuracy and Precision
TOC ¹	Direct Persulfate Oxidation	>5% (dry weight basis)	Duplicate samples of every homogenized half segment. Combined solids and drainable liquids.	±10% of notification limit; PQL=1%
Percent moisture ¹ (from safety screen)	Thermogravimetric Analysis	<17 weight %	Duplicate samples of every half segment.	±10% of notification limit; PQL=2%
Total fuel content (from safety screen)	Differential Scanning Calorimetry	≥125 cal/g (dry weight basis)	Duplicate samples of every homogenized half segment.	±10% of notification limit; PQL=1%
TOC ²	Furnace Oxidation	>5% (dry weight basis)	Duplicate samples of selected, homogenized half segments. Combined solids and drainable liquids.	±10% of notification limit; PQL=1%
Percent moisture ²	Gravimetry	<17 weight %	Duplicate samples of selected, homogenized half segments.	±10% of notification limit; PQL=2%
Adiabatic calorimetry ²	Adiabatic Calorimetry	≥125 cal/g (dry weight basis)	Duplicate samples of selected, homogenized half segments.	±10% of notification limit

Table 4-8 DQO-Based Analytical Requirements for Organic Fuel Rich Tanks

Analyte or Measurement	Analytical method	Notification Limit	Sample*	Desired Accuracy and Precision
Low molecular weight organic acids	GC/MS and/or HPLC ³	None specified	Duplicate samples of selected, homogenized half segments.	Detection limit of 3% by weight with an absolute error of 10% of sample mass for any single constituent
Equilibrium moisture content	Moisture loss as a function of relative humidity	None specified	Duplicate samples of selected, homogenized half segments.	not specified
Cs-137 ²	Gamma Energy Analysis	>1000 μ Ci/g	Water and fusion dissolution on duplicate samples of selected, homogenized half segments.	$\pm 10\%$ of notification limit; PQL=100 μ Ci/g
Cr and Mn oxidation state	method development required	None specified	Duplicate samples of selected, homogenized half segments.	Not specified
Cr and Mn concentration	Inductively Coupled Plasma	>5 weight % of dry sludge as MnO_4^- and $Cr_2O_7^{2-}$	Duplicate samples of selected, homogenized half segments.	Not specified
Nitrate	HPLC or equivalent	None specified	Duplicate samples of selected, homogenized half segments.	Not specified
Nitrite	HPLC or equivalent	None specified	Duplicate samples of selected, homogenized half segments.	Not specified

Table 4-8 DQO-Based Analytical Requirements for Organic Fuel Rich Tanks

Analyte or Measurement	Analytical method	Notification Limit	Sample*	Desired Accuracy and Precision
Hydroxide	Titration	None specified	Duplicate samples of selected, homogenized half segments.	Not specified

* Perform analyses on a dried sample of drainable liquid in addition to solid samples. TGA should be performed on liquid samples prior to drying. Primary analyte, Secondary analyte. See Tables 6-3 and 7-1 in *Tank Safety Screening Data Quality Objective* (Babad and Redus 1994) for criteria required before these analyses are performed. Analytical method currently under development.

WHC-SD-WM-PLN-091, REV. 0
FY 1995 Tank Waste Analysis Plan

Table 4-9 DQO-Based Analytical Requirements for Generic Tank Vapor Sampling

Analyte or Measurement	Analytical method	Notification Limit	Sample	Desired Accuracy and Precision
Combustible gasses	Combustible gas meter	>20% of Lower flammability limit	Tank headspace vapor sample	Not specified
Combustible gasses	Not specified	None specified	Tank headspace vapor sample	Not specified
Ammonia	Not specified	>50% of the consensus exposure standard	Tank headspace vapor sample	Not specified
Nitrogen dioxide	Not specified	>50% of the consensus exposure standard	Tank headspace vapor sample	Not specified
Nitric oxide	Not specified	>50% of the consensus exposure standard	Tank headspace vapor sample	Not specified
Water vapor	Not specified	None specified	Tank headspace vapor sample	Not specified
Hydrogen Cyanide	Not specified	>50% of the consensus exposure standard	Tank headspace vapor sample	Not specified
Volatile organic vapors	Not specified	>10% of the consensus exposure standard for any known or suspected carcinogen, teratogen, or mutagen present; or >50% of the consensus exposure standard for any non-carcinogen, non-teratogen, non-mutagen, or irritant present	Tank headspace vapor sample	Not specified

¹ If a single sample of tank vapor measures between 10% and 20% of the lower flammability limit, additional samples will be taken to determine the vapor constituents and concentrations of flammable constituents.

HHC-SD-MM-PLN-091, REV. 0
 FY 1995 Tank Waste Analysis Plan

Table 4-10 DQO-Based Analytical Requirements for Flammable Gas Tanks

Analyte or Measurement	Analytical method	Notification Limit	Sample	Desired Accuracy and Precision
Total Organic Carbon	Direct Persulfate Oxidation	> 3 wt% (30,000 μ g/g)	Unhomogenized auger sample	Acc: $\pm 20\%$ Pre: $\pm 20\%$
Percent Moisture	Thermogravimetric Analysis	None specified	Unhomogenized auger sample	Acc: $\pm 20\%$ Pre: $\pm 20\%$
Net Exothermic Energy	Differential Scanning Calorimetry	net exo. > 0	Unhomogenized auger sample	Acc: $\pm 20\%$ Pre: $\pm 20\%$
Total Exothermic Energy	Adiabatic Calorimetry	> 140 cal/g	Unhomogenized auger sample	Acc: $\pm 20\%$ Pre: $\pm 20\%$
Pu-239/240 ¹	Separation/ α counting	None specified	Unhomogenized auger sample	Acc: $\pm 20\%$ Pre: $\pm 20\%$
Cs-137 ¹	Gamma Energy Analysis	None specified	Unhomogenized auger sample	Acc: $\pm 20\%$ Pre: $\pm 20\%$
Sr-90 ¹	Separation/ β counting	None specified	Unhomogenized auger sample	Acc: $\pm 20\%$ Pre: $\pm 20\%$
I-129 ¹	Gamma Energy Analysis	None specified	Unhomogenized auger sample	Acc: $\pm 20\%$ Pre: $\pm 20\%$
Np-237 ¹	Separation/ α counting	None specified	Unhomogenized auger sample	Acc: $\pm 20\%$ Pre: $\pm 20\%$
Am-241 ¹	Gamma Energy Analysis	None specified	Unhomogenized auger sample	Acc: $\pm 20\%$ Pre: $\pm 20\%$

WHC-SD-WH-PLN-091, REV. 0
FY 1995 Tank Waste Analysis Plan

Table 4-10 DQO-Based Analytical Requirements for Flammable Gas Tanks

Analyte or Measurement	Analytical method	Notification Limit	Sample	Desired Accuracy and Precision
Tc-99 ¹	Liquid Scintillation	None specified	Unhomogenized auger sample	Acc: $\pm 20\%$ Pre: $\pm 20\%$

¹ Performed only if the DSC measurement indicates an energy content greater than 140 cal/g, or an in-tank camera indicates the presence of a dry crust ring.

This page intentionally left blank.

5.0 TANK CHARACTERIZATION PLANS

TCPs, letters of instruction, or test plans shall serve as the contracts for analytical work between the TWRS Characterization Program and the performing laboratory. As such, these documents require signature by the Characterization Program and the performing laboratory. TCPs integrate the results of the various issue- and process-based DQO efforts into specific sampling and analysis plans for a given tank. In addition, they specify the sample-specific quality assurance methods, the protocol for sampling and analysis, and the deliverables required of the laboratory. A TCP will be developed for most DSTs and SSTs sampled in FY 1995. Exceptions and the use of letters of instruction and test plans are discussed in Section 5.4.

5.1 TANK CHARACTERIZATION PLAN REQUIREMENTS

TCPs integrate the sampling and analytical interests of all relevant TWRS program elements for a given tank. Ultimately, each waste tank to be sampled will have a corresponding TCP that covers future sampling and analysis activities for that tank. These sampling and analysis requests shall be supported by (1) completed and approved DQO documents; (2) letters of request from programs that justify additional analyses. Other specific requirements concerning TCPs are as follows.

- One TCP shall cover Characterization Program-related sampling and analysis activities for a tank. Revisions of the TCP shall document any future sampling and analysis activities for that tank. Any sampling or analytical changes for a given sampling event shall be reflected in changes to that respective revision of the TCP, e.g., revision 0A.
- The TCP shall be approved before the respective sampling event. The 222-S Laboratory, 325 Laboratory, or other performing laboratories shall be signatories to ensure that the analytical requests are consistent with laboratory capabilities.
- The TCP shall be a WHC Supporting Document, making it amenable to change control.
- All DQO documents and/or letters of request used to prepare a TCP shall be referenced.

5.2 TANK CHARACTERIZATION PLAN PREPARATION

The sampling and analytical requirements of each tank on the FY 1995 Sampling Schedule are derived from the DQO-based information in Section 4.2. The TCP author shall consult Section 4.2 when preparing a TCP and it is recommended that the original DQO documents be studied as well. As mentioned above, many of the DQO efforts have overlapping sampling and analytical requirements. Each TCP shall employ the most stringent sampling and analytical requirements that apply. For example, one relevant DQO may specify

an analysis for percent water on a core sample at the segment level with a 20% accuracy while another relevant DQO may specify that the same analyte be measured on quarter segments with 10% accuracy. The TCP must then direct that percent water be measured on quarter segments with 10% accuracy.

5.3 TANK CHARACTERIZATION PLAN OUTLINE

The following is an outline of the TCP along with a brief description of each major section.

1. **Specific Tank Objectives:** This section shall identify the specific processes and safety or regulatory issues that relate to the characterization data to be gathered from this tank. This information should be available in the applicable DQO documents. The specific reasons for analyzing the tank waste shall be described, the appropriate DQO efforts shall be referenced, and how these DQO efforts were integrated into the TCP shall be explained. When preparing TCPs for process development sampling and analysis, the objectives may be provided through process memos and/or test plans in lieu of DQO efforts. The recommended outline for preparing a process development TCP is found in the Revised Interim Tank Characterization Plan Guidance (Schreiber 1994). The TCP should clearly identify the safety criteria, regulatory compliance, and process criteria that are important to decisions to be made from the data.
2. **Tank, Waste, and Sampling Information.** A summary of information describing the tank being analyzed is provided here. Information about the age, expected contents of the tank based on the tank's fill history, and the risers used for sampling shall be described or referenced. Note that the information about the age and expected tank contents exists in the respective tank characterization report, if it has been prepared. The amount and type (hardness and chemical composition) of waste in the tank shall be described or referenced. The number of cores, segments, potential layers, and expected recoveries shall be discussed. The sampling procedure(s) and/or work package, and the use of any hydrostatic head fluid or tracer shall be identified. The requirements for transporting samples to the laboratory shall also be specified.
3. **Sample Extrusion/Removal or Receiving Instructions.** The TCP shall describe the sample extrusion/removal and breakdown instructions to be used. The following items shall be identified or provided. Except for the fourth and last items, this information should be available in the applicable DQO documents.
 - Special observations (such as potential organic layers or solids) that are important during sample extrusion or removal
 - Samples to be taken before storage or homogenization

WHC-SD-WM-PLN-091, REV. 0
FY 1995 Tank Waste Analysis Plan

- Samples and analytes that have special holding times or need fast turn around times
- Clear instructions on how the phases are to be subsampled and analyzed if samples are expected to contain both solids and liquids
- Instructions on subsegment treatment and storage
- A description of compositing procedures and how partial segments or incomplete recovery will be handled
- Special quality control (QC) requirements (homogenization tests, duplicates, composites, blanks) associated with the extrusion/removal and hot cell work
- Instructions on how tracer concentration is to be monitored.

4. **Specific Sample Preparation, Analyte, Quality Control, and Data Criteria.** Topics described in Section 3.0 may be addressed in further detail in this section. A table in this section shall clearly identify each type of sample (field blank, hot cell blank, auger, grab, vapor, subsegment, segment, drainable liquid, separable solids/liquids, composite, or homogenization test) and the associated analyte; analytical method; procedure number and units; sample preparation; QC; safety, regulatory, or notification limits; and reporting format for each analyte being measured. The analytical procedure revision numbers should not be listed, as they will be identified in the data report/package. The table shall also contain the applicable task package identification numbers for the 222-S Laboratory and the appropriate work order number for the 325 Laboratory. A plan for addressing analytical priorities in case of incomplete sample recovery, and requests for reanalysis of samples shall also be included. This will be based on the priorities identified in the associated DQO efforts and the amount of sample needed for the different tests. Finally, this section shall identify applicable laboratory quality assurance and QC documentation, describe how it relates to the QC identified in the tables, and describe sample collection and handling activities.

5. **Organization.** A list of key personnel and their area of responsibility in the program management, sampling, extrusion/removal, and analysis shall be included. The objective of this list is not to reproduce the organizational structure for all operations, but to identify personnel that can answer questions about the data at a later date.

6. **Exceptions and Method Development.** This section shall address any DQO-based analyses for which methods do not exist, or for which present methods may be considered inadequate. It shall also address any exceptions to sampling, analytical, or QC demands specified in the respective DQO effort. Alternatives such as method development or the shipping of samples to another laboratory would be discussed.

7. **Deliverables.** The deliverables resulting from the characterization shall be specified in this section. The TCP shall clearly identify the notification limits for each analyte, whom shall be notified, the method of notification, and any other follow-up activities that may be required.
8. **References.** The TCP shall have a reference section that identifies all the appropriate program and laboratory documents that are used to support the characterization of the tank.

5.4 TANK CHARACTERIZATION PLAN EXEMPTIONS

All sampling and analysis of tank waste shall be supported by approved TCPs with the exceptions described below. Sampling and analysis activities not supported by TCPs shall be supported by letters of instruction or test plans.

5.4.1 Emergency Sampling Events

Emergency sampling events are defined at the discretion of the Characterization Program Manager, Field Sampling and Equipment. Normally, emergencies are based on tank conditions that exceed or may exceed the boundaries specified in operational safety requirements. These sampling events shall be placed at the top of the Sampling Schedule. Letters of instruction or TCPs shall be used to direct laboratory work.

5.4.2 Prior Agreements

Agreements may be made in advance to perform certain sampling and analysis activities without a TCP. Examples may include sampling and analysis contracted in a pre-existing Statement of Work.

5.5 TANK CHARACTERIZATION PLANS ISSUED IN FISCAL YEAR 1995

The FY 1995 Integrated Sampling Schedule details the tanks for which TCPs will be prepared and the required date of approval for FY 1995. It includes sampling from the 149 SSTs and 28 DSTs. Because of the commitment to comply with Recommendation 93-5, the majority of tanks to be core sampled in FY 1995 are Watch List tanks. The following assumptions were made in the preparation of the TCP schedule (1) The Sampling Schedule will be followed. (2) Writing and approval of each TCP will be accomplished in thirty calendar days. (3) There will exist adequate staff and funding to support TCP preparation.

6.0 TANK CHARACTERIZATION REPORT DELIVERABLES

6.1 INTRODUCTION

As stated in the Tri-Party Agreement (Ecology 1994), two functions of the *Tank Waste Analysis Plan* are to specify the contents of the tank characterization report and to identify the tank characterization reports to be submitted in FY 1995. A tank characterization report is an approved, publicly available document. Because it is intended to be a living document, it must be updated within 90 days as new tank information becomes available and as the waste tank contents change because of waste transfers, additions, or removals. The purpose of a tank characterization report is two-fold. First, a tank characterization report reviews, summarizes, and interprets the available historical knowledge regarding a waste tank. Second, it integrates that knowledge with recent sampling and analysis information contained in a characterization data report/package to identify the best estimate of the tank's contents.

A tank characterization report satisfies the following four functions.

- It verifies the quality and quantity of the historical and analytical data presented.
- It gives credible estimates of tank contents with documentable bases and interpretations.
- It provides a convenient reference for the various data users by presenting a relatively large amount of information in a compact, concise format.
- It reconciles discrepancies between sample results and tank model or historical data.

In this section, a general tank characterization report outline is presented, and tank characterization report delivery constraints are discussed. Also provided is a list of Tri-Party Agreement milestones and dates applicable to the delivery of tank characterization reports, and a list of the tank characterization reports to be delivered in FY 1995.

6.2 GENERAL TANK CHARACTERIZATION REPORT OUTLINE

This section gives a detailed explanation of each of the components that shall be included in a tank characterization report. Exceptions are granted for sections not applicable for a given tank characterization report (i.e., discussion of radiochemical analysis is not required if radiochemical analyses were not performed). This outline is based on *Tank Characterization Report (TCR) Procedure* (DeLorenzo 1993) and is not intended to be used as a procedure, given that each tank characterization report is unique to the specific nature of the tank for which it is written.

6.2.1 Executive Summary

The executive summary is a succinct overview of the most significant conclusions and information in the tank characterization report. This section should emphasize the most important features or issues associated with the tank. For instance, if there are any unreviewed safety questions for the tank, these should be summarized. The discussion should include features of the chemical, radiochemical, and physical properties of the waste. Also, a table showing the fractions of the major waste constituents and inventories of analytes affecting tank safety may be presented.

6.2.2 Introduction

6.2.2.1 Purpose

The purpose of the tank characterization report should be provided. Generally, a tank characterization report summarizes the available information regarding the waste in a tank, and arranges this information in a useful format that can be referenced by data users in both internal and external organizations.

6.2.2.2 Scope

The tank characterization report should present a broad background of preliminary information that was available before sampling and that initially guided the development of the sampling and analysis program. This material includes transfer records, observations from in-tank photographs, and inferences from waste simulant studies that may have been performed. The results of any core composite, segment, or other applicable analyses are summarized and presented in the tank characterization report, along with a statistical interpretation of the data. The information obtained from historical sources and possible synthetic waste studies is compared to the actual waste analyses. Tank constituents, inventories, and properties may then be established.

6.2.3 Historical Tank Information

6.2.3.1 Tank History

Examining the process history of a tank can uncover its physical characteristics as well as the processes that introduced waste into the tank. If these processes and subsequent waste types are studied in detail, hypotheses can be made about the expected contents of the tank. This section starts with a short history and description of the Hanford Site tank farms, SSTs, and DSTs. This description is intended to give an understanding of the layouts, processes, and conducts of operation at the Hanford Site to the reader. Basic tank design and typical configuration figures should be included in this section. This explanation is then followed by specific details about the tank that was analyzed, including facts about the tank design and history, process flows and waste streams, inter-tank transfers, and any stabilization or isolation activities.

6.2.3.2 Tank Status

This section discusses the present status of the tank. The bulk description and the current volume of the waste in the tank may be given, with estimates of salt cake, sludge, and supernate proportions. The estimated heat load, the tank bulk temperature, a tank schematic, and a montage showing the surface of the waste inside the tank, if available, are also incorporated into this section. If the tank is suspected or known to leak, this should also be discussed.

6.2.3.3 Process Knowledge

Although it is not the objective of a tank characterization report to determine the exact species concentrations in the tank from historical records, it is possible to give estimates of which components are expected to be found in the tank. This is accomplished by having a knowledge of the processes involved in creating the waste in the tank. By examining the approximate chemical composition of each waste stream, as well as the inflows, outflows, and transfers between tanks, estimated concentrations for selected isotopes, elements, and compounds can be determined. However, it is important to keep in mind that historical records are incomplete and were kept sporadically.

6.2.3.4 Historical Content Estimation

The Track Radioactive Constituents (TRAC) computer program was developed to estimate the radiochemical composition of the Hanford Site tank wastes. Waste inventories are estimated based on nuclear fuels production models, reprocessing and waste management flowsheets, tank transfers, and radioactive decay calculations. If TRAC estimates are given for the analyzed tank, these estimates for selected radionuclides and nonradioactive chemical constituents may be presented to support process knowledge estimates. Limitations in the TRAC model must be discussed, as well as the potential impact on TRAC estimate accuracy along with the verification of results from historical sampling events.

If the analyzed tank has been sampled previously, the results of these tank sampling and characterization actions are summarized in this section. Comments on data limitations and uncertainties, and the need for additional sampling should be addressed.

6.2.3.5 Tank Unreviewed Safety Questions

Many of the Hanford Site waste tanks have unreviewed safety questions associated with them. If the analyzed tank has an unreviewed safety question associated with it, this must be discussed in this section. This includes the actions or characterization required to resolve the unreviewed safety question. Processes and mechanisms that produced the waste are described and simulants and models of likely tank contents are included.

6.2.4 Sampling

6.2.4.1 Description of Sampling Event

This section should reference and provide the user with an understanding of the sampling plan and its implementation during sampling. Included in the discussion should be (1) a description of the equipment and procedures used for taking the samples from the tank being evaluated; (2) the tank risers used and the criteria for their selection; (3) the numbering system for cataloging the samples; and (4) the method of sampling. The reason for selecting that particular sampling method, and its impact on sample quality should be included.

6.2.4.2 Results of Sampling

Discussed in this section is sampling event information, which can reveal much about the physical characteristics of the waste. Such items as the time and location of sample acquisition, recoveries of the different segments, and problems and anomalies encountered while sampling and performing sample extrusion, or other hot cell work, should be included.

6.2.4.3 Chain of Custody

A chain of custody is maintained from sampling in the tank farm to delivery to the receiver laboratory for each sample container. Discussed should be a summary of the chain-of-custody forms, including any irregularities noted from the inspection that would merit a safety or sample integrity concern.

6.2.5 Description of Sample Handling and Analytical Scheme

This section discusses the sample handling and breakdown process, the analyses performed on each portion of the waste, and the program goals met by the various analyses. In general, separate suites of analyses are performed on segments, composites, drainable liquids, and homogenization samples from core samples. An explanation of these analyses would be divided into the following sections.

6.2.5.1 Homogenization Tests

Analyses are performed to measure the success in homogenizing the waste sample, and to provide an estimate of subsampling error. This section should include a list and description of the homogenization test procedures.

6.2.5.2 Rheological and Physical Measurements

The rheological and physical properties of the tank waste that were determined, and the identity of the portion of the sample upon which the analyses were performed, are discussed. Any sample preparation conducted before analysis is also described.

6.2.5.3 Sample Analyses

This section lists the type and description of the analytical tests performed on each core composite and segment, if a core sample was taken, or on other sample types if another sampling method was used. The preparation methods used for these samples or subsamples are also discussed. The procedures used for the analyses, general QA/QC and their specific execution in analysis, any meaningful differences to regulatory required procedures, and the basis for these procedural changes are also detailed.

6.2.6 Sample Extrusion/Removal and Preparation

6.2.6.1 Description of Sample Extrusion/Removal and Handling

In this section, the laboratory receipt of samples and holding times before extrusion or removal, whether samples were received and analyzed at the WHC 222-S Laboratory or at the Pacific Northwest Laboratory (PNL) 325 Laboratory, and any sample transfers between laboratories are discussed. Further, the laboratory extrusion process and procedures are reported, including any anomalies noted during extrusion of tank samples. The physical and chemical treatment of the samples before analysis is also addressed.

6.2.6.2 Description of Segments

During the sample extrusion process, the laboratory hot-cell chemist records the sample recoveries, liquid contents, phase changes within the sample, and sample consistency. These descriptions, along with photographs of the extruded segments, can aid in understanding the physical characteristics of the waste and are therefore included in the tank characterization report. General comments are given in this section regarding the stratification of the waste within the tank and any changing physical properties of the waste with waste depth are described. A synopsis of any chemical and radiological screening tests performed on the unhomogenized extruded segment is provided.

6.2.6.3 Physical and Thermal Analyses

In this section, physical property measurements such as particle size, viscosity, pH, percent water, shear strength, and settling and thermal properties are described. The discussion should include a description of the methods used, any difficulties encountered during analysis, and the results found for each sample. To help organization and presentation of the sample results and data, use of graphs, figures, and tables are recommended.

6.2.6.4 Chemical and Radiochemical Analyses

After the segment and composite samples are homogenized, they are prepared for analysis using one of the following methods; untreated aliquot, water digestion, acid digestion, acid dilution, extraction, or fusion dissolution. These preparations and the methods associated with these preparations are discussed in this section. The discussions should also include a summary of the effects on sample and analyte concentration because of the preparation method used and the digestion procedure employed. Further,

this section should address the methods of measuring chemical constituents. Finally, this section should include a description of the analytical methods used, any difficulties encountered during the analysis, and the results. Various methods are used in radiochemical analyses, such as alpha, beta, and gamma analyses, laser fluorimetry, and liquid scintillation counting. This section describes the analysis method used, any problems experienced during the analysis, and the results obtained for each sample. As with the physical and thermal analysis results, graphs, tables, and figures should be used to clarify the sample results and data.

6.2.7 Interpretation of Analytical Results

6.2.7.1 Tank Waste Profile

The objective of this section is to identify the waste profile of the tank or to develop a model for the spatial distribution of the compounds and radionuclides in the tank. This is accomplished by studying the segment results for those analytes distinct to the waste streams that were disposed in the tank (key indicator analytes) and relating these results with the process history.

6.2.7.2 Review of the Segment Analyte Profiles

Through investigation of segment results, vertical distribution of the analytes within a core can be ascertained. The horizontal distribution can be determined given the location of the risers where the sampling was performed. However, these spatial estimates are limited by the number of cores taken when the tank was sampled, the riser locations sampled, and the amount of segment recovery.

6.2.7.3 Tank Entrance/Exit Effects on Analyte Distribution

The process history of the tank can provide an indication of the chemicals and radionuclides expected to be present in the waste. With this knowledge, information regarding the location of the tank inlet and outlet nozzles can allow the effects of mixing, stratification, and combinations within the waste to be estimated.

6.2.7.4 In-Tank Chemistry

This section should describe the possible chemical reactions and other continuous changes in the tank waste characteristics, as well as the processes that could cause these changes. Plausible long-term thermal and radiological effects of these changes should also be included.

6.2.7.5 Calculated Bulk Inventories of Selected Analytes

Many safety issues are defined by weight percents or bulk amounts of specific analytes. This section presents the calculated bulk amounts of selected analytes and discusses their impact on the potential safety concerns. Disparities between historical or surveillance data and analytical results should also be discussed in this section.

6.2.7.6 Potential Waste Constituents

In evaluating the overall quality of the tank waste data, a material balance may be used. The material balance consists of summing the individual components of a sample to determine whether or not the entire sample mass was accounted for by the laboratory analysis.

6.2.8 Statistical Interpretation of the Data

This section should report the results of the statistical analysis of the sample data.

6.2.8.1 Mass Balances

A model that accurately describes the waste tank contents will have an average material balance composition near 100 percent and a very small standard deviation over the various samples taken. It should be assumed that the analytical data is accurate, and several models should be developed based on different assumptions on the waste forms and combinations present in the tank. These various models should then be compared, and the model that best depicts the waste should be selected to characterize the contents of the tank.

6.2.8.2 Charge Balances

A charge balance is a second tool in interpreting the composite data. In a charge balance, the charge associated with the cations should equal the charge of the anions. Several charge balance models should be developed, and the model that is most consistent with the laboratory analysis should be selected.

6.2.8.3 Concentration Estimates

This section should present the mean concentration estimates in the form of confidence intervals for each analyte of interest. The concentration estimates for each of the analytes found in the tank are presented as the mean concentration and the 95 percent confidence interval on the mean concentration.

6.2.8.4 Homogenization Tests

A core composite contains many segments of waste. Therefore, this section should explore the ability of the laboratory to effectively homogenize solid core and segment samples, which is a crucial step in preparing sample material.

6.2.8.5 Comparison Between Simulated and Actual Composites

A simulated composite is formed by combining the data obtained from the individual sub-samples used to generate the composite. To determine the ability of the laboratory to make composites that adequately represent the

tank waste, the results of the simulated composite should be compared with the data from the actual composite sample constructed in the laboratory.

6.2.8.6 Spatial Variability and Analytical Error Estimation

This section discusses the spatial variability, or the distribution of waste types within the tank, and the analytical error associated with the laboratory data. The spatial variability and the analytical error are represented statistically by a linear combination model and are then decoupled to determine the individual contributions from each source. Various constituent estimates and confidence intervals should also be presented and discussed.

6.2.9 Conclusions and Recommendations

The tank characterization report is intended to present the results of the analysis of the waste found in a Hanford Site waste tank. By examining the tank history and studying current tank data, the physical, thermal, chemical, and radiochemical properties of the waste may be identified. The conclusion should review important judgements and observations concerning the tank waste.

6.2.9.1 Results of the Data Validation Process

In this section, the laboratory data packages are reviewed and conclusions regarding data usability and defensibility are made. In this review, the limitations in data quality, laboratory procedural weaknesses, analytical and sampling errors, and QA/QC deficiencies are examined and explained. As well, the impact on the DQO-based decision rules is investigated based on the data restraints generated during the validation process.

6.2.9.2 Analytical Results

In this section, a summary of the tank characterization results is presented, including major waste constituents and the agreement between data results and historical model predictions.

6.2.9.3 Recommendations

This section should present recommendations regarding further characterization needs, safety issues, and impacts on future tank and sampling activities. These recommendations should be based on the data and analyses presented in the tank characterization report and the goals of the characterization effort. Conclusions about tank groupings should be made here to assist with future characterization and retrieval activities.

6.2.10 References

All documents, reports, manuals, and sources used in preparing the tank characterization report should be listed in this section.

6.3 TRI-PARTY AGREEMENT REQUIREMENTS

Within the Tri-Party Agreement (Ecology 1994), Milestone M-44-00 has been established regarding the delivery of tank characterization reports for each of the 177 Hanford Site waste tanks through FY 1999. Milestone M-44-00 has then been subdivided into various secondary milestones that detail the delivery schedule of these tank characterization reports. Table 6-1 lists these milestones and includes a description and the due date of each milestone.

Table 6-1 Tank Characterization Report-Related Tri-Party Agreement Milestones

Milestone	Description of milestone	Due date
M-44-03	Submit three tank characterization reports for initial evaluation and approval.	October, 1993 (completed)
M-44-05	Issue 20 tank characterization reports in accordance with the approved TCPs. If an approved TCP is not issued, the tank characterization reports must be approved by the Washington State Department of Ecology and the EPA.	September, 1994
M-44-08	Issue 30 tank characterization reports in accordance with the approved TCPs.	September, 1995
M-44-09	Issue 40 tank characterization reports in accordance with the approved TCPs.	September, 1996
M-44-10	Issue 40 tank characterization reports in accordance with the approved TCPs.	September, 1997
M-44-11	Issue 30 tank characterization reports in accordance with the approved TCPs.	September, 1998
M-44-12	Issue 14 tank characterization reports in accordance with the approved TCPs.	September, 1999

Milestone M-44-08 mandates that 30 tank characterization reports are to be delivered to the U.S. Department of Energy (DOE) by the end of FY 1995. Table 6-2 lists the specific tanks for which tank characterization reports will be delivered this fiscal year. Except for tanks C-111 and BX-112, waste from these tanks was sampled in FY 1994, and the sampling and analysis activities were directed by TCPs. It is anticipated that sampling and analysis of tanks C-111 and BX-112 in early FY 1995 will also be directed by a TCP. Therefore, the Tank Characterization Reports listed in Table 6-2 do not require approval by the Washington State Department of Ecology and the US EPA. It is necessary to note that this table lists the tanks in alpha-numeric order

WHC-SD-WM-PLN-091, REV. 0
FY 1995 Tank Waste Analysis Plan

and is not a prioritized list for delivery of the tank characterization reports.

Table 6-2 Specific Tank Characterization Report Deliverables by Tank for FY 1995

A-104	AN-107	AX-102	AX-104
AY-101	AY-102	AZ-102	B-102
BX-101	BX-102	BX-105	BX-108
BX-112	BY-104	BY-105	BY-106
C-102	C-103	C-104	C-105
C-106	C-108	C-111	S-106
SY-103	T-101	TX-118	U-106
	U-107	U-111	

6.4 TANK CHARACTERIZATION REPORT DELIVERY CONSTRAINTS

The production of a tank characterization report involves a multitude of participants, including the Tank Farms Operations personnel (sampling), the laboratories (analysis of sample), the tank characterization report author(s), and often Analytical Services (data validation). Because of the cooperative effort required to create a tank characterization report, the length of time required from the waste tank sampling event to the transmission of the data package to the tank characterization report author may present certain delivery constraints that could hinder the punctual completion of milestones.

Once the waste sample has been taken from the waste tank and sent to the laboratory, the laboratory has a specific amount of time to complete the analyses and prepare the data package. Table 6-3 summarizes the data analyses schedules required by the Tri-Party Agreement (Ecology 1994).

Table 6-3 Data Analysis Schedule*

Type of analyses	Time allowed for analysis and data package writing
SST samples	216 days, including validation
Transuranic and hot cell samples	136 days annual average; not to exceed 176 days, including validation
Low-level and mixed waste samples (up to 10 mrem/hour)	111 days annual average; not to exceed 126 days, including validation
Nonradioactive waste samples	86 days, including validation

*Taken from Ecology (1994).

WHC-SD-WM-PLN-091, REV. 0
FY 1995 Tank Waste Analysis Plan

All schedules are effective beginning with the date of the tank sampling activities.

Once the tank characterization report author has received the analytical data report or data package, a minimum of four months is required to write the report. Therefore, it may take from six months to one year to produce a tank characterization report once a tank is sampled. With this understanding, it is crucial that sampling activities are underway well in advance of tank characterization report milestones so that the tank characterization reports can be produced and the milestones can be met in a timely manner.

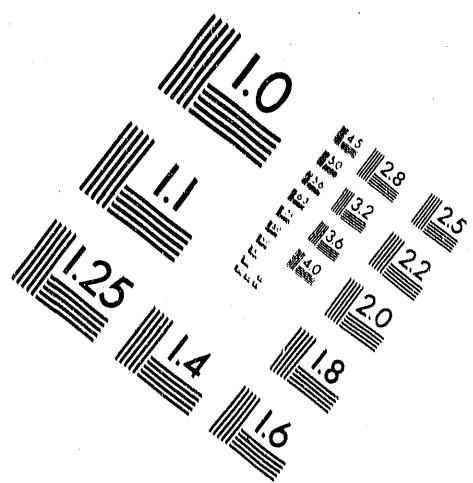
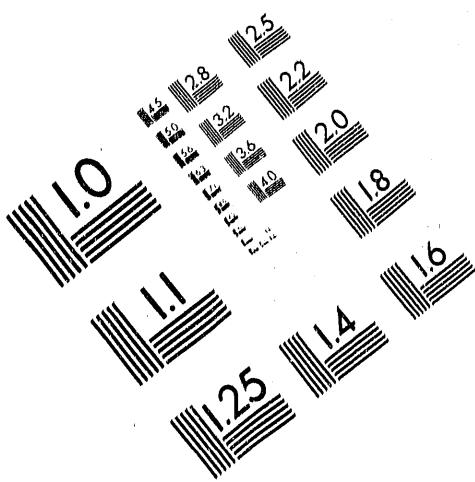
The tank characterization reports are intended to be living documents. Any tank characterization report affected by the addition/removal of waste, or new information about the waste, shall be updated within 90 days.



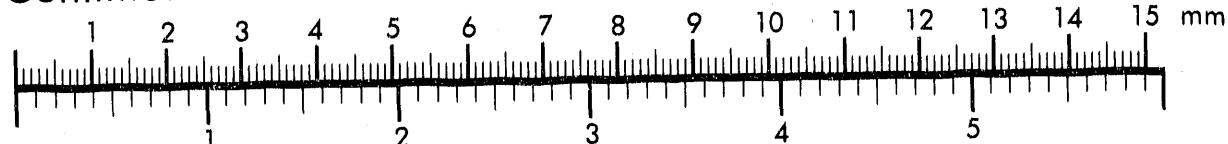
AIIM

Association for Information and Image Management

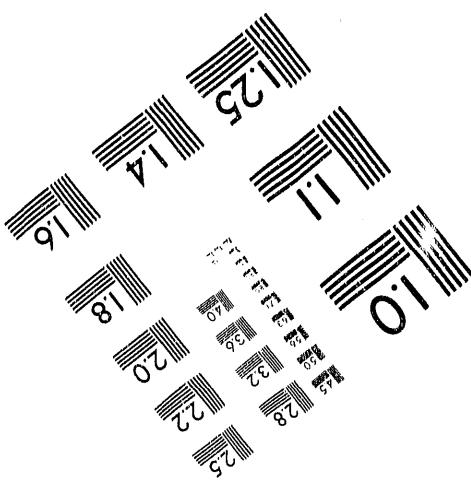
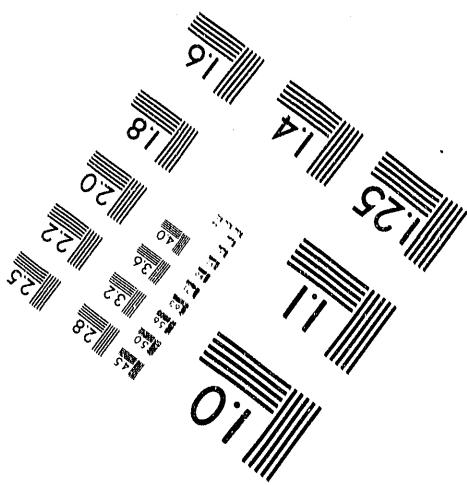
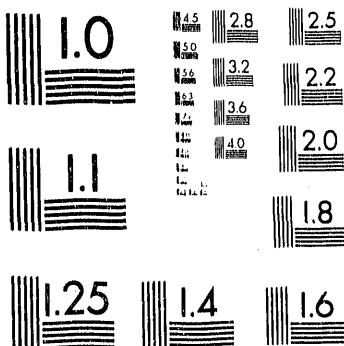
1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910
301/587-8202



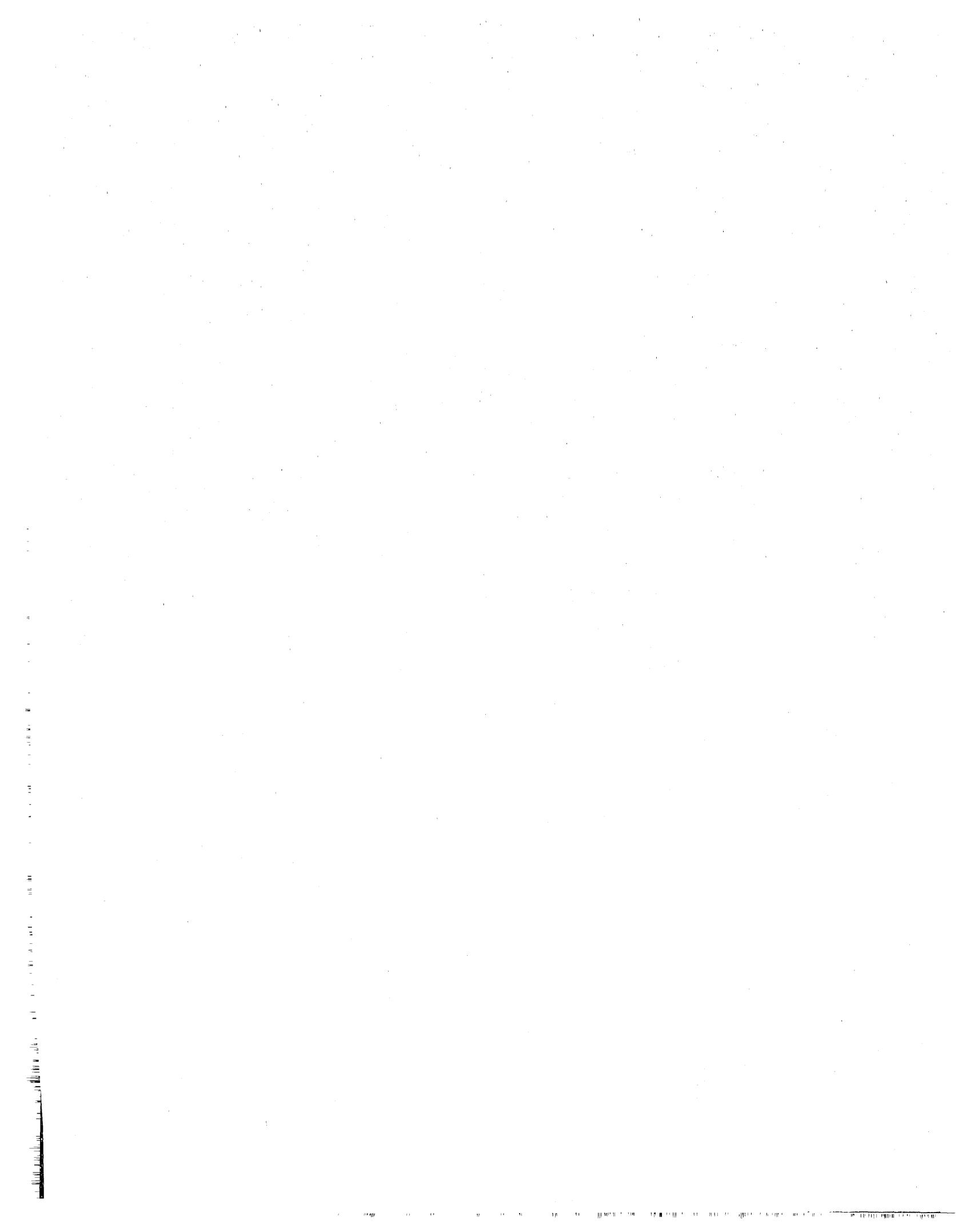
Centimeter



Inches



MANUFACTURED TO AIIM STANDARDS
BY APPLIED IMAGE, INC.



**DATE
FILMED**

6 / 14 / 95

END