W. I. Winters	R2-12	X
Central Files	L8-04	X
O.S.T.I. (2)	L8-07	X

OFFSITE

U. S. Department of Energy - Headquarters
Office of Environmental Restoration and
Waste Management EM-563
12800 Middlebrook Road
Germantown, MD 20874

K. T. Lang	X
J. A. Poppiti	X

Los Alamos Technical Associates
750 Swift, Suite 14
Richland, WA 99352

A. T. Dicenso	X
C. J. Lindquist	X
T. T. Tran	X
G. P. Westleigh	X

DISTRIBUTION SHEET

To	From	Page 1 of 2
Distribution	Characterization Support	Date 4/24/95
Project Title/Work Order		EDT No. 611602
Tank 241-SX-115 Tank Characterization Plan (WHC-SD-WM-TP-325, Revision 0)		ECN No.

Name	MSIN	Text With All Attach.	Text Only	Attach./ Appendix Only	EDT/ECN Only
<u>ONSITE</u>					
<u>U. S. Department of Energy - Richland Field Office</u>					
P. R. Hernandez	S7-54	X			
W. Liou	S7-54	X			
N. W. Willis	S7-54	X			
<u>MACTEC</u>					
J. P. Haney	S7-73	X			
<u>Pacific Northwest Laboratories</u>					
S. G. McKinley	P7-22	X			
J. T. Slankas	K9-81	X			
<u>Westinghouse Hanford Company</u>					
R. Akita	T6-20	X			
R. N. Campeau	S7-04	X			
T. F. Dale	T6-20	X			
S. J. Eberlein	R2-12	X			
C. A. Esvelt	S7-12	X			
G. D. Forehand	S7-31	X			
R. K. Fuller	T6-31	X			
V. W. Hall	H4-19	X			
W. J. Kennedy	S7-03	X			
J. G. Kristofzski	T6-06	X			
M. J. Kupfer	H5-49	X			
J. S. Lee	S7-03	X			
A. D. Olguin	S7-04	X			
A. D. Rice	T6-06	X			
L. M. Sasaki	R2-12	X			
P. Sathyanarayana (2)	R2-12	X			
J. S. Schofield	S7-12	X			
R. D. Schreiber (2)	R2-12	X			
R. H. Stubbs	S7-12	X			
C. L. Thomas	H4-19	X			
T. C. Trible	S1-57	X			
M. D. Webb	H4-25	X			

APR 24 1995
55 sta.5

ENGINEERING DATA TRANSMITTAL

Page 1 of 1

1. EDT № 611602

2. To: (Receiving Organization) SAMPLING OPERATIONS	3. From: (Originating Organization) TWRS/CHARACTERIZATION PLANS AND REPORTS	4. Related EDT No.: N/A
5. Proj./Prog./Dept./Div.: TWRS ENG/CPR	6. Cog. Engr.: L. M. SASAKI	7. Purchase Order No.: N/A
8. Originator Remarks: FOR ORIGINAL RELEASE		9. Equip./Component No.: N/A
		10. System/Bldg./Facility: TANK FARMS
11. Receiver Remarks:		12. Major Assm. Dwg. No.: N/A
		13. Permit/Permit Application No.: N/A
		14. Required Response Date: 4/24/95

15. DATA TRANSMITTED

(A) Item No.	(B) Document/Drawing No.	(C) Sheet No.	(D) Rev. No.	(E) Title or Description of Data Transmitted	(F) Approval Designator	(G) Reason for Transmittal	(H) Originator Disposition	(I) Receiver Disposition
1	WHC-SD-WM-TP-325		0	TANK 241-SX-115 TANK CHARACTERIZATION PLAN	Q	1,2	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 2. Release 5. Post-Review 3. Information 6. Dist. (Receipt Acknow. Required)	1. Approved 4. Reviewed no/comment 2. Approved w/comment 5. Reviewed w/comment 3. Disapproved w/comment 6. Receipt acknowledged

17. SIGNATURE/DISTRIBUTION (See Approval Designator for required signatures)

(G) Reason	(H) Disp.	(J) Name	(K) Signature	(L) Date	(M) MSIN	(J) Name	(K) Signature	(L) Date	(M) MSIN	(G) Reason	(H) Disp.
1	1	Cog.Eng. L. M. SASAKI	L M Sasaki	4/20/95	R2-12						
1		Cog. Mgr. J. G. KRISTOFZSKI	[signature]	4/21/95	T6-06						
1		QA T. C. TRIBLE	T.C. Trible	4/20/95	S1-57						
		Safety									
		Env.									
1	1	J. T. Slankas	L M Sasaki for JTSlankas (per telecon)	4/20/95							

18.	19.	20.	21. DOE APPROVAL (if required)
L. M. SASAKI L M Sasaki 4/20/95 Signature of Originator / EDT Date	W. J. Kennedy [signature] 4/24/95 Authorized Representative for Receiving Organization / Date	[signature] 4/21/95 J. G. KRISTOFZSKI Cognizant Manager / Date	Ctrl. No. [] Approved [] Approved w/comments [] Disapproved w/comments

BD-7400-172-2 (04/94) GEF097

BD-7400-172-1

RELEASE AUTHORIZATION

Document Number:	WHC-SD-WM-TP-325, REV 0
Document Title:	Tank 241-SX-115 Tank Characterization Plan
Release Date:	4/24/95

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 M. Broz — April 24, 1995

SUPPORTING DOCUMENT

1. Total Pages	31

2. Title	3. Number	4. Rev No.
TANK 241-SX-115 TANK CHARACTERIZATION PLAN	WHC-SD-WM-TP-325	0

5. Key Words

CHARACTERIZATION, SAFETY SCREENING, SINGLE-SHELL TANK, SAMPLING, ANALYSIS, TANK CHARACTERIZATION PLAN, NON-WATCH LIST

6. Author

Name: L. M. SASAKI

L. M. Sasaki 4/20/95
Signature

Organization/Charge Code 71520/N4168

7. Abstract

This document is a plan which serves as the contractual agreement between the Characterization Project, Sampling Operations, and WHC 222-S Laboratory. The scope of this plan is to provide guidance for the sampling and analysis of samples for tank 241-SX-115.

8. RELEASE STAMP

OFFICIAL RELEASE
BY WHC
DATE APR 24 1995
55 Sta. 5

A-6400-073 (08/94) WEF124

WHC-SD-WM-TP-325
Revision 0

Tank 241-SX-115 Tank Characterization Plan

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

by

Los Alamos Technical Associates
8633 Gage Boulevard
Kennewick, Washington 99336

TABLE OF CONTENTS

APPENDICES

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

DNFSB	Defense Nuclear Facilities Safety Board
DOE	U.S. Department of Energy
DQO	Data Quality Objective
DST	Double-Shell Tank
RCRA	Resource Conservation and Recovery Act of 1976
SAP	Sampling and Analysis Plan
SST	Single-Shell Tank
SX-115	Tank 241-SX-115
TCP	Tank Characterization Plan
TOC	Total Organic Carbon
TPA	Federal Facility Agreement and Consent Order (Tri-Party Agreement)
TWRS	Tank Waste Remediation System
WHC	Westinghouse Hanford Company

1.0 INTRODUCTION

The Defense Nuclear Facilities Safety Board (DNFSB) has advised the U.S. Department of Energy (DOE) to concentrate the near-term sampling and analysis activities on identification and resolution of safety issues (Conway 1993). The data quality objective (DQO) process was chosen as a tool to be used to identify the information needed for the resolution of safety issues. As a result, a revision in the Federal Facility Agreement and Consent Order (Tri-Party Agreement or TPA) milestone M-44 has been made, which states that "A Tank Characterization Plan (TCP) will be developed for each double-shell tank (DST) and single-shell tank (SST) using the DQO process ... Development of TCPs by the DQO process is intended to allow users (e.g., Hanford Facility user groups, regulators) to ensure their needs will be met and that resources are devoted to gaining only necessary information" (Ecology et al, 1994). This document satisfies that requirement for tank 241-SX-115 (SX-115) sampling activities.

2.0 DATA QUALITY OBJECTIVES APPLICABLE TO TANK 241-SX-115

The sampling and analytical needs associated with the Hanford Site underground storage tanks on one or more of the four Watch Lists (ferrocyanide, organic, flammable gas, and high heat) and the safety screening of all 177 tanks have been identified through the DQO process. A DQO identifies the information needed by a program group concerned with safety issues, regulatory requirements, tank waste processing, or the transport of tank waste. The DQOs that have beenm completed and are applicable to tank SX-115 are discussed in the following sections.

2.1 SAFETY SCREENING DATA QUALITY OBJECTIVES

The *Tank Safety Screening Data Quality Objective* (Babad and Redus 1994) describes the sampling and analytical requirements that are used to screen the waste tanks for unidentified safety issues. Both Watch List and non-Watch List tanks will be sampled and evaluated to classify waste tanks into one of three categories (SAFE, CONDITIONALLY SAFE, or UNSAFE). The safety screening DQO identifies the guidelines to determine to which classification a tank belongs based on analyses that indicate if certain measurements are within certain parameters. The primary analytical requirements for the safety screening of a tank are energetics, total alpha activity, moisture content, and flammable gas concentration. If a specified parameter is exceeded, further analysis of a second set of properties and a possible Watch List classification would be warranted. A tank can be removed from a Watch List if it is classified as SAFE. As of January 1995, tank SX-115 was classified as a non-Watch List tank,

To meet the sampling requirements of this DQO effort, a vertical profile of the tank waste shall be obtained from at least two widely spaced risers. This vertical profile may be obtained using core, auger, or grab samples. The safety screening analyses shall be applied to all core samples, DST Resource Conservation and Recovery Act (RCRA) samples, and all auger samples, except those taken exclusively to assess the flammable gas crust burn issue.

2.2 PRETREATMENT DATA QUALITY OBJECTIVES

Interim Data Quality Objectives for Waste Pretreatment and Vitrification (Kupfer et al. 1994) addresses the characterization needs for the Pretreatment, High-Level Waste Disposal, and Low-Level Waste Disposal programs. These programs are responsible for developing long-term treatment and storage processes for the Hanford Site Waste. This effort will require comprehensive physical and chemical information from waste tank samples. The Pretreatment process must be able to separate the waste into feed streams that satisfy the safety issues associated with the operating requirements for the low-level and high-level vitrification facilities.

3.0 TANK AND WASTE INFORMATION

This section summarizes the available historical information for SX-115. Included are the age of the tank, process history, and the expected contents of the tank based on historical information in *Historical Tank Content Estimate for the SW Quadrant of the Hanford 200 West Area* (Brevick et al. 1994). The fill history information is available in *A History of the 200 Area Tank Farms* (Anderson 1990).

3.1 TANK STATUS

As of December 1994, tank SX-115 is a non-Watch List tank and is passively ventilated with interim stabilization completed in 1978. The tank is classified as an assumed leaker in 1965 and intrusion prevention measures were completed in 1982. Approximately 45,000 liters (12,000 gallons) of waste, consisting of 22,700 liters (6,000 gallons) of sludge and 22,700 liters (6,000 gallons) of unknown waste with no pumpable liquid remaining are contained in the tank. The waste level measures about 25 centimeters (10 inches) in depth. The last solids update was obtained April 28, 1982. The last photograph taken March 18, 1988, revealed a dry, dark brown surface (Brevick et al. 1994). Temperature data, have not been available since 1991 because the thermocouple tree has been out of service (Hanlon 1995).

3.2 TANK CONFIGURATION

Single-shell tank SX-115 was constructed as a type IV tank between 1953 and 1954 and is located in the 200 West Area. Tank SX-115 is 23 meters (75 feet) in diameter and has a capacity of 3,800,000 liters (1,000,000 gallons). The tank is third in a three tank cascade flow system which includes tanks SX-113, 241-SX-114, and 241-SX-115. When the primary tank in the system became full, the waste would then flow to the secondary tanks in the system.

3.3 TANK HISTORY

Single-shell tank SX-115 was constructed between 1953 and 1954. Tank SX-115 was declared as an assumed leaker and removed from service in 1965 with a leak volume of 190,000 liters (50,000 gallons). Interim stabilization was declared in November 1978 and instursion prevention completed in September 1982. This tank contains non-complexed waste (NCPLX) with a total waste volume of 45,000 liters (12,000 gallons). The waste is comprised of 22,700 liters (6,000 gallons) of unknown waste and 22,700 liters (6,000 gallons) of sludge with no pumpable liquid remaining. Figure 3-1 summarizes the influx and effluent history of tank SX-115 (Anderson 1990).

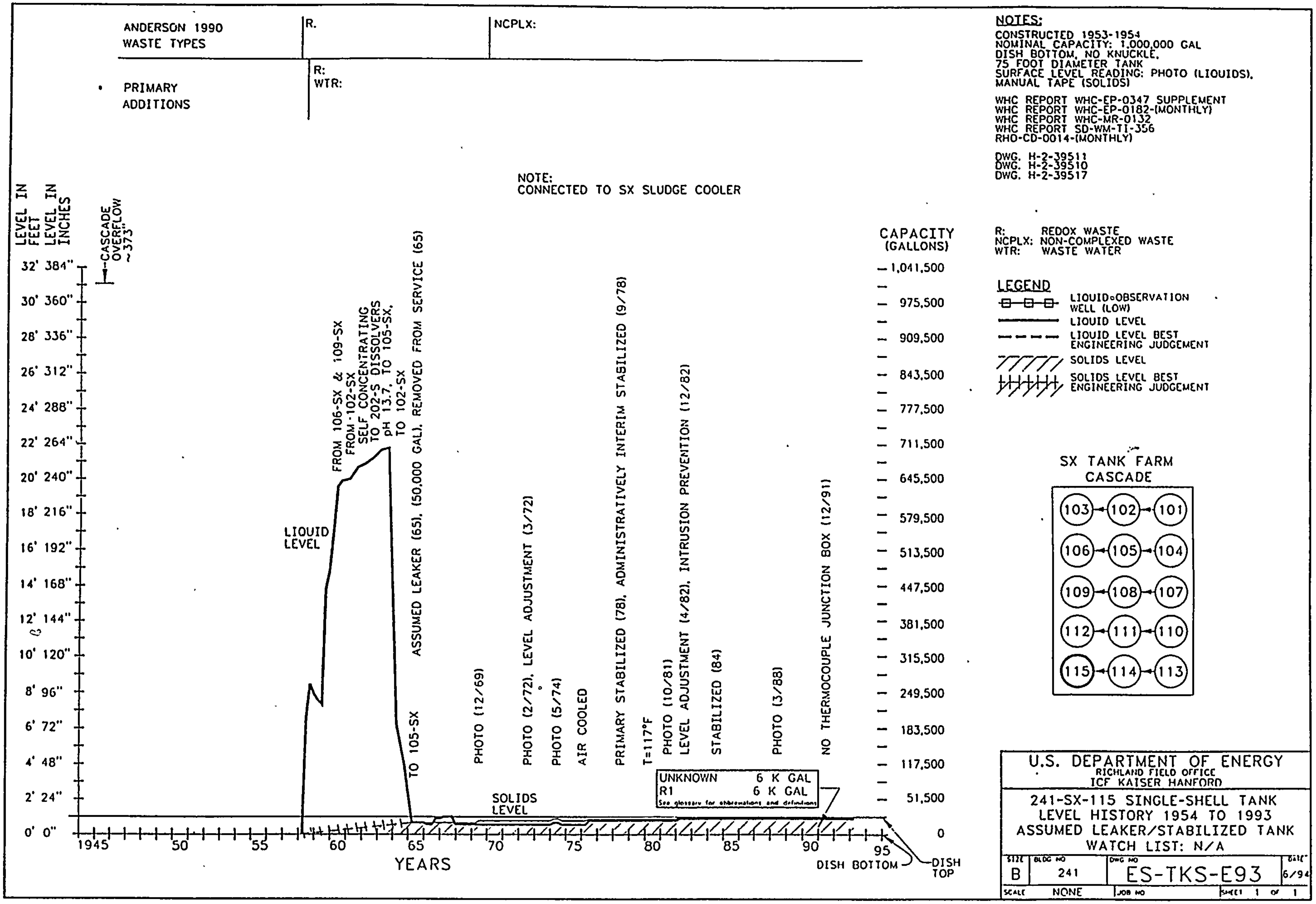
3.4 EXPECTED TANK CONTENTS

Tank SX-115 is expected to contain two primary layers of waste in the following order: Redox waste and an upper layer which is a supernate composed of unknown waste. Nitrate is present in high concentrations and plutonium is present in low concentrations (Brevick et al. 1994). An estimated inventory based on historical sample and analysis data is shown in Table 3-1 (Brevick et al. 1994).

Table 3-1: Tank SX-115 Solid Composite Inventory Estimate

Physical Properties		
Total solid waste	6.92E+04 kg (12 kgal)	
Heat load	0.16 kW (5.53E+02 BTU/hr)	
Bulk density	1.52 g/cc	
Void Fraction	0.68	
TOC wt% C (wet)	0.01	
Water wt%	43.66	
Chemical Constituents	**µg/g**	**kg**
Na^{+}	9.76E+04	6.76E+03
Al^{3+}	4.40E+04	3.04E+03
Fe^{3+} (total Fe)	1.54E+03	1.07E+02
Cr^{3+}	9.50E+03	6.57E+02
OH^{-}	9.60E+04	6.64E0+03
NO^{3-}	2.25E+05	1.56E+04
NO^{2-}	1.69E+03	1.17E+02
CO_3^{2-}	8.12E+03	5.62E+02
PO_4^{3-}	1.67E+03	1.16E+02
SO_4^{2-}	7.77E+03	5.37E+02
F^{-}	2.25E+02	15.6
Cl^{-}	84.47	5.84
$C_6H_5O_7^{3-}$	2.69E+02	18.61
$HEDTA^{3-}$	0.62	4.32E-02
Radiological Constituents		
Pu	5.83E-02 (µCi/g)	6.72E-02 (kg)
U	1.98E+03 (µg/g)	1.37E+02 (kg)
Cs	1.02E+02 (µCi/g)	7.03E+03 (Ci)
Sr	2.77E+02(µCi/g)	1.92E+04 (Ci)

Figure 3-1: Fill History of Tank 241-SX-115



4.0 TANK SX-115 SCHEDULED SAMPLING EVENTS

Because there is only a small amount of waste in tank SX-115, sampling of this tank will not add much to the knowledge of waste in the tank farms as a whole. However, in order to address the data requirements of the *Tank Safety Screening Data Quality Objective* (Babad and Redus 1994), sampling of the tank will be performed. The only known sample from tank SX-115 was in 1975; that sample indicated a low moisture content, which is of concern.

Because of the low inventory of waste and lack of pumpable liquids in tank SX-115, auger sampling is the most appropriate sampling method to employ. Using the auger sampling technique, conservative energetics and moisture content data will be established for the waste currently contained in tank SX-115. These conservative data will enable a specific safety category to be determined for tank SX-115 in accordance with the *Tank Safety Screening Data Quality Objective* (Babad and Redus 1994).

Only one sampling event for tank SX-115 is currently scheduled: an auger sample in June 1995. No other sampling of tank SX-115 is scheduled through Fiscal Year 1997 (Stanton 1995). The auger sampling shall be conducted following the *Tank Safety Screening Data Quality Objective* (Babad and Redus 1994) and *Interim Data Quality Objective for Waste Pretreatment and Vitrification* (Kupfer et al. 1994). Sampling and analytical requirements from these DQOs are summarized in Table 4-1. A more complete list of analytical requirements are given, as an appended attachment, in the appropriate Sampling and Analysis Plan (SAP).

Table 4-1: Integrated DQO Requirements

Sampling Event	Applicable DQO	Sampling Requirements	Analytical Requirements*
Auger	▪ Tank Safety Screening ▪ Pretreatment	Samples from 2 risers separated radially to the maximum extent possible	▪ Energetics ▪ Moisture Content ▪ Total Alpha

* These analytical requirements are for the Safety Screening DQO. Currently the Pretreatment Program does not require that any analyses be performed. See Section A6.1.

5.0 REFERENCES

Anderson, J. D., 1990, *A History of the 200 Area Tank Farms*, WHC-MR-0132, Westinghouse Hanford Company, Richland, WA.

Babad, H. and K. S. Redus, 1994, *Tank Safety Screening Data Quality Objective*, WHC-SD-WM-SP-004, Rev. 0, Westinghouse Hanford Company, Richland, WA.

Brevick, C. H., L. A. Gaddis, and W. W. Pickett, 1994, *Historical Tank Content Estimate for the SW Quadrant of the Hanford 200 West Area*, WHC-SD-WM-ER-352, Rev. 0, ICF Kaiser Hanford Company, Richland, WA.

Conway, J. T., Letter to H.R. O'Leary, DOE, "DNFSB Recommendation 93-5 to the Secretary of Energy." 9400070, dated July 19, 1993.

Ecology, EPA, and DOE, 1994, *Hanford Federal Facility Agreement and Consent Order, Fourth Amendment*, Washington State Department of Ecology, U.S. Environmental Protection Agency and U.S. Department of Energy, Olympia, Washington.

Hanlon, B. M., 1995, *Waste Tank Summary for Month Ending December 31, 1994*, WHC-EP-0182-81, Westinghouse Hanford Company, Richland, WA.

Kupfer, M. J., J. M. Conner, R. A. Kirkbride, and J. R. Mobley, 1994, *Interim Data Quality Objective for Waste Pretreatment and Vitrification*, WHC-SD-WM-DQO-011, Rev. 1, Westinghouse Hanford Company, Richland, Washington.

Stanton, G. A., 1995, *Baseline Sampling Schedule, Revision* 4.1, (Internal Memo 74320-95-01, to distribution, February 2), Westinghouse Hanford Company, Richland, WA.

APPENDIX A

SAMPLING AND ANALYSIS PLAN

FOR AUGER SAMPLING IN FISCAL YEAR 1995

TABLE OF CONTENTS FOR APPENDIX A

LIST OF TABLES FOR APPENDIX A

LIST OF FIGURES FOR APPENDIX A

LIST OF ABBREVIATIONS FOR APPENDIX A

ACL	Analytical Chemistry Laboratory
DOE	Department of Energy
DQO	Data Quality Objective
DSC	Differential Scanning Calorimetry
DST	Double-Shell Tank
GEA	Gamma Energy Analysis
HPGE/MCA	High Purity Germanium-multi channel analysis
IC	Ion Chromatography
ICP	Inductively Coupled Plasma - atomic emission spectroscopy
LIMS	Laboratory Information Management Systems
RCRA	*Resource Conservation and Recovery Act of 1976*
RSST	Reactive System Screening Tool
SARP	Safety and Analysis Report for Packaging
SAP	Sampling and Analysis Plan
SST	Single-Shell Tank
SX-115	Tank 241-SX-115
TCP	Tank Characterization Plan
TGA	Thermogravimetric Analysis
TOC	Total Organic Carbon
TWRS	Tank Waste Remediation System
USQ	Unreviewed Safety Question
WHC	Westinghouse Hanford Company

A1.0 SPECIFIC TANK CHARACTERIZATION OBJECTIVES

This Sampling and Analysis Plan will identify characterization objectives for sample collection, hot cell sample breakdown, and laboratory analytical evaluation and reporting requirements in accordance with the *Tank Safety Screening Data Quality Objective* (Babad and Redus 1994) and *Interim Data Quality Objective for Waste Pretreatment and Vitrification* (Kupfer 1994). These Data Quality Objectives (DQOs) are described in the Tank Characterization Plan (TCP) for tank 241-SX-115 (SX-115). The pretreatment DQO, at the request of the Pretreatment Program, will have limited use in this SAP (refer to section A6.1). This Sampling and Analysis Plan will also identify procedures and requirements, for collecting and characterizing samples from tank SX-115 by the auger sampling method.

A2.0 TANK STATUS AND SAMPLING INFORMATION

A2.1 TANK STATUS

Tank SX-115 was classified as an assumed leaker in 1965. Tank SX-115 is a non-Watch List tank and is passively ventilated with interim stabilization completed in 1978 and intrusion prevention measures completed in 1982. Tank SX-115 currently contains 45,000 liters (12,000 gallons) of non-complexed waste. The waste is comprised of 22,700 liters (6,000 gallons) of unknown waste and 22,700 liters (6,000 gallons) of sludge with no pumpable liquid remaining. This volume of waste corresponds to approximately 25 centimeters (10 inches) of waste. The last solids update was obtained April 28, 1982 and in the latest photograph, taken March 18, 1988, the surface appears a dry dark brown. The temperature is not availabel because the thermocouple tree has been out of service since December 1991 (Hanlon 1995).

A2.2 SAMPLING INFORMATION

Tank SX-115 is scheduled to be sampled by the auger sampling method. Samples are expected to be taken from risers 3 and 6. If a different riser is necessary to meet sampling and analysis requirements, this change must be recorded and approved in writing by the sampling cognizant engineer before sampling. The risers used may be recorded on a permanent data sheet or recorded directly in a work package. Sampling shall be conducted following procedures and documentation included in tank SX-115 work package WS-95-0070. If the sampling depth is within $\pm$5 inches of the current depth information, one 20 inch auger bit will be used for the sampling of each riser. In the event that the current depth information is incorrect, a different sized auger bit may be used. The objective of the sampling event is to reach the inner bottom of the tank (bottom of the waste) and the number of samples might change depending on the depth of the waste in the tank.

A3.0 SAMPLE EXTRUSION AND BREAKDOWN INSTRUCTIONS

A3.1 TANK-SPECIFIC ANALYTICAL PROCEDURES

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

As a precautionary measure, the Safety and Analysis Report for Packaging (SARP) in the work procedure TO-080-090 ("Load/Transport Sample Cask(s)") has been reviewed for an safety issued involved with transportation of tank SX-115 auger samples. **For tank SX-115 auger samples, the tranport sample casks <u>must</u> be vented every fifteen days from the time of the cask sealing to release any accumulated gas.**

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

Step 1 Receive auger samples at the laboratory in accordance with approved procedures.

Step 2 Conduct the following on the material from each sample:

- Perform a visual examination of the sample(s)
- Record observations. This may include a sketch of the sample in addition to written documentation of pertinent descriptive information such as color, texture, homogeneity, consistency.
- Note color and clarity of any drainable liquid.
- Report sample recovery results to the Characterization Program within one working day of sample breakdown.
- Take color photographs and/or a videotape to visually document the sample.

Step 3A Is drainable liquid present?

Yes: Proceed to Step 3B
No: Proceed to Step 5A

Step 3B Separate any drainable liquid from the solids. Measure and record the volume. Retain drainable liquids for further processing.

Step 4 Is the sample 100% drainable liquid?

Yes: Proceed to Step 14
No: Proceed to Step 5A

SOLIDS PATH

Step 5A Is there a hard, dry layer on the top of the auger sample?

Yes: Proceed to Step 5B
No: Proceed to Step 5C

Step 5B Separate the hard, dry layer and retain for analysis.

Step 5C Divide each auger sample into two equal subsample (i.e., half samples).

Step 6 Homogenize each subsample using the appropriate approved procedure.

Step 7 Will a homogenization test be performed ?

Yes: Proceed to Step 8
No: Proceed to Step 9

NOTE: One subsample per auger, at a minimum, should be used if a homogenization test is to be performed. Additional tests may be performed at the laboratory's discretion.

Step 8 Conduct the homogenization test by taking 1 to 2 g aliquot from widely separated locations of the homogenized subsample. Conduct the homogenization test in accordance with Bell (1993).

Step 9 Collect sufficient aliquots from each homogenized subsample to perform the appropriate preparations and analyses listed in Table A-1 in duplicate.

NOTE: If there is an insufficient amount of sample available in any subsample to perform all required analyses on the subsample, notify the Characterization Program within one business day and follow the prioritization of analyses given in Section A3.3.

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

Step 11 Combine subsamples proportional to the sludge recovery of the sample to build the solid composite.

Step 12 Remove 100 mL of the solid composite as the pretreatment solid composite archive (Bratzel 1994).

Step 13 Remove 125 mL of the solid composite for pretreatment process development work (see Section A6.2).

NOTE: If insufficient sample material is available to provide an archive and a sample for process development of the sizes described, divide the material remaining after Step 10 into equal portions (i.e., equal-sized portions for archive and process development work).

LIQUIDS PATH

Step 14 Closely inspect the liquid sample for the presence and approximate volume of any potential organic layers. Does the sample contain any immiscible (potentially organic) layers?

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

Step 15A Report any visually observed immiscible (potential organic) layer immediately by the early notification system (see Section A7.2).

Step 15B Separate and retain the potential organic layer for possible future analysis.

NOTE: Steps 16 through 22 shall be performed on the remaining (probable aqueous) liquid layer only.

Step 16 Filter the remaining liquid sample through a 0.45 micron filter.

Step 17 Is there greater than 1 gram of solid on the filter?

Yes: Proceed to Step 18
No: Proceed to Step 19

Step 18 Archive the solids for possible future analysis (Bratzel 1994).

Step 19 Remove sufficient aliquots from the liquid sample to perform the appropriate analyses listed in Table A-1 in duplicate.

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

Step 21 Combine the sample-level liquid proportional to the liquid recovery of the sample to build a liquid composite of the auger sample.

Step 22 Remove 100 mL of the liquid composite as the Pretreatment liquid composite archive (Bratzel 1994).

PRIMARY ANALYSIS PATH

Step 23 Perform primary analyses as listed in Table A-1.

Step 24 Compare the primary analysis data with notification limits.

Step 25A Do the results exceed the notification limits (Table A-1)?

Yes: Proceed to Step 25B.
No: Proceed to Step 28.

Step 25B Report results exceeding the notification limits using Format I reporting deliverable requirements as listed in Section A7.2.

SECONDARY ANALYSIS PATH

Step 26 Perform secondary analyses according to Table A-1.

Step 27A Do the secondary analyses exceed the notification limits?

Yes: Proceed to Step 27B
No: Proceed to Step 28

Step 27B Report results exceeding the notification limits using Format I reporting deliverable requirements as listed in Section A7.2.

Step 28 Report results as listed in Section A7.0.

A3.2 INSUFFICIENT SAMPLE RECOVERY

If the amount of material recovered from the samples taken from tank SX-115 is insufficient to perform the analyses requested and to permit a minimum 10 mL archive per sample, the laboratory shall notify the Tank Cognizant Engineer within one working day (See Table A-2). A prioritization of the analyses requested in this document is given in Section A3.3. Any analyses prescribed by this document, but not performed, shall be identified in the appropriate data report, with justification for non-performance.

A3.3 PRIORITIES OF REQUESTED ANALYSES

Confirmation of prioritization levels or revision of sample breakdown procedures may be provided to the laboratory by the Characterization Program based upon the sample recovery, readily observable physical property distinctions within the sample, and the requested sample breakdown procedures as provided in Section A3.1. The priority of an analysis is specified by its designation as a primary or secondary analysis. Further prioritization will be determined by the program on a DQO basis.

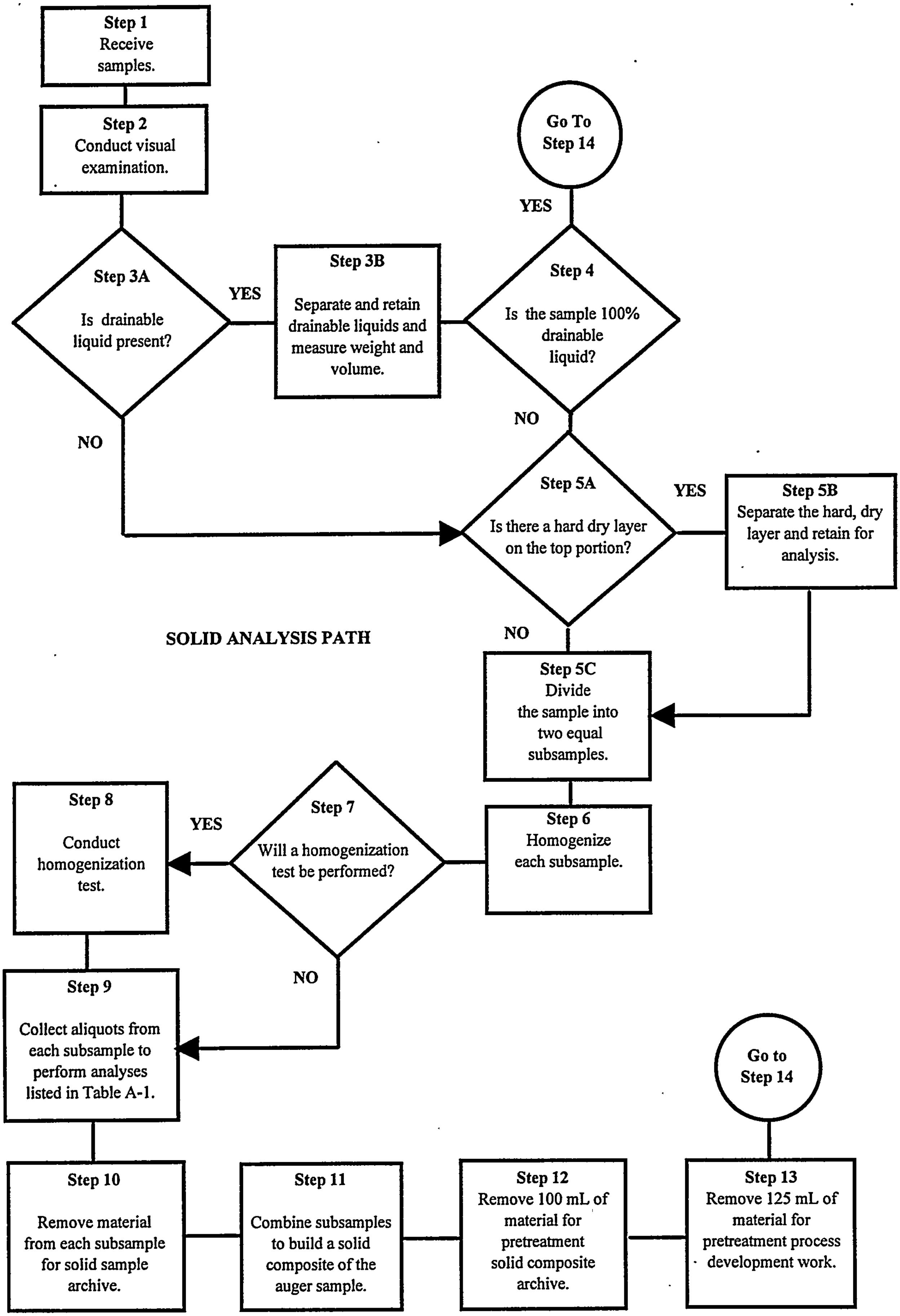


Figure A-1: Solid Analysis Flow Chart

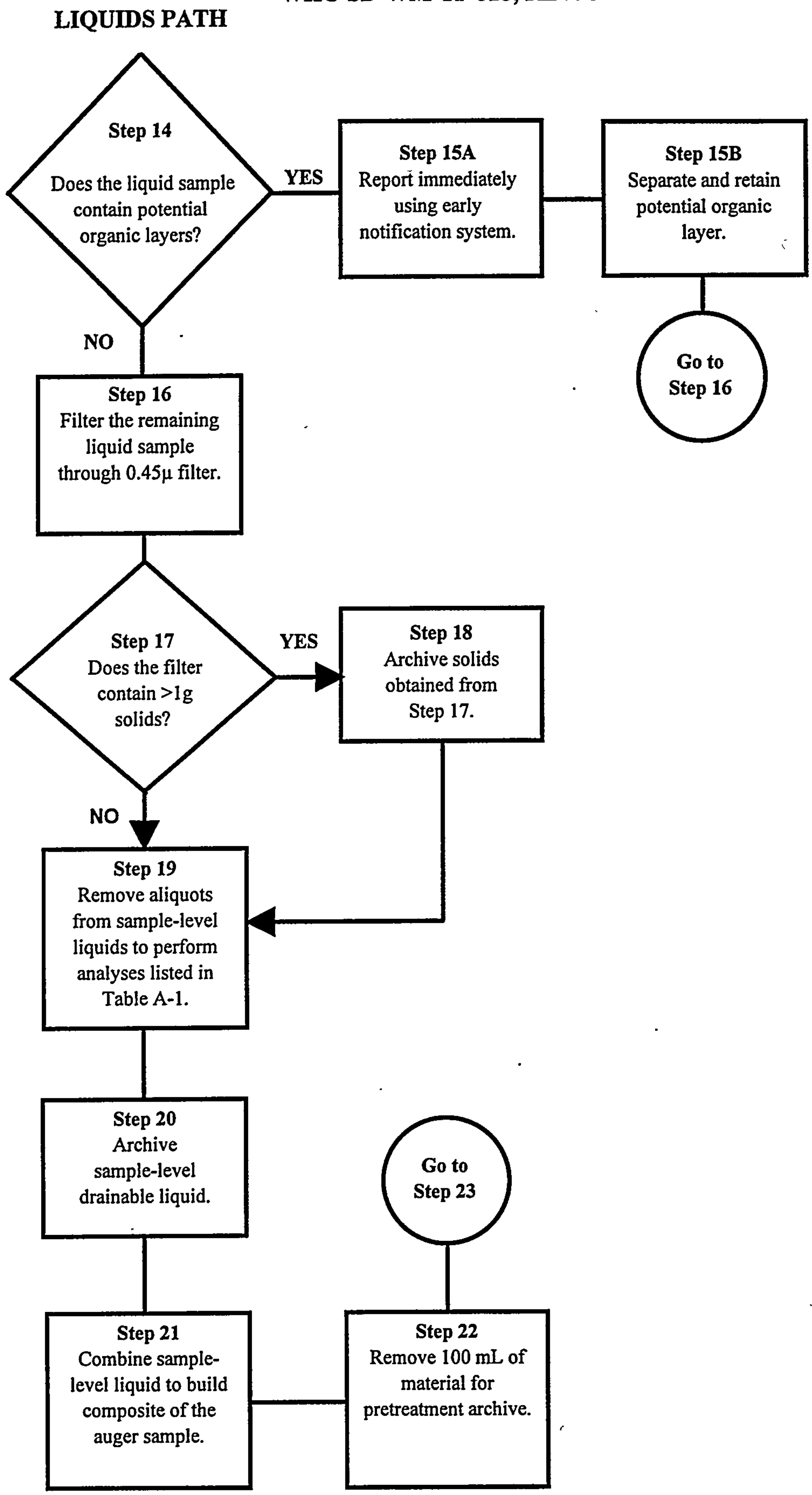


Figure A-2: Liquid Analysis Flow Chart

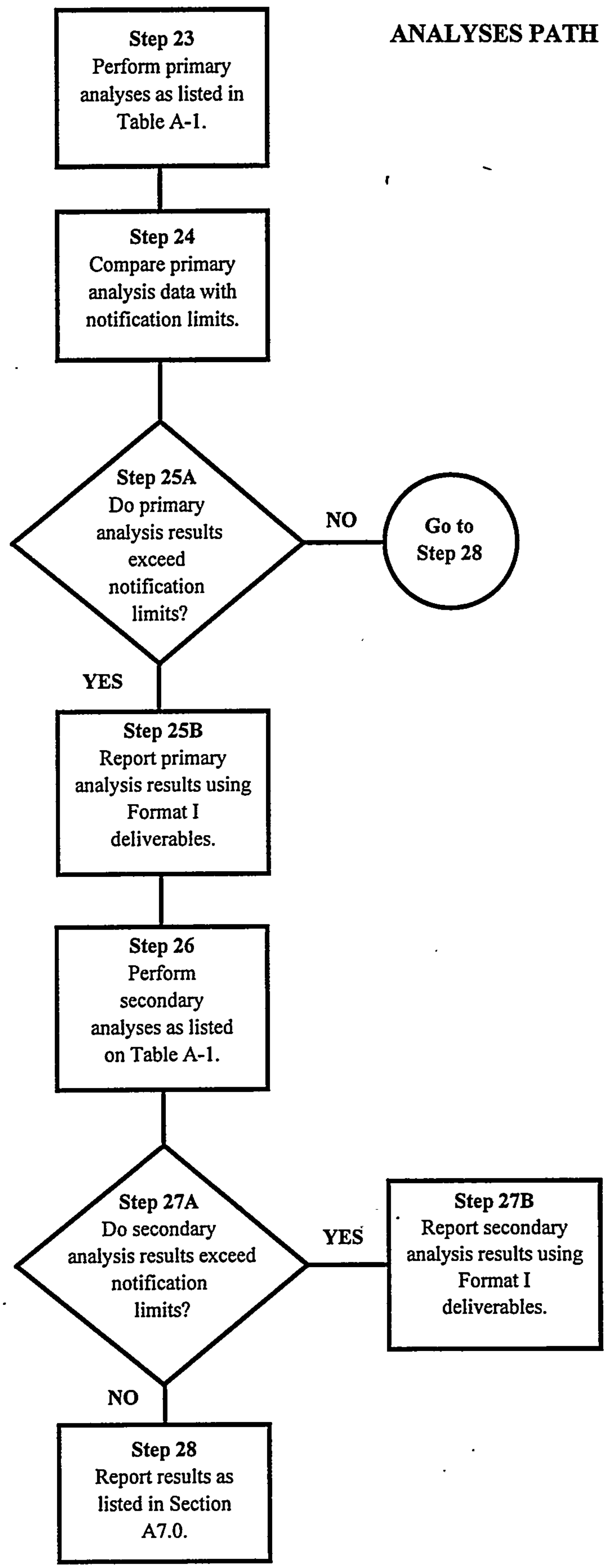


Figure A-3: Sample Analysis and Reporting Flow Chart

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

A4.1 SPECIFIC METHODS AND ANALYSES

The analyses in Table A-1 to be performed on the tank SX-115 samples are based on the safety screening DQO referenced in Section A1.0. The laboratory procedure numbers, which shall be used for the analyses, are included in this table.

A4.2 QUALITY ASSURANCE

A4.2.1 Laboratory Operations

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

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

A4.2.2 Sample Collection

Two auger samples are to be taken from tank SX-115 and shipped to the performing laboratory by Sampling Operations in accordance with work package WS-95-0070. That work package shall also initiate the chain-of-custody for the samples. Approved work procedure TO-080-090 ("Load/Transport Sample Cask(s)") is to be used during the sampling event. Samples shall be identified by a unique number before being shipped to the performing laboratory. The sampling team is responsible for documenting any problems and procedural changes affecting the validity of the sample in a field notebook. Sampling Operations shall enter this information in the comment section of the chain-of-custody form for addition to the data reports.

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

A4.2.3 Sample Custody

The chain-of-custody form is initiated by the sampling team as described in work package WS-95-0070. Samples are shipped in a cask and sealed with a Waste Tank Sample Seal.

WASTE TANK SAMPLE	
Supervisor:	Sample No.:
Date of Sampling:	Time of Sampling:
Shipment No.:	Serial No.:

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

Table A-1: Tank SX-115 Chemical, Radiological and Physical Analytical Requirements

SOLID ANALYSES

Project Name	SX-115 Auger Sample	**COMMENTS**		**REPORTING LEVELS**	
Plan Number	WHC-SD-WM-TP-325, REV. 0	Homogenization Test - Per Laboratory Discretion		FORMAT I	Early Notify
		Field Blank - Not Required		FORMAT II	Process Control
PROGRAM	**PROGRAM CONTACTS**	Hot Cell Blank - Per Laboratory Discretion		FORMAT III	Safety Screen
A. Safety Screening	Safety Screening E. J. Lipke			FORMAT IV	Waste Management
	TWRS L. M. Sasaki	**TANK**	**# AUGERS**	FORMAT V	RCRA Compliance
		SX-115	2	FORMAT VI	Special

PROGRAM	PRIMARY ANALYSES			SAMPLE[1]	PREP[2]	QUALITY CONTROL[3]						CRITERIA			FOR-MAT
	METHOD	ANAL.	WHC PROCEDURE	½ SEG SOLID		DUP	SPK/MSD	BLK	CALIB STD	PR	AC	UNITS	NOTIFICATION LIMIT[4]	EXPECTED RANGE[4]	
A	DSC	Energy	LA-514-113	X	d	ea smpl	N/A	N/A	ea AB	±10	90-110	J/g[5]	> 481	unknown	I, III
A	TGA	% H_2O	LA-560-112	X	d	ea smpl	N/A	N/A	ea AB	±10	90-110	wt%	< 17	unknown	I, III
A	Alpha	Total Alpha	LA-508-101	X	f or a	ea smpl	1/mtrx	ea PB	ea AB	±10	90-110	µCi/g	> 41	unknown	I, III
PROGRAM	**SECONDARY ANALYSES**			**SAMPLE[1]**	**PREP[2]**	**QUALITY CONTROL[3]**						**CRITERIA**			**FOR-MAT**
	METHOD	ANAL.	WHC PROCEDURE	½ SEG SOLID		DUP	SPK/MSD	BLK	CALIB STD	PR	AC	UNITS	NOTIFICATION LIMIT[4]	EXPECTED RANGE[4]	
A	RSST[9]	Energy	see 9 below	X	d	N/A	N/A	N/A	ea AB	±20	80-120	J/g	> 481	unknown	I, III
A	Distillation[9]	CN	LA-695-102	X	d	ea smpl	1/mtrx	ea AB	ea AB	±10	90-110	µg/g	> 39,000	unknown	I, III
A	Hot Persulfate[9]	TOC	LA-342-100	X	d	ea smpl	1/mtrx	ea AB	ea AB	±10	90-110	µg C/g	> 30,000	unknown	I, III
A	Sep. & α counting[10]	Pu-239/240	LA-503-156	X	f	ea smpl	1/mtrx[7]	ea PB	ea AB	±15	85-115	µCi/g	> 41	unknown	I, III
A	ICP[10]	Fe Mn U	LA-505-151	X	f or a	ea smpl	see[8]	ea PB	ea AB	±10	90-110	µg/g	none none none	unknown unknown unknown	III III III

[1]½ SEG SOLID-½ segment, solids
[2]d-direct, f-fusion dissolution, a-acid dissolution, w-water dissolution
[3]PR-precision, AC-accuracy, ea-each, smpl-sample, DUP-duplicate, SPK/MSD-spike and matrix spike duplicate, AB-analytical batch, PB-preparation blank, N/A-not applicable, mtrx-matrix
[4]Units for notification limits and expected range are those listed in the "units" column.
[5]Dry weight basis.
[6]Direct liquid samples may be diluted in acid or water to adjust to proper sample size and/or pH.
[7]Tracer or carrier may be used in place of a spike and results corrected for recovery.
[8]Either serial dilutions or matrix spikes will be performed.
[9]This analysis required if DSC exceeds notification limits. The RSST method, yet to be proceduralized, may be found in WHC-SD-WM-TP-104.
[10]Performed only if total alpha exceeds notification limit.

Table A-1: Tank SX-115 Chemical, Radiological and Physical Analytical Requirements

LIQUID ANALYSES

Project Name	SX-115 Auger Sample		COMMENTS		REPORTING LEVELS	
Plan Number	WHC-SD-WM-TP-325, REV. 0		Homogenization Test - Per Laboratory Discretion		FORMAT I	Early Notify
PROGRAM	PROGRAM CONTACTS		Field Blank - Not Required		FORMAT II	Process Control
			Hot Cell Blank - Per Laboratory Discretion		FORMAT III	Safety Screen
A. Safety Screening	Safety Screening	E. J. Lipke	TANK	# AUGERS	FORMAT IV	Waste Management
	TWRS	L. M. Sasaki	SX-115	2	FORMAT V	RCRA Compliance
					FORMAT VI	Special

PROGRAM	PRIMARY ANALYSES			SAMPLE[1]	PREP[2]	QUALITY CONTROL[3]						CRITERIA			FORMAT
	METHOD	ANAL.	WHC PROCEDURE	LIQUID		DUP	SPK/MSD	BLK	CALIB STD	PR	AC	UNITS	NOTIFICATION LIMIT[4]	EXPECTED RANGE[4]	
A	DSC	Energy	LA-514-113	X	d	ea smpl	N/A	N/A	ea AB	±10	90-110	J/g[5]	> 481	unknown	I, III
A	TGA	% H_2O	LA-560-112	X	d	ea smpl	N/A	N/A	ea AB	±10	90-110	wt%	< 17	unknown	I, III
A	Visual	Organic Layer	LA-519-151	X	d	N/A	N/A	N/A	N/A	N/A	N/A	none	presence	unknown	I, III
PROGRAM	SECONDARY ANALYSES			SAMPLE[1]	PREP[2]	QUALITY CONTROL[3]						CRITERIA			FORMAT
	METHOD	ANAL.	WHC PROCEDURE	LIQUID		DUP	SPK/MSD	BLK	CALIB STD	PR	AC	UNITS	NOTIFICATION LIMIT[4]	EXPECTED RANGE[4]	
A	RSST[10]	Energy	see 10 below	X	d	N/A	N/A	N/A	ea AB	±20	80-120	J/g[5]	> 481	unknown	I, III
A	Distillation[10]	CN	LA-695-102	X	d[6]	ea smpl	1/mtrx	ea AB	ea AB	±10	90-110	µg/mL	> 39,000[7]	unknown	I, III
A	Hot Persulfate[10]	TOC	LA-342-100	X	d[6]	ea smpl	1/mtrx	ea AB	ea AB	±10	90-110	µg C/mL	> 30,000[7]	unknown	I, III

[1] LIQUID- segment level liquid

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

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

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

[5] Dry weight basis.

[6] Direct liquid samples may be diluted in acid or water to adjust to proper sample size and/or pH.

[7] Action limit converted from weight basis assuming liquid density of 1.0 g/mL.

[8] Tracer or carrier may be used in place of a spike and results corrected for recovery.

[9] Either serial dilutions or matrix spikes will be performed.

[10] This analysis required if DSC exceeds notification limits. The RSST method, yet to be proceduralized, may be found in WHC-SD-WM-TP-104.

A5.0 ORGANIZATION

The organization and responsibility of key personnel involved with this tank SX-115 characterization project are listed in Table A-2.

Table A-2: Tank SX-115 Project Key Personnel List

Individual	Organization	Responsibility
L. M. Sasaki	TWRS Characterization Plans and Reports	TWRS Tank SX-115 Cognizant Engineer
E. J. Lipke	WHC Safety Program	Safety Screening Point of Contact
West Tank Farm Operations Shift Manager	Tank Farm Operations	200 West Tank Farm Point of Contact if Action Limit is Exceeded (373-3475)

A6.0 EXCEPTIONS, CLARIFICATIONS, AND ASSUMPTIONS

A6.1 EXCEPTIONS TO DQO REQUIREMENTS

In the safety screening DQO, it is specified that cyanide analyses are to be run on a quarter-segment level and that the notification limit for the DSC analysis is 125 cal/g. The revised ferrocyanide DQO (Meacham et al. 1994) has changed the requirements such that the cyanide analysis is now to be run on a half-segment level and the DSC notification limit is 115 cal/g (dry weight basis). This change will be incorporated in the next revision to the safety screening DQO. Therefore, although this Sampling and Analysis Plan uses the current safety screening DQO, it specifies that cyanide is to be run on a half-segment basis and that notification shall be made if the DSC value exceeds 481 J/g (115 cal/g) dry weight basis.

In the pretreatment DQO, a wide array of analyses has been requested. However, it has been determined by the Pretreatment Program that all of these analyses are not necessary for these samples. If necessary, the Pretreatment Program will personally contact the laboratory to run analyses on the archived composite samples. Therefore, the Pretreatment Program has directed that only a 125 mL composite solid sample for process development and a 100 mL composite sample for archive shall be obtained from this sampling event (Slankas 1995).

A6.2 CLARIFICATIONS AND ASSUMPTIONS

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

- Any exotherm (in cal/g or J/g) determined by differential scanning calorimetry (DSC) must be reported on a dry weight basis as shown in equation (1) using the weight percent water determined from Thermogravimetric Analysis

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

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

- The safety screening DQO (Babad and Redus 1994) requires that additional analyses be performed if total alpha activity measures greater than 1 g/L. Total alpha is measured in μCi/g rather than g/L. To convert the notification limit for total alpha into a number more readily usable by the laboratory, it was assumed that all alpha decay originates from Pu-239. The notification limit may then be calculated as shown in equation (2):

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

NOTE: If a density of 1.5 g/mL is assumed for solid material, the notification limit becomes 41 μCi/g.

- The safety screening DQO, upon which the analyses in Table A-1 are based, does not sufficiently address the analyses of any drainable liquid present. To characterize the tank waste adequately, all analyses performed on the solids for the safety screening DQO, with the exception of total alpha analyses, shall also be performed on any drainable liquid.

- The Pretreatment Program has requested 125 mL of the solid composite material for process development work. A test plan (Lumetta and Rapko 1994; Temer 1994) will be used to guide this process development work. Since the Characterization Program is responsible for the taking of tank samples, the Characterization Program will need to approve the test plan. This approval will not only ensure that the DQO process has been used in the generation of the test plan and that there is justification for the samples, but also that the facility receiving the samples is in an adequate position to handle radioactive material. At such time that the test plan is approved by the Characterization Program, the Characterization Program will direct the performing laboratory, via a letter of instruction, to allow shipment of the sample material to the performing laboratory.

A7.0 DELIVERABLES

All analyses of tank SX-115 waste material shall be reported as Formats I and/or III as indicated in Table A-1. Additional information regarding reporting formats is given in Schreiber (1994a).

A7.1 PROGRESS REPORTS

Each laboratory performing analyses on tank SX-115 waste material from this sampling project shall provide monthly status reports to the Characterization Program. This report shall contain 1) a summary of the activities on the analysis of tank SX-115, 2) preliminary results to the program, and 3) schedule and cost information on a DQO basis.

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

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

Schedule reporting shall consist of the following:

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

A7.2 FORMAT I REPORTING

Table A-1 contains the notification limits for each analyte. Any results exceeding their notification limits shall be reported by calling the West Tank Farm Operations Shift Manager at 373-3475 and the Characterization Program Office (Schreiber 1994b). This verbal notification must be followed within 1 working day by written communication, documenting the observations, to Characterization Plans and Reports, Characterization Program Office, Safety Screening Representative, and Process Control. Points of contact within each program/project are defined by Schreiber (1995). Additional analyses for verification purposes may be contracted between the performing laboratory and the contacts above by a revision to this document or by a letter of instruction.

A7.3 FORMAT III REPORTING

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

A8.0 CHANGE CONTROL

Under certain circumstances, it may become necessary for the performing laboratory to make decisions concerning a sample without review of the data by the customer or the Characterization Program. These changes shall be documented through the use of internal characterization change notices or analytical deviation reports for minor low-impact changes and documented in applicable laboratory reports. All significant changes (such as changes in scope) shall be documented by Characterization Plans and Reports via an Engineering Change Notice to this Tank Characterization Plan. All changes shall also be clearly documented in the final data report.

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

A9.0 REFERENCES

Babad, H., 1992, *An Overview of Progress Made Toward Resolving Priority One Safety Issues: Fiscal Year 1992*, WHC-SD-WM-EP-0606, Westinghouse Hanford Company, Richland, Washington.*

Babad, H. and K. S. Redus, 1994, *Tank Safety Screening Data Quality Objective*, WHC-SD-WM-SP-004, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Bell, K. E., 1993, *Tank Waste Remediation System Tank Waste Characterization Plan*, WHC-SD-WM-PLN-047, Rev. 1, Westinghouse Hanford Company, Richland, Washington.

Bratzel, D. R., Letter to S. M. Joyce, "Archiving Requirements", 7E720-94-125, dated June 23, 1994.

DOE, 1994, *Hanford Analytical Services Quality Assurance Plan*, DOE/RL-94-55, Rev. 0, U. S. Department of Energy, Richland Field Office, Richland, Washington.

Haller, C. S., 1994, *Fiscal Year 1995 Tank Waste Remediation System Tank Waste Analysis Plan*, WHC-SD-WM-PLN-091, Rev. 0, Westinghouse Hanford Company, Richland, Washington.*

Hanlon, B. M., 1995, Waste Tank Summary for Month Ending December 31, 1994, WHC-EP-0182-81, Westinghouse Hanford Company, Richland, Washington.

Hill, J. G., W. I. Winters, and B. C. Simpson, J. W. Buck, P. J. Chamberlain, V. L Hunter, 1991, *Waste Characterization Plan for the Hanford Site Single-Shell Tanks*, WHC-EP-0210, Rev. 3, Westinghouse Hanford Company, Richland, Washington.*

Kupfer, M. J., J. M. Conner, R. A. Kirkbride, and J. R. Mobley, 1994, *Interim Data Quality Objective for Waste Pretreatment and Vitrification*, WHC-SD-WM-DQO-011, Rev. 1, Westinghouse Hanford Company, Richland, Washington.

Lumetta, G. J. and B. M. Rapko, 1994, *TWRS Pretreatment Technology Development Project: Sludge Washing and Caustic Leaching Screening Tests*, PRT-TP-4.2, Rev. 0, Pacific Northwest Laboratory, Richland, Washington.

Meacham, J. E., R. J. Cash, G. T. Dukelow, H. Babad, J. W. Buck, C. M. Anderson, B. A. Pulipher, J. J. Toth, and P. J. Turner, 1994, *Data Requirements for the Ferrocyanide Safety Issue Developed through the Data Quality Objectives Process*, WHC-SD-WM-DQO-007, Westinghouse Hanford Company, Richland, Washington.

Meznarich, H. K., 1994, *Quality Assurance Program Plan for Laboratory Analysis and Process Testing*, WHC-SD-CP-QAPP-003, Rev. 1, Westinghouse Hanford Company, Richland, Washington.

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

Schreiber, R. D., 1994b, Letter to J. G. Kristofzski, "Format I Reporting Requirement", 7E720-94-128, dated August 15, 1994.

Schreiber, R. D., 1995, Letter to J. G. Kristofzski, "**REVISION:** Point of Contact/Distribution List", 71520-95-108 Reissue, dated March 23, 1995.

Slankas, J. T., 1995, Letter to R. D. Schreiber, TWRS-TDPO-95-009, dated February 2, 1995.

Taylor, L. H., 1993, *Quality Assurance Project Plan for Chemical Analysis of Highly Radioactive Mixed Waste Samples in Support of Environmental Activities on the Hanford Site*, WHC-SD-CP-QAPP-002 Rev. 0A, Westinghouse Hanford Company, Richland, Washington.

Temer, D. 1994, *Los Alamos National Laboratory Test Plan for Sludge Washing and Caustic Leaching Test*, Los Alamos National Laboratory, Los Alamos, New Mexico.

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

*included as a bibliographical reference