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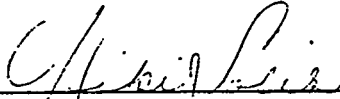
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Tank 241-TY-104 Tank Characterization Plan

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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

MASTER

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LIST OF ABBREVIATIONS

1C	1st cycle decontamination-BiPO ₄ process
ACL	Analytical Chemistry Laboratory
BL	B-Plant low level waste
DOE	Department of Energy
DQO	data quality objective
DST	double shell tank
DW	decontamination waste
NCPLX	noncomplexed waste
OWW	organic wash waste
R	redox waste
RIX	redox ion exchange waste
RCRA	<i>Resource Conservation and Recovery Act of 1976</i>
SST	single shell tank
TBP	tri-butyl phosphate
TCP	Tank Characterization Plan
TOC	total organic carbon
TWRS	Tank Waste Remediation System
TY-104	tank 241-TY-104
USQ	unreviewed safety question
WHC	Westinghouse Hanford Company

1.0 INTRODUCTION

The Defense Nuclear Facilities Safety Board has advised the DOE to concentrate the near-term sampling and analysis activities on identification and resolution of safety issues (Conway 1993). The data quality objective (DQO) process was chosen as a tool to be used to identify the analytical sampling needs for the resolution of safety issues. As a result, a revision in the Federal Facility Agreement and Consent Order (Tri-Party Agreement) milestone M-44 has been made, which states that "A Tank Characterization Plan (TCP) will 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-TY-104 (TY-104).

2.0 DATA QUALITY OBJECTIVES APPLICABLE TO TANK TY-104

The sampling and analytical needs associated with the 177 single-shell and double-shell underground storage tanks have been identified through the DQO process. DQOs identify information needed by a program group concerned with safety issues, regulatory requirements, or the transporting and processing of tank waste. As of February 1995, the DQOs that may apply to tank TY-104 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 waste tanks for unidentified safety issues. Both Watch List and non-Watch List tanks will be sampled and evaluated to classify the waste tanks into one of three categories: SAFE, CONDITIONALLY SAFE, or UNSAFE. A tank can be removed from a Watch List if it is classified as SAFE. The safety screening DQO identifies the requirements used to determine to which classification a tank belongs, based on analyses that indicate if certain measures are above or below established thresholds. The measures begin with the determination of the concentration of primary analytes which are considered indicators of potentially unsafe conditions within a tank. The primary analytical requirements for the safety screening of a tank are energetics, total alpha activity, moisture, and flammable gas concentrations. If a specific criteria level on one of these items is exceeded, further analysis and a possible change in tank classification may be required.

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 analyses shall be applied to all core samples, DST Resource Conservation and Recovery Act (RCRA) samples, and all auger samples, except auger samples taken exclusively to assess the flammable gas tank crust burn issue.

2.2 WATCH LIST DATA QUALITY OBJECTIVES

Based on the current classification of the tank, the Watch List DQOs applicable to tank TY-104 are: *Data Requirements for the Ferrocyanide Safety Issue Developed through the Data Quality Objective Process* (Meacham et al. 1994) and *Data Quality Objective to Support Resolution of the Organic Fuel Rich Tank Safety Issue* (Babad et al. 1994).

The DQO for the ferrocyanide safety issue concluded that the most reliable information is obtained from two widely spaced core samples. Two primary parameters, sodium nickel ferrocyanide concentration and moisture content, determine whether a tank is SAFE, CONDITIONALLY SAFE, or UNSAFE.

As with the ferrocyanide DQO effort, the sampling requirements of the organic fuel rich DQO effort are for a minimum of two widely spaced core samples. The primary analyses employed are organic carbon, presence of a free organic liquid phase, moisture content, and tank temperature. Additional analyses, if needed, include major organic species, certain oxidizing agents, hydroxide level, or radiochemical species.

2.3 FUGITIVE VAPOR EMISSION DATA QUALITY OBJECTIVES

DQOs concerned with fugitive vapor emissions from tank TY-104 are: *Data Quality Objectives for Generic In-Tank Health and Safety Vapor Issue Resolution* (Osborne et al. 1994a) and *Rotary Sampling Core Vapor Sampling Data Quality Objective* (Price 1994). Characterization of the tank headspace is needed to: 1) identify those tanks which can be sampled safely with intrusive equipment without risk of gas ignition; 2) identify and estimate concentrations of toxicologically significant compounds present in the tank headspace to establish worker safety precautions; and 3) support the startup and operation of the portable exhaustor used during rotary-mode core sampling.

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. Following resolution of the flammability issue, tank headspace samples will be taken to assess vapor toxicity. 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.

Tank TY-104 is one of the 36 tanks on the "Suspect Tank List" (Osborne and Huckaby 1994b). This list is composed of 20 Ferrocyanide Watch List tanks, 9 Organic Watch List tanks (one of which is also on the Ferrocyanide Watch List), and 8 tanks with a history of vapor incidents.

2.3 PRETREATMENT DATA QUALITY OBJECTIVES

Interim Data Quality Objectives for Waste Pretreatment and Vitrification (Kupfer et al. 1994), describes the sampling and analytical requirements to support the TWRS technical strategy by identifying the chemical and physical composition of the waste in the tank. In addition, the DQO works to guide development efforts to define waste pretreatment processes, which will in turn define high-level and low-level waste feed to vitrification processes.

3.0 TANK TY-104 HISTORICAL INFORMATION

This section summarizes the available information on tank TY-104. Included are the present status and physical description of the tank, its age, process history, and the expected contents of the tank based on historical information. The fill history information is available in *A History of the 200 Area Tank Farms* (Anderson 1990) and *Historical Tank Content Estimate for the Northwest Quadrant of the Hanford 200 West Area* (Brevick 1994). Characterization data on ferrocyanide tanks, including TY-104, are available in *Compendium of Characterization Data on Ferrocyanide Tanks* (Sathyanarayana 1993) and references therein.

3.1 FEBRUARY 1995 TANK STATUS

Tank TY-104, an assumed leaker, was officially added to the Ferrocyanide Watch List in January 1991 and to the Organic Watch List in May 1994. The amount of FeCN reported for the tank is 12,000 g-mol. A total organic carbon (TOC) level of 1 wt.% and a waste moisture content of 50 wt. % H₂O are listed for TY-104 (Hanlon 1994).

The tank waste temperature is monitored continuously by the Tank Monitor and Control System (TMACS). The highest waste temperature reading taken on October 22, 1994, from riser #4, was 22 °C (72 °F), which did not exceed the maximum temperature criteria (Hanlon 1994). The highest temperature in January 1995, obtained from Tank Farm Surveillance, is 20 °C (68 °F).

This tank currently contains non-complexed waste (NCPLX) with a total waste volume of 170 kL (46 kgal), which is equivalent to 60 cm (24 in) of waste as measured from the absolute bottom of the tank. The January 1995 surface level, as read automatically with a Food Instrument Corporation gauge located on riser #1, is 59.94 cm (23.60 in). The waste is comprised 160 kL (43 kgal) of sludge and 10 kL (3 kgal) of supernatant liquid with no saltcake present. A portion of the waste volume, 45 kL (12 kgal), is considered as drainable interstitial liquid (Hanlon 1994).

3.2 TANK CONFIGURATION

Tank TY-104 is one of six single-shell tanks in the 200 West Area TY Farm. It is 23 m (75 ft) in diameter and 7 m (23 ft) in operating depth. It has a concave-shaped base and a design capacity of 2,870 kL (758 kgal). However, safety issues require a maximum operating capacity of 2,840 kL (750 kgal). The tank has four active dry wells monitoring radiation in the surrounding soil (Hanlon 1994). Tank TY-104 is second in a cascade series consisting also of tank TY-103 (Brevick 1994).

3.3 TANK HISTORY

Tank TY-104 began to receive waste in the third quarter of 1953 from the tributyl phosphate (TBP) uranium extraction process at U-Plant. It was filled above operating capacity by 41 cm (16 in.). In 1955 waste was transferred to TY #1 cavern, and first-cycle decontamination waste from B-Plant and T-Plant was received from tank 241-TY-103. From 1959 through 1961, TY-104 received T-Plant decontamination waste from 241-TX-118.

In 1966, waste was transferred to tank 241-TX-118. From 1967 through 1970 decontamination waste was received from 241-TX-115 and organic wash water plus reduction oxidation ion-exchange waste from 241-TY-103. Waste was then transferred to 241-TX-118.

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Throughout 1974, waste was transferred to tank 241-TY-102 and 241-S-110. Tank TY-104 was removed from service in the fourth quarter of 1974 and labeled inactive in 1976. Table 2-1 summarizes the fill history from when tank TY-104 was first placed on active status to the present time.

Table 3-1: Tank TY-104 Fill History*

YEAR	QTR	TRANSACTION	LOCATION	WASTE TYPE	TOTAL VOLUME kL (kgal)
1953	3	Received	U-Plant	TBP	666 (176)
1953	4	Transfer	TX-118	TBP	534 (141)
1955	1	Received	TY-103	TBP, 1C	2,870 (758)
1955	3	Transfer	TY #1 Cavern	TBP, 1C	314 (83)
1959	2	Received	TX-118	TBP, 1C	1,140 (301)
1960	2	Received	TX-118	TBP, 1C	1,880 (498)
1961	1	Received	TX-118	TBP, 1C, DW	1,720 (456)
1961	3	Received	TX-118	TBP, 1C, DW	2,780 (736)
1966	3	Transfer	TX-118	TBP, 1C, DW	2,170 (574)
1966	4	Transfer	TX-118	TBP	235 (62)
1967	2	Received	TX-115	TBP, DW	647 (171)
1967	3	Received	TX-115	TBP, DW	1,400 (369)
1969	4	Add	TY-104	WATER	
1969	4	Transfer	TX-118	TBP, DW	2,700 (714)
1970	1	Received	TY-103	DW-R	
1970	1	Transfer	TX-118	DW-R	2,570 (679)
1970	2	Transfer	TX-118	DW	689 (182)
1970	4	Received	TY-103	DW-OWW-RIX	2,740 (724)
1974	1	Transfer	S-110	DW-OWW-RIX	193 (51)
1974	3	Transfer	TY-102	----	155 (41)
1974	4	Transfer	TY-102	BL-OWW-RIX	151 (40)
1974	2	Removed from service		BL-OWW-RIX	174 (46)
1976	1	Inactive		NCPLX	163 (43)
1978	4	Primary Stabilized		NCPLX	174 (46)
1983	4	Interim Stabilized		NCPLX	174 (46)
1994	3			NCPLX	174 (46)

*(Anderson 1990)

3.4 ESTIMATED TANK CONTENTS

Tank TY-104 is expected to contain two primary layers of waste. The upper supernatant liquid layer consists of REDOX high-level waste, B Plant low-level waste, organic wash waste, REDOX ion exchange waste, and decontamination waste. The lower sludge layer should contain several types of waste including TBP waste, first cycle waste, and decontamination waste (Hill et al. 1990).

A summary of the most current analytical data available on tank TY-104 is reported in Table 3-2 (Weiss and Mauss 1987). The characterization results of analyses performed by the 222-S Laboratory represent average analyte concentrations from two core samples.

Table 3-2: TY-104 Core Composite Chemical, Radiochemical, and Physical Characterization Data¹

Physical Data			
Total tank waste (kgal)		46	
Radiation (mR/hr)		1375	
Bulk Density (g/mL)		1.625	
Particle Size (μm)		8.1	
pH		11.95	
Viscosity (cP)		10,000	
Chemical Constituents ($\mu\text{g/g}$)		Chemical Constituents ($\mu\text{g/g}$)	
Al	8.80E+03	SO ₄ ²⁻	3.93E+03
Ba	4.25E+02	NO ₃ ⁻	1.12E+04
Bi	1.80E+04	CO ₃ ²⁻	1.80E+04
Cd	1.70E+01	TOC	1.93E+03
Cr	1.65E+03	OH ⁻	1.38E+03
Fe	4.26E+04	Radionuclides ($\mu\text{Ci/g}$)	
Pb	6.15E+02	^{239/240} Pu	1.98E-01
Mn	1.51E+03	Total Alpha	2.52E-01
Ni	1.74E+03	¹⁴ C	3.59E-03
P	2.89E+04	⁹⁰ Sr	2.25E+02
Si	1.00E+04	⁹⁹ Tc	3.23E-02
Ag	8.62	Total Beta	6.58E+02
Na	1.16E+05	²⁴¹ Am	3.41E-02
Zr	1.88E+02	⁶⁰ Co	1.68E-02
U	2.46E+04	¹³⁷ Cs	3.56E+01
Cl ⁻	5.58E+02	¹²⁹ I	5.38E-02
F ⁻	5.11E+03	Total Gamma	3.62E+01
NO ₃ ⁻	4.38E+04		

¹(Weiss and Mauss 1987)

Tank TY-104 headspace samples were collected through triple sorbent traps using the in situ sampler on August 5, 1994. Table 3-3 lists the mean headspace concentrations of target analytes detected in tank TY-104 samples at Oak Ridge National Laboratory (Dindal et al. 1995). A total of 142 additional compounds were tentatively identified in a mass spectral library search of by operator evaluation in at least one of the samples. Several organic compounds were tentatively detected at high concentrations (0.2 - 0.5 mg/m³) such as 3-methyl-hexane, 3,3-dimethyl-pentane, and 2-methyl-hexane. Several polychlorinated biphenyls were detected at low levels (~0.003 mg/m³). Organic concentrations were estimated by GC/MS at 1.6 mg/m³ for target and 3.2 mg/m³ for non-target analytes, yielding a mean total organic concentration of 4.8 mg/m³. Total organic load was estimated by GC-FID to be 1.5 mg/m³.

Table 3-3: Mean Headspace Concentrations of Target Analytes, GC/MS Analysis for Tank TY-104 samples.¹

Target Analyte	Mean Concentration, ppm	Standard Deviation	Target Analyte	Mean Concentration, ppm	Standard Deviation
Acetonitrile*	0.075	0.0042	Pentanenitrile	0.0026	0.00020
Acetone*	0.14	0.030	2-Hexanone	0.0014	0.000039
Methylene Chloride*	0.0013	0.000017	Octane	0.0051	0.00047
Propanenitrile	0.011	0.0010	Hexanenitrile	0.0014	0.000022
Butanal	0.016	0.0059	2-Heptanone*	0.0011	0.000084
Hexane	0.0056	0.00043	Nonane*	0.00087	0.000015
Benzene	0.0017	0.00043	Heptanenitrile*	<0.00091	-
1-Butanol*	0.098	0.0024	2-Octanone*	0.00060	0.000056
Butanenitrile	0.0030	0.00026	Octanenitrile*	<0.0012	-
2-Pentanone	0.0036	0.00021	Nonanenitrile*	<0.0010	-
Heptane*	0.025	0.0012	Dodecane	0.013	0.00069
Toluene	0.022	0.00049	Tridecane*	0.036	0.0029

1 (Dindal et al. 1995)

* Indicates that one or more samples fell outside the calibration range.

† Only analytes which were detected are listed.

In addition, calculation models have been developed using vapor liquid equilibria, tank farm measurements, and empirical correlations to estimate tank farm vapor space composition. By using the available Westinghouse Hanford Company (WHC) analytical data on the waste composition and volume, a model input has been developed and implemented. The resulting estimated vapor composition for tank TY-104 (Scott 1994) is summarized in Table 3-4.

Table 3-4: Tank TY-104 Estimated Vapor Composition¹

Analyte	Vapor Concentration*	Analyte	Vapor Concentration*
Al	1.09E-06	P	6.18E-06
CO ₃ ²⁻	3.11E-05	PO ₄ ³⁻	1.60E-06
Cr	3.77E-07	SiO ₃ ²⁻	2.68E-07
F ⁻	8.52E-08	SO ₄ ²⁻	3.37E-07
Fe	2.20E-07	TOC [†]	7.98E-06 g C/L
Na	1.52E-04	ZrO ₂ ⁺	2.16E-07
Ni	2.11E-08	¹³⁷ Cs	2.81E-06
NO ₂ ⁻	5.39E-07	²⁴¹ Pu	1.32E-07
NO ₃ ⁻	6.61E-06	⁹⁹ Tc	1.66E-07
OH ⁻	6.07E-07	Water	2.04E+04

¹(Scott 1994)

*Estimated vapor composition ppm by volume for volatiles, ppm by mass for non-volatiles, and microcurie/L for radionuclides.

[†]Sample data reported only unspiciated TOC. Some species may be volatile.

4.0 STRATEGY FOR WASTE CHARACTERIZATION AND SAFETY ISSUE RESOLUTION

In this section, the DQO requirements for sampling and analysis are integrated and compared with scheduled sampling and analysis activities.

4.1 TANK TY-104 SCHEDULED SAMPLING EVENTS

The characterization objectives in fiscal year 1995 involve sampling of tanks to identify and resolve safety issues. Two sampling events of tank TY-104 are scheduled: an auger sampling in February 1995 and a vapor sampling in March 1995. No other sampling is scheduled through fiscal year 1997 (Stanton 1994).

The headspace vapor sampling shall be performed in accordance with the two DQO's dealing with fugitive vapor emissions: *Data Quality Objectives for Generic In-Tank Health and Safety Vapor Issue Resolution* (Osborne et al. 1994a) and *Rotary Sampling Core Vapor Sampling Data Quality Objective* (Price 1994). Vapor sampling will satisfy part of the requirement specified in TPA Milestone M-40-08 to complete the vapor sampling of all organic Watch List tanks (Osborne and Huckaby 1994b).

The auger sampling shall be conducted following *Tank Safety Screening Data Quality Objective* (Babad and Redus 1994), *Data Requirements for the Ferrocyanide Safety Issue Developed through the Data Quality Objective Process* (Meacham et al. 1994) and *Data Quality Objective to Support Resolution of the Organic Fuel Rich Tank Safety Issue* (Babad et al. 1994). These two sampling and analysis events, if successful, will also satisfy the February 1995 applicable DQO requirements. These requirements are summarized in Table 4-1. A more complete list of analytical requirements is given, as an appended revision, in the appropriate sampling and analysis plan.

Table 4-1: Integrated DQO Requirements

Sampling Event	Applicable DQO's	Sampling Requirements	Analytical Requirements
Auger Sampling	-Safety Screening DQO -Ferrocyanide DQO -Organics DQO -Pretreatment DQO	2 auger samples from risers separated radially to the maximum extent possible	Energetics, TOC, Total Alpha, Beta & Gamma, Moisture, CN, Major Anions & Cations, TIC, Radionuclides, Density, Flammable Gas Concentrations
Vapor Sampling	-Health & Safety Vapor Issue Resolution DQO -Rotary Sampling Core Vapor Sampling DQO	6 SUMMA® canisters 12 Triple Sorbent Traps 6 Sorbent Trap Systems	Gas Flammability Gas Toxicity -Organic Vapors -Permanent Gases

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APPENDIX A

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

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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
NCPLX	non-complexed waste
PNL	Battelle Pacific Northwest Laboratory
RCRA	<i>Resource Conservation and Recovery Act of 1976</i>
RSST	reactive system screening tool - adiabatic calorimetry
SST	single shell tank
TCP	Tank Characterization Plan
TGA	thermogravimetric analysis
TIC	total inorganic carbon
TOC	total organic carbon
TWRS	Tank Waste Remediation System
TY-104	Tank 241-TY-104
USQ	unreviewed safety question
WHC	Westinghouse Hanford Company

A1.0 SPECIFIC TANK CHARACTERIZATION OBJECTIVES

There are four Watch List tank classifications (ferrocyanide, organic, hydrogen/flammable gas, and high heat load). These classifications cover the six safety issues related to public and worker health that have been associated with the Hanford Site underground storage tanks. These safety issues are as follows: ferrocyanide, flammable gas, organic, criticality, high heat, and vapor safety issues (Babad 1992). Tank TY-104 is one of the twenty tanks currently on the Organic Watch List and one of the eighteen tanks currently on the Ferrocyanide Watch List. This Sampling and Analysis Plan (SAP) will identify characterization objectives pertaining to sample collection, hot cell sample isolation, and laboratory analytical evaluation and reporting requirements in accordance with the appropriate DQO documents.

A1.1 RELEVANT SAFETY ISSUES

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

The ferrocyanide safety issue arises from the development of a process to scavenge the ^{137}Cs and other soluble radionuclides from the tank waste liquids (Sloat 1954, Abrams 1956) using ferrocyanide compounds in a carrier-precipitation process. This treatment was used on U-Plant effluent as well as selected waste previously discharged to tanks.

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

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

A1.1.1 Tank TY-104 Characterization Objectives

The characterization effort applicable to this Sampling and Analysis Plan is focused on the relevant safety issues listed above. The Organic Safety Program has identified two key safety questions that should be answered from analytical data on tank TY-104 waste are as follows:

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

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

The Ferrocyanide Safety Program has identified two key safety questions that should be answered from analytical data on the tank's waste (Postma et al. 1994):

- ▶ "Is a significant exothermic reaction possible during interim storage?"
- ▶ "Is a significant exothermic reaction possible under present conditions of waste moisture content?"

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

To satisfy other objectives of this sampling and analysis effort, the tank contents shall be safety screened in order to identify any other potential safety issues associated with TY-104, and to ensure that the tank should not be placed on an additional Watch List.

A1.1.2 Safety Screening, Pretreatment, Organic and Ferrocyanide Data Quality Objectives

The sampling and analytical needs associated with organic and ferrocyanide tanks and the Pretreatment Program, as well as the safety screening of all tanks, have been identified through the data quality objective (DQO) process. Additional data needs associated with tank TY-104 may be identified in subsequent DQO efforts.

Pertinent documents to this effort include the following:

- ▶ *Tank Safety Screening Data Quality Objective* (Babad and Redus 1994), which describes the sampling and analytical requirements for screening all waste tanks for unidentified safety issues.
- ▶ *Data Quality Objective to Support Resolution of the Organic Fuel Rich Tank Safety Issue* (Babad et al. 1994), which describes the sampling and analytical requirements for tanks on the Organic Watch List, including tank TY-104.
- ▶ *Data Requirements for the Ferrocyanide Safety Issue Developed through the Data Quality Objectives Process* (Meacham et al. 1994), which describes the sampling and analytical requirements for tanks on the Ferrocyanide Watch List, including tank TY-104.
- ▶ *Interim Data Quality Objectives for Waste Pretreatment and Vitrification* (Kupfer et al. 1994), which describes the sampling and analytical requirements to support the TWRS technical strategy by identifying the chemical and physical composition of the waste in the tank. In addition, the DQO works to guide development efforts to define waste pretreatment processes, which will in turn define high-level and low-level waste feed to vitrification processes. This DQO, at the request of the Pretreatment Program, will have a limited use in this sampling and analysis plan (refer to Section B6.1).

A1.1.3 Data Quality Objectives Integration

The safety screening, pretreatment, organic and ferrocyanide DQO efforts require a minimum of two core samples to be taken from risers separated radially to the maximum extent possible by the existing installed risers. From each riser, one auger sample shall be taken.

For sample breakdown, both the safety screening DQO and organic DQO request primary and secondary analyses on a half-segment level.

It should be noted that for this Sampling and Analysis Plan, the Pretreatment Program has requested that only composite samples for archive and a composite sample for process development be obtained. For further information, refer to Section A6.1.

Anticipating near-term approval of the new characterization strategy, the Ferrocyanide Safety Program has re-evaluated its need to sample all ferrocyanide tanks. A revised priority tank sampling list includes tanks with the highest initial ferrocyanide concentration, the least exposure to high caustic solutions, the lowest radionuclide inventory, and the lowest historic temperature profile. Assuming aging has occurred in these tanks, then it can be extrapolated that the other tanks have aged to the same or to a greater extent as well (Cash 1994). Tank TY-104 is not on the priority sampling list; however, as a precaution in the event that the new strategy is not approved, sample material will be archived. If analyses are necessary at a later time, the Ferrocyanide Program will contact the laboratory to run analyses on the archived samples (see Section A6.1).

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

A2.0 TANK STATUS AND SAMPLING INFORMATION

A2.1 TANK STATUS

Tank TY-104 currently contains 174 kL (46 kgal) of non-complexed waste. The waste consists of 163 kL (43 kgal) of sludge and 11 kL (3 kgal) of supernate; of which 57 kL (15 kgal) is drainable liquid (Hanlon 1994). This volume of waste corresponds to approximately 60 cm (24 in) of waste, as measured from the absolute bottom of the tank. The tank is classified as an assumed leaker and it is currently on the Organic and Ferrocyanide Watch Lists. It was added to the Ferrocyanide Watch List in January 1991 and the Organic Watch List in May 1994 (Hanlon 1994).

A2.2 SAMPLING INFORMATION

Tank TY-104 is currently scheduled to be sampled by the auger sampling method. Samples are expected to be taken from riser 15 and riser 18. Although there are approximately 60 cm (24 in) of material in tank TY-104 as measured at the deepest point in the tank (the middle), since the auger samples shall be taken from risers situated on the side of the tank during this sampling event, 38 cm (15 in) of

material is expected. If a different riser is necessary to meet sampling and analysis requirements, this change must satisfy the intent of the applicable DQOs and must be recorded and approved by the sampling cognizant engineer prior to sampling. Risers used may be recorded on a permanent data sheet or recorded directly in the work package. Sampling shall be conducted according to procedures and documentation included in tank TY-104 work package WS-94-0858. If the sampling depth is within ± 5 inches of the current depth information, one 20 inch auger sample is expected to be obtained from each riser. However, 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 bottom of the tank; therefore the number of samples might change depending on the depth of the waste.

A3.0 LABORATORY SAMPLE RECEIPT AND ANALYSIS INSTRUCTIONS**A3.1 TANK-SPECIFIC ANALYTICAL PROCEDURES**

A flowchart depicting the general safety screening 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) has been reviewed for any safety issues involved with transportation of TY-104 auger samples. For TY-104 auger samples, the transport sample casks must be vented every 15 days to release retained gas. Sampling Operations has a maximum of three days to ship the samples; therefore, no safety issues exist for auger samples with respect to transportation.

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 sample material from each isolated auger sample:
- ▶ Perform a visual examination of the sample(s)
 - ▶ Record observations. This may include a sketch of the isolated auger sample in addition to written documentation of pertinent descriptive information such as color, texture, homogeneity, and consistency.
 - ▶ Note the color and clarity of any drainable liquid.
 - ▶ Report sample recovery results to the Organic Safety Program within one working day of sample breakdown.
 - ▶ Take color photographs and/or a videotape to visually document the isolated auger samples.
- Step 3 Does the sample contain drainable liquid?
- Yes: Proceed to Step 4A
No: Proceed to Step 5
- Step 4A Separate any drainable liquid from the solids. Measure and record the volume. Retain drainable liquids for further processing.
- Step 4B Is the sample 100% drainable liquid?
- Yes: Proceed to Step 15

No: Proceed to Step 5

SOLIDS PATH

- Step 5 Remove 50 g of material from the uppermost region of the top sample and store for future analysis. It is important that this material represent the top layer of the waste in the tank. If it can be seen that removing this 50 g of material will result in insufficient sample for the analyses and archiving requirements below, this amount may be reduced to as low as 25 g if necessary. If there is not enough material in this particular subsegment to store 25 g and satisfy the analysis and archiving requirements below, notification is to be made to the Organic Safety Program, the Characterization Program, and Characterization Support so that alternate instructions may be given.
- Step 6A Is there a hard, dry layer on the top of the auger sample?
- Yes: Proceed to Step 6B
No: Proceed to Step 6C
- Step 6B Separate the hard, dry layer and retain for analysis.
- Step 6C Divide each auger sample into four 12 cm quarter samples (segments). The first 12 cm segment removed from the sampler originates from the lowest portion of the tank relative to the other segments and therefore shall be assigned to the fourth quarter segment and shall be uniquely identified as (Tank-Core No.-Segment No.-D). The following three 12 cm sections of the isolated auger sample shall be labelled as C, B, and A, respectively. If the isolated auger sample is less than 48 cm long, then the same labeling convention shall still apply until no solid material is left to make a complete 12 cm quarter segment.
- Step 7 Homogenize each quarter segment using the appropriate approved procedure.
- Step 8 Will a homogenization test be performed?
- Yes: Proceed to Step 9
No: Proceed to Step 10
- NOTE:** One quarter segment per core, at a minimum, should be used if a homogenization test is to be performed. Additional tests may be performed at the laboratory's discretion.
- Step 9 Conduct the homogenization test by taking 1 to 2 g aliquot from widely separated locations of the homogenized quarter segment. Conduct the homogenization test in accordance with Bell (1993).
- Step 10 Remove at least 10 mL and up to 20 mL of each homogenized quarter segment for the ferrocyanide archive sample (Bratzel 1994).
- Step 11 Combine the remainder of quarter segments A and B to create a half segment. Do the same with quarter segments C and D.

- Step 12 Homogenize each half segment from Step 11 using the appropriate approved procedures.
- Step 13A Collect sufficient aliquots from each homogenized half segment 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 half segment, notify the Characterization Program within one business day and follow the prioritization of analyses given in Section A3.3.
- Step 13B Remove at least 20 mL and up to 40 mL of each homogenized half segment for the archive sample (Bratzel 1994).
- Step 14A Combine portions of each subsample proportional to the sludge recovery of each segment to build a core composite. This composite must be large enough to include 125 mL of material for process development work and 100 mL for archive.
- Step 14B Remove 100 mL of the solid composite as the Pretreatment solid composite archive (Bratzel 1994).
- Step 14C Remove 125 mL of the solid composite for 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 14A into equal portions (i.e., equal-sized portions for archive and process development work).

LIQUIDS PATH

- Step 15 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 16A
No: Proceed to Step 17
- Step 16A Report any visually observed immiscible (potential organic) layer immediately by the early notification system (see Section A7.2).
- Step 16B Separate and retain the potential organic layer for possible future analysis.
- NOTE:** Steps 17 through 21 shall be performed on the remaining (probable aqueous) liquid layer only.
- Step 17 Filter the remaining liquid sample through a 0.45 micron filter.
- Step 18 Is there greater than 1 gram of solid on the filter?
- Yes: Proceed to Step 19
No: Proceed to Step 20

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- Step 19 Archive the solids for possible future analysis (Bratzel 1994).
- Step 20 Remove sufficient aliquots from the liquid sample to perform the appropriate analyses listed in Table A-1 in duplicate.
- Step 21 Archive at least 20 mL and up to 40 mL of the drainable liquid as the liquid archive (Bratzel 1994).

PRIMARY ANALYSIS PATH

- Step 22 Perform primary analyses as listed in Table A-1.
- Step 23 Compare the primary analysis data with notification limits.
- Step 24A Do the results exceed the notification limits (Table A-1)?
 - Yes: Proceed to Step 24B.
 - No: Proceed to Step 27.
- Step 24B Report results exceeding the notification limits using Format I reporting deliverable requirements as listed in Section A7.2.

SECONDARY ANALYSIS PATH

- Step 25 Perform secondary analyses according to Table A-1.
- Step 26A Do the secondary analyses exceed the notification limits?
 - Yes: Proceed to Step 26B
 - No: Proceed to Step 27
- Step 26B Report results exceeding the notification limits using Format I reporting deliverable requirements as listed in Section A7.2.
- Step 27 Report results as listed in Section A7.0.

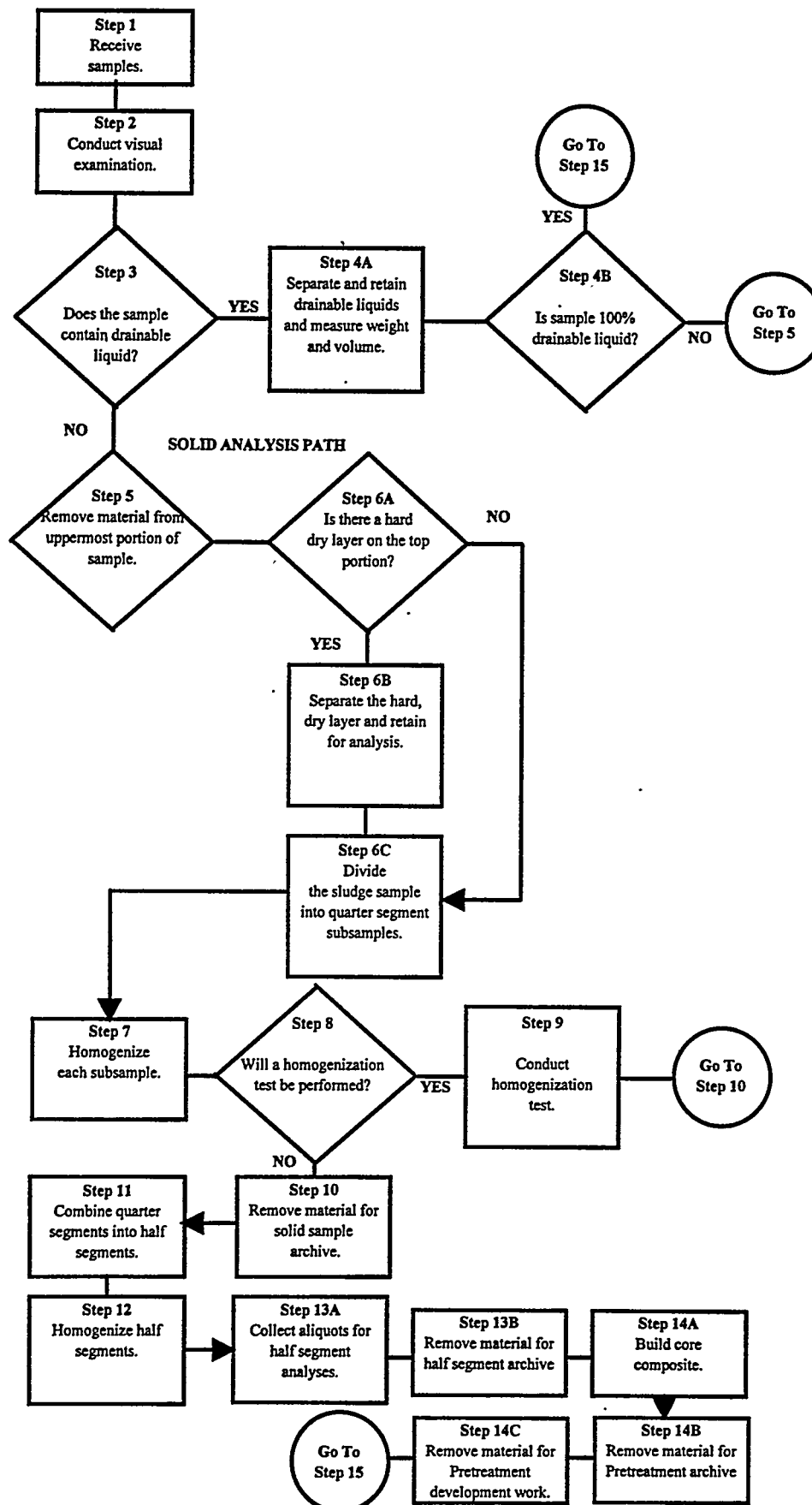


Figure A-1: Solid Analysis Flow Chart

LIQUID PATH

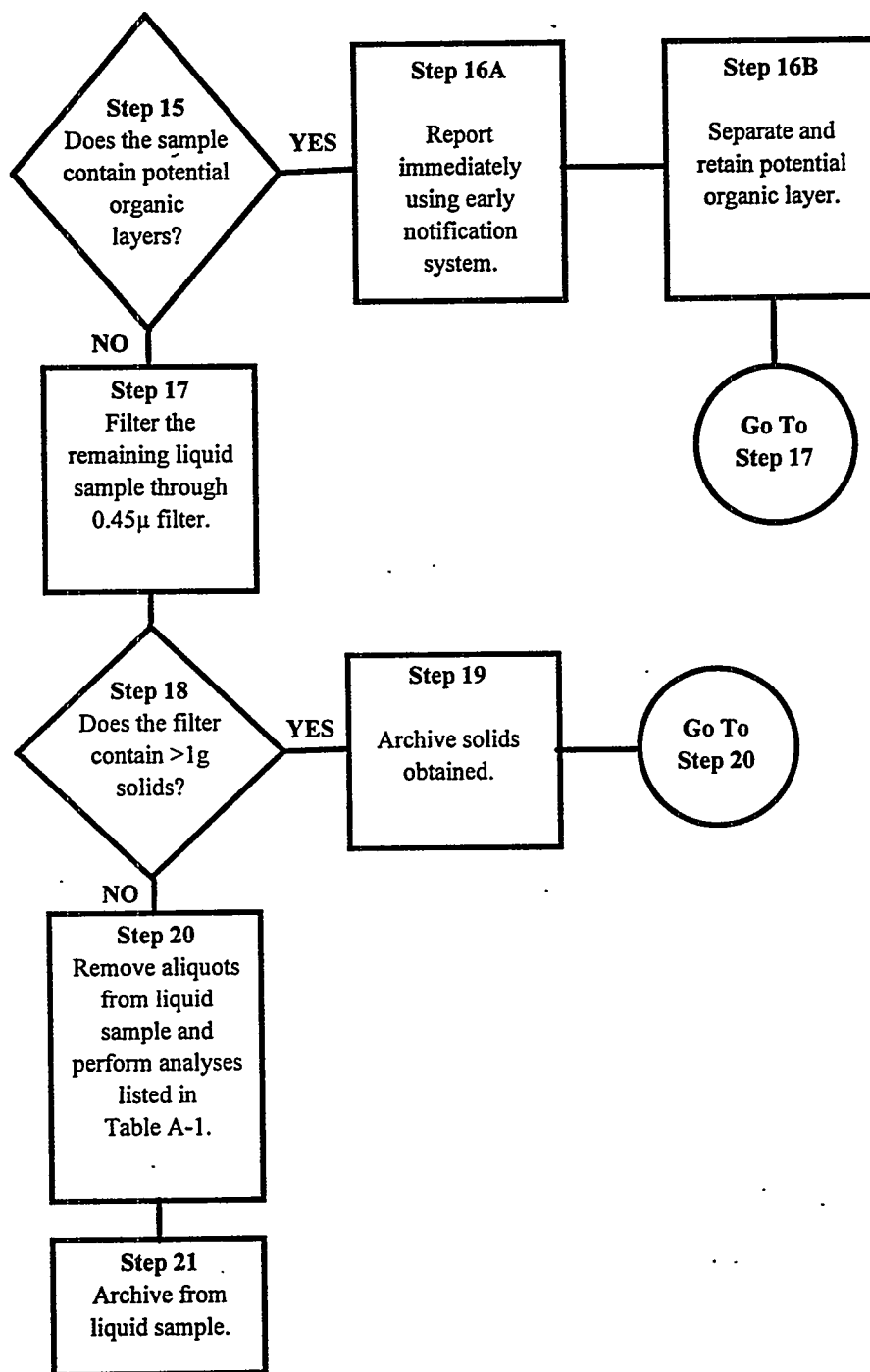


Figure A-2: Liquid Analysis Flow Chart

ANALYSIS AND REPORTING PATH

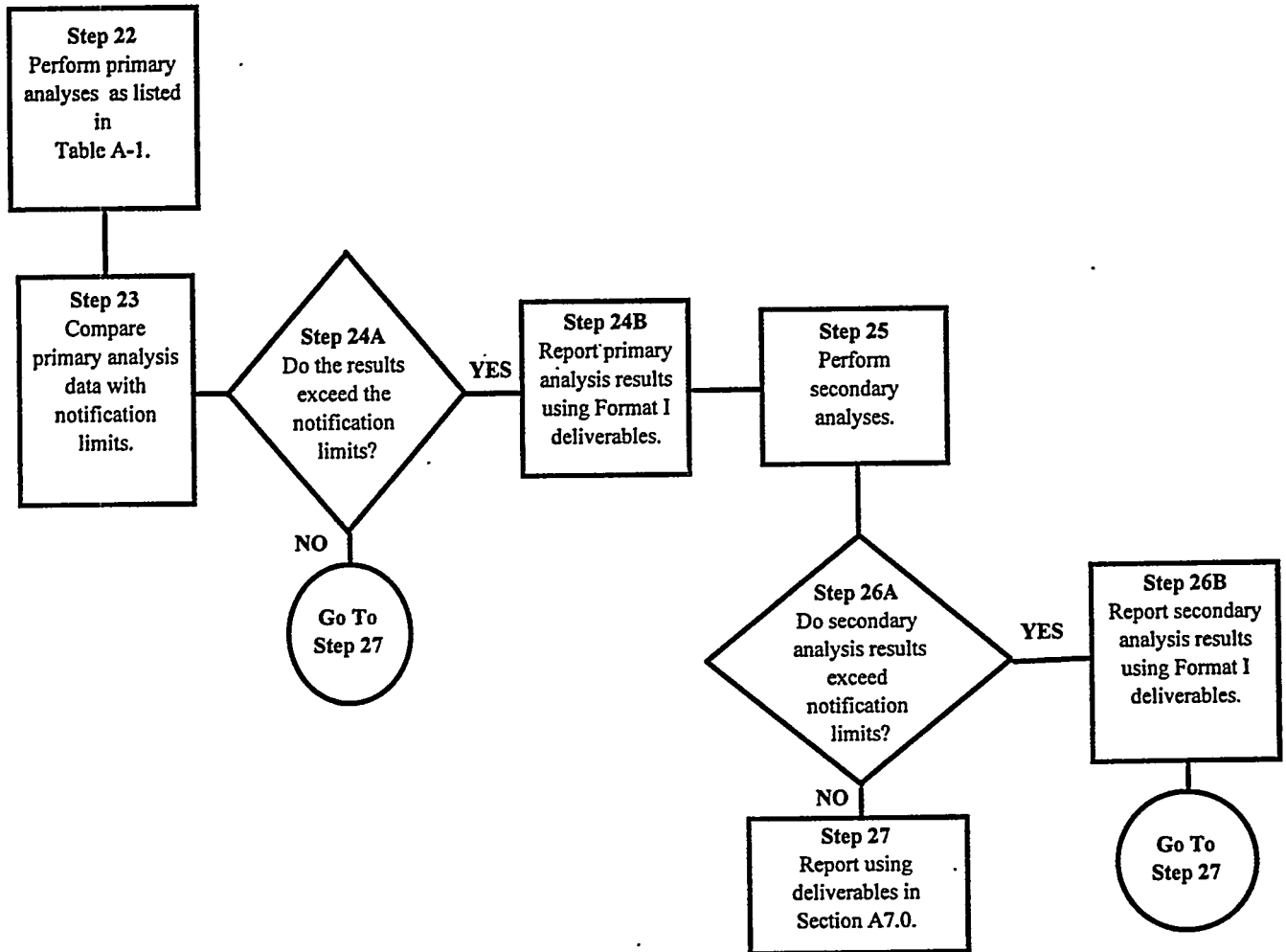


Figure A-3: Sample Analysis and Reporting Flow Chart

A3.2 INSUFFICIENT SEGMENT RECOVERY

If the amount of material recovered from core samples taken from tank TY-104 is insufficient to perform the analyses requested and permit a minimum 10 mL archive per sample, the laboratory shall notify the Tank Cognizant Engineer and the manager of Analytical Services, Program Management and Integration 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

The analyses to be performed for the tank safety screening and organic programs have been prioritized below. Confirmation of prioritization levels or revision of sample breakdown procedures may be provided to the laboratory based upon the sample recovery, readily observable physical property distinctions within the sample, and the requested sample breakdown procedures provided in Section A3.1.

PRIORITY LEVEL 1

The total organic carbon (TOC) by Hot.Persulfate, DSC, TGA, and Total Alpha analyses shall be performed.

PRIORITY LEVEL 2

The cyanide, total organic carbon (TOC) by Furnace Oxidation, RSST, ^{239/240}Pu, Fe, Mn, U, hydroxide, nitrate, nitrite, and gravimetric analyses shall be performed.

PRIORITY LEVEL 3

The Cr analyses shall be performed.

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 TY-104 auger samples are based on the organic and safety screening DQOs referenced in Section A1.1.2. The laboratory procedure numbers, which shall be used for the analyses, are included in the table.

A4.2 QUALITY ASSURANCE

A4.2.1 Laboratory Operations

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

Method specific quality control such as calibrations and blanks are also found in the analytical procedures. Sample quality control (duplicates, spikes, 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 TY-104 and shipped to the performing laboratory by Sampling Operations in accordance with work package WS-943-0858. That work package shall also initiate the chain-of-custody for the samples. Approved auger sampling procedure TO-080-008 and procedure TO-080-090 ("Load/Transport Sample Cask(s)") are to be used during the sampling event. Samples shall be identified by a unique number before being shipped to the performing laboratory. The sampling team is responsible for documenting any problems and procedural changes affecting the validity of the sample in a field notebook. Sampling Operations shall enter this information in the comment section of the chain-of-custody form for addition to the data reports.

Sampling Operations should transport each sample collected to the performing laboratory within 1 working day of removing the sample from the tank, but must transport each sample within 3 calendar days. 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-94-0858. Core samples are shipped in a cask and sealed with a Waste Tank Sample Seal.

WASTE TANK SAMPLE SEAL	
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: TY-104 Chemical, Radiological and Physical Analytical Requirements

SOLID ANALYSES																		
Project Name		TY-104 Auger Sample				COMMENTS				REPORTING LEVELS								
Plan Number		WHC-SD-WM-TP-301, 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				H. Babad				FORMAT IV		Waste Management						
C. Organic		Organic				D. A. Turner				FORMAT V		RCRA Compliance						
		TWRS				TANK				#AUGERS		FORMAT VI		Special				
		222-S Laboratory				TY-104				2								
PROGRAM	METHOD	PRIMARY ANALYSES			SAMPLE ¹		PREP ²	QUALITY CONTROL ³					UNITS	CRITERIA		FOR-MAT		
		ANAL.	WHC PROCEDURE	WHC	½ SEG SLDG	½ SEG SC		DUP	SPK/ MSD	BLK	CALIB STD	PR		AC	NOTIFICATION LIMIT ⁴		EXPECTED RANGE ⁴	
A,C	DSC	Energy	LA-514-113		X	X	d	ea smpl	N/A	N/A	ea AB	±10	90-110	J/g ⁵	unknown	I, III, IV		
A,C	TGA	% H ₂ O	LA-560-112		X	X	d	ea smpl	N/A	N/A	ea AB	±10	90-110	wt%	unknown	I, III, IV		
A	Alpha	Total Alpha	LA-508-101		X		f or a	ea smpl	1/mtrix	ea PB	ea AB	±10	90-110	µCi/g	0.202 to 0.302	I, III, IV		
A,C	Hot Persulfate	TOC	LA-342-100		X ¹²	X ¹²	d	ea smpl	1/mtrix	ea AB	ea AB	±10	90-110	µg C/g	1,540 to 2,320	I, III ¹² , IV		
PROGRAM	METHOD	SECONDARY ANALYSES			SAMPLE ¹		PREP ²	QUALITY CONTROL ³					UNITS	CRITERIA		FOR-MAT		
		ANAL.	WHC PROCEDURE	WHC	½ SEG SLDG	½ SEG SC		DUP	SPK/ MSD	BLK	CALIB STD	PR		AC	NOTIFICATION LIMIT ⁴		EXPECTED RANGE ⁴	
A,C	RSST ¹⁰	Energy	see 10 below		X	X	d	N/A	N/A	N/A	ea AB	±20	80-120	J/g	unknown	I, III, IV		
A	Distillation ¹⁰	CN	LA-695-102		X	X	d	ea smpl	1/mtrix	ea AB	ea AB	±10	90-110	µg/g	unknown	I, III, IV		
A	Sep. & α counting ¹¹	Pu-239/240	LA-503-156		X		f	ea smpl	1/mtrix ⁸	ea PB	ea AB	±10	90-110	µCi/g	0.158 to 0.238	I, III, IV		
A	ICP ¹¹	Fe	LA-505-151		X		f or a	ea smpl	see ⁹	ea PB	ea AB	±10	90-110	µg/g	34,100 to 51,100	III, IV		
		U						ea smpl		ea PB	ea AB	±10	90-110	µg/g	19,700 to 29,500	III, IV		
A,C	ICP ^{11,13}	Mn	LA-505-151		X		f or a	ea smpl	see ⁹	ea PB	ea AB	±10	90-110	µg/g	1,210 to 1,800	III, IV		
C	ICP ¹⁵	Cr	LA-505-151		X		f or a	ea smpl	see ⁹	ea PB	ea AB	±10	90-110	µg/g	1,320 to 1,980	III, IV		
C	IC ¹³	NO ₂ ⁻	LA-533-105		X		w	ea smpl	1/mtrix	ea PB	ea AB	±10	90-110	µg/g	2,710 to 4,070	IV		
		NO ₃ ⁻						ea smpl		ea PB	ea AB	±10	90-110	µg/g	35,000 to 52,600	IV		
C	Titration ¹³	OH ⁻	LA-661-103		X		d	ea smpl	N/A	ea AB	ea AB	±10	90-110	µg/g	1,100 to 1,660	IV		
A,C	Furnace	TOC	LA-344-105		X	X	w	ea smpl	1/mtrix	ea PB	ea AB	±10	90-110	µg C/g	1,540 to 2,320	I, III, IV		
C	Gravimetric ¹⁶	% H ₂ O	LA-564-101		X		d	ea smpl	N/A	N/A	ea AB	±20	80-120	wt%	unknown	I, IV		

¹½ SEG SLDG-½ segment, sludge; ½ SEG SC-½ segment, saltcake

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

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

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

⁵Dry weight basis.

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

⁷Tracer or carrier may be used in place of a spike and results corrected for recovery.

⁸Either serial dilutions or matrix spikes will be performed.

Table A-1: TY-104 Chemical, Radiological and Physical Analytical Requirements

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

Table A-1: TY-104 Chemical, Radiological and Physical Analytical Requirements

LIQUID ANALYSES														
Project Name			COMMENTS				REPORTING LEVELS							
TY-104 Auger Sample			Homogenization Test - Per Laboratory Discretion				FORMAT I		Early Notify					
Plan Number			Field Blank - Not Required				FORMAT II		Process Control					
PROGRAM			Hot Cell Blank - Per Laboratory Discretion				FORMAT III		Safety Screen					
A. Safety Screening			Safety Screening				FORMAT IV		Waste Management					
C. Organic			Organic				FORMAT V		RCRA Compliance					
TWRS			TANK				#AUGERS		FORMAT VI					
222-S Laboratory			TY-104				2							

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

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

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

⁵Dry weight basis.

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

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

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

⁹Either serial dilutions or matrix spikes will be performed.

¹⁰RSST performed only if DSC exceeds notification limits. The RSST method, yet to be proceduralized, may be found in WHC-SD-WM-TP-104.

Table A-1: TY-104 Chemical, Radiological and Physical Analytical Requirements

- ¹²These analyses are primary analyses for the organic DQO, but also are secondary analyses for the safety screening DQO. Therefore, if the DSC limit is exceeded, these analyses must be performed and reported within 90 days of receipt of the last sample at the laboratory dock.
- ¹³This analysis is required if the energy equivalent of the TOC assay by hot persulfate is > 125% of the DSC value.
- ¹⁴This analysis is required if the energy equivalent of the TOC by hot persulfate is < 75% of the DSC value.
- ¹⁵This analysis is required if the energy equivalent of the TOC assay by furnace oxidation is < 75% of the DSC value.
- ¹⁶This analysis is required if moisture analysis by TGA exceeds the notification limit.

A5.0 ORGANIZATION

The organization and responsibility of key personnel involved with this tank TY-104 characterization project are listed in Table A-2.

Table A-2: Tank TY-104 Project Key Personnel List

Individual	Organization	Responsibility
J. G. Kristofzski	222-S Analytical Operations	Program Support Manager of Analytical Operations
R. D. Schreiber	TWRS Characterization Support	Tank TY-104 Tank Characterization Plan Cognizant Engineer
D. A. Turner	Organic Tanks Safety Program	Organic Safety Program Manager
H. Babad	Characterization Program	Safety Screening Point of Contact
J. L. Deichman	Analytical Services	Manager of Analytical Services Program Management and Integration
J. T. Slankas	Technology Development Program Office	Pretreatment 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 (Babad and Redus 1994), 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. However, 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 made to the safety screening DQO when it is revised. Therefore, although this Sampling and Analysis Plan uses the current safety screening DQO, it specifies that cyanide is to be run on a half-segment basis and that notification shall be made if the DSC value exceeds 481 J/g (115 cal/g dry weight basis).

In the organic DQO (Babad et al. 1994), ^{137}Cs and ^{90}Sr on half-segments are requested as secondary analyses. However, these have not been requested as primary analyses, nor are there any other primary analyses that would require ^{137}Cs or ^{90}Sr to be conducted should it exceed a notification limit. Therefore, it has been decided by both the Organic Safety Program and the Characterization Program that ^{137}Cs and ^{90}Sr on a half-segment level should not be analyzed.

In the organic DQO, the method of analyses for principal organic species, equilibrium moisture content, and Cr and Mn oxidation states has not been developed

at this point. Therefore, if it is necessary to analyze these secondary constituents, archived samples will be used for analyses at a later date.

Anticipating near-term approval of the new characterization strategy, the Ferrocyanide Safety Program has re-evaluated its need to sample all ferrocyanide tanks. The Ferrocyanide Safety Program is also attempting to accelerate resolution of the Ferrocyanide Safety Issue to mid Fiscal Year 1996 (approximately 1½ years earlier than previously planned). Experiments on waste simulants and waste tank sampling to date indicate that ferrocyanide (fuel) no longer exists in sufficient quantities because of radiolytic and chemical degradation (aging). The revised priority tank sampling list includes tanks with the highest initial ferrocyanide concentration, the least exposure to high caustic solutions, the lowest radionuclide inventory, and the lowest historic temperature profile. Assuming aging has occurred in these tanks, then it can be extrapolated that the other tanks have aged to the same or to a greater extent as well (Cash 1994, see Section A9.0). Tank TY-104 is not on the priority sampling list; however, as a precaution in the event that the new strategy is not approved, a sample will be archived. If analyses are necessary at a later time, the Ferrocyanide Program will contact the laboratory to run analyses on the archived samples.

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 the samples taken. If necessary, the Pretreatment Program will personally contact the laboratory, via letter of instruction, to run analyses on the archived composite samples. Therefore, the Pretreatment Program has directed that only a 125 mL solid composite sample for process development and a 100 mL solid composite sample for archive shall be obtained from this sampling event (Slankas 1994).

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.

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

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

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

$$\left(\frac{1 \text{ g}}{\text{L}}\right)\left(\frac{1 \text{ L}}{10^3 \text{ mL}}\right)\left(\frac{1}{\text{density}} \frac{\text{mL}}{\text{g}}\right)\left(\frac{0.062 \text{ Ci}}{1 \text{ g}}\right)\left(\frac{10^6 \text{ } \mu\text{Ci}}{1 \text{ Ci}}\right) = \frac{61.5}{\text{density}} \frac{\text{ } \mu\text{Ci}}{\text{g}} \quad (2)$$

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

- ▶ Neither the safety screening nor the organic DQO, upon which the analyses in Table A-1 are based, sufficiently addresses the analyses of any drainable liquid present. To adequately characterize the tank, all analyses performed on the solids for the safety screening and organic DQOs, with the exception of total alpha analyses, shall also be performed on any drainable liquids.
- ▶ The Organic Safety Program has requested that 50 g of material from the uppermost section of the uppermost segment of the core be stored. Presently, the Organic Safety Program is writing a DQO that will specify the analytical requirements on the stored sample. If there is not enough sample material to provide for the requested analyses on Table A-1 and archive the required amount, the material to be stored may be reduced as long as a minimum of 25 g is stored. If this is not possible, notify the Organic Safety Program, the Characterization Program, and Characterization Support so that alternate instructions may be given.
- ▶ In the organic DQO it is unclear as to when secondary analyses are to be run. Whether or not a secondary DQO is run depends on the comparison between the value of the energy equivalent for TOC, "X", and the DSC energetics value. The energy equivalent of TOC is given in equation (3).

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

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

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

- ▶ If X by hot persulfate is $\leq 75\%$ of the DSC value, run TOC by furnace combustion on the half-segment.
- ▶ If X by hot persulfate is $\geq 125\%$ of the DSC value, run nitrite, nitrate, and hydroxide analyses on the half-segment.
- ▶ If X by furnace combustion is $\leq 75\%$ of the DSC, analyze for the presence of Mn and Cr on the half-segment.
- ▶ The Pretreatment Program has requested 125 mL of the solid composite material for process development work. Two test plans (Lumetta 1994, and 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 plans. This approval will not only ensure that the DQO process has been used in the generation of the test plans and that there is

justification for the samples, but also that the facility receiving the sample is in a position to adequately handle radioactive material. At such time that the test plans are approved by the Characterization Program, the Characterization Program will direct the performing laboratory, via letter of instruction, to allow shipment of the sample material.

A7.0 DELIVERABLES

All analyses of tank TY-104 waste material shall be reported as Formats I, III, and/or IV as indicated in Table A-1. Additional information regarding reporting formats is given in Schreiber (1994a).

A7.1 PROGRESS REPORTS

Each laboratory performing analyses on tank TY-104 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 TY-104, 2) preliminary results to the program, and 3) schedule and cost information on a DQO basis.

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

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

Schedule reporting shall consist of the following:

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

A7.2 FORMAT I REPORTING

Table A-1 contains the notification limits for each analyte. Any results that exceed the notification limits defined in the DQO processes 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 to the Organic Safety Program, Analytical Services, Characterization Support, the Characterization Program Office, the Safety Screening Representative, and Waste Tanks Process Engineering, documenting the observations. Additional analyses for verification purposes may be contracted between the performing laboratory and the contacts above either 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, the Organic Safety Program,

Characterization Support, Waste Tanks Process Engineering, the Characterization Program Office, Los Alamos Technical Associates (LATA), the Tank Characterization Resource Center, and the Tank Characterization Database representative (Schreiber 1994c) 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).

A7.4 FORMAT IV REPORTING

Analytical results requested for the characterization project of tank TY-104 shall be compiled into a Format IV type data package. The data package shall be provided to Analytical Services, the Organic Safety Program, the Tank Characterization Resource Center representative and the Characterization Program within 216 days of the sampling event. Detailed information regarding the contents of this reporting format are given in (Schreiber 1994a).

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

A8.0 CHANGE CONTROL

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

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

A9.0 ATTACHMENTS

The following memorandum is intended to be used as interim guidance pertaining to the requested tanks to be sampled for ferrocyanide safety issues until the Ferrocyanide DQO is revised (scheduled release date of April 1995).

Westinghouse
Hanford CompanyInternal
Memo

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

74260-95-003

To: G. A. Stanton S7-31

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

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

RECEIVED
 DEC 01 1994
 C. S. HALLER

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

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

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

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

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

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

74260-95-003

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

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



R. J. Cash
Manager

p11

A10.0 REFERENCES

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