Sampling and Analysis Plan for Liquid and Solids in the 204-AR-TK-1 Catch Tank

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Abstract: This tank sampling and analysis plan describes the steps necessary in order to characterize the supernatant and solids in catch tank 204-AR-TK-1 for the Effluent Treatment Facility Waste Acceptance Criteria and the Double Shell Tank Compatibility evaluation.

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LIST OF TERMS

Abbreviations and Acronyms

AEA	alpha energy analysis
AES	Atomic emission spectroscopy
ASTM	American Society for Testing and Materials
ATL	Advanced Technologies and Laboratories International, Inc.
CAS	Chemical Abstracts Service
CCN	Characterization Change Notice
CVAA	Cold Vapor Atomic Absorption
DOECAP	Department of Energy's Consolidated Audit Program
DQO	data quality objective
DRF	Document Release Form
DST	double-shell tank
DUP	duplicate
EPA	U.S. Environmental Protection Agency
ETF	200 Area Effluent Treatment Facility
FB	field blank
GC	Gas chromatography
GEA	gamma energy analysis
HASQARD	Hanford Analytical Services Quality Assurance Requirements Documents
IC	ion chromatography
ICP	inductively coupled plasma
LCS	Laboratory control sample
LERF	Liquid Effluent Retention Facility
LSC	Liquid scintillation counting
MS	mass spectrometry
MSD	matrix spike duplicate
NA	Not applicable or not available
O&M	Operations and Maintenance
P&ID	Piping and instrumentation design/diagram/drawing
PCB	Polychlorinated biphenyl
QA	quality assurance
QC	quality control
QSAS	Quality Systems for Analytical Services
RDL	Required Detection Limit
RPD	Relative percent difference
SOW	statement-of-work
SpG	specific gravity
SVOC	semi-volatile organic compound
TC	Total carbon
TGA	thermogravimetric analysis
TIC	Total Inorganic Carbon
TOC	Total Organic Carbon
TSAP	Tank Sampling and Analysis Plan

VOC	volatile organic compound
WAC	waste acceptance criteria
WRPS	Washington River Protection Solutions, LLC

Units

°C	degrees Celsius
%	percent
Ci	curies
cm	centimeter
cP	centipoises
g	gram
J	Joule
kg	kilogram
kgal	kilo-gallon
L	Liter
mL	milliliter
wt%	weight percent
µCi	microcuries
µg	micrograms
µgC	micrograms carbon
µS	microSiemen

1.0 SAMPLING AND ANALYSIS OBJECTIVES

This Tank Sampling and Analysis Plan (TSAP) was written in accordance with TFC-ENG-CHEM-D-23, *Preparation of Tank Sampling and Analysis Plans*. This TSAP provides direction and specifies requirements for field sampling, laboratory analysis, and data reporting for liquid and solid grab samples that will be taken from the 204-AR-TK-1 catch tank. The analytical data are needed for removal of liquid and entrained solids from the catch tank. The method of transferring the contents will be determined based upon the results of this sampling event. This will also determine whether the catch tank contents will be transported to the 200 Area Effluent Treatment Facility (ETF) or a double-shell tank (DST).

Sampling and analyses are necessary to determine if the waste in the 204-AR-TK-1 catch tank (a) meets the waste acceptance criteria (WAC) for shipping and acceptance at the ETF as described in HNF-3172, *Liquid Waste Processing Facilities Waste Acceptance Criteria*, or (b) meets waste compatibility requirements for transfer into a DST, with controls identified in HNF-SD-WM-OCD-015, *Tank Farms Waste Transfer Compatibility Program*. These documents require that a waste assessment be completed prior to acceptance of a waste transfer. Liquid and solids data required to evaluate ETF WAC and Tank Farms waste compatibility are specified in HNF-3172 and HNF-SD-WM-DQO-001, *Data Quality Objectives for Tank Farms Waste Compatibility Program*, respectively. Liquid and solid samples will be taken using the "bottle-on-string" method and the clamshell method, respectively.

In addition, sample data may be needed to address miscellaneous needs including safety basis evaluation, emergency preparedness, shipping, and environmental compliance. The safety basis evaluation will require data to calculate radiological unit liter dose and the toxicological sum of fractions. These calculations are also required by the Compatibility Data Quality Objective (DQO); therefore, no additional analyses are required to address this need. Analytes required for emergency preparedness purposes are listed in HNF-SD-WM-DQO-001.

2.0 FACILITY AND WASTE DESCRIPTION

Catch tank 204-AR-TK-1 is located in the 204-AR Waste Unloading Facility, south of the 244-AR Vault and west of the 241-AX Tank farm in the 200 East Area. The facility was completed in 1981 and is a two-story reinforced concrete structure approximately 64 feet long, 49 feet wide, and 25.5 feet high. The 204-AR-TK-1 catch tank is located below-grade in the Rail Tank Car Unloading Canyon, beneath the floor of the unloading area. The tank has a nominal volume of 1,500 gallons and a maximum operating capacity of 1,200 gallons. It is cylindrical in shape with its axial centerline oriented vertically. The tank was fabricated from a ¼-inch thick, welded 304L stainless steel. It is approximately 102 inches high by 66 inches in diameter with the tank floor sloped at $1/16^{th}$ of an inch per foot. The catch tank is equipped with liquid-level instrumentation and drain/overflow lines.

In 2000, a backflow preventer failure/leak in the catch tank overflowed into the sump, resulting in a high-contamination area. The tank was subsequently pumped out and rinsed. In 2005, the last transfer occurred from 204-AR-TK-1 to 241-AP-107. Since then, the additions to the tank have been mostly from weekly additions of water to the seal loops and weekly eyewash and safety shower inspections.

The current tank level reading is 63.5 inches (927 gallons) [e-mail from J. W. Deline to S. J. Harrington, "RE: 204 AR catch tank information," (Deline, J. W., 2011-02-24); see Appendix B]. Sludge level in the tank is not known and will be measured during this sampling event. Estimates for the sludge level have been obtained from RPP-33928, *Spreadsheet Description Document for Estimation of Catch Tank 204-AR-TK-1 Liquid and Solid Wastes*. As indicated in this document, the sludge volume is assumed to be 5% of the total tank volume, or 5.25 inches (74 gallons). This leads to a supernatant volume of 58.25 inches (853 gallons).

One separable organics sample will be taken just above the surface of the supernate when tank 204-AR-TK-1 is sampled. Two additional aqueous subsurface samples and one duplicate will be taken to satisfy Compatibility and ETF WAC requirements (HNF-SD-WM-DQO-001 and HNF-3172). One solids sample and one duplicate will also be taken (if solids are found to be present) as required by HNF-SD-WM-DQO-001 and HNF-3172. The exact sample locations will be determined based on level measurements, as described in Section 3.0.

The table of estimated mean radionuclide activities for the supernatant and solid samples to be taken from tank 204-AR-TK-1 are detailed in Appendix A at the end of this document. This information is provided to support shipment of the samples to the laboratory. The references that were available for this estimate included:

- RPP-33928, *Spreadsheet Description Document for Estimation of Catch Tank 204-AR-TK-1 Liquid and Solid Wastes*;
- SVF-1332, *204-AR-TK-1 Liquid & Solid Composition Estimates.xls*;
- RPP-RPT-25889, *Waste Compatibility Assessment of Catch Tanks 244-A and 204-AR Waste with Tank 241-AP-107 Waste*;
- RPP-17754, *Waste Compatibility Assessment of Catch Tank 204-AR Waste with Tank 241-AP-107 Waste*; and
- Internal letter CL3120-00-015, "Extension of Waste Compatibility Assessment of WESF Waste (WESF-99-01, Rev. 4) with Tank 241-AP-108 Waste" (CL3120-00-015 – Letter).

Radionuclide concentrations in the waste are estimated using available process knowledge information, as no sample data could be found for this tank. These rough estimates are conservative, and should be used with caution.

3.0 SAMPLING EVENT REQUIREMENTS

All sampling activities shall be conducted in accordance with this TSAP, along with the appropriate sampling procedures and work packages. Changes to the specified sampling requirements must be made in accordance with the Change Control direction provided in Section 9.0. Liquid samples will be taken using the "bottle-on-string" method. Sludge samples will be collected (if solids are present) using the clamshell sampler. Brief descriptions of these sampling methods are provided below.

The "bottle-on-string" technique is based on the weighted bottle sampling method as described in the American Society for Testing and Material (ASTM) ASTM E-300-03, *Standard Practice for Sampling Industrial Chemicals*. A clean bottle is placed in a metal cage. The cage is lowered through an access port (e.g. a riser) into the liquid. In this instance, the riser will be the 4 inch pipe attached to MOV-101 valve (see H-14-020814 001, *Waste Transfer (WT) System O&M System P&ID*, July 2003), which will be cut to allow access to the tank contents. The bottle is allowed to fill with liquid and then removed from the tank. The bottle is capped, removed from the cage, and placed in a shipping container for transport to a laboratory for analysis. Another clean bottle is placed in the cage for collecting the next sample, and the process is repeated until sampling is complete. A photograph of a "bottle-on-string" sampler is shown on the left of Figure 3-1. The rubber stopper seen in this photograph is used for sampling below the surface. The stopper is inserted into the bottle prior to lowering into the liquid waste. It is then removed through a "tug" on the sampling string, allowing the bottle to fill at the appropriate sample depth.

The clamshell sampler is a remotely operated end-effector tool designed for obtaining residual waste samples from underground storage tanks. It consists of a battery-powered control unit with cable, a push-pole adaptor, a motorized retrieval claw that has been modified to accept a sampling scoop, and the sampling scoop. The sampling scoop may be used repeatedly to collect and deposit solids into a sample jar. A photograph of a clamshell sampler is shown on the right of Figure 3-1.

Figure 3-1. Photograph of a "Bottle-on-String" Sampler (Left) and Clamshell Sampler (Right).

3.1 SAMPLE COLLECTION

Prior to sampling, sampling bottles and jars shall be cleaned using a procedure that is consistent with the cleaning protocol outlined in SW-846, *Test Methods for the Evaluation of Solid Waste, Physical/Chemical Methods*. Sampling equipment, including the sample holder with the attached bonding wire, stopper, including the eye bolt, nuts, and washers, and the clamshell sampling scoop shall be cleaned per the approved laboratory sampling equipment cleaning procedure. Clear, wide mouth, 250-mL glass bottles shall be used for all liquid samples, including field blanks, with 240-mL Teflon jars being used for solid samples. These bottles shall be sealed with Teflon®[1] lined caps.

The primary need for data from this sampling event is to determine whether the tank waste meets the ETF WAC in HNF-3172 and/or the HNF-SD-WM-DQO-001 waste compatibility limits. To satisfy the need for compatibility, a total of three grab samples [and a duplicate] will be taken as well as a solids sample and duplicate. This will satisfy the combined needs for the ETF WAC and waste compatibility. The strategy for collecting the required samples is discussed below and summarized in Table 3-1.

A zip cord shall be used to measure (1) the elevation of the surface (to an accuracy of ¼ inch or better) prior to sampling, as well as (2) the solids level after all samples except 204AR-11-04 and 204AR-11-04DUP have been taken. A measurement device with a resolution of 1/8 inch shall be used in conjunction with the zip cord.

One field blank is required. The field blank bottle shall be filled at the laboratory with water that is de-ionized, filtered, and free of volatile organic compounds before it is brought to the field.

[1] Teflon ® is a registered trademark of I. E. DuPont De Nemours and Company, Inc., Wilmington, Delaware.

The field blank shall be uncapped and lowered into the tank riser to the depth specified in Table 3-1. The Tank Sampling first line manager or designee shall verify that the field blank is properly prepared and shipped to the laboratory for use.

The separable organic surface sample, 204AR-11-01, shall be taken after the surface zip cord measurement. The sample carrier is lowered to a location where the mouth of the sample bottle (without a stopper) is approximately ¼-inch above the zip cord reading. The sample shall be held at the sample location elevation for about 30 seconds to allow the bottle to fill to approximately ¾ full or more. If the sampling device fails to collect any liquid at this depth, sampling shall be repeated ¼ inch below the previous level until liquid is observed in the bottle.

Table 3-1. Sampling Requirements

Sample Identification Number	Sample Type	Sample Location, From Top to Bottom[1]	Sample Jar/Lid	Description
204AR-11-01FB	Field blank(FB)	24 inches ABOVE liquid surface zip cord level	250-mL wide mouth clear glass bottle with Teflon®-lined lid.	FB sample.
204AR-11-01	Surface sample	¼ inch ABOVE aqueous surface zip cord reading		Separable organic surface sample, taken without stopper.
204AR-11-02	Subsurface liquid samples	Approximately 20 inches BELOW the aqueous surface level measurement		TOP subsurface sample.
204AR-11-03	Subsurface liquid samples	Approximately 40 inches BELOW the surface level measurement		BOTTOM subsurface sample.
204AR-11-03DUP				DUP BOTTOM subsurface sample.
204AR-11-04	Solid samples	Solids layer	240-mL Teflon® jars and lids.	Solids sample.
204AR-11-04DUP				DUP solids sample.

Notes: [1]The sample assembly must be placed such that the mouth of the sample bottle is at the specified location.

After taking the 204AR-11-01 sample, liquid subsurface samples required in Table 3-1 shall be taken from top to bottom to minimize disturbance of the liquid. Each sample bottle shall be at least ¾ full unless otherwise directed by the Tank Coordinator.

A sludge level measurement shall be made after all liquid samples have been taken to avoid disturbing the liquid. A measurement device with a resolution of 1/8-inch shall be used in conjunction with the sludge level measurement device. The clamshell shall be used repeatedly to obtain solids until each 240-mL jar is at least half-full (not including liquids). If the scoop is empty (or nearly empty) on at least two consecutive attempts, sampling may be discontinued with concurrence by the Tank Coordinator. The liquid surface and solids zip cord level measurements shall be recorded in the work package.

Sample pigs should be stored in a heated building prior to sampling, and staged in the field just prior to use. This ensures the samples do not cool substantially, or freeze. The Tank Sampling

organization shall be responsible for transporting each sample to the performing laboratory on the same day the sample is collected, or shall store the samples in a heated facility until shipment is possible. A verbal notification by Tank Sampling shall be made to the 222-S Laboratory at 373-2435 at least 24 hours in advance of an expected shipment.

3.2 SAMPLE CUSTODY AND SHIPPING

The sampling team shall initiate a chain of custody form for each sample jar. The chain of custody form shall accompany each sample through to its final destination. The following sampling information is required on the completed chain-of custody form, as a minimum:

- Project name (e.g., "204-AR-TK-1 2011 Compatibility Samples");
- Signature of sampler;
- An identification number unique to each sample as assigned in Table 3-1;
- Date, time, and location (riser and depth) at which the sample was obtained;
- Matrix (e.g., liquid, solid, color, consistency, etc.) along with a rough estimate of the volume of each present in the sample;
- Signature(s) of individual(s) involved in the sample transfer; and
- Date and time of possession.

Personnel shall record pertinent sampling information (e.g., separable organic layer(s), unusual waste characteristics, or sampling problems) in the comments section of the chain of custody form. Specifically, include a description of any solids observed in each grab sample and, if present, note the color and settling characteristics (e.g., hard settled, loosely settled, suspended in sample). To the extent that field conditions permit, Tank Sampling personnel should provide a rough estimate of the volume of solids present in each sample containing solids. Sample preservation and analysis requirements are documented elsewhere in this TSAP, and therefore need not be recorded on the chain-of-custody form. Each sample shall be shipped to the laboratory in an approved shipping container per approved procedures. Each sample shall be sealed with a waste tank sample seal to demonstrate that the samples reached the laboratory without alteration. Radionuclide concentration information that may be used to determine the required shipping container type is provided in Appendix A.

4.0 LABORATORY ANALYSIS REQUIREMENTS

After the samples are received at the laboratory, the samples shall be prepared and analyzed according to the directions and requirements specified in this section. Section 4.1 provides

sample handling requirements. Analytical requirements are specified in Section 4.2, while directions for addressing insufficient sample recovery are provided in Section 4.3. The Quality Assurance/Quality Control (QA/QC) requirements for the analyses are specified in Section 5.0. Changes to the analysis requirements in this TSAP shall be controlled in accordance with the change control direction provided in Section 9.0.

4.1 DIRECTION FOR SAMPLE HANDLING

4.1.1 Liquid Sample Handling

The laboratory shall perform the following steps on each liquid sample:

- Verify that the identification number on each sample bottle matches the sample seal on the sample container and chain-of-custody form.
- Record visual observations (e.g. color, clarity of the liquid, presence of solid particles, etc.). Take close-up photographs of the samples/sample material. The photographs should show, as clearly as possible, color and consistency of the samples. Estimate and record the volume percent settled solids, if present.
- Closely inspect each sample for the presence of any organic (separable) layers. Estimate and record the volume of the separable organic phase, if present. If present, retain the immiscible material in a separate labeled jar.
- If solids are observed visually and are less than 10% of the total sample volume, allow the solids to settle. If solids appeared to be precipitates caused by cooling of the sample, allow the solids to re-dissolve by holding the sample at the temperature of the hotcell until no further dissolution is observed. Remove sufficient aliquots of liquid from all of the samples, and perform the analyses as listed in Table 4-1. Do not re-suspend settled solids. If solids are ‘flighty’, separate the liquid from the solids (via centrifugation or filtration) prior to analysis.
- If solids are visually observed in the samples and constitute greater than 10% by volume, contact the Tank Coordinator for additional instructions.
- Archive the remainder of each sample.

4.1.2 Solids Sample Handling

The laboratory shall verify that the identification number on each sample bottle matches the sample seal on the sample container and chain-of-custody form. The laboratory shall observe and record physical characteristics such as color and consistency of the solids in each sample jar.

Close-up photographs of the sample materials shall be taken. The photographs should show, as clearly as possible, color and consistency of the samples.

If a liquid phase is present in a sample jar, the liquid shall be decanted into another jar after the sample is allowed to settle. The decanted liquid shall be weighed and the net weight recorded. The decanted liquid shall be placed in archive until further notice from the Tank Coordinator.

The solids shall be weighed and the net weight recorded. Subsamples shall be taken for analysis of volatile organic chemicals (VOCs), semi-volatile organic chemicals (SVOCs), Polychlorinated biphenyls (PCBs), and ammonia. These subsamples shall be taken prior to homogenization to avoid losses of volatile constituents. The bulk density shall also be measured prior to homogenization. The remaining solids in each sample shall be homogenized. The laboratory shall contact the Tank Coordinator for further direction if sample material cannot be homogenized effectively. Subsamples shall be taken from each sample to perform the analyses as listed in Table 4-2. Unused solids shall be placed in archive until further notice.

4.2 REQUIREMENTS FOR ANALYSIS

Liquid and solid waste samples shall be analyzed in separate batches. The liquid and solid subsamples shall be analyzed per Table 4-1 and Table 4-2, respectively. Concentration limits and direction for notification are provided in Section 8.1. All unused sample material shall be stored in archive until further notice.

Table 4-1. Analytical Requirements for Liquid Samples (3 pages)

Analytes	Analytical Technique	Reference Method[1]	Sample to be Analyzed[2]	Preparation Method	Units	Report Format[3]
Separable organics layer	Visual	Not Available (NA)	204AR-11-01, 204AR-11-02, 204AR-11-03, 204AR-11-03DUP	NA	NA	I, VI
Volume percent settled solids	Visual	NA	204AR-11-02, 204AR-11-03, 204AR-11-03DUP	NA	NA	VI
Al, Ag, As, Ba, Be, Bi, Ca, Cd, Cr, Co, Cu, Fe, K, La, Mg, Mn, Na, Ni, P, Pb, Rh, S, Sb, Se, Si, Sr, U, V, W, Zn, Zr	Inductively coupled plasma (ICP)/atomic emission spectrometry (AES)	6010	204AR-11-01FB, 204AR-11-02, 204AR-11-03, 204AR-11-03DUP	Direct	µg/mL	VI
Br^-, Cl^-, F^-, NO_2^-, NO_3^-, $C_2H_3O_2^-$, CHO_2^-, $C_2H_3O_3^-$, $C_2O_4^{2-}$, PO_4^{3-}, SO_4^{2-}	Ion chromatography (IC)	9056	204AR-11-01FB, 204AR-11-02, 204AR-11-03, 204AR-11-03DUP	Direct	µg/mL	I[5], II[5], VI
pH	pH probe	9040	204AR-11-01FB, 204AR-11-02, 204AR-11-03, 204AR-11-03DUP	Direct	unitless	I, II, VI

Table 4-1. Analytical Requirements for Liquid Samples (3 pages)

Analytes	Analytical Technique	Reference Method[1]	Sample to be Analyzed[2]	Preparation Method	Units	Report Format[3]
Hydroxide	Titration	NA	204AR-11-02, 204AR-11-03, 204AR-11-03DUP	Direct	µg/mL	I, II, VI
Specific Gravity (SpG)	Gravimetric	NA	204AR-11-01 204AR-11-02, 204AR-11-03, 204AR-11-03DUP	Direct	unitless	VI
Percent Water	Thermogravimetric analysis (TGA)	NA	204AR-11-02, 204AR-11-03, 204AR-11-03DUP	Direct	wt%	VI
Conductivity	Conductivity meter	9050	204AR-11-02, 204AR-11-03, 204AR-11-03DUP	Direct	µS/cm at 25°C	VI
Energetics	Differential scanning calorimetry	NA	204AR-11-02, 204AR-11-03, 204AR-11-03DUP	Direct	J/mL	VI
Total Dissolved Solids	Evaporation of filtrate	SM 2540 C	204AR-11-02, 204AR-11-03, 204AR-11-03DUP	Direct	µg/mL	VI
Total Suspended Solids	Evaporation of filtration residuals	SM 2540 D	204AR-11-02, 204AR-11-03, 204AR-11-03DUP	Direct	µg/mL	VI
Total inorganic carbon (TIC) / Total organic carbon (TOC)	Silver-catalyzed Oxidation / Coulometric Auto titration	ASTM D Method 4129, *Annual Book of ASTM Standards*	204AR-11-01FB, 204AR-11-02, 204AR-11-03, 204AR-11-03DUP	Direct	µg C/mL	VI
Total carbon (TC) / TOC[4]	Combustion / Coulometry	ASTM D Method 4129	204AR-11-01FB, 204AR-11-02, 204AR-11-03, 204AR-11-03DUP	Direct	µg C/mL	VI
Ammonium	IC	EPA 300.7	204AR-11-01FB, 204AR-11-02, 204AR-11-03, 204AR-11-03DUP	Distillation	µg/mL	VI
Mercury	Cold Vapor Atomic Absorption (CVAA)	7470	204AR-11-02, 204AR-11-03, 204AR-11-03DUP	Direct	µg/mL	VI
VOC	Gas chromatography (GC)/ mass spectrometry (MS)	8260	204AR-11-01FB, 204AR-11-02, 204AR-11-03, 204AR-11-03DUP	Direct	µg/L	VI
SVOC [4]	GC/MS	8270	204AR-11-01FB, 204AR-11-02, 204AR-11-03, 204AR-11-03DUP	Extraction	µg/L	VI
PCBs (Arochlors 1016, 1221, 1232, 1242, 1248, 1254, and 1260)	GC/ electron capture detector	8082	204AR-11-01FB, 204AR-11-02, 204AR-11-03, 204AR-11-03DUP	Extraction	µg/L	VI

Table 4-1. Analytical Requirements for Liquid Samples (3 pages)

Analytes	Analytical Technique	Reference Method[1]	Sample to be Analyzed[2]	Preparation Method	Units	Report Format[3]
^{3}H	Separation/liquid scintillation (LSC)	NA	204AR-11-02, 204AR-11-03, 204AR-11-03DUP	Direct	µCi/mL	VI
^{14}C, ^{63}Ni	Separation/LSC	NA	204AR-11-02, 204AR-11-03, 204AR-11-03DUP	Direct	µCi/mL	VI
^{79}Se	Anion-cation exchange/LSC	NA	204AR-11-02, 204AR-11-03, 204AR-11-03DUP	Direct	µCi/mL	VI
^{99}Tc, ^{233}U, ^{234}U, ^{235}U, ^{237}Np, ^{238}U	ICP/MS	6020	204AR-11-02, 204AR-11-03, 204AR-11-03DUP	Direct	µg/mL	I, II, VI
^{129}I	Separation/gamma energy analysis (GEA)	NA	204AR-11-01FB, 204AR-11-02, 204AR-11-03, 204AR-11-03DUP	Direct	µCi/mL	VI
^{60}Co, ^{94}Nb, ^{106}Ru, ^{134}Cs, ^{137}Cs, ^{154}Eu, ^{155}Eu, ^{226}Ra	GEA	NA	204AR-11-01FB, 204AR-11-02, 204AR-11-03, 204AR-11-03DUP	Direct	µCi/mL	II, VI
^{90}Sr	Separation/beta counting	NA	204AR-11-02, 204AR-11-03, 204AR-11-03DUP	Direct	µCi/mL	II, VI
^{238}Pu, $^{239/240}Pu$, ^{241}Am, $^{243/244}Cm$	Separation/alpha energy analysis (AEA)	NA	204AR-11-01FB, 204AR-11-02, 204AR-11-03, 204AR-11-03DUP	Direct	µCi/mL	I, II, VI
Gross alpha/beta	Direct mount (Gas proportional counting)	NA	204AR-11-01FB, 204AR-11-02, 204AR-11-03, 204AR-11-03DUP	Direct	µCi/mL	I, II, VI

Notes: [1] The SW-846 methods are listed without suffixes indicating method revisions; however, the latest updates are preferred.
[2] Sample 204AR-11-02 shall be analyzed in duplicate, as required by HNF-SD-WM-DQO-001.
[3] See Section 8.0 for descriptions of report formats.
[4] SVOC analyses will only be performed if directed by the Tank Coordinator and if an organic phase is observed in the liquid samples. Specific VOCs and SVOCs for the ETF WAC are detailed in Table 4-3.
[5] Formats I and II apply to NO_2^- and NO_3^- only.

Table 4-2. Analytical Requirements for All Solids Samples (2 pages)

Analytes	Analytical Technique	Reference Method[1]	Preparation Method	Units	Report Format[2]
Organic Layer	Visual	NA	Direct	N/A	I, VI
Ag, Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, La, Mg, Mn, Na, Ni, P, Pb, Pd, S, Sb, Se, Si, Sn, Sr, U, V, Te, Th, Tl, Zr.	ICP/AES	6010	Acid	µg/g	VI
Br^-, Cl^-, CHO_2^-, $C_2H_3O_2^-$, $C_2H_3O_3^-$, $C_2O_4^{2-}$, F^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}.	IC	9056	Water	µg/g	I[4], II[4], VI
pH	pH probe	9045	1 to 1 water to solids leach	unitless	I, II, VI
Hydroxide	Titration	NA	1 to 1 water to solids leach	µg/mL	I, II, VI
Bulk density	Gravimetric	NA	Direct	g/mL	VI
Percent Water	Thermo-gravimetric analysis	NA	Direct	wt %	VI
Energetics	Differential scanning calorimetry	NA	Direct	J/g dry weight basis	VI
Conductivity	Conductivity meter	9050	1 to 1 water to solids leach	µS/cm at 25 degree Celsius	II, VI
TIC/TOC	Silver-catalyzed Oxidation / Coulometric Auto titration	ASTM D Method 4129	Direct	µg C/g	VI
TC / TOC	Combustion / Coulometry	ASTM D Method 4129	Water	µg C/g	VI
Ammonium	IC	EPA 300.7	Distillation	µg/g	VI
Mercury	CVAA	7471	Direct	µg/g	VI
VOC [3]	GC/MS	8260	Direct	µg/kg	VI
SVOC [3]	GC/MS	8270	Extraction	µg/kg	VI
PCBs (Aroclors 1016, 1221, 1232, 1242, 1248, 1254, and 1260)	GC/ electron capture detector	8082	Extraction	µg/kg dry weight	VI
^{3}H	Separation/LSC	NA	Water	µCi/g	VI
^{14}C	Separation/LSC	NA	Water	µCi/g	VI
^{63}Ni	LSC	NA	Fusion	µCi/g	VI
^{79}Se	Anion-cation exchange/LSC	NA	Acid	µCi/g	VI
^{99}Tc	Radiochemical separation/LSC	NA	Acid	µCi/g	VI
^{99}Tc, ^{233}U, ^{234}U, ^{235}U, ^{237}Np, ^{238}U	ICP/MS	6020	Acid	µg/g	I, II, VI
^{129}I	Separation/GEA	NA	Fusion	µCi/g	VI
^{60}Co, ^{94}Nb, ^{106}Ru, ^{134}Cs, ^{137}Cs, ^{154}Eu, ^{155}Eu, ^{226}Ra	GEA	NA	Fusion	µCi/g	II, VI
^{90}Sr	Separation/beta counting	NA	Fusion	µCi/g	II, VI
^{238}Pu, $^{239/240}Pu$, ^{241}Am, $^{243/244}Cm$	Separation/AEA	NA	Fusion	µCi/g	I, II, VI

Table 4-2. Analytical Requirements for All Solids Samples (2 pages)

Analytes	Analytical Technique	Reference Method[1]	Preparation Method	Units	Report Format[2]
Gross alpha/beta	Direct mount (Gas proportional counting)	NA	Fusion	µCi/g	I, II, VI

Notes: [1]The SW-846 methods are listed without suffixes indicating method revisions; however, the latest updates are preferred.

[2]See Section 8.0 for descriptions of report formats.

[3]Specific VOCs and SVOCs required for the ETF WAC are detailed in Table 4-3.

[4] Formats I and II apply to NO_2^- and NO_3^- only.

The list of analyses was developed from HNF-3172 and HNF-SD-WM-DQO-001. The laboratory project manager and/or chemist shall select the appropriate sample preparation procedure based on sample matrix and analysis requirements. The selected procedure shall be documented in the data report narrative. Tank corrosion is affected primarily by soluble constituents; therefore, acid digestions of liquid samples shall not be performed in order to minimize dissolution of suspended solids.

Solids digestion methods are specified in Table 4-2. If required results cannot be achieved with the specified methods, the Tank Coordinator shall be contacted for further direction. A description of the digests and residues shall be provided in the laboratory data report narrative. ICP/MS analysis shall be performed on the acid digest to maintain low detection limits. If acid digestion is inadequate, fusion digestion shall be attempted.

Sampling organizations and analytical laboratories are expected to meet the holding times specified in SW-846 and laboratory QA plans and procedures. However, it is recognized that high radioactivity and difficult sample matrices may require additional time to ship, prepare, and analyze the samples. Also, if samples were taken during cool weather, solids may precipitate after samples are removed from the tank. Allowing the samples to reheat until the solids re-dissolve could affect holding times. Therefore, the laboratory is requested to perform the analyses as quickly as possible, during normal working hours, after sample receipt to minimize the time between sampling and analysis. All analytical data that exceed holding times shall be identified and discussed in the data report.

The preferred methods of analysis for the analytes listed in this document are from SW-846 or other approved standardized methods. The methods are listed without suffixes that indicate method revisions; however, the most recent revisions are preferred. Where no approved regulatory methods exist, the laboratory should use the technique specified in the analysis table(s). It is understood that the laboratory analytical procedures may have changes to the SW-846 methods to accommodate analysis of samples from Hanford waste tanks and to reduce radiological exposure to the analysts. It is also understood that those changes and their effect on method performance have been documented to demonstrate that their procedures can provide satisfactory performance for the intended use of the data. The documentation of changes (e.g., substitutions, deviations or modifications) to the methods shall be in writing, maintained at the laboratory, and available for inspection upon request by authorized representatives of regulatory authorities and Washington River Protection Solutions, LLC (WRPS). Additional regulatory or

DOE/RL-96-68, *Hanford Analytical Services Quality Assurance Requirements Documents* (HASQARD) requirements for documenting procedure modifications should also be followed.

Duplicate analyses shall be performed on subsurface sample 204AR-11-02, as specified by HNF-SD-WM-DQO-001.

Semi-volatile organic analyses (SVOA) shall only be performed if directed by the Tank Coordinator. Required volatile organic analytes (VOA) and potentially required SVOA (as described in HNF-3172) necessary for transfers to the ETF are provided in Table 4-3.

Table 4-3. Organic Analytes Required for ETF WAC

Parameter	Chemical Abstract Service (CAS) Identification Number	Parameter	CAS Identification Number
Carbon Tetrachloride	56-23-5	2,4,6-Trichlorophenol	88-06-2
Acetone	67-64-1	Acetophenone[1]	98-86-2
Chloroform	67-66-3	Methyl isobutyl ketone	108-10-1
1-Butyl alcohol	71-36-3	Tetrahydrofuran	109-99-9
Benzene	71-43-2	Pyridine	110-86-1
1,1,1-Trichloroethane	71-55-6	Di-n-octyl phthalate	117-84-0
Methylene chloride	75-09-2	Hexachlorobenzene	118-74-1
Carbon disulfide	75-15-0	Tributyl phosphate	126-73-8
Methyl ethyl ketone	78-93-3	Tetrachloroethylene	127-18-4

Note: [1]Analysis of Acetophenone, a SVOA, will depend upon direction by the Tank Coordinator if SVOA is run.

4.3 INSUFFICIENT SAMPLE MATERIAL

If sample material is insufficient to perform the analyses requested in this TSAP, the laboratory shall notify the Tank Coordinator within one working day. The amounts of material available and the amounts required for the individual analyses shall be provided at that time. Priorities for the analyses will be confirmed based on available sample material and discussion with representatives from the ETF and Washington River Protection Solutions, LLC. Any analyses prescribed by this TSAP, but not performed shall be identified in the data report. In addition, justification for not performing the analyses shall be provided.

5.0 QUALITY ASSURANCE AND QUALITY CONTROL

Quality requirements for conducting River Protection Project sampling and analysis are described in DOE/RL-96-68. Document HNF-SD-WM-DQO-001 provides quality requirements specific to the sampling and analysis of tanks for compatibility. Conditions (e.g., quality problems) that do not conform to requirements specified in this TSAP or references herein shall be controlled to prevent inadvertent use. These quality problems shall be identified, documented, controlled, and reported to prevent re-occurrence as required by Advanced Technologies and Laboratories International, Inc. (ATL) ATL-312 Section 4.26, *Analytical Project Process Flow* procedure and ATS-310, Section 1.25, *222-S Analytical Project Process Flow* procedure parts 4.17, 4.18 and 4.19. Off-site laboratories shall initiate their corrective

action process as applicable to the Department of Energy Consolidated Audit Program (DOECAP) Quality Systems for Analytical Services (QSAS) requirements detailed within QSAS, *Consolidated Audit Program Quality Systems for Analytical Services Document*.

All sampling and analysis activities shall be performed using approved methods, procedures, and work packages, which are written in accordance with approved operational and laboratory QA plans, consistent with the requirements of this TSAP. Qualified personnel, who meet site and job specific training requirements and use properly maintained and calibrated equipment, shall perform all activities specified in this TSAP.

5.1 QUALITY ASSURANCE/QUALITY CONTROL REQUIREMENTS FOR SAMPLING

Sample labeling and chain-of-custody is performed as described in Table 3-1 and Section 3.2.

5.2 QUALITY ASSURANCE/QUALITY CONTROL REQUIREMENTS FOR LABORATORY ANALYSIS

Document ATL-MP-1011, *ATL Quality Assurance Project Plan for 222-S Laboratory*, shall govern analyses performed by ATL for this sampling event. Analyses performed by WRPS shall be governed by ATS-MP-1032, *222-S Laboratory Quality Assurance Plan.* All tank waste analyses shall be performed in accordance with these requirements. Laboratories performing analyses in support of this TSAP shall have approved and implemented QA plans. These QA plans shall meet the DOE/RL-96-68 minimum requirements as the baseline for laboratory quality systems. If subcontracting any portion of this TSAP to a commercial laboratory off the Hanford site, the Subcontractor's implementing QA program shall comply with the QSAS.

The laboratory shall perform QC analyses at the frequency specified in the referenced methods. Where such methods are not available, QC analyses shall be performed at the frequency specified in the laboratory analytical procedure.

Analytical QC acceptance criteria [duplicates, spikes, and laboratory control samples (LCSs)] for both liquids and solids are identified in Table 5-1. The laboratory shall also use calibration and calibration check standards appropriate for the analytical instrumentation being used (see DOE/RL-96-68 for definitions of QC samples and standards). The criteria presented in the tables are goals for demonstrating reliable method performance. The laboratory will use its internal QA system for addressing any QC failures. If the QC failures are systematic and cannot be resolved by the internal protocols, the Tank Coordinator shall be consulted to determine the proper action. The laboratory should suggest a course of action at that time. All data not meeting the QC requirements shall be properly noted, and the associated QC failures shall be discussed in the narrative of the data report.

Table 5-1. Quality Control Criteria for Analytes

Method or Analyte	QC Acceptance Criteria[1]			
	LCS % Recovery	Spike % Recovery	Duplicate/MSD RPD[2] for Liquid	Duplicate/MSD RPD[2] for Solids
ICP/ AES	80 – 120%	75 – 125%	≤20%	≤30%
IC	80 – 120%	75 – 125%	≤20%	≤30%
pH meter	± 0.1 pH units	NA	NA	NA
Hydroxide	80 – 120%	75 – 125%	≤20%	≤30%
Density	NA	NA	NA	≤20%
SpG (for liquids)	80 – 120%	NA	≤20%	NA
Percent water	80 – 120%	NA	≤20%	≤30%
Energetics	80 – 120%	NA	≤30%	≤30%
TIC/TOC	80 – 120%	75 – 125%	≤20%	≤30%
Hg	80 – 120%	75 – 125%	≤20%	≤30%
Spectrophotometric for CN^-	80 – 120%	75 – 125%	≤20%	≤30%
VOC and SVOC	70-130%	70-130%	≤20%	≤30%
PCB	54-144% [3]	51-128% [3]	≤30%	≤30%
ICP/MS	80 – 120%	75 – 125%	≤20%	≤30%
^{3}H	Not specified	Not specified	Not specified	Not specified
^{14}C	Not specified	Not specified	Not specified	Not specified
^{63}Ni	Not specified	Not specified	Not specified	Not specified
^{79}Se	Not specified	Not specified	Not specified	Not specified
GEA	80 – 120%	NA	≤20%	≤30%
Beta counting	80 – 120%	NA [4]	≤20%	≤30%
Separation/AEA [5]	80 – 120%	NA [4]	≤20%	≤30%
Gas proportional counting	80 – 120%	NA [4]	≤20%	≤30%

Abbreviations: MSD = Matrix spike duplicate; RPD = Relative percent difference; LCS = Laboratory control sample; NA = Not applicable.

Notes: [1] The specified LCS and spike recovery criteria are applicable only if the analytical procedure requires these QC samples. Also, only analytes required by the analytical procedure will be included in the LCS or spike.

[2] If primary and duplicate results are available above detection limits, RPD will be based on these results.

[3] For solids, the LCS is 53-125% and the spike is 70-130%.

[4] Matrix spike analyses are not required for this method because a carrier or tracer is used to correct for constituent loss during sample preparation and analysis. The result generated using the carrier or tracer accounts for any inaccuracy of the method on the matrix. The reported results reflect this correction.

[5] ^{241}Pu is calculated from ^{238}Pu, $^{239/240}Pu$, therefore all % recovery and Duplicate/MSD RPD for liquids and solids are NA for this analyte.

5.3 ANALYTICAL DETECTION LIMITS

Analytical detection limits are specified in the Compatibility DQO and provided in Table 5-2. Maximum bounding concentrations and liner compatibility limits for the Liquid Effluent Retention Facility (LERF) for the ETF are provided in HNF-3172. Detection limits for these bounding concentrations are set to one order of magnitude lower than the bounding limit unless otherwise specified by D. Halgren at ETF, and are provided in Table 5-3 below. The laboratory shall meet the required detection limits (RDLs) specified in Table 5-4, which provides the most stringent detection limits from those provided in Table 5-2 and Table 5-3. The units for the RDLs in Table 5-4 are adjusted to match those in Table 4-1. For all analytes, including those without specified RDLs, the laboratory shall take necessary steps (e.g., use the least dilutions, large sample sizes, etc.) to minimize the method detection limits.

Table 5-2. Compatibility Required Detection Limits

Analyte	Required Detection Limit[1]
$^{239/240}Pu$	0.0001 g/L 0.000016 Ci/L
^{233}U	0.0001 g/L
^{235}U	0.0001 g/L
^{99}Tc	8.3E-6 Ci/L
^{90}Sr, ^{90}Y	0.022 Ci/L
^{137}Cs	0.15 Ci/L
^{241}Am	0.00013 Ci/L
PCB	3.7 µg/g (solids) 0.0065 µg/mL (liquid) [2]
NO_2^-	50.6 µg/mL
NO_3^-	310 µg/mL
PO_4^{3-}	950 µg/mL
OH^-	17 µg/mL

Notes: [1] Use bulk density measurement to convert the stated units of the required detection limits to units on mass basis for solid samples.

[2] Based on highest detection limit for individual Aroclor (not sum of detection limits).

Table 5-3. Required Detection Limits Based upon LERF Bounding Concentrations

Analyte	Required Detection Limit [1]
^{3}H	2.4E-05 Ci/L
^{14}C	1.6E-07 Ci/L
^{60}Co	2.4E-07 Ci/L
^{79}Se	1.5E-08 Ci/L
^{90}Sr	4.2E-06 Ci/L
^{94}Nb	2.6E-08 Ci/L
^{99}Tc	1.8E-06 Ci/L
^{106}Ru	6.5E-08 Ci/L
^{129}I	1.8E-07 Ci/L
^{134}Cs	4.1E-08 Ci/L
^{137}Cs	1.0E-06 Ci/L
^{144}Ce	2.0E-06 Ci/L
^{154}Eu	9.8E-07 Ci/L
^{155}Eu	6.3E-06 Ci/L
^{226}Ra	6.4E-09 Ci/L
U (gross; as ^{234}U)	2.1E-11 Ci/L
^{237}Np	2.1E-10 Ci/L
^{238}Pu	2.8E-10 Ci/L
$^{239/240}Pu$	1.8E-09 Ci/L
^{241}Pu	2.6E-09 Ci/L
^{241}Am	1.4E-10 Ci/L
^{244}Cm	2.5E-09 Ci/L
Alcohol/glycol (1-butanol)	1.0E-02 mg/L [3]
Alkanone (Acetone) [2]	1.0E-02 mg/L [3]
Aromatic/cyclic hydrocarbons (Acetophenone, benzene, carbozole, chrysene, cresol, di-n-octyl phthalate, diphenylamine, isophorone, pyridine, tetrahydrofuran)	0.01 mg/L [3]
Halogenated hydrocarbons (Arochlors, carbon tetrachloride, chloroform, hexachlorobenzene, lindane (gamma-BHC), hexachlorocyclopentadiene, methylene chloride, p-chloroaniline, tetrachloroethylene, 2,4,6-trichlorophenol)	200 mg/L
Ethers (Dichloroisopropyl ether)	200 mg/L
Other hydrocarbons (Acetonitrile, carbon disulfide, n-nitrosodimethylamine, Tributyl phosphate)	0.01 mg/L [3]
Acids, bases, and salts (Ammonia, cyanide, anions, cations)	1.0E+01 mg/L [3]

Notes: [1] Detection limits are set to one order of magnitude less than bounding limits described in Table D-1 and E-1 of HNF-3172. To convert the stated units of the required detection limits to units on a mass basis for solid samples, use the bulk density measurement.

[2] This includes ketones which contain saturated alkyl group(s). Those that contain unsaturated alkyl groups do not have detection or compatibility limits for the LERF.

[3] These detection limits were set based upon e-mail communication with the ETF WAC point of contact, D. Halgren.

Table 5-4. Required Detection Limits For 204-AR-TK-1 Laboratory Sample Analyses[1]

Analyte	Required Detection Limit [2]
^{3}H	2.4E-02 µCi/mL
^{14}C	1.6E-04 µCi/mL
^{60}Co	2.4E-04 µCi/mL
^{79}Se	1.5E-05 µCi/mL
^{90}Sr, ^{90}Y	4.2E-03 µCi/mL
^{94}Nb	2.6E-05 µCi/mL
^{99}Tc	1.1E-01 µg/mL
^{106}Ru	6.5E-05 µCi/mL
^{129}I	1.8E-04 µCi/mL
^{134}Cs	4.1E-05 µCi/mL
^{137}Cs	1.0E-03 µCi/mL
^{144}Ce	2.0E-03 µCi/mL
^{154}Eu	9.8E-04 µCi/mL
^{155}Eu	6.3E-03 µCi/mL
^{226}Ra	6.4E-06 µCi/mL
^{233}U	1.0E-01 µg/mL
U (gross; as ^{234}U)	2.1E-08 µCi/mL
^{235}U	1.0E-01 µg/mL
^{237}Np	3.0E-4 µg/mL
^{238}Pu	2.8E-7 µCi/mL
$^{239/240}Pu$	1.8E-06 µCi/mL
^{241}Pu	2.6E-06 µCi/mL
^{241}Am	1.4E-07 µCi/mL
^{244}Cm	2.5E-06 µCi/mL
Alcohol/glycol (1-butanol)	10 µg/L[5]
Alkanone (Acetone) [3]	10 µg/L[5]
Aromatic/cyclic hydrocarbons (Acetophenone, benzene, carbozole, chrysene, cresol, di-n-octyl phthalate, diphenylamine, isophorone, pyridine, tetrahydrofuran)	10 µg/L[5]
Halogenated hydrocarbons (Arochlors, carbon tetrachloride, chloroform, hexachlorobenzene, lindane (gamma-BHC), hexachlorocyclopentadiene, methylene chloride, p-chloroaniline, tetrachloroethylene, 2,4,6-trichlorophenol)	For Arochlors/PCBs: 3.7E+03 µg/kg (solids); 6.5 µg/L (liquid) [4] For all others: 2E+05 µg/L
Ethers (Dichloroisopropyl ether)	2E+05 µg/L
Other hydrocarbons (Acetonitrile, carbon disulfide, n-nitrosodimethylamine, Tributyl phosphate)	10 µg/L[5]
NO_2^-	50.6 µg/mL
NO_3^-	310 µg/mL
PO_4^{3-}	950 µg/mL
OH^-	17 µg/mL
All other acids, bases, and salts (Ammonia, cyanide, anions, cations)	1.0E+01 µg/mL[5]

Notes: [1] The RDL for an analyte is not applicable if it is detected above the laboratory quantitation limit.

[2] RDLs presented in this column were adjusted to be consistent with the units provided in Table 4-1. To convert the stated units of the required detection limits to units on mass basis for solid samples, use the bulk density measurement.

[3] This includes ketones that contain saturated alkyl group(s). Those that contain unsaturated alkyl groups do not have detection or compatibility limits for the LERF.

[4] Based on highest detection limit for individual Aroclor (not sum of detection limits).

[5] These Required Detection Limits are based upon requests from the ETF WAC Point of Contact.

6.0 EXCEPTIONS, CLARIFICATIONS, AND ASSUMPTIONS

6.1 EXCEPTIONS TO DATA QUALITY OBJECTIVE REQUIREMENTS

The laboratory shall report all analytical results recovered from ICP/AES, IC, ICP/MS, GEA, and AEA, even though only specific analytes are requested. These non-requested analytes will be reported only if no additional preparatory work is required and associated errors are documented. This requirement may be met by applying appropriate qualifiers to any results that do not meet internal laboratory QC limits. No reruns or additional analyses will be performed to improve recovery for analytes not specified in Table 4-1 and Table 4-2 unless formally requested by the Tank Coordinator. Minimum detection limits as specified in this TSAP are not applicable to analytes that exceed the laboratory's estimated quantitation limit.

For GEA, report the requested analytes as well as any other analytes detected above the method detection limit. The non-requested analytes are also to be reported only if no additional preparatory work is required (e.g., running additional standards) and if the associated errors are reported. This requirement may be satisfied by reporting the counting statistics and applying appropriate qualifiers to any results that do not meet internal laboratory QC limits.

Ammonia analysis is being performed by IC instead of ion selective electrode, and is reported as ammonium ion (NH_4^+). The detection limits and the action level have been adjusted accordingly.

Percent water and hydroxide are not requested on field blanks. The field blank is analyzed for pH.

Currently there is no method for analysis of ^{241}Pu. As described in HNF-SD-WM-DQO-001, until a method is developed, ^{241}Pu will be calculated from ^{238}Pu and $^{239/240}$Pu.

This TSAP includes a number of analytes that are important to tank inventory determinations, including ^{3}H, ^{79}Se, ^{99}Tc, ^{237}Np, $^{243/244}$Cm, S, and P. For the solids analysis, ^{99}Tc will be measured using both radiochemical separation/LSC and ICP/MS to ensure accuracy of the results. Similarly for both liquid and solid sample analyses, U will be measured both as individual isotopes using ICP/MS and as U via ICP/AES.

The Compatibility DQO (HNF-SD-WM-DQO-001) requires analysis of ^{151}Sm for transfers from inactive tank farm facilities as atomic mass unit 151. The laboratory does not believe that ICP/MS would provide a meaningful estimate for the concentration of this analyte due to interferences from other analytes. With e-mail concurrence of the Compatibility Point of Contact, this analyte was removed from the required analyte list for this sampling event.

Analysis for PCBs will be performed according to SW-846 Method 8082, which specifies amber-colored sample bottles. However, clear sample bottles will be used so that separable organics, if present, can be more easily identified. PCBs are stable compounds and any loss due to exposure to light is expected to be negligible.

SVOA shall only be performed on liquid samples if directed by the Tank Coordinator. The VOA and SVOA in Table 4-3 have been approved via telephone and e-mail conversation with the ETF WAC Point of Contact, Dale Halgren. If a separable organic layer is observed in sample 204AR-11-01, or if solids are obtained, the Tank Coordinator shall be notified and, per direction after discussion with all data users, all required SVOA may be performed to obtain concentration data for the SVOA listed in Table 4-3.

DOE/RL-96-68 does not include a description of a data qualifier for blank sample contamination. A 'B' qualifier shall be used to flag sample results in an analytical batch when an analyte is detected in both the sample and the blank and the blank sample result is greater than 5% of the sample result.

This TSAP specifies 250-mL sample bottles because additional sample material is needed to perform waste compatibility analyses and may be needed if additional testing is desired. The larger sample size does not affect quality of the sample.

Grab Sampling procedure follows the American Society for Testing and Materials (ASTM) E-300 'bottle on a string' procedure for sampling (ASTM E300-03, *Standard Practice for Sampling Industrial Chemicals*). The deviations from the ASTM E300-03 'bottle on a string' procedure are documented below.

- Requirement: The sampling apparatus shall be filled and allowed to drain before drawing the sample.
  - Deviation: The sampling apparatus is lowered into the tank to the desired level within the waste to collect the sample. To meet this requirement, the sample would have to be taken, retrieved, the contents poured out, and then retaken. Each sample would therefore have to be handled twice, increasing the radiation dose to the sample personnel. Furthermore, allowing the radioactive liquids "to drain" in the field could result in spreading of radiological contamination. Hence, this requirement is not implemented.

- Requirement: Bottles and jars may be made of clear or brown glass or polyethylene with necks shaped to receive glass stopper or a screw cap made of metal or plastic material.
  - Deviation: A rubber stopper is used when an empty bottle is lowered to the desired sample depth. (Glass stoppers were used at one time but their use often resulted in broken sample bottles during sampling). The stopper is then removed to allow the liquid to flow into the bottle. A plastic screw cap is used to close the bottle once it is removed from the tank.

- Requirement: Stopper and label bottles immediately after taking the samples and deliver them to the laboratory.
  - Deviation: Samples are placed in radiation shielded casks for shipping. Past experience indicates that sample labels often did not remain on the bottles during shipping. The sample bottles are therefore etched with sample identification numbers before the samples are collected. The samples are shipped to the

laboratory as soon as resources are available, within three days of sample collection.

- Requirement: To prevent the loss of the liquid during shipment and to protect against moisture and dust, cover the closure of the glass bottle with plastic caps, which have been swelled in water, wiped dry, placed over the top of the stoppered bottle, and allowed to shrink tightly in place. Screw-top bottles are recommended. The cap should be lined with material inert to the sample. The screw caps should be secured by use of adhesive tape or similar material.
  - Deviation: To minimize the handling of radioactive samples, only Teflon®-lined screw caps are used to close sample jars. The caps are not secured with tape since it is difficult to remove the tape remotely with manipulators in the laboratory hotcell.

6.2 CLARIFICATIONS AND ASSUMPTIONS

It is anticipated that all of the analyses will be performed at the 222-S Laboratory Complex. If necessary, the laboratory may subcontract certain analyses to another qualified laboratory. The subcontracted laboratory shall meet all QA/QC requirements in this TSAP. The 222-S Laboratory will prepare a statement-of-work (SOW) authorizing the subcontracted laboratory to perform the analyses. The SOW shall be reviewed by Tank Waste Inventory and Characterization Models manager and QA prior to approval. The subcontractor's implementing QA program shall comply with DOE/RL-96-68 for Hanford site laboratories. When subcontracting any portion of this TSAP to a commercial laboratory off the Hanford site, the subcontractor's implementing QA program shall comply with QSAS.

The IC method shall be able to distinguish fluoride from low molecular weight organic acids, such as formate and acetate. Low molecular weight organic acid results shall be reported opportunistically.

Requested analyses are required by DOE/RL-96-68 to be listed on the chain-of-custody. This TSAP will be used to communicate the analytical requirements instead. Additionally, DOE/RL-96-68 requires sample preservation in accordance with SW-846. The applicable DQOs do not require sample refrigeration or the addition of preservatives to tank samples because of concerns with high radiation exposure that would result from additional handling of sample solutions. Sample refrigeration would cause precipitation of dissolved salts in the sample, precluding achievement of the primary goal of this TSAP. Acidification or the addition of preservatives would likewise cause unacceptable alteration of the samples.

7.0 ORGANIZATION

The organization and responsibility of key personnel involved with this characterization effort are shown in Table 7-1.

Table 7-1. Tank 204-AR-TK-1 Characterization Project Key Personnel

Roles and Responsibility	Individual Name & Number [1]
Tank Coordinator	**S. J. Harrington, 376-1336**
222-S Laboratory Point of Contact	R. A. Bushaw, 373-4314
222-S Laboratory Point of Contact (off hours)	222-S Laboratory Leader, 373-2435
Tank Farms Shift Office	**Base Operations Shift Manager, 373-2689**
Compatibility Point of Contact	**J. Jo, 373-9322**
Tank Farms Criticality Safety Representative (Criticality Point of Contact)	**M. V. Shultz, 373-3740**
Back-up Tank Farms Criticality Safety Representative	**J. N. Appel (Acting), 372-3635**
Manager, Tank Waste Inventory and Characterization	**J. G. Reynolds, 373-5999**
Manager, Process Modeling	N. W. Kirch, 373-2380
Corrosion Mitigation Controls Technical Point of Contact	K. G. Carothers, 373-4556
Project Manager / A/AX/AY/AZ Facility Area Operations Specialist	J. W. Deline, 373-5511
ETF WAC Point of Contact	D. L. Halgren, 376-9988
Waste Technical Services	D. C. Hetzer, 372-3304
Nuclear Safety	S. D. Kozlowski, 373-1360
Base Ops Environmental	D. L. Dyekman, 372-2678
Radiation Control	W. R. Cooper, 373-2031
Sampling Operations	S. L. Kooiker, 372-3101
Grab Sampling Component Engineer	A. B. Cockrell, 373-4189
WRPS Sample Management Office	J. R. Prilucik, 373-3830

Notes: [1] Individuals in bold are those that require notification per Section 8.1

8.0 DELIVERABLES

All analyses of tank waste material shall be reported as Format I, II, and/or VI as indicated in Table 4-1. These standard formats for laboratory data reports are described in detail in ATL-MP-1011. Brief descriptions of these reporting formats are provided below.

8.1 FORMAT I REPORTING

This format requires immediate notification for certain analytes when the notification limits specified below are exceeded. Two types of notifications are required, as described in the following paragraphs.

If any of the limits identified in Table 8-1 are exceeded, the laboratory shall notify the Tank Farms Shift Office and Tank Farms Criticality Safety Representative immediately by telephone, with confirmatory e-mail or memo as soon as practical. The notification shall include the

anomalous sample value and the notification limit that was exceeded. In addition, the notification shall include the following wording:

"This notification indicates a potential Criticality Prevention Specification non-conformance."

Table 8-1. Immediate Telephone Notification Limits for Criticality

Constituent	Notification Limit	
	Liquid [1]	Solid [2]
$^{239/240}Pu$	> 2.2 g/L > 136 µCi/mL	> 1,100 µg/g > 68 µCi/g
^{233}U	> 2.2 g/L	> 1,100 µg/g
^{235}U (only if $^{235}U/^{238}U$ exceeds 0.0072)	> 2.2 g/L	> 1,100 µg/g
Sum of $^{239/240}Pu$, ^{233}U and ^{235}U (only include ^{235}U in sum if $^{235}U/^{238}U$ exceeds 0.0072)	> 2.2 g/L	> 1,100 µg/g

Notes: [1] Mass/volume limits based on 85% of bulk fissile material concentration limit (2.6 g/L) specified in CPS-T-149-00012.
[2] Mass/mass limits converted from mass/volume limits using an assumed density of 1.33 g/mL (RPP-33928). Use maximum density for sample event if available.

Any results exceeding the surveillance notification limits in Table 8-2 and Table 8-3 shall be reported via e-mail at the earliest opportunity the next business day, after the data are obtained and reviewed by the responsible scientist. Notifications shall be made to:

- Tank Coordinator and Manager, Tank Waste Inventory and Characterization: Limits in Table 8-2 and Table 8-3.
-
- Tank Farms Criticality Safety Representative: Limits in Table 8-2 only.

Table 8-2. Surveillance Notification Limits for Criticality

Constituent	Notification Limit	
	Liquid [1]	Solid [2]
$^{239/240}Pu$	> 1 g/L > 62 µCi/mL	> 500 µg/g > 31 µCi/g
^{233}U	> 1 g/L	> 500 µg/g
^{235}U (only if $^{235}U/^{238}U$ exceeds 0.0072)	> 1 g/L	> 500 µg/g
Total alpha	> 62 µCi/mL	> 31 µCi/g

Notes: [1] Mass/volume limits based on surveillance concentration limit (1 g/L) specified in CPS-T-149-00012, *Tank Farm Operations, Criticality Prevention Specification*.
[2] Mass/mass limits converted from mass/volume limits using an assumed density of 1.33 g/mL (RPP-33928). Use maximum density for sample event if available.

Table 8-3. Notification Limits for Separable Organic Phase

Constituent	Notification Limit	
	Liquid	Solid
Separable organic phase	If observed	If observed

Subsequent notifications will be made by Tank Waste Inventory and Characterization personnel per TFC-ENG-CHEM-P-18, *Response to Anomalous Sample Results*. Additional analyses for verification purposes may be contracted between the performing laboratory and Tank Waste Inventory and Characterization by a revision to this TSAP.

8.2 FORMAT II REPORTING

This format requires early transmittals of interim results for analyses identified in Table 4-1 and Table 4-2. The deliverables shall consist of data summary tables from the Laboratory Information Management System. The data may be transmitted to the Tank Coordinator via electronic mail. Format II reporting requirements for the 204-AR-TK-1 samples are as follows:

1. Within 7 calendar days of receiving the last liquid sample, interim results for pH, specific gravity, electrical conductivity, gamma energy analysis analytes, and strontium-90 in the liquid samples (not including the field blank) shall be transmitted.

2. Within 30 calendar days of receiving the last sample (liquid or solid), interim results for the following analytes in the liquid and solid samples shall be transmitted:
   - strontium-90,
   - neptunium-237 by inductively-coupled plasma/mass spectrometry, and
   - all analytes by gamma energy analysis and alpha energy analysis.

8.3 FORMAT VI REPORTING

A technical report documenting the results of all the analyses and QC data shall be released in accordance with TFC-ENG-DESIGN-C-25, *Technical Document Control*, with the assistance of the Sample Management Office. The report format shall be similar to a Format IV report with the exception that the only raw data required to be included are the raw data for the hydroxide and weight percent water by TGA. The report shall be distributed as shown in Table 8-4. The report shall be issued within 60 days of the receipt of the samples at the laboratory loading dock. The raw data shall be accessible to the program in accordance with the laboratory's Records Inventory and Disposition Schedule and until the respective waste tank is closed or the waste is treated.

The data package shall also include chromatograms of tentatively identified compounds found in VOAs and SVOAs. The narrative shall include a summary table containing all tentatively

identified compounds and the associated estimated concentrations. A discussion of the tentatively identified compound evaluation process shall be provided in the narrative.

An electronic version of the analytical results shall be loaded into the Tank Characterization Database within seven (7) calendar days of release of the data package. The electronic version shall be in the standard electronic format as directed in HNF-3638, *Standard Electronic Format Specification for Tank Characterization Data Loader: Version 3.5* (or higher revision). Sample photographs shall be added to the "HotCellPhoto" share drive, which is accessible to the Tank Coordinator. In addition, the laboratory shall provide an Excel®[2] spreadsheet containing the reviewed and approved data to the Tank Coordinator. The generation date and time on the spreadsheet shall match those on the data summary table in the laboratory data report.

Table 8-4. Final Report Distribution

Recipient	Report Type[1]
S. J. Harrington	E, H
J. H. Rasmussen	E
D. M. Nguyen	E
D. L. Banning	E
D. L. Dyekman	E
J. D. Guberski	E
S. D. Kozlowski	E
D. P. Mackay	E
A. L. Beerman	E
W. R. Cooper	E
S. L. Metzger	E
K. J. Hull	E
M. F. Pascual	E
N. W. Kirch	E
J. W. DeLine	E
J. N. Appel	E
J. G. Reynolds	E
J. Jo	E
J. Y. Houchin	E
D. L. Halgren	E
J. F. Cheadle	E
DOE Reading Room	H

Notes: [1] H = hard copy, E = electronic copy

[2] Excel® is a registered trademark of the Microsoft Corporation, Redmond, Washington.

9.0 CHANGE CONTROL

Sampling-related changes to the risers, sample location, sampling method, and/or number of grab samples, etc., must be approved by the Tank Coordinator. The changes shall be recorded on a Document Release Form (DRF), a Characterization Change Notice (CCN), a permanent data sheet, or directly in the sampling work package(s). Justification for the changes shall be provided in sufficient details.

The Tank Coordinator shall document significant changes to the analytical requirements in the TSAP (changes impacting scope, cost, or budget) with a DRF. Minor changes (as determined by the Tank Coordinator) may be made by the Tank Coordinator using a CCN. All changes shall be clearly documented in the final data report. The laboratory shall append the CCNs affecting sampling and analysis to the final data report. The Tank Coordinator has the responsibility of exercising technical judgment in modifying the described work and in justifying the level of documentation required when changes to the described work in the TSAP are made.

10.0 **REFERENCES**

ASTM D Method 4129, *Annual Book of ASTM Standards*, as revised, American Society for Testing and Materials, West Conshohocken, Pennsylvania.

ASTM E300-03, 2009, *Standard Practice for Sampling Industrial Chemicals,* ASTM International, West Conshohocken, Pennsylvania.

ATL-312 Section 4.26, *ATL Analytical Project Process Flow,* Advanced Technologies and Laboratories International, Inc., Richland, Washington.

ATL-MP-1011, *ATL Quality Assurance Project Plan for 222-S Laboratory*, as revised, Advanced Technologies and Laboratories International, Inc., Richland, Washington.

ATS-310, Section 1.25, *222-S Analytical Project Process Flow,* Washington River Protection Solutions, LLC, Richland, Washington.

ATS-MP-1032, *222-S Laboratory Quality Assurance Plan*, as revised, Washington River Protection Solutions, LLC, Richland, Washington.

CPS-T-149-00012, *Tank Farm Operations, Criticality Prevention Specification*, as revised, Washington River Protection Solutions, LLC, Richland, Washington.

DeLine, J. W., 2011-02-24, "RE: 204 AR catch tank information," (e-mail to S. J. Harrington), Washington River Protection Solutions, LLC, Richland, Washington.

CL3120-00-015, 2000, "Extension of Waste Compatibility Assessment of WESF Waste (WESF-99-01, Rev. 4) with Tank 241-AP-108 Waste," (internal letter from J. A. Lechelt to R. J. Brown, December 27), CH2M Hill Hanford Group, Inc., Richland, Washington.

DOE/RL-96-68, 2007, *Hanford Analytical Services Quality Assurance Requirements Documents*, Rev. 3, U.S. Department of Energy, Richland Operations Office, Richland, Washington.

EPA Method 300.7, 1986, *Dissolved Sodium, Ammonium, Potassium, Magnesium, and Calcium in Wet Deposition by Chemically Suppressed Ion Chromatography*, U.S. Environmental Protection Agency, Washington, D.C.

H-14-020814 001, 2003, *Waste Transfer System (WT) O&M System P&ID*, Rev. 02, U.S. Department of Energy, Office of River Protection, Richland, Washington.

HNF-3172, 2009, *Liquid Waste Processing Facilities Waste Acceptance Criteria*, Rev. 4, CH2M Hill Plateau Remediation Company, Richland, Washington.

HNF-3638, 2001, *Standard Electronic Format Specification for Tank Characterization Data Loader: Version 3.5*, Rev. 2, prepared by Pacific Northwest National Laboratory for CH2M HILL Hanford Group, Inc., Richland, Washington.

HNF-SD-WM-DQO-001, *Data Quality Objectives for Tank Farms Waste Compatibility Program*, as revised, Washington River Protection Solutions, LLC, Richland, Washington.

HNF-SD-WM-OCD-015, 2010, *Tank Farms Waste Transfer Compatibility Program*, Rev. 22, Washington River Protection Solutions, LLC, Richland, Washington.

QSAS, *Quality Systems for Analytical Services*, as revised, U. S. Department of Energy, Oak Ridge Office, Oak Ridge, Tennessee. https://doecap.oro.doe.gov/Readings/uploads/QSAS%20Rev%202%206%20Final%20w%20signature.pdf.

RPP-17754, 2003, *Waste Compatibility Assessment of Catch Tank 204-AR Waste with Tank 241-AP-107 Waste*, Rev. 0, CH2M Hill Hanford Group, Inc., Richland, Washington.

RPP-33928, 2007, *Spreadsheet Description Document for Estimation of Catch Tank 204-AR-TK-1 Liquid and Solid Wastes*, Rev. 0, Washington River Protection Solutions, LLC, Richland, Washington.

RPP-RPT-25889, 2005, *Waste Compatibility Assessment of Catch Tanks 244-A and 204-AR Waste with Tank 241-AP-107 Waste*, Rev. 1, CH2M Hill Hanford Group, Inc., Richland, Washington.

SVF-1332, 2007, *204-AR-TK-1 Liquid & Solid Composition Estimates.xls*, Rev. 0, CH2M Hill Hanford Group, Inc., Richland, Washington.

SW-846, 1986, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, 3rd ed., as amended, U.S. Environmental Protection Agency, Washington, D.C.

TFC-ENG-CHEM-P-18, *Response to Anomalous Sample Results*, as revised, Washington River Protection Solutions, LLC, Richland, Washington.

TFC-ENG-CHEM-D-23, *Preparation of Tank Sampling and Analysis Plans*, as revised, Washington River Protection Solutions, LLC, Richland, Washington.

TFC-ENG-DESIGN-C-25, *Technical Document Control*, as revised, Washington River Protection Solutions, LLC, Richland, Washington.

APPENDIX A

ESTMATES OF RADIONUCLIDE CONCENTRATIONS IN THE 204-AR-TK-1 CATCH TANK SAMPLES

ESTMATES OF RADIONUCLIDE CONCENTRATIONS IN 204-AR-TK-1 CATCH TANK SAMPLES

The liquid and sludge currently in catch tank 204-AR-TK-1 have not been recently sampled. Radionuclide concentrations in the waste are estimated using available process knowledge information. These rough estimates should be used with caution.

Liquid radionuclide estimates are based on estimates made in RPP-RPT-25889, *Waste Compatibility Assessment of Catch Tanks 244-A and 204-AR Waste with Tank 241-AP-107 Waste*. This information is the most conservative when compared to other available estimates, such as those in RPP-17754, *Waste Compatibility Assessment of Catch Tank 204-AR Waste with Tank 241-AP-107 Waste*, or RPP-33928, *Spreadsheet Description Document for Estimation of Catch Tank 204-AR-TK-1 Liquid and Solid Wastes*. The radionuclide concentrations were then decayed from 06/24/2005 to 02/24/2011. This does not take into consideration any dilutions due to volume changes that may have occurred between the compatibility assessment performed in 2005 and 02/24/2011. The rough estimate of radionuclides in the 204-AR-TK-1 catch tank liquid is provided in Table A-1.

The estimated solids radionuclide concentrations were based on information provided in RPP-33928. These values were based upon facility shielding calculations (e.g. estimates). The estimated 204-AR-TK-1 solids composition provided in Table 6-2 of RPP-33928 was used as a starting point for the solids' radionuclide concentration. These constituents were decayed, as was done for the liquids, from 05/25/2007 to 02/24/2011. The rough estimates of radionuclides in the 204-AR-TK-1 catch tank solids are provided in Table A-2.

Table A-1. Estimates of Radionuclide Concentrations in 204-AR-TK-1 Catch Tank Liquid Samples

Analyte	Estimated Concentration (µCi/mL)	Estimated Radioactivity (Ci in each 250-mL Sample)
Maximum total alpha (as Americium-241)[1]	2.90E-02	7.25E-06
Cesium-137	6.43E+01	1.60E-02
Barium-137m	6.07E+01	1.50E-02
Plutonium-239/240	6.60E-04	1.70E-07
Strontium-90	5.80E+00	1.45E-03
Yttrium-90	5.80E+00	1.45E-03

Notes: [1] The Maximum Total Alpha concentration provided on page B-7 of RPP-RPT-25889 was obtained from RPP-17754. In this reference, the concentration provided on page B-2 for Am-241 is the same as that for the Total Alpha, which is the same number provided on page B-7 of RPP-RPT-25889 for the concentration (µCi/mL) of Maximum Total Alpha.

Table A-2. Estimates of Radionuclide Concentrations in 204-AR-TK-1 Solid Samples

Analyte	Estimated Concentration (µCi/g)	Estimated Concentration (Ci in each 240 mL jar of solids) [1]
Cesium-137	2.22E+01	7.09E-03
Barium-137m	2.09E+01	6.67E-03
Strontium-90,	1.02E+02	3.26E-02
Yttrium-90	1.02E+02	3.26E-02

Note: [1] Determined using an estimated solid density of 1.33 g/mL from assumptions in RPP-33928.

APPENDIX A REFERENCES

RPP-17754, 2003, *Waste Compatibility Assessment of Catch Tank 204-AR Waste with Tank 241-AP-107 Waste*, Rev. 0, CH2M Hill Hanford Group, Inc., Richland, Washington.

RPP-33928, 2007, *Spreadsheet Description Document for Estimation of Catch Tank 204-AR-TK-1 Liquid and Solid Wastes*, Rev. 0, CH2M Hill Hanford Group, Inc., Richland, Washington.

RPP-RPT-25889, 2005, *Waste Compatibility Assessment of Catch Tanks 244-A and 204-AR Waste with Tank 241-AP-107 Waste*, Rev. 1, CH2M Hill Hanford Group, Inc., Richland, Washington.

APPENDIX B

E-MAIL CORRESPONDENCE CONCERNING THE 204-AR-TK-1 CATCH TANK LIQUID LEVEL

(DeLine, J. W., 2011-02-24, "RE: 204 AR catch tank information," (e-mail to S. J. Harrington), Washington River Protection Solutions, LLC, Richland, Washington.)

Harrington, Stephanie J

From: DeLine, Jeffery W (Jeff)
Sent: Thursday, February 24, 2011 2:48 PM
To: Harrington, Stephanie J
Cc: DeLine, Jeffery W (Jeff); Metzger, Stephen
Subject: RE: 204 AR catch tank information

Hi Stephanie,

Operators due a daily level reading as part of the rounds sheets. The current reading is 63.5" or 927 gallons. Based on process knowledge, the tank level is due to water addition to the seal loops and weekly safety shower inspections. However, for Catch Tank to Farm transfers, the catch tank is not pumped below 150 gallons.

Hope this helps

Jeff

From: Harrington, Stephanie J
Sent: Wednesday, February 23, 2011 11:14 AM
To: DeLine, Jeffery W (Jeff)
Subject: 204 AR catch tank information

Jeff,

You stated that the tank level was approximately 900 gallons. Do you have any records for the exact volume held in this tank? Also, do you have any records on the changes in tank volume since 2009? I have looked for this information on PCSACS and TWINS, but both have no new data since early 2009. I would appreciate any references you can provide for inclusion in the sampling and analysis plan.

Thank you,
Stephanie Harrington, PhD
Core (Process) Engineer
Washington River Protection Solutions,
contractor to the United States Department of Energy
(509) 376-1336

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DISTRIBUTION SHEET

To	From	Page 1 of 1
Distribution	Tnk Wst Inv & Characterization	Date 04/13/2011
Project Title/Work Order		EDT No. N/A
RPP-PLAN-43865, Rev. 0, Sampling and Analysis Plan for Liquid and Solids in the 204-AR-TK-1 Catch Tank		ECN No. N/A

Name	MSIN	Text With All Attach.	Text Only	Attach./ Appendix Only	EDT/ECN Only
S. J. Harrington	B1-55	X			
J. G. Reynolds	B1-55	X			
D. M. Nguyen	B1-55	X			
J. H. Rasmussen	B1-55	X			
S. L. Kooiker	S7-03	X			
T. W. Craft	S7-20	X			
R. A. Bushaw	T6-10	X			
J. R. Prilucik	T6-02	X			
J. M. Johnson	T6-02	X			
J. W. Deline	S5-60	X			
J. Jo	B1-55	X			
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