CHAPTER 3.0
WASTE ANALYSIS PLAN

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CHAPTER 3.0
WASTE ANALYSIS PLAN

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GLOSSARY

ASTM	American Society for Testing and Materials
AWWA	American Water Works Association
CAS#	Chemical Abstract Service Number
CFR	Code of Federal Regulations
C_T	total carbon
DOE	U. S. Department of Energy
DQO	data quality objective
DSC	differential scanning calorimeter
DST	Double-Shell Tanks
Ecology	Washington State Department of Ecology
EPA	U.S. Environmental Protection Agency
ETF	200 Area Effluent Treatment Facility
GC	gas chromatography
HDPE	high-density polyethylene
IC_T	total inorganic carbon
IR	infrared
LERF	Liquid Effluent Retention Facility
MS	mass spectrometry
N/A	not applicable
QA	quality assurance
QC	quality control
RCRA	*Resource Conservation and Recovery Act of 1976*
RPD	relative percent difference
TGA	Thermogravimetric analysis
TOC	total organic carbon
TSD	treatment, storage, and/or disposal
VOA	volatile organic analysis
WAC	Washington Administrative Code
WAP	waste analysis plan

METRIC CONVERSION CHART

Into metric units			Out of metric units		
If you know	Multiply by	To get	If you know	Multiply by	To get
Length			**Length**		
inches	25.40	millimeters	millimeters	0.0393	inches
inches	2.54	centimeters	centimeters	0.393	inches
feet	0.3048	meters	meters	3.2808	feet
yards	0.914	meters	meters	1.09	yards
miles	1.609	kilometers	kilometers	0.62	miles
Area			**Area**		
square inches	6.4516	square centimeters	square centimeters	0.155	square inches
square feet	0.092	square meters	square meters	10.7639	square feet
square yards	0.836	square meters	square meters	1.20	square yards
square miles	2.59	square kilometers	square kilometers	0.39	square miles
acres	0.404	hectares	hectares	2.471	acres
Mass (weight)			**Mass (weight)**		
ounces	28.35	grams	grams	0.0352	ounces
pounds	0.453	kilograms	kilograms	2.2046	pounds
short ton	0.907	metric ton	metric ton	1.10	short ton
Volume			**Volume**		
fluid ounces	29.57	milliliters	milliliters	0.03	fluid ounces
quarts	0.95	liters	liters	1.057	quarts
gallons	3.79	liters	liters	0.26	gallons
cubic feet	0.03	cubic meters	cubic meters	35.3147	cubic feet
cubic yards	0.76456	cubic meters	cubic meters	1.308	cubic yards
Temperature			**Temperature**		
Fahrenheit	subtract 32 then multiply by 5/9ths	Celsius	Celsius	multiply by 9/5ths, then add 32	Fahrenheit
Force			**Force**		
pounds per square inch	6.895	kilopascals	kilopascals	0.14504	pounds per square inch

Source: *Engineering Unit Conversions*, M. R. Lindeburg, P.E., Second Ed., 1990, Professional Publications, Inc., Belmont, California.

3.0 WASTE ANALYSIS PLAN

3.1 Introduction

This waste analysis plan (WAP) addresses analysis necessary to manage the waste at the 242-A Evaporator according to requirements included in the *Hanford Facility Resource Conservation and Recovery Act, Dangerous Waste Portion, Permit,* WA7 89000 8967 (Permit), and Washington Administrative Code (WAC), Chapter 173-303.

Modifications of the WAP require modifications of the Permit. Permit modifications are discussed in Permit Condition I.C and WAC 173-303-830.

Where information regarding treatment, management, and disposal of the radioactive source byproduct material and/or special nuclear components of mixed waste (as defined by the Atomic Energy Act of 1954 as amended) has been incorporated into this document, it is not incorporated for the purpose of regulating the radiation hazards of such components under the authority of this Permit or chapter 70.105 RCW and its implementing regulations but is provided for information purposes only.

3.2 Purpose

The purpose of the WAP is to ensure waste at the 242-A Evaporator is managed properly in accordance with WAC 173-303-300. To ensure the waste analysis is comprehensive, a data quality objectives (DQO) analysis was performed on all streams at the 242-A Evaporator. Sampling and analysis identified in the DQO analysis related to meeting RCRA requirements are included as an integral part of this WAP.

Regulatory and safety issues are addressed in the WAP by establishing boundary conditions for waste to be received and treated at the 242-A Evaporator. The boundary conditions are set by establishing limits for items such as reactivity, waste compatibility, and control of vessel vent organic emissions. Waste that exceeds the boundary conditions would not be acceptable for processing without further actions, such as blending with other waste. In some cases, individual waste streams not acceptable at the 242-A Evaporator may be pre-treated or blended with other compatible waste streams to meet the 242-A waste acceptance criteria. Such pre-treatment or blending, however, would occur at dangerous waste management unit(s) other than the 242-A Evaporator.

3.3 Scope

This WAP discusses sampling and analysis of waste to determine the acceptability of the waste in 'candidate feed tank(s)' for processing at the 242-A Evaporator and characterization of dangerous waste streams generated from the treatment process. A 'candidate feed tank(s)' means one or more tanks in the Double Shell Tank (DST) System, and is typically not the feed tank (241-AW-102). Refer to additional discussion in Section 3.5 for 'candidate feed tanks.'

- **Candidate Feed Tank Acceptance Process** – This process determines the acceptability of DST System waste at the 242-A Evaporator operating capabilities prior to acceptance of the waste at the 242-A Evaporator for treatment. Refer to Section 3.7.
- **Dangerous waste generated from the treatment process** – Sampling and analysis is used to characterize the process condensate waste stream generated from the treatment process. The process condensate is transferred to the Liquid Effluent Retention Facility (LERF). Sampling can be performed either at the 242-A Evaporator or at LERF. A discussion of process condensate sampling at the 242-A Evaporator is included in this WAP, while discussion of process condensate sampling at LERF is included in the Permit, Part III, Liquid Effluent Retention Facility and 200 Area Effluent Treatment Facility, *Waste Analysis Plan*. Refer to Section 3.8.
- Samples of other 242-A Evaporator waste streams, such as steam condensate, cooling water, and 242-A-81 back flush water, are taken as required for process control but are excluded from this plan because these streams have been previously characterized and determined to be nondangerous waste streams.

3.4 242-A Evaporator Process Description

The 242-A Evaporator, located in the 200 East Area of the Hanford Site, separates the incoming waste from the DST System into two mixed waste aqueous streams the slurry and the process condensate as described in the following paragraph. The 242-A Evaporator also generates utility waste streams such as cooling water and steam condensate, which do not designate as dangerous waste. Description of the waste processed by the 242-A Evaporator is described in Section 3.5.

The 242-A Evaporator process uses a conventional forced-circulation, vacuum evaporation system to concentrate mixed waste solutions from the DST System tanks. The incoming stream is separated by evaporation into two liquid streams: a concentrated slurry stream and a process condensate stream. The slurry contains the majority of the radionuclides and inorganic constituents. After the slurry is concentrated to the desired amount, the slurry stream is pumped back to the DST System and stored for further treatment. Vapor from the evaporation process is condensed, producing process condensate. The process condensate is transferred to LERF for storage and treatment. Vacuum for the evaporator vessel is provided by two steam jet ejectors. The 242-A Evaporator vessel vent stream is filtered and discharged through an exhaust stack. Figure 3.1 shows a simplified schematic of the 242-A Evaporator process. A more detailed description of the 242-A Evaporator process is provided in Chapter 4.0.

3.5 Waste Identification

All of the waste accepted by the 242-A Evaporator is stored in the DST System. Waste characterization for a campaign is based on sampling and analysis results and/or process knowledge. Based on this information, certain DST System tanks are selected as 'candidate feed tanks' for processing in the 242-A Evaporator. The contents of these candidate feed tanks are subjected to closer scrutiny and evaluated against 242-A Evaporator waste acceptance criteria before the final tank selection is made. To meet waste acceptance criteria, the contents of several tanks could be blended together in the feed tank (241-AW-102) prior to processing. The 241-AW-102 tank is not typically considered a candidate feed tank but can become a candidate feel tank if waste is staged and sampling is performed there. Selection of candidate feed tank(s) for a campaign is outside the scope of this WAP and based on operational needs of the DST system.

Process knowledge is used to determine whether actions to add waste to a tank are acceptable after a candidate feed tank(s) or the 241-AW-102 feed tank has been isolated for a campaign. Operational and maintenance activities can occur at the 242-A Evaporator or the DST System which results in the introduction of operational and maintenance additions into a candidate feed tank(s) or the 241-AW-102 feed tank. In most cases, operational and maintenance waste solution additions are anticipated. Prior to anticipated activities occurring, documentation will be placed in the Hanford Facility Operating Record, 242-A Evaporator unit-specific portion, to show waste acceptance criteria will still be met. The calculation(s) will use, as appropriate, candidate feed tank sampling and analysis results for the proposed campaign, candidate feed tank sampling and analysis results from the previous campaign for waste residing in the 241-AW-102 feed tank, coupled with information about the type and quantity of solutions to be introduced into the isolated waste. When the operational and maintenance waste solution addition occurs and is unanticipated, documentation will be prepared after the event and prior to processing and will be placed in the Hanford Facility Operating Record, 242-A Evaporator unit-specific portion, in a similar fashion to the anticipated event.

Anticipated or unanticipated water additions to isolated candidate feed tank(s) or the 241-AW-102 feed tank do not require documentation. Water additions will not affect whether the waste acceptance criteria will be met.

3.5.1 General Constituent Description

The only waste stream processed at the 242-A Evaporator is the DST System waste stream. The mixed waste is an aqueous solution containing dissolved inorganic salts such as sodium, potassium, aluminum, hydroxides, nitrates, and nitrites. The mixed waste in some tanks has detectable levels of heavy metals such as lead, chromium, and cadmium. The radionuclide content includes fission products such as Sr-90 and Cs-137, and actinide series elements such as uranium and plutonium. Small quantities of ammonia and organics, such as acetone, butanol, and tri-butyl phosphate, could be present. Waste received in the DST System has been chemically adjusted to ensure the waste is compatible with materials used for construction of the waste tanks and the 242-A Evaporator. The physical consistency of the waste in the DST System ranges from liquid supernate to thick sludge. Waste fed to the 242-A Evaporator is supernate taken from the DST System; the sludge is not processed through the 242-A Evaporator.

The slurry, which results from treatment of DST System waste in the 242-A Evaporator, is an aqueous solution containing the same components as the feed stream with increased concentrations of non-volatile organic and inorganic constituents. The slurry may also contain solids precipitated due to the liquid volume reduction. Most of the volatile constituents in the feed are separated into the process condensate. The process condensate, a mixed waste, is a dilute aqueous solution with ammonia, volatile organics, and trace quantities of non-volatile constituents.

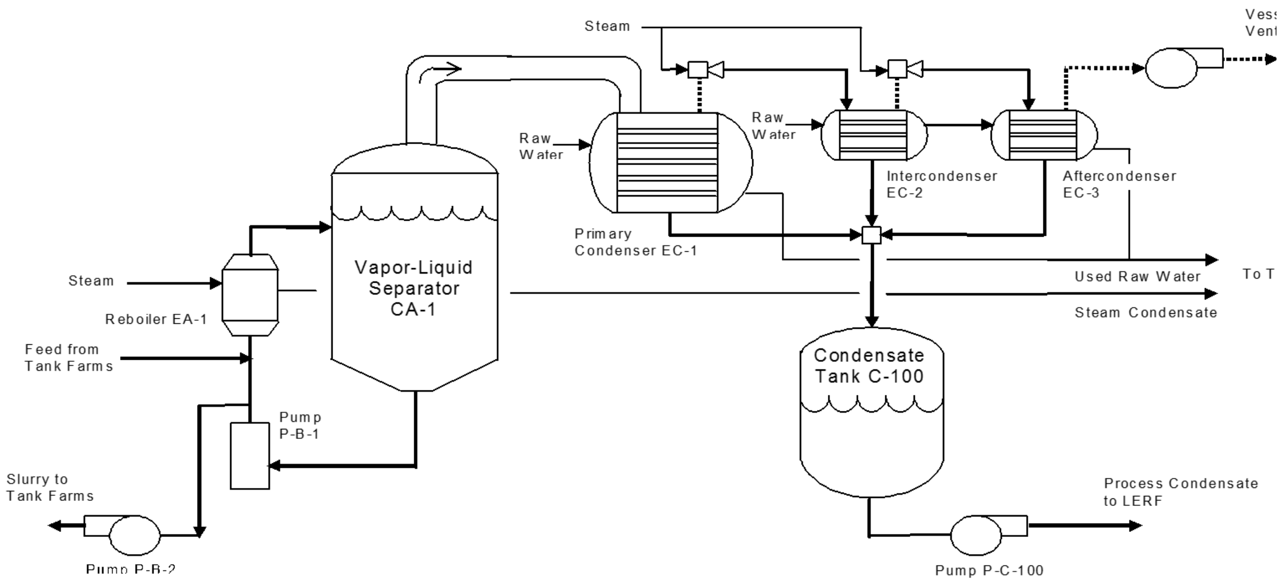

Figure 3.1. 242-A Evaporator Simplified Schematic

3.5.2 Classification of Waste

The waste processed at the 242-A Evaporator is classified as a mixed waste because it contains a radioactive component and a chemical component that designates as a dangerous waste. The waste processed is designated and assigned dangerous waste codes for waste stored in the DST System as follows.

- Waste generated from the evaporation treatment process includes slurry and process condensate. The concentrated slurry and process condensate are mixed waste since they are derived from the treatment of the DST System listed dangerous waste due to waste codes F001 through F005. The two waste streams may also exhibit one or more dangerous waste characteristics (WAC 173-303-090).
- Other 242-A Evaporator waste streams do not contact mixed waste solutions, such as cooling water and steam condensate. These waste streams are not discussed in this WAP because these streams do not designate as dangerous waste under WAC 173-303. Any waste sampling and analysis for purposes of designation would be conducted pursuant to WAC 173-303-170, outside the scope of this Permit.

3.5.3 Dangerous Waste Numbers

The 242-A Evaporator is specifically designed to accept DST System waste directly from feed tank 241-AW-102. Waste acceptable for transfer to the 242-A Evaporator could be assigned any of the dangerous waste numbers found in Chapter 1.0, Part A, Form (latest Revision). These numbers are identical to the ones in the Part A, Form (latest Revision) for the DST System. Process knowledge and historical data indicate that the slurry stream returning to the DST System contains the same dangerous waste constituents as the waste feed, so the same dangerous waste numbers are applicable to the feed and slurry.

Table 3.1 lists the dangerous waste numbers assigned to the process condensate. The process condensate is designated with the dangerous waste numbers F001 to F005 because the process condensate is derived from treatment of DST System waste assigned these numbers.

Table 3.1. Waste Designation for Process Condensate.

Waste number	Characteristic/Source	Basis for designation
F001	Spent halogenated solvents	Derived from F001 waste
F002	Spent halogenated solvents	Derived from F002 waste
F003	Spent nonhalogenated solvents	Derived from F003 waste
F004	Spent nonhalogenated solvents	Derived from F004 waste
F005	Spent nonhalogenated solvents	Derived from F005 waste
F039	Multi-source leachate from waste disposal operations	Future receipt of waste with the F039 number, derived from F001 through F005.

The slurry waste stream generated at the 242-A Evaporator is also a mixed waste, but the slurry waste is not stored at the 242-A Evaporator, as it is transferred back to the DST system, and therefore not subject to the WAP. In addition to the F001–F005 dangerous waste numbers, the slurry waste may designate for one or more applicable characteristic dangerous waste numbers.

3.6 Waste Acceptance Process

This section describes the actions performed before every campaign to determine candidate feed tank waste is acceptable for treatment at the 242-A Evaporator. Because initial acceptance of the process condensate at LERF is based on completion of a waste stream profile using candidate feed tank data, LERF waste acceptance criteria are also considered in the selection of a candidate feed tank. DST wastes are not accepted for treatment in the 242-A Evaporator unless the 242-A Evaporator waste acceptance criteria are satisfied, and the process condensate projected to be generated via treatment in the 242-A Evaporator satisfies LERF waste acceptance criteria.

The 242-A operates as a batch treatment system. Feed for each evaporator campaign must follow this waste acceptance process for waste verification and waste acceptance. Therefore, there is no need to periodically re-evaluate any waste stream.

Evaluation of data produced from the sampling and analysis of candidate feed tank waste for each campaign are documented in the campaign specific process control plan, process memo and associated engineering calculations, which are maintained in the Hanford Facility Operating Record, 242-A Evaporator, unit specific portion. Process control plans are prepared to describe and define the specific controls required for a planned campaign. Each process control plan includes the information described below:

- Waste Feed Description - describes the source, volume, and any potential mixing or blending data.
- Campaign Objectives – details the waste reduction volume estimates and specific gravities expected for each campaign.
- Candidate Feed Tank Sampling and Analysis Evaluation– describes the actual sampling and analysis data for each candidate feed tank for each campaign. This evaluation includes review of data to the 242-A Evaporator waste acceptance criteria, other health and safety controls beyond the scope of the Permit for operation of the 242-A Evaporator, and calculation of the expected process condensate constituent concentrations for review to the LERF waste acceptance criteria.
- Process Controls and Campaign Recommendations – describes the limits and conditions for each campaign based on the campaign objectives and candidate feed tank analytical data.

3.7 Candidate Feed Tank Waste Acceptance Process

Once possible feed candidate tanks have been identified, the method for determining if the waste in a candidate feed tank is acceptable for processing is followed. This section describes the waste acceptance process and Figure 3.2 provides an overall process flow.

The following activities are performed to determine if candidate waste feed will meet the 242-A Evaporator waste acceptance criteria.

- Perform a boil down study to evaluate the impacts of solids formation as specified in the Evaporator DQO (Banning 2009).
- Evaluate Potential for Energetics/Uncontrolled Chemical Reactions: There must be no exothermic reaction of waste constituents that occur below 168°C (335ºF), and the ratio of exotherm-to-endotherm energy be less than 1.
- Evaluate Potential for Separable Organic Phase: Prior to operation of the evaporator, the absence of separable organics in the feed must be verified or managed to preclude transfer to the 242-A Evaporator.
- Calculate Process Condensate Ammonia and Organic Concentrations: Ammonia and volatile organic concentrations are needed for the LERF waste profile sheet (refer to the Permit, Part III, LERF and 200 Area ETF, unit-specific conditions and Chapter 3.0, Waste Analysis Plan.)

3.7.1 Selecting Candidate Feed Tanks

For each 242-A Evaporator campaign, DST System tanks are selected as candidate feed tanks based on process knowledge of chemical properties with respect to waste acceptance criteria (Section 3.6.1). The initial determination of possible candidate feed tanks is outside the scope of this WAP and is based on operational needs of the DST system.

3.7.2 Candidate Feed Tank Sampling

After a candidate tank is selected, the waste in the tank is sampled and analyzed and the data evaluated to confirm waste acceptability through development of a Tank Sampling and Analysis Plan (Figure 3.2). Every candidate feed tank is sampled and analyzed to confirm waste acceptability. Sampling of a candidate feed tank waste for treatment in the 242-A Evaporator is performed according to the requirements of this WAP. The WAP reflects the rationale for determining the number of samples in the DQO (Banning 2009). The waste is sampled in the DST System, prior to transfer and acceptance at the 242-A Evaporator.

Four (4) representative samples of aqueous candidate feed tank waste supernatant, from one tank riser, are required. These samples are adequate to ensure the resulting waste characterization data are of sufficient quality for the data's planned purposes. The data are compared to the 242-A Evaporator waste acceptance criteria, applied to the 242-A Evaporator Process Control Plan for purposes of predicting process condensate properties, and used for comparison to LERF waste acceptance criteria for liner compatibility. The rationale for this statement is that the estimates of the variability of DST System content wastes properties is sufficiently defined and consistent that four (4) samples are sufficient. No solid samples are collected.

The four (4) samples will be collected from the following depths. One (1) surface sample to address the possible existence of a separable organic layer and three (3) subsurface samples are obtained from each waste candidate feed tank. The depths of the subsurface samples are determined by the Permittees based on best professional judgment (based on Table 3.3). In the event multiple candidate feed tanks are identified, sampling can occur after wastes are blended. The identified candidate feed tanks coupled with process knowledge of the feed tank (241-AW-102) provide a representative set of data for determining waste acceptance in the 242-A Evaporator. This is due to the consistency in the type of feed waste and the source of the waste. Waste in candidate feed tanks must first be accepted into the DST System by meeting the corresponding DST System waste acceptance criteria. Waste management in the DST System results in supernatant that is relatively homogeneous within each tank recognizing some concentration gradients may exist vertically within each tank caused by the transfer history and limited mixing actions within the DST System. Lateral stratification is not expected.

3.7.3 Assessing Candidate Feed Tank Sampling and Analysis Results

Candidate feed tank sampling and analysis, in conjunction with the waste acceptance criteria in Section 3.9, are used to assess whether established limits (limits are defined in the 242 Evaporator DQO, Banning 2009 and Permit, Part III, LERF and 200 Area ETF, unit-specific conditions and Chapter 3.0, Waste Analysis Plan) would be exceeded. Based on the results, three possible options are implemented:

- The waste is acceptable for processing at the 242-A Evaporator without further actions.
- The waste is unacceptable for processing as a single batch, but is acceptable if blended with other waste to be processed or the waste can be pre-treated as necessary to fully satisfy the 242-A Evaporator waste acceptance criteria.
- The waste is unacceptable for processing, and no acceptable pre-treatment or blending options can be identified.

3.8 Sampling Process for Dangerous Wastes Generated From Treatment

Two mixed waste streams are generated as the result of the 242-A Evaporator process: process condensate and concentrated waste slurry. Sampling of the concentrated waste slurry is not necessary under this WAP in order to return the waste back to the DST System.

Sampling of process condensate is required for confirmation that the waste meets the LERF waste acceptance criteria with respect to LERF liner compatibility. Depending on programmatic needs, this sampling can be performed at the 242-A Evaporator during a campaign or at LERF after the campaign is completed.

Before the start of a 242-A Evaporator campaign, the decision whether process condensate sampling will be performed at the 242-A Evaporator or at LERF is documented in the process control plan, which is maintained in the Hanford Facility Operating Record, 242-A Evaporator Unit specific portion. Planning for process condensate sampling at the 242-A Evaporator (i.e., number of samples, when samples are taken, etc.) is completed before starting the campaign. Sampling at LERF is beyond the scope of this WAP.

3.8.1 Determining the Number of Process Condensate Samples

The purpose of sampling the process condensate stream at the 242-A Evaporator is to confirm that the stream is acceptable for treatment at the ETF. Before starting a 242-A Evaporator campaign where sampling will be performed at the 242-A Evaporator instead of LERF, characterization of the process condensate will be developed based on process knowledge. Process knowledge includes previous documented process condensate analysis, estimated concentrations based on documented candidate feed tank sampling and analysis, etc. Sampling of the process condensate stream at the 242-A Evaporator is performed during the campaign to confirm the characterization. Sampling frequency is determined using the following equation:

> Number of process condensate = N + 1 samples required (per campaign). Where N is the number of candidate feed tanks to be processed during the campaign.

For example, a campaign processing waste from only one candidate feed tank would require two samples, while a campaign processing waste from three candidate feed tanks would require four samples. Sampling is spread approximately evenly through the campaign, allowing for operational events such as unexpected shutdowns and planned maintenance outages. This sample frequency represents a confirmation rate of about one sample every 5 to 8 days of processing. This is reasonable based on the relatively homogeneous tank waste feed and the more or less steady state of evaporator operations. Therefore, the process condensate waste stream should also be relatively homogeneous, and multiple samples are not necessary to document or account for waste stream variability. A minimum of two samples is taken to meet LERF waste acceptance criteria.

3.8.2 Assessing Process Condensate Sampling and Analysis Results

The process condensate sample and analysis results are assessed against the LERF waste acceptance criteria.

3.9 242-A Evaporator Waste Acceptance Criteria

Waste acceptance criteria for the 242-A Evaporator have been established from regulatory requirements, operating experience, previous sample analyses, and engineering calculations. Processing criteria are maximum and/or minimum values of a waste analyte that, if exceeded, alert the operator that management of the waste requires further attention. The rationale for selecting a given analyte for inclusion in this WAP, as required by WAC 173-303-300, is indicated in this section for each test and/or analyte.

Additional analyses (such as specific gravity and radionuclide analysis) of the feed tanks, process condensate, and other streams are performed to ensure that the facility is operating within established parameters. This process control sampling and analysis is outside the scope of this plan because it is not used to assess compatibility of the waste with other waste and with the 242-A Evaporator tank systems.

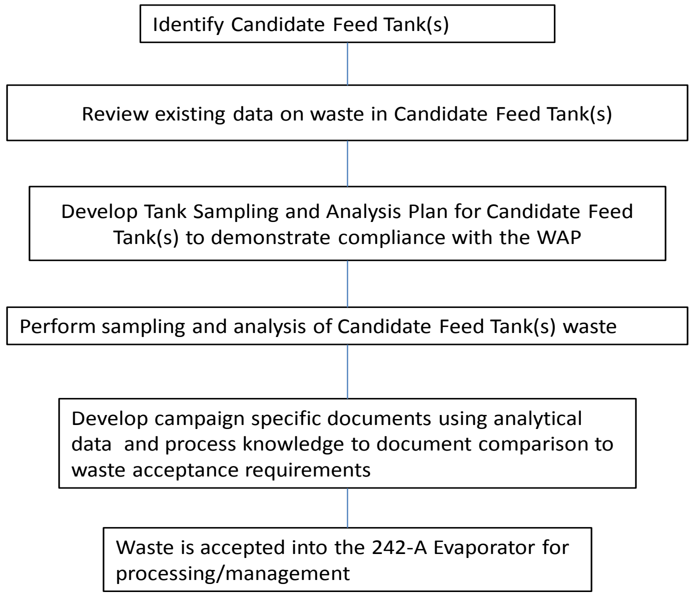

Figure 3.2. 242-A Evaporator Waste Acceptance Process

3.9.1 Candidate Feed Tank Waste Acceptance Criteria

The following sections discuss waste acceptance criteria for candidate feed tanks to be processed in the 242-A Evaporator.

3.9.1.1 Exothermic Reactions

WAC 173-303-395(1) requires waste handling be conducted to prevent an uncontrolled reaction that could damage the tank system structural integrity or threaten human health or the environment. To evaluate the possibility of an uncontrolled reaction at the elevated temperatures in the evaporator vessel, a differential scanning calorimeter (DSC) test is performed on samples of all candidate waste to be processed. DSC measures the amount of heat absorbed or released by a sample as the temperature is increased. Waste exhibiting exotherms below 168 ºC (335 ºF), or with an absolute value of the exotherm-to-endotherm ratio greater than one, will not be processed in the 242-A Evaporator without further technical evaluation.

3.9.1.2 Compatibility

WAC 173-303-640(10) and WAC 173-303-395(1) requires waste handling be conducted to prevent an uncontrolled reaction that could damage the 242-A Evaporator tank system structural integrity or threaten human health or the environment. To verify there will be no adverse affects because of mixing the contents of different candidate feed tanks in the feed tank (241-AW-102) and the 242-A Evaporator vessel (C-A-1), a compatibility evaluation is performed on waste in the candidate feed tanks. As samples from each of the planned waste sources are mixed, observations are made to note any changes in color, temperature, clarity, or other visually determinable characteristic. This would indicate an unexpected chemical reaction that might have an impact on 242-A Evaporator operations. If such visible changes are observed when mixing samples, the waste would not be processed in the 242-A Evaporator without further technical evaluation.

3.9.1.3 Separable Organics

The waste surface layer sample collected from each candidate feed tank or combined feed in 241-AW-102 is visually inspected to determine whether separable organics are present in the waste and requires the waste feed to be rejected for processing or allows waste processing. In addition, testing of the sample is performed by either percent water to determine if the whole sample is organic and cannot be discerned visibly or by total carbon/total inorganic carbon. The action limit of 25% water will indicate if the sample is all organic. Results of the visual inspection and testing are used together to determine if the waste can be accepted at the 242-A Evaporator for processing. If there is a separate visible organic layer in the candidate feed tank samples then the waste transfer to 242-A Evaporator must incorporate engineering controls to eliminate (exclude) the organic layer during the transfer.

3.9.1.4 Organic Constituents

Because process condensate generated at the 242-A Evaporator is transferred only to the LERF, the 242-A Evaporator will not accept waste for treatment whose data review does not allow treatment and storage in LERF. Process condensate could contain trace quantities of chemicals that could cause degradation of the liner material if found to exceed specifications. To predict the concentrations expected in the process condensate, the candidate feed tank waste is sampled and analyzed for organics and the results are then used to predict the concentrations in the campaign specific process condensate. The level of volatile organics in the feed is limited to ensure organic constituents that transfer to the process condensate are compatible with the LERF liner as specified in the LERF waste acceptance criteria.

The 242-A Evaporator performs distillation of waste containing organic concentrations greater than 10 parts per million by weight; therefore, organic air emissions are subject to WAC 173-303-690 (which incorporates 40 CFR 264, Subpart AA, by reference). Organic emissions from TSD units on the Hanford Site subject to 40 CFR 264, Subpart AA are controlled to ensure emissions to do not exceed 1.4 kilograms per hour and 2,800 kilograms per year. To ensure these requirements are met, the levels of volatile organics in the 242-A Evaporator feed must be limited to prevent excessive organic emissions during processing. Engineering calculations were used to determine the feed limits given in Table 3.2. The limits include a modifier "(R-1)/R", which adjusts the limits based on the campaign's planned boiloff rate. R is the ratio of feed flow rate to slurry flow rate. Typically, R is between 1 to 2, making the range of (R-1)/R 0 to 0.5.

In addition, analysis of the individual components in Table 3.2, total carbon (C_T) and total inorganic carbon (IC_T) analysis are performed as a screening tool to account for other organic species that might be present in the waste. The value of C_T minus IC_T represents the total organic concentration in the waste. If the C_T minus IC_T limit is exceeded, additional volatile organic species might be present and a more detailed evaluation will be conducted to determine organic emissions out of the vessel vent. The limit for evaluation is 174.4 milligrams per liter, based on the conservative assumption that all organic species present in the waste are as volatile as acetone. Acetone was chosen because of its relatively high volatility and low percentage of carbon.

Based on the liner manufacturer's compatibility data, waste acceptance criteria from the LERF will impose concentration limits on classes of constituents that could potentially degrade the liner. To ensure that these limits are not exceeded in the process condensate, the concentration limits are applied to the candidate feed tanks as well, with the modifier "(R-1)/R". A C_T minus IC_T analysis, similar to the one described previously, is also applied to the LERF liner limits. The strictest limit for organic species is 2,000 milligrams per liter. Assuming the organic is acetone (with its low percentage of carbon); this converts to a carbon value of 1,240 milligrams per liter.

The calculations in Table 3.2 require use of the ∍sum of the fractions∍ technique. A calculation is performed where the analysis of each constituent is divided by its associated limit to produce a fraction of the limit. If the sum of these fractions is less than 1, the waste meets the requirements in the tables.

3.9.2 Process Condensate Waste Acceptance Criteria

The waste acceptance criteria for process condensate sampling, including treatability, LERF liner compatibility, compatibility with other waste, etc., is given in the Permit, Part III, LERF and 200 Area ETF unit-specific conditions and Chapter 3.0, Waste Analysis Plan.

Table 3.2. Candidate Feed Tank Limits for Vessel Vent Organic Discharge[a].

Feed constituent	Limit (milligrams per liter) b, c
Acetone	174.4 ([R-1]/R)
1-Butanol	452 ([R-1]/R)
2-Butoxyethanol	190.4 ([R-1]/R)
2-Butanone	116 ([R-1]/R)
Tri-butyl phosphate	2.03E+4 ([R-1]/R)
Total carbon and Total inorganic carbon	(CT-ICT) < 174.4 ([R-1]/R) (as acetone)

[a] Limits are based on a maximum continuous operating time equivalent to 6 months per year. If total operating time is expected to exceed 6 months per year, the limits must be re-evaluated.

$$\sum_{n=1}^{i}\left(\frac{Conc_n}{LIMIT_n}\right) \leq 1$$

[b] The limits are applied using the sum of the fractions technique: where i is the number of organic constituents detected in analysis of the waste feed tank. Total carbon and total inorganic carbon analysis are not part of the summation.

[c] R is the ratio of feed flow rate to slurry flow rate (typically R = between 1 and 2).

3.10 Sample Collection and Analysis

This section discusses sampling and analysis, including sampling procedures, sample collection points, sample quality assurance/quality control (QA/QC), and selection of analytes.

3.10.1 Sample Collection

This section describes collection of candidate feed tank waste and process condensate samples. Candidate feed tank waste is sampled and analyzed before the start of each 242-A Evaporator campaign. Process condensate samples are taken at the 242-A Evaporator only if the decision is made before the start of the campaign that sampling will be done at the 242-A Evaporator instead of LERF.

3.10.1.1 Candidate Feed Tank Sample Collection

Candidate feed tank waste samples are obtained by using a grab sampling method (e.g. "bottle on a string method") specified in ASTM E300-86. The number of lateral sampling locations in candidate feed tanks is limited by the availability of tank risers providing access into the tank. Generally, only a few risers in each tank are actually available for sampling because the risers are dedicated to instrumentation or other uses. Sampling within a vertical column is generally limited only by the depth of waste in the tank.

Riser selection is determined using best professional judgment. Previous waste feed tank sampling campaigns used two or more risers, and showed that negligible lateral variability exists in the DST System waste supernatants; therefore, only one riser will be used. Sample depths are determined depending on whether layering is suspected to exist and applying the requirements given in Table 3.3.

3.10.1.2 Candidate Feed Tank Sampling Quality Assurance and Quality Control

For each candidate feed tank waste sample, a sample solution is drawn from the sample riser using one or more sample bottles. Sample bottles are precleaned, amber-colored glass bottles sealed with Teflon* caps or septum caps. The exceptions to the sample bottle requirements are: a clear bottle is used for the surface sample to determine the existence of separable organics and the bottle for VOA analysis must be sealed with a septum cap.

For candidate feed tank sampling quality control, one field blank, consisting of one or more sample bottles, is taken during the sample event. Field blanks are inserted at least 1-foot into the head space through the sample riser used during the sample event. One trip blank, also consisting of one or more sample bottles, is taken during each sample event. Trip blanks are analyzed as independent samples for VOA. Field and trip blanks use the same types of sample bottles as the actual samples and are filled with reagent-grade water before shipment to the field.

Preservatives are not used with candidate feed tank samples because of concerns with high radiation exposure that would result from additional handling of sample solutions. It is not practical to refrigerate the bulky, shielded sample pigs and shipping containers. Biological activity, generally the largest problem in environmental samples, is unlikely in candidate feed tank samples because of the high salt content, pH, and radioactivity of the sample.

The chain of custody is documented on a data sheet that includes a unique sample number, date and time sample was taken, custody seal number, and signature of the sampler. When possession of the sample is transferred to other persons, such as the shipper or laboratory, the signature of the relinquisher and receiver are recorded, along with date and time of the transfer. The receiver at the laboratory also documents on the data sheet that the sample seal number is correct and the seal is intact. The chain-of-custody data sheets are included in the operating record.

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*Teflon is a trademark of E.I. DuPont de Nemours & Company

3.10.1.3 Deviations from Specified Sampling Practices

The WAP requires ASTM E 300 'bottle on a string procedure' for sampling (ASTM E300-86). Due to high radiation fields, some deviations to the standard have been necessary to implement safely the sampling practices in the field. These deviations are documented below.

- Requirement: The sampling apparatus be filled and allowed to drain before drawing the sample.

  Deviation: Sampling personnel lowers the sampling apparatus to the specified level and collects the sample. To pour the contents out and resample would encourage the spread of radiological contamination and additional whole body and extremity radiation exposure.

- 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: Sampling personnel uses clear or amber glass with necks shaped to receive rubber stoppers. Glass stoppers were used at one time but resulted in broken sample bottles during the removal of the glass stoppers from the glass bottles.

- Requirement: Stopper and label bottles immediately after taking the samples and deliver them to the laboratory.

  Deviation: Sampling personnel screws on the bottle cap after the sample has been collected. Because of the alkalinity of the tank waste sample labels will not stay on bottles after samples are collected. Therefore, sample bottles are etched with the sample 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: Select wiping cloths so that lint is not introduced, contaminating the samples.

  Deviation: Sampling personnel uses damp cotton towels to wipe down sample bottles after the sample bottles have been capped. The intent is to remove any waste that may have been deposited on the bottle during the sampling event to minimize contamination and personnel exposure.

- 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: Sampling personnel uses screw caps and 4-mil plastic bags. The cap is Teflon-lined which is inert to the sample. The sample bottle is placed inside a plastic bag, which is placed inside a steel pig (or sample pig). The steel pig is placed inside a shipping pig. The screw cap is not secured with adhesive tape. Securing the sample bottle caps with tape would present the laboratory with difficulty of removing the caps remotely (in the hot cell). If the sample leaks from the sample bottle, it is trapped in the plastic bag. The custody seal is placed on the shipping pig per procedure.

- Requirement: All sampling apparatus and closures shall be clean, dry, free of contaminants, and constructed of materials that are inert to the product to be sampled.

  Deviation: Prior to sampling, sampling equipment such as the sample holder shall be cleaned using a procedure that is consistent with SW-846, *Test Methods for the Evaluation of Solid Waste, Physical/Chemical Methods*, sampling equipment cleaning protocol. The bottles with screw caps are washed and certified and are not opened until at the time of the sampling event. The bottles are opened when the previous sample is completed so that only one bottle is opened at the time of sampling to insert the rubber stopper from the sample holder. The stopper and bottles are constructed from materials that are inert to the product to be sampled.

3.10.1.4 Process Condensate Sample Collection

Process condensate samples, when performed at 242-A Evaporator instead of LERF, are taken from the process condensate transfer line in the condenser room of the 242-A Building. Grab sampling is performed during the campaign at the SAMP-RC3-2 sampler or other sample port by opening a valve and allowing a small volume of process condensate to flush valve and line/piping. The required volume of sample is collected into labeled bottles and chain of custody is maintained. Samples of process condensate are collected in a manner to produce a representative sample. Testing methods are used consistent with SW-846 procedures as listed in Table 3.4.

3.10.1.5 Process Condensate Sampling Quality Assurance and Quality Control

For information on process condensate sample collection, including the number and types of sample bottles, sampling QA/QC, etc., refer to the Permit, Part III, LERF and 200 Area ETF unit-specific conditions and Chapter 3.0, Waste Analysis Plan.

3.10.2 Analyte Selection and Rationale

The DQO analysis for the 242-A Evaporator examined the data needs for sampling the candidate feed tanks and determined that the analyses in Table 3.4 should be conducted to satisfy WAC 173-303-300 requirements. Table 3.4 also contains the rationale for these parameters being selected. Section 3.7 provides additional detail on the rationale.

For information on process condensate sample analyte selection and rationale, refer to the Permit, Part III, LERF and 200 Area ETF unit-specific conditions and Chapter 3.0, Waste Analysis Plan.

Table 3.3. Candidate Feed Tank Sample Point Selection.

Number of Samples	Location of Sample Points
Four samples, no layering suspected	One surface sample to address the potential for a separable organic layer and three subsurface samples: one sample each obtained from the upper third (near the half way point), one sample in the middle third and one sample in the lower third (near the lower limit) of the supernatant layer.
Four samples, layering suspected	One sample taken from the waste surface to address the potential for a separable organic layer. Three samples targeting the expected midpoint of the suspected layers. If more than three layers are suspected, The larger layers have sampling priority.

Table 3.4. Analytes for Candidate Feed Tanks

Parameter	Test technique	Analyte (CAS#)	Rationale
Exotherm	Differential scanning calorimeter	Temperature and energy	Verify the waste will not undergo an exothermic reaction (Section 3.9.1.1).
Compatibility test	Mixing and compatibility study	Visual physical changes	Verify the waste is chemically compatible (Section 3.9.1.2).
Separable Organics	Visual Inspection	Visual Inspection	Process control information needed to evaluate campaign parameters and status.(Section 3.9.1.3)
	TGA OR Carbon coulometric detector	Percent Water OR Total carbon, Total Inorganic carbon	Verify surface sample is not a single layer of homogeneous liquid (Section 3.9.1.3)
Organic compounds	Gas chromatograph/ mass spectrometer	Acetone (67-64-1), 1-Butanol (71-36-3), 2-Butoxyethanol (111-76-2), 2-Butanone (78-93-3), Tri-butyl phosphate (126-73-8)	Used in calculations to verify that vessel vent emissions will not exceed regulatory limits and to prevent compatibility problems with the LERF liner (Section 3.9.1.4).
	Carbon coulometric detector	Total carbon, Total inorganic carbon	Used in calculations to verify that vessel vent emissions will not exceed regulatory limits and to prevent compatibility problems with the LERF liner (Section 3.9.1.4).
Ammonia	Ion selective electrode or Ion chromatography	Ammonia (7664-41-7)	To prevent compatibility problems with the LERF liner (Section 3.9.1.4).
CAS#=Chemical Abstract Service Number LERF=Liquid Effluent Retention Facility TGA = Thermogravimetric analysis			

3.11 Analytical Methods and Quality Assurance and Quality Control

This section provides information on the analytical methods and QA/QC for candidate feed tank samples, including discussions concerning laboratory selection and analytical methods. For information on process condensate analytical methods and QA/QC, refer to the Permit, Part III, LERF and 200 Area ETF unit-specific conditions and Chapter 3.0, Waste Analysis Plan.

3.11.1 Laboratory Selection

Because of the nature of the samples, it is anticipated that candidate feed tank waste sample testing will be conducted at the 222-S Laboratory Complex. Other laboratories at the Hanford Facility could be used provided they are equipped to handle such samples. Laboratory selection depends on availability, analytical needs, and the ability of the laboratory to meet Permit and quality assurance requirements.

3.11.2 Analytical Methods

The analytical methods that must be followed for testing candidate feed tanks are included in Table 3.5. Performance-based specifications rather than procedure-based specifications are used for determining the appropriate analytical methods. This allows for necessary adjustments to the methods for Hanford Facility-specific issues; related to high radioactivity of the sample matrix, while ensuring acceptable data quality. Because of the high radioactivity, the analytical method will in some cases deviate from those in national standards such as *Test Methods For Evaluating Solid Waste*, SW-846 (EPA 1986) and *Standard Methods for the Examination of Water and Waste Water* (AWWA 2005).

3.11.3 Laboratory Quality Assurance and Quality Control

Candidate feed tank waste testing and sampling methods conducted as part of this plan must meet the data quality requirements contained in Table 3.6 to be considered acceptable for decision-making purposes. Quality control check samples (i.e., calibration samples and/or laboratory control samples) generally are performed once per sample event (e.g., once for all samples from one candidate feed tank). Matrix spike and duplicate analysis are performed once per sample event for all methods except differential scanning calorimetry (DSC). A duplicate analysis is performed for DSC analysis to determine method precision. Accuracy for DSC is evaluated by using the laboratory control standard.

The QA/QC program for sampling and analysis related to this unit must, at a minimum, comply with the applicable regulatory requirements. All analytical data will be defensible and will be traceable to specific, related quality control samples and calibrations.

Table 3.5. Analytical Methods for Candidate Feed Tank Stream Analytes.

Category	Analyte	Performance-based analytical methods	Method
Organics	Acetone 1-Butanol 2-Butanone	Purge and trap and GC/MS (VOA)	SW-846 Method 8260
	2-Butoxyethanol Tri-butyl Phosphate	Solvent extraction and GC/MS (semi-VOA)	SW-846 Method 3520B and 8270A
Inorganic	Ammonia	Ion selective electrode and Micro-distillation Ion Chromatography	AWWA Method 4500-NH3 and EPA method 300.7
Other	Exotherm	Differential scanning calorimeter	A sample is placed in the DSC unit and heated to 500° C (932° F). The differential heat flow between the sample and a reference pan is monitored by thermocouples.
	Mixing and compatibility study	Lab specific	Representative samples of each candidate feed tank are mixed and visually checked for gas evolution, heat generation, precipitation, dissolution of solids, color change, clarity, and any other observable characteristics.
	Separable Organics	TGA OR Carbon coulometric detector	A small subsample (typically about 20 mg) is heated to approximately 500° C (932° F). The percent weight loss in the boiling range of water is reported as sample percent water. OR Coulometry: ASTM 5310
	Total carbon	Combustion with IC_T/C_T coulometric detection OR Persulfate oxidation with IC_T/TOC coulometric detection	Combustion and persulfate treatment: AWWA Method 5310 Coulometry: ASTM 5310
	Total Inorganic Carbon	Acidification with IC_T/TOC coulometric detection	Acidification: AWWA Method 5310. Coulometry: ASTM 5310

ASTM=American Society of Testing and Materials
AWWA=American Water Works Association
GC/MS=Gas Chromatograph/Mass Spectrometer
IC_T= Total Inorganic Carbon
TGA= Thermogravimetric analysis
TOC=Total Organic Carbon
VOA= Volatile Organic Analysis

Table 3.6. Quality Assurance Requirements for Candidate Feed Tank Stream Analytes

Category	Analyte	Estimated quantitation limit (matrix specific)	Precision (RPD between duplicates), %	Accuracy (recovery of matrix spike), %	Action level [1]
Organics	Acetone	28 mg/L	<25	40-110	> 87 mg/L[2]
	1-Butanol	20 mg/L	<25	30-110	> 226 mg/L[2]
	2-Butoxyethanol	30 mg/L	<25	30-110	> 95.2 mg/L[2]
	2-Butanone (methyl ethyl ketone)	18 mg/L	<25	40-110	> 58 mg/L[2]
	Tri-butyl phosphate	50 mg/L	<25	40-125	> 1.015E+4 mg/L[2]
Inorganic	Ammonia	400 ug/ml	<20	75-125	> 50,000 mg/L
Other	Exotherm	None	<20[3]	Not applicable [3]	< 168 EC or absolute value of ratio of exotherm to endotherm > 1
	Mixing and compatibility study	Not applicable	Not Applicable	Not Applicable	Visual: unusual changes in color, temperature, clarity, etc.
	Total carbon	25 ug/mL	<20	75-125	C_T-IC_T > 87 mg/L
	Total inorganic carbon	25 ug/mL	<20	75-125	C_T-IC_T > 87 mg/L

1=In deriving the action levels, the ratio of feed flow rate to slurry flow rate (R) is assumed to be 2.
2=For organic species limits, sum of the fractions rule apply (refer Table 3.2). Total carbon and total inorganic carbon are not included in the summation of organics.
3=Precision for this method is evaluated by the deviation between sample (unspiked) and sample replicate. Accuracy for DSC is evaluated by using the laboratory control standard.
RPD - relative percent difference; C_T - total carbon; IC_T - total inorganic carbon
mg/L - milligram per liter; ug/L - microgram per liter

3.12 References

ASTM, 1986, *Standard Practice for Sampling Industrial Chemicals*, ASTM E300-86, American Society for Testing and Materials, West Conshohocken, Pennsylvania, updated periodically.

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AWWA, 2005, *Standard Methods for the Examination of Water and Wastewater*, 17th edition, American Public Health Association/America Water Works Association, Washington, D.C., updated periodically.

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EPA, 1986, *Test Methods for Evaluating Solid Waste Physical/Chemical Methods*, SW-846, U.S. Environmental Protection Agency, Washington, D.C., updated periodically.

EPA, 1994a, *Waste Analysis at Facilities that Generate, Treat, Store, and Dispose of Hazardous Wastes, A Guidance Manual*, PB94-963603, OSWER 9938.4-03, U.S. Environmental Protection Agency, Washington D.C.

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