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1 **6.0 WASTE ANALYSIS PLAN**

2 **6.1 GENERAL**

3 The Waste Analysis Plan (WAP) provides the basis for measuring the adequacy of waste
4 treatment and assists in optimizing the waste treatment operation based on treated waste analysis
5 results. It also provides information on secondary waste streams to determine the required type
6 and level of treatment or the appropriate disposal path.

7 The WAP objective is to develop a sampling approach for the final vitrified waste form to ensure
8 compliance with the waste acceptance criteria of the IDF or another permitted disposal facility
9 and the land disposal restrictions listed in WAC 173-303-140. As depicted in Figure 6-1, the
10 WAP identifies assumptions, sample points, sampling methods and frequencies, and analytical
11 objectives.

12 **6.2 WASTE FEED CHARACTERISTICS AND SAMPLING**

13 **6.2.1 Dangerous Waste Designations**

14 Tank 241-S-109 has the dangerous waste designations listed in Table 6-1, per the SST Part A
15 Form 3 (DOE/RL-88-21).

16 Process knowledge, process history, pertinent literature on waste chemistry and tank history, and
17 analysis on the waste retrieved during Phase 1 and Phase 2 will be used to address the Dangerous
18 Waste Codes D001 (Ignitability), D002 (Corrosivity), and D003 (Reactivity) before transfer to
19 the DBVS to ensure characteristics associated with these waste codes do not exist in the waste
20 feed. Sections 6.2.4 and 6.2.5 discusses sampling frequency in greater detail.

21 **6.2.2 Waste Physical Properties**

22 The DBVS has been designed to receive waste that has the physical properties listed in Table 6-2
23 (RPP-17403). The waste will not contain a visible separate organic phase.

Table 6-1. Dangerous Waste Designation and Sampling/Analysis Strategy (2 pages)

Waste Code	Chemical/Characteristic (40 CFR 268.40)	Strategy			
		Phase 1		Phase 2	
		Waste Feed	Vitrified Waste	Waste Feed	Vitrified Waste
D001	Ignitable Characteristic Waste	√	1	2	2
D002	Corrosive Characteristic Waste	√	1	2	2
D003	Reactive Characteristic Waste	√	1	2	2
D004	Arsenic	√	√	2	3
D005	Barium	√	√	2	3
D006	Cadmium	√	√	2	3
D007	Chromium (total)	√	√	2	3
D008	Lead	√	√	2	3
D009	Mercury	√	√	2	3
D010	Selenium	√	√	2	3
D011	Silver	√	√	2	3
D018	Benzene	√	√	2	3
D019	Carbon Tetrachloride	√	√	2	3
D022	Chloroform	√	√	2	3
D028	1,2-Dichloroethane	√	√	2	3
D029	1,1-Dichloroethylene	√	√	2	3
D030	2,4-Dinitrotoluene	√	√	2	3
D033	Hexachlorobutadiene	√	√	2	3
D034	Hexachloroethane	√	√	2	3
D035	Methyl ethyl ketone	√	√	2	3
D036	Nitrobenzene	√	√	2	3
D038	Pyridine	√	√	2	3
D039	Tetrachloroethylene	√	√	2	3
D040	Trichloroethylene	√	√	2	3
D041	2,4,5-Trichlorophenol	√	√	2	3
D043	Vinyl chloride	√	√	2	3
F001 F002 F003 F004 F005	Acetone Benzene n-Butyl alcohol Carbon disulfide Carbon Tetrachloride Chlorobenzene Cresol – mixed isomers Cyclohexanone o-Dichlorobenzene Ethyl Acetate Ethyl Benzene Ethyl ether Isobutyl alcohol Methanol Methylene chloride Methyl ethyl ketone Methyl isobutyl ketone Nitrobenzene	√	√	2	3

Table 6-1. Dangerous Waste Designation and Sampling/Analysis Strategy (2 pages)

		Strategy			
	Pyridine Tetrachloroethylene Toluene 1,1,1-Trichloroethane 1,1,2-Trichloroethane 1,1,2-Trichloro-1,2,2-trifluoroethane Trichloroethylene Trichloromonofluoromethane Xylenes – mixed isomers				
WP01	Persistent Dangerous Waste	4	4	4	4
WP02	Extremely Persistent Dangerous Waste	4	4	4	4
WT01	Toxic Dangerous Waste	5	5	5	5
WT02	Extremely Toxic Dangerous Waste	5	5	5	5

¹ Analyze if exists in waste feed

² Analyze first waste feed tank

³ Analyze first ten containers, then randomly

⁴ Book designate per WAC 173-303-100(6)

⁵ Book designate per WAC 173-303-100(5)

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Table 6-2. Waste Feed Physical Properties

Property	Value
Density	1.2 – 1.3 g/ml (10.0 – 10.8 lb/gal)
Viscosity	10 cP Maximum at 25 °C (77 °F)
Percent Solids	<3%

3
4

6.2.3 Waste Feed Chemical and Radiochemical Properties

6.2.3.1 Saltcake Key Chemical and Radiological Contaminants.

6 The average concentrations of major constituents important for glass performance and key
 7 contaminants in the Tank 241-S-109 saltcake waste are shown in Tables 6-3 and 6-4. The major
 8 constituents listed in Table 6-3 are important to ensure proper glass processing and good glass
 9 performance. The key contaminants indicated in Table 6-3, column 3, are important to ensure
 10 compliance with LDRs listed in 40 CFR 268 and to determine the compliance with performance
 11 assessment objectives. Concentrations have been normalized to 5 M sodium, the sodium
 12 concentration in the expected feed to the bulk vitrification process. Note that not all of these
 13 constituents will be present in the retrieval stream, since some of the solids (in particular the
 14 metals and transuranics) have very low solubility and will mostly be left in the tank or removed
 15 via a solids/liquid hydroclone separator.

1

Table 6-3. Chemical Constituents/LDR Contaminants in Average Tank 241-S-109 Saltcake Waste

Constituent/ Contaminant	Average Saltcake Normalized to 5 M Na ¹ (µg/ml)	Key Contaminants Land Disposal Restriction Level)
Aluminum	1300	
Calcium	49	
Chloride	270	
Total Chromium	770	√ (0.75 mg/L TCLP)
Fluoride	110	
Iron	270	
Potassium	170	
Manganese	8	
Nickel	6	√ ²
Nitrite ³	3000	√ ²
Nitrate ³	290000	√ ²
Lead	29	√ (0.75 mg/L TCLP)
Phosphate	5500	
Silica	160	
Sulfate	3700	
Total Inorganic Carbon as CO ₃	11000	
Total Organic Carbon	320	
Total Uranium	28	√ ²

¹The composition is based on the saltcake portion of the Tank 241-S-109 Best Basis Inventory (BBI 2001), normalized to 5 M Na (115000 µg/ml)

²Not listed as an LDR contaminant

³ Destroyed or removed in the vitrification process

TCLP = Toxic Characteristic Leaching Procedure

Table 6-4. Key Radionuclide Contaminants in Average Tank 241-S-109 Saltcake Waste

Contaminant	Average Saltcake Normalized to 5 M Na ¹ (μCi/ml)
TRU (total)	3.7 x 10 ⁻³
Cesium-137	6.2 x 10 ⁰
Strontium-90	2.3 x 10 ⁰
Technetium-99	4.7 x 10 ⁻²
Cobalt-60	5.5 x 10 ⁻³
Europium-154	2.5 x 10 ⁻²
Iodine-129	9.1 x 10 ⁻⁵

¹The composition is based on the saltcake portion of the Tank 241-S-109 Best Basis Inventory (BBI, 2001), normalized to 5 M Na (115000 μg/ml)

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6.2.3.2 Expected Concentrations of Retrieved Waste Streams

The composition of the waste retrieved during different phases of RD&D operations depends on the relative amounts of interstitial liquid and the dissolution brine retrieved. The interstitial liquid is the liquid phase that currently exists in the tank and contains the highly soluble components including the bulk of the Cs-137. The composition of this liquid is constant and established by analysis of saltwell grab samples. The dissolution brine is the liquid phase formed as the solid saltcake is dissolved through the addition of water and is composed of the relatively soluble components in the salt phase. The composition of the dissolution brine is established through modeling and changes over the course of the retrieval process. The exact ratio of these liquids retrieved in the different phases is not known but an approximate composition can be established via a general understanding of the effects of dissolution on the waste.

Retrieval operations that attempt to remove cesium from Tank 241-S-109 and route it to the DST system will focus on removing the interstitial liquid. These operations will maximize removal of the liquor and minimize the addition of water that might create dissolution brine that will dilute the liquor. The interstitial liquid concentrations for any contaminant that might end up in the glass waste form (e.g., all contaminants other than NO₂ and NO₃ which are destroyed or removed during vitrification) are bounded by the concentrations in the interstitial liquid.

The Phase 1 and Phase 2 retrieval operations will obtain an acceptable feed for the DBVS. These retrieval phases will maximize the quantity of dissolution brine retrieved while minimizing the incorporation of the interstitial liquid. This strategy will minimize the concentration of all key contaminants other than NO₂ and NO₃ that are collected as the salt dissolves but are destroyed or removed during vitrification. In all cases, the contaminant concentrations of all key contaminants listed in Tables 6-3 and 6-4 (other than NO₂ and NO₃) will be lower than those in the interstitial liquid.

1 **6.2.3.3 Compositions of Interstitial Liquid and Dissolution Brine.** Tables 6-5 and 6-6 show
2 the concentrations of key constituents/contaminants that are expected for the interstitial liquid
3 and the dissolution brine at three different points in the retrieval process. The brine and liquor
4 have been normalized to 5 M sodium. The interstitial liquid composition is based on grab
5 samples taken in the saltwell.

6 The dissolution brine compositions are based on the Environmental Simulation Program (ESP), a
7 chemical thermodynamic model, which used the Tank 241-S-109 Best Basis Inventory
8 (BBI 2001) as input. The contaminants F, NO₃, PO₄, SO₄, CO₃, and TOC (in the form of
9 oxalate) are present with sodium primarily in the soluble solids fraction. Sodium nitrate
10 (NaNO₃) is the dominant solid and produces most of the solute in the dissolution brine. Because
11 sodium phosphate, sulfate, and carbonate are present in small quantity, they are entirely
12 dissolved early in the dissolution process, subsequently washing out of the waste. Sodium
13 fluoride and oxalate salts are also present in small quantity, but their dissolution is effectively
14 suppressed by the other salts until middle or late dissolution, so their concentrations rise later in
15 the process. Contaminants that do not dissolve in water are excluded from the dissolution brine,
16 as are contaminants that are present entirely in dissolved form in the original waste. The key
17 contaminants excluded because the solid forms have very low solubility in water are Al, Ca,
18 Cr(III), Fe, Mn, Ni, Pb, Si, U, TRU, Sr-90, Co-60, and Eu-154. The key contaminants excluded
19 because they are present completely in dissolved form in the original waste are Cl, Cr(VI), K,
20 NO₂, Cs-137, Tc-99, and I-129.

21 **6.2.3.4 Waste Acceptance Criteria**

22 Other waste feed characteristics have a role in determining how the waste feed will be handled in
23 the DBVS, but do not represent limiting specifications that would prevent the tank waste from
24 being processed to generate the data necessary to determine if bulk vitrification is a viable
25 production process. As an RD&D facility, it is important to maintain the flexibility to accept and
26 test a wide range of feed compositions and to adequately challenge the process. Waste feed
27 variations can be accommodated through blending of the waste with chemical simulant,
28 adjusting waste loading, or through processing modifications. The limiting specifications for
29 waste feed from Tank 241-S-109 to the DBVS are:

- 30 1. Cesium concentration must be less than 0.05 Ci/L (on a 7 M sodium basis),
- 31 2. The average solids concentration must be less than 3%,
- 32 3. TRU concentration must be less than 100 nCi/g.

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Table 6-5. Key Chemical Constituents/Contaminants in Interstitial Liquid and Dissolution Brine Fractions of Tank 241-S-109 Retrieval Stream

Contaminant	In Interstitial Liquid Normalized to 5 M Na ¹ (µg/ml)	In Dissolution Brine at 5 M Na (µg/ml)		
		During Early Dissolution	During Middle Dissolution	During Late Dissolution
Al	24000	Low Sol	Low Sol	Low Sol
Ca	25	Low Sol	Low Sol	Low Sol
Cl	5000	In Interstitial Liquid	In Interstitial Liquid	In Interstitial Liquid
total Cr	4700	Cr III Low Sol Cr VI in Interstitial Liquid	Cr III Low Sol Cr VI in Interstitial Liquid	Cr III Low Sol Cr VI in Interstitial Liquid
F	39	75	280	21
Fe	15	Low Sol	Low Sol	Low Sol
K	1200	In Interstitial Liquid	In Interstitial Liquid	In Interstitial Liquid
Mn	3	Low Sol	Low Sol	Low Sol
Ni	4	Low Sol	Low Sol	Low Sol
NO ₂	45000	In Interstitial Liquid	In Interstitial Liquid	In Interstitial Liquid
NO ₃	69000	186000	281000	301000
Pb	21	Low Sol	Low Sol	Low Sol
PO ₄	840	17000	3200	1100
Si	71	Low Sol	Low Sol	Low Sol
SO ₄	900	8000	5400	750
TIC as CO ₃	5100	34000	6200	2100
TOC	580	38	99	120
Total U	1	Low Sol	Low Sol	Low Sol

¹The interstitial liquid composition is based on grab-samples taken in the saltwell. The dissolution brine compositions are based on runs of the ESP code using the Tank 241-S-109 Best Basis Inventory (BBI, 2001) as input

Early dissolution: 1 part water has been added to 4 parts waste

Middle: 1 part water has been added to 1.6 parts waste

Late: 1 part water has been added to 1 part waste

Low Sol: Low solubility in water

In Interstitial Liquid: As modeled in ESP, not present in dissolution brine because 100% is in the interstitial liquid

TIC: total inorganic carbon

TOC: total organic carbon

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Table 6-6. Key Radionuclide Contaminants in Interstitial Liquid and Dissolution Brine Fractions of Tank 241-S-109 Retrieval Stream

Contaminant	In Interstitial Liquid Normalized to 5 M Na ¹ (μCi/ml)	In dissolution brine at 5 M Na (μCi/ml)		
		During Early Dissolution	During Middle Dissolution	During Late Dissolution
TRU (total)	7.6 x 10 ⁻⁴	Low Sol	Low Sol	Low Sol
Cesium-137	1.6 x 10 ²	In Interstitial Liquid	In Interstitial Liquid	In Interstitial Liquid
Strontium-90	1.4 x 10 ⁻¹	Low Sol	Low Sol	Low Sol
Technetium-99	1.6 x 10 ⁻¹	In Interstitial Liquid	In Interstitial Liquid	In Interstitial Liquid
Cobalt-60	2.0 x 10 ⁻³	Low Sol	Low Sol	Low Sol
Europium-154	9.7 x 10 ⁻²	Low Sol	Low Sol	Low Sol
Iodine-129	3.1 x 10 ⁻⁴	In Interstitial Liquid	In Interstitial Liquid	In Interstitial Liquid

¹The interstitial liquid composition is based on grab-samples taken in the saltwell. The dissolution brine compositions are based on runs of the ESP code using the Tank 241-S-109 Best Basis Inventory (BBI 2001) as input

Early dissolution: 1 part water has been added to 4 parts waste

Middle: 1 part water has been added to 1.6 parts waste

Late: 1 part water has been added to 1 part waste

Low Sol: Low solubility in water

In Interstitial Liquid: As modeled in ESP, not present in dissolution brine because 100% is in the interstitial liquid

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3 6.2.4 Waste Feed Verification

4 In the course of the RD&D test project, waste feed batches will be received from the
 5 Tank 241-S-109 WRS to the waste receipt tanks. These waste feed batches will be sampled for
 6 constituents in the assigned waste codes for SST waste. Sampling will determine if these
 7 constituents are detectable in the waste feed and the vitrified treated waste will not be tested for
 8 the undetected LDR constituents. Processing will not begin until either the results of material
 9 analyses are received and reviewed, or a determination has been made that the existing analyses
 10 are valid. If necessary, the test plan for that campaign will include procedures to prevent the
 11 mixing of materials not suitable for processing. The analytical methods used for measuring
 12 concentrations will follow the analytical methods listed in Table 3.3 of the Waste Treatment
 13 Plant Waste Analysis Plan (24590-WTP-RPT-ENV-01-003) and the analytical methods listed in
 14 Appendix D from the *Regulatory Data Quality Objectives Optimization Report* for the WTP
 15 (24590-WTP-RPT-MGT-04-001). Additional sampling and analyses to support risk and
 16 performance assessment activities may be conducted and will be defined in test plans, as
 17 applicable. Waste feed verification is part of the testing protocol to verify presence of a
 18 bounding waste envelope.

1 The waste material composition as treated in the DBVS will represent the vitrification system
2 waste stream provided by the WTP during full-scale operation. To ensure that the range of waste
3 properties used during testing properly bounds the WTP waste properties, simulants will be
4 added as required.

5 **6.2.5 Sampling Methods and Frequency**

6 Sampling during Phase 1 will be performed at the WRS waste staging tank prior to transfer to the
7 DBVS waste receipt tank. The frequency of analysis of the waste during Phase 2 will be once
8 per full DBVS waste receipt tank, unless a determination has been made that existing waste
9 analyses are valid. Samples will be collected and analyzed consistent with the applicable
10 portions of Section 9.0 in the *Regulatory Data Quality Objectives Optimization Report* (24590-
11 WTP-RPT-MGT-04-001)(Appendix D), which consists of LDR and underlying hazardous
12 constituent analytical methods.

13 **6.2.5.1 Treated Waste Sampling and LDR Compliance.** The final vitrified waste will be
14 sampled to provide data for waste form qualification, risk assessment, performance assessment,
15 and regulatory compliance. The vitrified waste will be tested for waste constituents on the SST
16 Part A, which are LDR restricted for disposal in WAC 173-303-140 and 40 CFR 268.40. The
17 constituents analyzed for are based on documented process knowledge, analysis of the waste
18 feed, and are reasonably expected to be present in the final waste form. A composited vitrified
19 waste core sample will be analyzed for the dangerous waste constituents that were detected in the
20 tank waste feed to determine compliance with LDR requirements. The frequency of sampling
21 the treated waste will be once per vitrified container of waste for an initial 10-sample set, after
22 which random sampling will take place, as agreed to in the final test matrix.

23 Table 6-7 lists some of the physical properties that the treated waste will be analyzed for in order
24 to determine waste form qualifications.

25 **6.3 SECONDARY WASTE STREAMS**

26 A variety of secondary wastes will be generated during DBVS operations. This section covers
27 general requirements for management of expected secondary wastes.

28 **6.3.1 Secondary Liquid Waste**

29 Secondary liquid waste streams will be stored at the Test and Demonstration Facility area in
30 portable tanks, prior to being disposed at the 200 Area ETF. Therefore, waste will be
31 characterized in accordance with the waste characterization requirements specified in Section 3
32 of the *Hanford Site Liquid Waste Acceptance Criteria* (HNF-3172). The sampling frequency
33 will initially be once per tank. The long-term sampling frequency will be determined by the
34 results of initial testing. The secondary liquid waste will be sampled with an appropriate
35 sampler.

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Table 6-7. Physical Properties Sampling and Analysis¹

Property	Requirement	Citation
Vapor Hydration Test	Glass alteration rate shall be less than 50 grams/(m ² -day) when measured using at least a seven day vapor hydration test run at 200 °C	ASTM WK84, <i>Test Method for Measuring Waste Glass Durability by Vapor Hydration Test.</i>
Compressive Strength after subjecting the samples to conditions noted:	Mean compressive strength of the waste form shall be at least 3.45E6 Pa and not less than 75% of the initial compressive strength	ASTM C39/C39M-01, <i>Standard Test Methods for Compressive Strength Specimens</i>
	Thermal Degradation - Thirty thermal cycles between a high of 60° C and a low of -40° C	ASTM B553-79, <i>Test Method for Thermal Cycling of Electroplated Plastics</i>
	Biodegradation - No evidence of culture growth when representative samples are tested	ASTM G21-96, <i>Standard Practice for Determining Resistance of Synthetic Polymeric Materials to Fungi</i> , and ASTM G22-76, <i>Standard Practice for Determining Resistance of Plastics to Bacteria</i>
Compression Testing	Each fully loaded package shall be able to withstand a compression load of 50,000 kg with the seal remaining intact	Integrated Disposal Facility Waste Acceptance Criteria

¹ Not all tests will be performed on all treated waste. Results from simulant tests may be used where applicable.

2 **6.3.2 Secondary Solid Waste**

3 A wide variety of solid and semisolid wastes will be generated during DBVS operation. Waste
 4 streams include, but are not limited to, waste material residues in receipt and holding tanks,
 5 collected air pollution control equipment dusts/sludges, discarded protective equipment, and
 6 discarded samples taken during testing. These materials will be properly designated and
 7 packaged per HNF-EP-0063 and managed at the appropriate TSD unit in accordance with the
 8 unit's waste acceptance criteria.

9 Solid waste streams that are designated as dangerous or mixed waste will be transferred to a
 10 Hanford Site TSD unit in accordance with the current *Hanford Site Solid Waste Acceptance*
 11 *Criteria* (HNF-EP-0063) and the waste acceptance criteria of the receiving TSD unit. The waste
 12 will meet the acceptance criteria as outlined in HNF-EP-0063 as well as the receiving TSD unit
 13 acceptance criteria. Process knowledge will be used to better identify the final disposal method.

14 **6.4 OFFGAS TREATMENT SYSTEM**

15 The main offgas treatment system exhaust will be monitored continuously for radionuclides
 16 contributing greater than 0.1 mrem/year using a record sample collection system. The offgas
 17 treatment system will also be continuously monitored for criteria pollutants (i.e., particulate
 18 matter, CO, NO_x, SO_x).

6.5 QUALITY ASSURANCE AND QUALITY CONTROL

6.5.1 General

This Quality Assurance (QA) and Quality Control (QC) section is prepared to support sampling and analysis to be implemented for DBVS operations. It will be used to support verification and characterization of the waste feed, treated waste form and the characterization of secondary waste streams.

6.5.1.1 The QA/QC program ensures that an activity or project meets a required quality standard. QA is associated with recordkeeping, tracking, audits and assessments, and involves determining the desired level of quality and setting limits in advance. The analytical methods and associated QA/QC for the constituents of concern and for supplemental analytes identified in 24590-WTP-RPT-MGT-04-001, *Regulatory Data Quality Objectives Optimization Report*, will be imposed on waste feed samples. The laboratory(s) selected to do the analyses will have QA plans approved by Ecology prior to waste sample receipt and performing the selected analytical methods.

6.5.1.2 Chain-of-Custody. Chain-of-custody forms are used to document the possession of samples from the time they are collected through completion of laboratory analysis. The following information will be recorded for samples of waste, treatment residuals, and secondary wastes:

- The type of waste collected
- Names and signatures of sampling personnel
- Sample number, date and time of collection, and designation (e.g., grab, core)
- Names and signatures of persons involved in transferring and analyzing samples
- If applicable, the shipping number (air bill number) for samples shipped to off-site laboratories
- Analyses to be performed.

6.5.2 Trip Blanks and Equipment Blanks

The trip blank will be a water sample carried during the sample collection activities to ensure that contamination is not occurring during the different steps of sample collection and transportation to the laboratory. The equipment blank is a sample of analyte-free water used to rinse the sampling equipment. It is used to document the adequate decontamination of sampling equipment. Decontamination will be performed if disposable sampling equipment cannot be used. Analysis for the trip blank and equipment blank will be the same analytical tests performed for the specified procedures.

6.5.3 Duplicate Samples

The duplicate sample is a second aliquot of the collected sample and is used to determine method precision. The relative percent difference of the two samples is calculated by first obtaining the

1 difference of the two samples, dividing the difference by the average of the two samples, and
2 finally multiplying by 100.

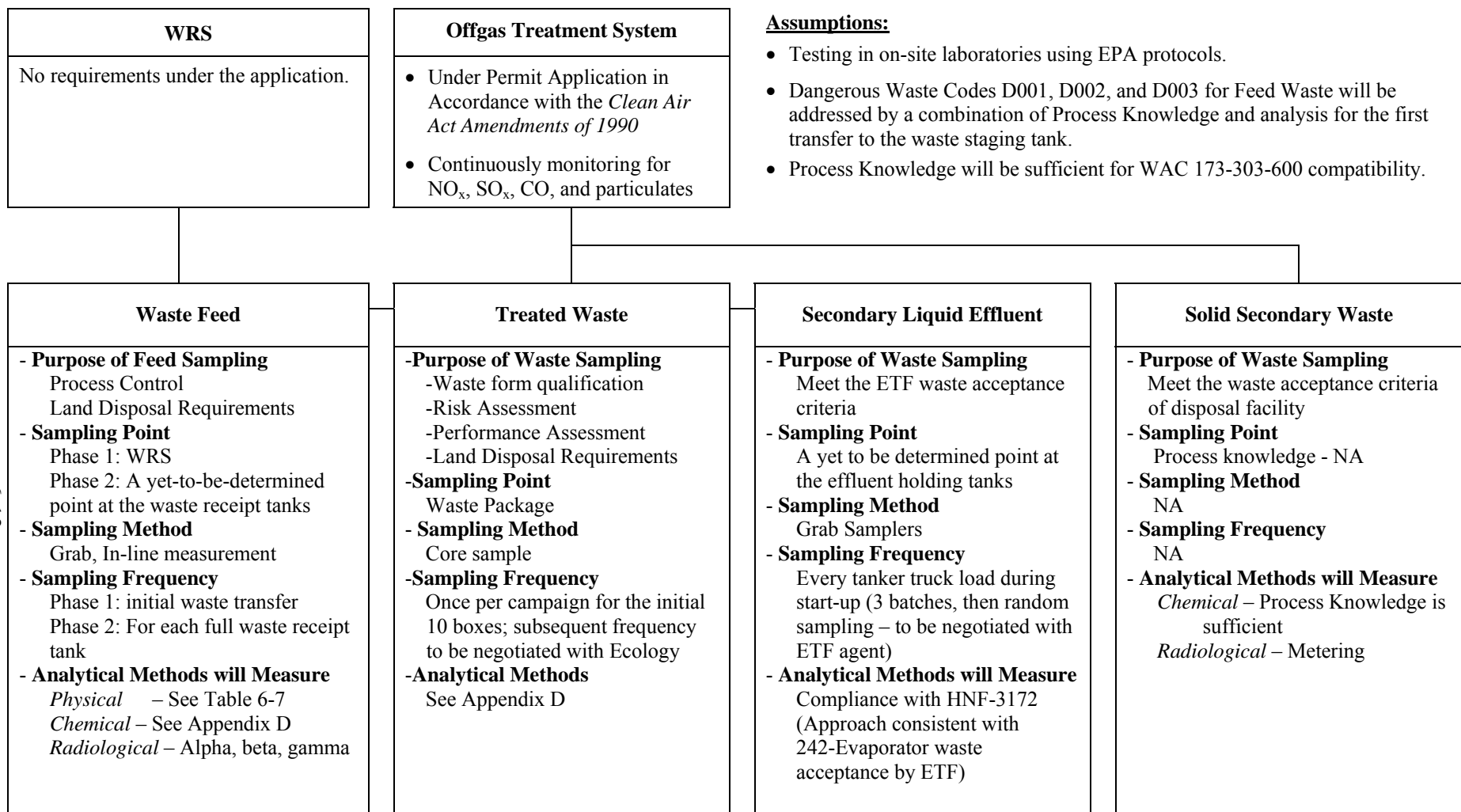
3 **6.5.4 Matrix Spike and Matrix Spike Duplicate Samples**

4 The matrix spike and matrix spike duplicate (MS/MSD) samples are QC samples spiked with
5 known quantities of analytes. MS/MSD samples ensure that the analysis is testing for the
6 specific analytes. Precision of a given sample can be calculated by the relative percent
7 difference between the analytical results for the MS/MSD samples.

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Figure 6-1. Flow Diagram for DBVS Waste Analysis Plan



6-13