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DATA QUALITY OBJECTIVES FOR SELECTING WASTE SAMPLES TO TEST THE FLUID BED STEAM REFORMER PROCESS

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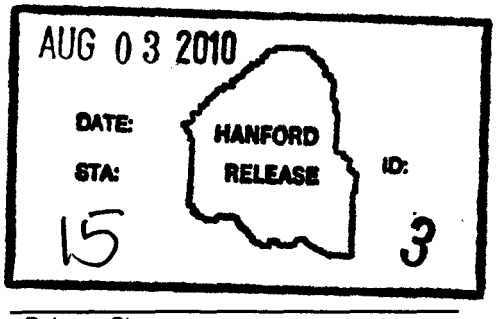
Abstract: This document describes the data quality objectives to select archived samples located at the 222-S Laboratory for Fluid Bed Steam Reformer testing. The type, quantity and quality of the data required to select the samples for Fluid Bed Steam Reformer testing are discussed.



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Abbreviations and Acronyms

DQO	data quality objective
FBSR	fluid bed steam reformer
PSQ	principle study questions
TRU	transuranic

1.0 INTRODUCTION

In order to maximize the efficiency and minimize the time to treat Hanford tank waste in the Waste Treatment and Immobilization Plant, additional treatment processes may be required. One of the potential treatment processes is the fluid bed steam reformer (FBSR). A determination of the adequacy of the FBSR process to treat Hanford tank waste is required. The initial step in determining the adequacy of the FBSR process is to select archived waste samples from the 222-S Laboratory that will be used to test the FBSR process. Analyses of the selected samples will be required to confirm the samples meet the testing criteria.

This document describes the Data Quality Objective (DQO) process undertaken to ensure appropriate samples are selected to support FBSR process testing. The DQO process was implemented in accordance with TFC-ENG-CHEM-C-16, *Data Quality Objectives for Sampling and Analyses* and the U.S. Environmental Protection Agency EPA QA/G4, *Guidance on Systematic Planning Using the Data Quality Objectives Process*. As stated in these documents, the DQO process is iterative. Therefore, changes to this DQO document will be made during the project if data are obtained that change the requirements or if additional requirements or data are needed. As the FBSR process testing proceeds and data to support the testing are obtained, specific constituents for analysis can be added or deleted from the document as required.

In addition to this DQO document, other documents will be prepared to guide the overall testing program including a test plans for the sample preparation and analysis, FBSR testing, and the subsequent analysis of samples.

2.0 PROBLEM STATEMENT

The objective of a problem statement is to clearly define the problem (the reason analytical data are required) so the focus of the project (selecting archived waste samples to test the FBSR waste treatment process) will be unambiguous.

With the objective of the problem statement and the focus of this DQO process in mind the problem statement can be written as follows:

> Select appropriate archived samples from the 222-S Laboratory that meet the requirements for shipping, FBSR testing, and subsequent analyses.

The primary study question developed from the problem statement can be stated as:

> Are appropriate archived samples available at the 222-S Laboratory that meet the requirements for shipping, FBSR testing, and subsequent analyses?

3.0 DECISION STATEMENTS

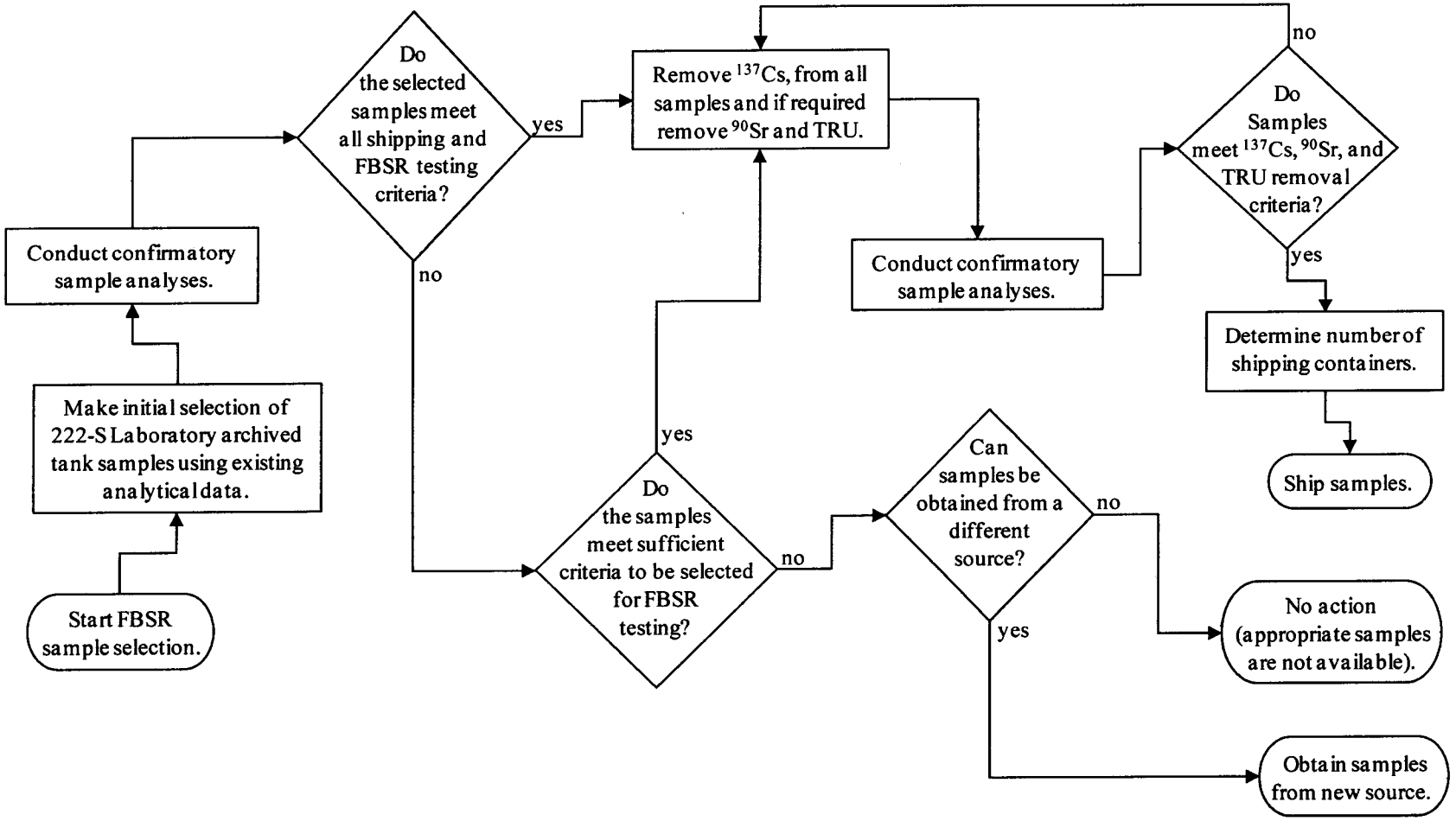
Decision statements are developed by combining principle study questions (PSQ) with alternative actions. The PSQ identifies key unknown conditions or unresolved issues that reveal the solution to the problem. Alternative actions are the possible actions that might be taken once a PSQ has been resolved.

The decision statement is as follows:

> Determine whether appropriate archived samples are available at the 222-S Laboratory that meet FBSR testing requirements and can be shipped or requires a determination of the adequacy of samples that do not meet all of the criteria, requires obtaining samples from an alternative source, or requires no action (appropriate samples are not available).

Figure 3-1 shows the general logic flow chart for selecting Hanford waste samples to test the FBSR process. The flow chart shows the decisions and activities that are covered by this DQO document and are needed to address sample selection for FBSR testing.

Figure 3-1. Sample Selection Logic Flow Chart



4.0 DATA INPUTS

Three separate samples, with different properties, will be shipped for FBSR process testing. Each one of the three samples may be made up of several 222-S Laboratory archived samples from the same tank. The shipped samples will be liquid; however, the samples may be made from dissolved archived solid samples. The general requirements for each of the three samples are shown below.

1. Contains high SO_4^{2-} (sufate), Cl^- (chloride), F^- (fluoride), and PO_4^{3-} (phosphate) relative to Na (sodium),
2. Contains low SO_4^{2-}, Cl^-, F^-, and PO_4^{3-} relative to Na, and
3. Complexant waste (relatively high total organic carbon).

As can be seen in Figure 3-1, the samples to be shipped will be analyzed to confirm the expected concentrations of the required analytes shown in Table 4-1. After the samples have been selected for shipping and their constituent concentrations confirmed, ^{137}Cs (cesium 137) will be removed from the samples. In addition, ^{90}Sr (strontium 90) and transuranic (TRU) constituents will be removed if required by the project. The samples will be analyzed again to confirm removal of ^{137}Cs, ^{90}Sr, and TRU constituents to the action limits shown in Table 4-1. The samples will be shipped after these requirements are confirmed.

Table 4-1. Required Information and Action Limits

Data Inputs	Action Limits[a]	Comments
Na	≥ 100 grams per sample	
SO_4^{2-}	High Sample ≥ 0.03 Low Sample ≤ 0.006	The action limits are ratios of SO_4^{2-} M/Na M.
Cl^-	High Sample ≥ 0.017 Low Sample ≤ 0.006	The action limits are ratios of Cl^- M/Na M.
F^-	High Sample ≥ 0.05 Low Sample ≤ 0.004	The action limits are ratios of F^- M/Na M.
PO_4^{3-}	High Sample ≥ 0.035 Low Sample ≤ 0.005	The action limits are ratios of PO_4^{3-} M/Na M.
^{137}Cs	< 1.5 μCi/g	
^{90}Sr	< 400 μCi per sample	
TRU constituents (^{241}Am, ^{243}Cm, ^{244}Cm, ^{237}Np, ^{238}Pu, ^{239}Pu, ^{240}Pu)	< 100 nCi/g	
^{99}Tc	None	Information only. Knowledge of amount in the samples is needed for testing; however, no limits are required to ship the sample.
TOC	None	Information only. Knowledge of amount in the samples is needed for testing; however, no limits are required to ship the sample.
RCRA metals (Ag, As, Ba, Be, Cd, Cr, Hg, Pb, Ni, Sb, Se, Tl, V, Zn)	None	Information only. Knowledge of amount in the samples is needed for testing; however, no limits are required to ship the sample.
Sample mass	< 1000 kg	Limit for treatability studies.[b]

Notes:

TRU = transuranic
TOC = total organic carbon
RCRA = Resource Conservation and Recovery Act
M = moles

[a]As can be seen in Figure 3-1, a sample may be selected for testing when all of the action limits are not met.

[b]WAC 173-303-071, "Excluded Categories of Waste," *Washington Administrative Code*

A sample meeting all of the action limits for the anion ratios (SO_4^{2-}, Cl^-, F^-, and PO_4^{3-}) shown in Table 4-1 may not be achievable; therefore, a priority of importance for the anions was developed. The order of importance for meeting the action limits is SO_4^{2-}, Cl^-, F^-, and PO_4^{3-}.

4.1 QUALITY CONTROL

Laboratories and/or subcontracted laboratories performing analyses in support of this DQO document shall have approved and implemented quality assurance (QA) plans. These QA plans shall meet DOE/RL-96-68, *Hanford Analytical Services Quality Assurance Requirements Documents* (HASQARD) minimum requirements as the baseline for laboratory quality systems. ATL-MP-1011, *ATL Quality Assurance Project Plan for 222-S Laboratory* specifies the analyses

conducted at the 222-S Laboratory. Analyses performed by WRPS shall be performed by ATS-MP-1032, *222-S Laboratory Quality Assurance Plan.*

If subcontracting any portion of this DQO to a commercial laboratory off the Hanford Site, the Subcontractor's implementing quality assurance program shall comply with the Department of Energy Consolidated Audit Program (DOECAP) *Quality Systems for Analytical Services.*

Each sample in the analytical batch will require duplicate analysis; therefore, each client sample will have a primary and duplicate value for each analyte. Other laboratory quality control will be conducted according to the criteria outlined in Table 4-2.

The preferred methods of analysis are SW-846, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, or other approved standardized methods. The most recent revisions are preferred. Conditions (e.g., quality problems) that do not conform to requirements specified in this DQO or references herein shall be controlled to prevent inadvertent use. These quality problems shall be identified, documented, controlled, and reported to prevent reoccurrence as required by ATL-312, *ATL Analytical Project Process Flow* procedure (Section 4.26) and ATS 310, *222-S Analytical Project Process Flow* procedure (Section 1.25) parts 4.17, 4.18 and 4.19. Off-site laboratories shall initiate their corrective action process as applicable to DOECAP.

A letter report shall be prepared within 30 days after selection of the archived samples for analysis. The letter report will document the results of all the analyses and quality control data.

Table 4-2. Quality Control Parameters.

Analytes	Quality Control Acceptance Criteria				
	Proposed Analytical Methods	LCS % Recovery[a]	Spike % Recovery[b]	Duplicate RPD[c] Liquids	Duplicate RPD[c] Solids
Ag, As, Ba, Be, Cd, Cr, Hg, Pb, Na, Ni, Sb, Se, Tl, V, Zn	ICP/AES	80 - 120	75 - 125	≤20%	≤30%
Hg	CVAA	80 - 120	75 - 125	≤20%	≤30%
Cl^-, F^-, PO_4^{3-}, SO_4^{2-}	IC	80 - 120	75 - 125	≤20%	≤30%
^{90}Sr	Beta Counting	80 - 120	N/A[d]	≤20%	≤30%
^{241}Am, ^{238}Pu, $^{239/240}Pu$	Alpha Counting	80 - 120	N/A[d]	≤20%	≤30%
^{99}Tc, ^{237}Np	ICP/MS	80 - 120	75 - 125	≤20%	≤30%
^{243}Cm, ^{244}Cm	Alpha Counting	N/A[e]	N/A[e]	N/A[e]	N/A[e]
^{137}Cs	GEA	80 - 120	N/A[f]	≤20%	≤30%
TOC	Silver catalyzed persulfate oxidation	80 - 120	75 - 125	≤20%	≤30%

Notes:

N/A = Not Applicable
TOC = total organic carbon

(a) LCS = Laboratory Control Sample. This sample is carried through the entire method. The accuracy of a method is usually expressed as the percent recovery of the LCS. The LCS is a matrix with known concentration of analytes processed with each preparation and analyses batch. It is expressed as percent recovery; i.e., the amount measured, divided by the known concentration, times 100.

(b) For some methods, the sample accuracy is expressed as the percent recovery of a matrix spike sample. It is expressed as percent recovery; i.e., the amount measured, less the amount in the sample, divided by the spike added, times 100. One matrix spike is performed per analytical batch. Samples are batched with similar matrices.

(c) RPD = Relative Percent Difference between the analytical samples. Analytical precision is estimated by analyzing duplicates taken separately through preparation and analysis. RPD for PCBs may be calculated using matrix spike and matrix spike duplicate results. Acceptable analytical precision is usually ≤20% RPD for liquids and ≤30% for solids if the sample result is at least 10 times the instrument detection limit.

RPD = ((absolute difference between primary and duplicate)/mean) x 100

(d) 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.

(e) The measurement is calculated from ^{241}Am analyses and therefore LCS, spike recovery, and RPD are not applicable.

(f) The measurement is a direct reading of the energy and the analysis is not affected by the sample matrix; therefore, a matrix spike is not required.

5.0 STUDY BOUNDARIES

This step in the DQO process defines the spatial and temporal boundaries for the required sampling and analyses needed to make the necessary decisions. The spatial boundaries define the physical area to which the decisions will apply and where the samples should be taken. The temporal boundaries describe the timeframe the data will represent, and when the samples should be taken. In addition, this portion of the DQO addresses any sampling constraints.

5.1 SPATIAL AND TEMPORAL BOUNDARIES

Presently, the spatial boundaries for this DQO include only the archived samples (liquid and solid) of Hanford tank waste located at the 222-S Laboratory. If appropriate samples cannot be located at the 222-S Laboratory and samples will be obtained from another source, this activity will be addressed in a revision of this DQO.

This DQO will be in effect until the FBSR testing is concluded and no additional sample selections are required.

5.2 SAMPLING CONSTRAINTS

The biggest constraint to obtaining the required samples is the availability of appropriate waste (quantity and type) in the 222-S Laboratory. However, as stated in Section 4.0, each one of the samples to be shipped may be made up of several 222-S Laboratory archived samples from the same tank or several tanks.

6.0 DECISION RULES

The DQO process includes development of decision rules, which define the actions to be taken as a result of exceeding an action limit. Decision rules are expressed as "if...then" statements that incorporate, as available, the parameter of interest, the scale of decision making, the action limit, and the actions that would result from resolution of the decision rule.

Commonly, an action limit is a concentration at which point a predetermined action is taken depending on whether the results of the analyses are above or below the specified action limit. To account for uncertainty in the data, analytical results are compared to the action limit at a statistical confidence interval previously agreed upon. In the case of this DQO, the means of the analytical data (primary and duplicate) are considered adequate to make the comparison to the action limits shown in Table 4-1 and no additional statistical calculations are required.

As can be seen in Figure 3-1, there are several decisions made in selecting samples for FBSR testing and these decisions are sequential. The first decision rule addresses the requirements needed to determine if the samples meet the FBSR testing requirements shown in Section 4.0.

1. If the average of the confirmatory analytical data shows the samples meet the FBSR testing requirements (see Table 4-1), then remove the radionuclides as needed (decision rule 3); otherwise, determine if the samples meet sufficient criteria (decision rule 2), when compared to the action limits (see Table 4-1), to be selected for FBSR process testing.

The second decision rule is a subjective determination of the suitability of the sample for FBSR testing when only a portion of the requirements listed in Table 4-1 are met.

2. If it is subjectively determined the analytical data indicate the samples meet sufficient criteria, when compared to the action limits (see Table 4-1), then remove the radionuclides as needed (decision rule 3); otherwise, obtain samples from a different source or discontinue sample selection.

The third decision rule addresses radionuclide removal of the selected samples and can be written as follows.

3. If the average of the confirmatory analytical data for the radionuclide removal meets the requirements (see Table 4-1), then determine the required number of shipping containers and ship samples; otherwise, conduct radionuclide removal again.

7.0 ERROR TOLERANCE

The uncertainty in the DQO process provides an evaluation of the probability of decision error based on an estimation of the mean, variance, and number of samples. The uncertainty evaluation is used to assess the accuracy and precision specified for sample collection and analysis, the level of decision error, and the number of samples required to meet a given decision error rate.

As stated in Section 6.0, the project team determined the means of the analytical data (primary and duplicate) are adequate to make the comparison to the action limits shown in Table 4-1. Therefore, if the mean of the analytical data meets the appropriate action limits or if a subjective determination is made the sample is suitable for testing then the samples can be used and no additional error calculations will be required.

8.0 SAMPLING DESIGN

Sampling for this DQO consists of selecting archived tank waste samples from the 222-S Laboratory. Three samples will be selected and shipped for FBSR testing. The sample selection will be based on previous analytical data and sufficient quantity for FBSR process testing. Each FBSR test sample will be from the same tank. However, separate archived samples from the same tank may be combined to provide a sufficient quantity for the test sample.

As stated in Section 4.0, one of the samples selected will be complexant waste. This sample should be obtained from a tank containing complexant waste (e.g., tank 241-AN-107).

Because of the nature of "sampling" for this DQO, sample optimization is not applicable. Sample collection will be based on the criteria described above.

9.0 REFERENCES

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

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

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