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Title/Desc:

DATA QUALITY OBJECTIVE TO SUPPORT RESOLUTION OF  
THE ORGANIC COMPLEXANT SAFETY ISSUE

## ENGINEERING CHANGE NOTICE

1. ECN 609985

Page 1 of 2

Proj.  
ECN

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## ENGINEERING CHANGE NOTICE

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1. ECN (use no. from pg. 1)

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## 15. Design Verification Required

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SDD/DD	<input type="checkbox"/>	Seismic/Stress Analysis	<input type="checkbox"/>	Tank Calibration Manual	<input type="checkbox"/>
Functional Design Criteria	<input type="checkbox"/>	Stress/Design Report	<input type="checkbox"/>	Health Physics Procedure	<input type="checkbox"/>
Operating Specification	<input type="checkbox"/>	Interface Control Drawing	<input type="checkbox"/>	Spares Multiple Unit Listing	<input type="checkbox"/>
Criticality Specification	<input type="checkbox"/>	Calibration Procedure	<input type="checkbox"/>	Test Procedures/Specification	<input type="checkbox"/>
Conceptual Design Report	<input type="checkbox"/>	Installation Procedure	<input type="checkbox"/>	Component Index	<input type="checkbox"/>
Equipment Spec.	<input type="checkbox"/>	Maintenance Procedure	<input type="checkbox"/>	ASME Coded Item	<input type="checkbox"/>
Const. Spec.	<input type="checkbox"/>	Engineering Procedure	<input type="checkbox"/>	Human Factor Consideration	<input type="checkbox"/>
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OM Manual	<input type="checkbox"/>	Operational Safety Requirement	<input type="checkbox"/>	ICRS Procedure	<input type="checkbox"/>
FSAR/SAR	<input type="checkbox"/>	IEFD Drawing	<input type="checkbox"/>	Process Control Manual/Plan	<input type="checkbox"/>
Safety Equipment List	<input type="checkbox"/>	Cell Arrangement Drawing	<input type="checkbox"/>	Process Flow Chart	<input type="checkbox"/>
Radiation Work Permit	<input type="checkbox"/>	Essential Material Specification	<input type="checkbox"/>	Purchase Requisition	<input type="checkbox"/>
Environmental Impact Statement	<input type="checkbox"/>	Fac. Proc. Samp. Schedule	<input type="checkbox"/>	Tickler File	<input type="checkbox"/>
Environmental Report	<input type="checkbox"/>	Inspection Plan	<input type="checkbox"/>		<input type="checkbox"/>
Environmental Permit	<input type="checkbox"/>	Inventory Adjustment Request	<input type="checkbox"/>		<input type="checkbox"/>

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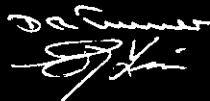
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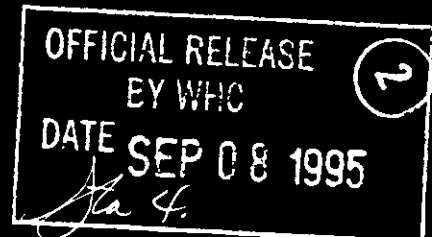
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7. Abstract

This document records the data quality objectives (DQO) process applied to the Organic Complexant Safety Issue at the Hanford Site. Two important outputs of this particular DQO application were the following: (1) decision rules for categorizing organic tanks; and (2) analytical requirements that feed into the tank-specific characterization plans.

The decision rules developed in this DQO allow the organic tanks to be categorized as *safe*, *conditionally safe*, or *unsafe* based on fuel and moisture concentrations. The analytical requirements from this DQO process fall into two groups, primary and secondary. The primary data requirements are always applied, while the secondary requirements are only necessary on those half segment samples that violate the fuel and moisture decision rules or that propagate during adiabatic calorimetry testing.

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# Data Quality Objective to Support Resolution of the Organic Complexant Safety Issue

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DATA QUALITY OBJECTIVE TO SUPPORT RESOLUTION OF THE  
ORGANIC COMPLEXANT SAFETY ISSUE

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EXECUTIVE SUMMARY

This document records the data quality objectives (DQO) process applied to the Organic Complexant Safety Issue at the Hanford Site. Two important outputs of this particular DQO application were the following: (1) decision rules for categorizing organic tanks; and (2) analytical requirements that feed into the tank-specific characterization plans.

The decision rules developed in this DQO allow the organic tanks to be categorized as *safe*, *conditionally safe*, or *unsafe* based on fuel and moisture concentrations. The analytical requirements from this DQO process fall into two groups, primary and secondary. The primary data requirements are always applied, while the secondary requirements are only necessary on those half segment samples that violate the fuel and moisture decision rules or that propagate during adiabatic calorimetry testing.

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# LIST OF TERMS

AC	Adiabatic Calorimetry
D2EHPA	Di-2-Ethylhexyl phosphoric acid
DBBP	Dibutyl-butyl phosphonate
DQO	Data Quality Objective
DSC	differential scanning calorimetry
EDTA	ethylenediaminetetraacetic acid
GC	gas chromatography
HEDTA	hydroxyethylene(ethylenediamine)triacetic acid
HPLC	high-performance liquid chromatography
ICP	inductively coupled plasma
MS	mass spectrometry
PUREX	Plutonium-Uranium Extraction
SAP	Sampling Analysis Plan
TBP	tributyl phosphate
TCP	Tank Characterization Plan
TGA	thermogravimetric analysis
TOC	total organic carbon



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**DATA QUALITY OBJECTIVE TO SUPPORT RESOLUTION OF THE  
ORGANIC COMPLEXANT SAFETY ISSUE**

**1.0 INTRODUCTION**

The primary purpose of this document is to assist in determining the interim safe storage status of organic complexant waste in Hanford Site tanks, and to provide information for resolving the Organic Complexant Safety Issue. Specifically, this DQO process defines the type, quantity, and quality of data required to categorize the organic complexant waste tanks (as *safe*, *conditionally safe*, or *unsafe*) and to resolve the safety issue.

All available sources of characterization information are used including original process flowsheets, waste transfer histories, waste laydown models, simulant experiments, organic complexant degradation (aging) data, and sampling results. The scope of this DQO is limited to organic complexant waste; however, this DQO process does provide linkage with safety screening (Dukelow et al. 1995) and other safety issues. This is a living document, and the assumptions contained within will be refined as more data from sampling and characterization become available.

## 2.0 STATEMENT OF THE PROBLEM

During the defense mission at the Hanford Site, organic complexants (see Table 2-1) were used during fuel reprocessing, metal recovery operations, and waste management operations. Nitrate salts have also been precipitated in the tanks (a source of oxidizer) and an intimate mixture of organic complexant and nitrite/nitrate may exist in some Hanford Site tanks. Organic complexants, in sufficiently high concentrations and mixed with oxidizing material such as sodium nitrate/nitrite, can be made to react exothermically by heating to high temperatures (Fauske 1995). Therefore, it is desired to know if there exists a potential for exothermic organic complexant reactions in the waste that could produce a radioactive release.

Table 2-1. Organic Complexants used at Hanford

Process or operation	Organic chemical	Amounts purchased or used (times 1000) <sup>1</sup>
PUREX/B Plant	NPH/TBP	140 kg (308 lb) <sup>2</sup>
B Plant	TBP-NPH-D2EHPA	0.06 cubic meters (12.7 gal)
Z Plant	TBP-DBBP bottoms that contained some carbon tetrachloride	1.8 cubic meters (400 gal)
B Plant (strontium recovery)	Glycolic acid	694 kg (1,530 lb)
B Plant (strontium recovery)	Citric acid	633 kg (1,396 lb)
B Plant (strontium recovery)	HEDTA	745 kg (1,642 lb)
B Plant (strontium recovery)	EDTA	166 kg (366 lb)
N Reactor, T Plant	Turco <sup>3</sup> brand detergents	Unknown
PUREX, B Plant	Ion-exchange resins	Unknown

<sup>1</sup> Quantities derived from Klem (1990) and Gerber (1992).

<sup>2</sup> These solvents degrade to alkali-soluble materials under tank conditions (Camaioni et al. 1994).

<sup>3</sup> Turco (a trademark of Turco Products, Inc.) detergents were used in decontamination procedures, which are estimated to contain 5 - 10 wt% TOC.

D2EHPA = Di-2-Ethylhexyl phosphoric acid  
 DBBP = Dibutyl-butyl phosphonate  
 EDTA = Ethylenediaminetetraacetic acid  
 HEDTA = Hydroxyethylene(ethylenediamine)triacetic acid  
 NPH = Normal paraffin hydrocarbons  
 PUREX = Plutonium-Uranium Extraction  
 TBP = Tributyl phosphate

Reviews of waste transfer records (Babad and Turner 1993) and the available sampling data (Webb et al. 1995) indicate that 36 tanks may contain greater than 3 wt% total organic carbon (TOC), and thus currently fall under the scope of this DQO. These tanks currently have controls in place to prevent propagating reactions (WHC 1995); however, controls will be added to or removed from tanks as more characterization information becomes available. These 36 tanks include the following:

- |              |              |              |
|--------------|--------------|--------------|
| • 241-A-101  | • 241-BY-107 | • 241-TX-105 |
| • 241-A-102  | • 241-BY-108 | • 241-TX-118 |
| • 241-AX-102 | • 241-BY-110 | • 241-TY-104 |
| • 241-B-102  | • 241-C-102  | • 241-U-103  |
| • 241-B-103  | • 241-C-103  | • 241-U-105  |
| • 241-B-202  | • 241-C-201  | • 241-U-106  |
| • 241-BX-104 | • 241-C-202  | • 241-U-107  |
| • 241-BX-105 | • 241-S-102  | • 241-U-108  |
| • 241-BX-110 | • 241-S-111  | • 241-U-109  |
| • 241-BY-103 | • 241-SX-103 | • 241-U-111  |
| • 241-BY-105 | • 241-SX-106 | • 241-U-203  |
| • 241-BY-106 | • 241-T-111  | • 241-U-204  |

### 3.0 DECISIONS

#### 3.1 SAFETY CATEGORIES FOR ORGANIC COMPLEXANT TANKS

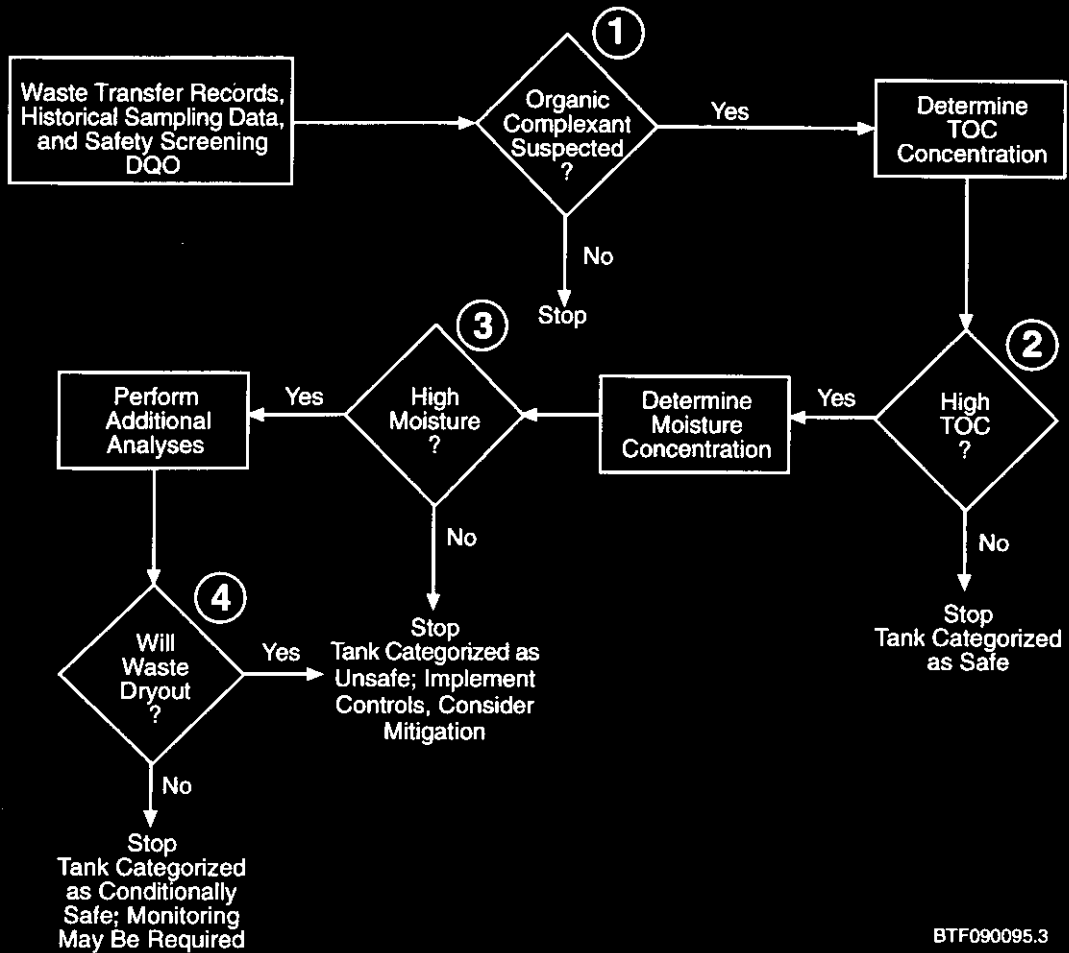
The chemical reactivity of organic complexant waste stored in some Hanford Site tanks places the tanks into one of three categories: *safe*, *conditionally safe*, or *unsafe* (Grumbly 1993). Numerical criteria for the three safety categories have been developed for organic complexant waste based on empirical data (Fisher 1990, Babad and Turner 1993). Tanks categorized as *safe* contain insufficient fuel and cannot support a propagating reaction. Tanks categorized as *conditionally safe* contain waste that cannot support a propagating reaction under current storage conditions and might require periodic monitoring. *Unsafe* tanks require controls to avoid conditions that could lead to reaction ignition. Mitigation will be considered to remove a tank from the *unsafe* category.

#### 3.2 DECISION LOGIC

The decision logic for placing organic complexant waste tanks into one of the three categories is shown in Figure 3-1. The decisions are listed in a logical order such that some decisions only need to be addressed based on the outcome of previous decisions. The decisions are broken down into four distinct questions. The decision rules or action limits corresponding to these general questions are stated in Section 6.0.

1. Is the tank suspect of receiving organic complexant waste? Reviews of waste transfer records (Fisher 1990) and historic sampling data (Webb et al. 1995), and the safety screening DQO (Dukelow et al. 1995) help determine which tanks should be evaluated by this Organic Complexant DQO.
2. Does the waste have enough fuel to support a propagating reaction when dried? If not, the waste is categorized as *safe* and the decision process ends here.
3. Is enough moisture present in the waste to prevent a propagating reaction? If not, the waste is categorized as *unsafe*, controls are implemented, and mitigation is considered. The decision process ends here.
4. Does the waste have the potential to dry during interim storage? If not, then the tank is categorized as *conditionally safe* and monitoring might be required to confirm the tank remains *conditionally safe*. The decision process ends here. If the moisture concentration could decrease to below safe levels during interim storage, then the tank is categorized as *unsafe*.

Figure 3-1. Decision Logic for Organic Complexant Waste Tanks



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## 4.0 DECISION INPUTS

### 4.1 REQUIRED DECISION INPUTS

Decision inputs may consist of any piece of information or data that can help answer the decision. The decision inputs required to make the decisions are summarized in Table 4-1. The decision input is listed along with the reason it is needed. Each of the decision inputs are connected to one of the four decisions listed in Section 3.2.

Table 4-1. Summary of Decision Inputs

Decision Input	Decision	Reason for Required Decision Input
1. Identification of Organic Complexant tanks	Did tank receive organic complexants?	Identification of tanks that contained organic complexants focuses analyses and sampling efforts.
2. TOC	Is there enough fuel to support a propagating reaction?	Determines if the waste has the potential to support an exothermic propagating reaction.
3. TOC and moisture	Will moisture prevent a propagating reaction?	Even if sufficient fuel is present, a propagating reaction cannot occur if enough moisture is present.
4. Temperature, cations, and waste dry out analyses	Will the waste dry out?	Evaluates whether the waste will dry out, possibly moving the waste to the <i>unsafe</i> category.

### 4.2 BASES FOR DECISION INPUTS

Data on fuel and moisture concentration are necessary to categorize a organic complexant tank as *safe*, *conditionally safe*, or *unsafe*. The waste must exceed a minimum fuel concentration to support a propagating reaction. This minimum fuel concentration, based on empirical data (Fisher 1990), is 3 wt% TOC (480 J/g) on a dry-weight basis. To judge whether waste exceeds this minimum, the TOC concentration or the exothermic energy (in J/g) must be determined experimentally.

TOC is a primary analyte that provides information on the fuel content of the waste. Direct persulfate oxidation is recommended to determine TOC; however, other techniques that meet the desired analytical uncertainty are also acceptable. If the energy equivalent TOC (based on sodium acetate) is low by 25%, then TOC will also be determined by furnace oxidation (Burger 1994).



Together, the TOC concentration and the energetics measurement provide corroborative data on the fuel content of the waste.

Differential Scanning Calorimetry (DSC) will be used to screen the exothermic energy concentration of organic complexant waste samples. For each tank, the sample that exhibits the greatest exothermic energy during DSC analysis will also be analyzed by adiabatic calorimetry (AC) analysis. However, if no exotherms above 480 J/g (dry-weight basis) are found in any of the samples, AC analysis is not required.

The reasons for adiabatic calorimetry testing are twofold. First, relatively large samples (10 grams or more) are tested. This provides greater assurance that the sample tested is representative of the bulk of the sampled material. Second, the observed self-heating behavior is evidence of the kinetics and energetics of the reactions in dried waste, and is a more direct test of whether a waste could support an exothermic propagating reaction.

Waste that exhibits propagation during AC testing will be analyzed for the major organic constituents by gas chromatography (GC) flame ionization detection or mass spectrometry (MS). High performance liquid chromatography (HPLC) will be used to identify the low molecular weight organic acids. Other Analytical techniques other than GC, MS, and HPLC are also acceptable if the technique can meet the desired analytical uncertainty.

In sufficient quantity, moisture can prevent a propagating reaction. Tube propagation tests using organic complexant waste surrogates have shown that propagating reactions cannot occur if the moisture exceeds 17 wt% (Babad and Turner 1993). Moisture concentration should be measured by thermogravimetric analysis (TGA). If the TOC concentration is greater than 3 wt% and the moisture measurement is below 17 wt%, then the moisture measurement will be confirmed by gravimetric analysis.

Analyses for aluminum, bismuth, calcium, iron, phosphorus, sodium, and other cations and temperature data help corroborate waste dry out models. These analyses are used to confirm that actual waste is bounded by the waste simulant experiments used to model waste dry out.

## 5.0 DECISION BOUNDARIES

The number of samples required to characterize a tank is a function of waste variability (heterogeneity) and the desired confidence to make a correct decision. An effort to understand variabilities in tank waste is currently underway, and data generated as a result of this DQO will be used to help bound potential waste variability. If valid assay data exist from prior sampling efforts, replication of those assays need not be done.

An optimum number of profiles will be determined for a specific tank during preparation of the Tank Characterization Plan (TCP) or Sample Analysis Plan (SAP). The number of profiles will be based on evaluation of historical data, prior sampling activities, and requirements of program specific DQOs. Comparisons with threshold values will be made using one-sided 95% confidence limits. If inadequate information exists to determine an appropriate number of samples, two vertical profiles of the liquid and solid portions of a tank will be obtained. Review of the data from these two profiles may indicate additional samples are necessary.

The boundaries for rotary-mode, push-mode core sampling, and auger sampling are applied to homogenized half-segments of waste [a 24-cm (9.5-in.) high cylinder of waste]. Where possible, sampling locations should be chosen to increase the likelihood for obtaining samples that represent the true spatial variations within a tank (e.g., opposite sides or side-center for two cores, side-center-side for three cores).

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## 6.0 DECISION RULES

To formulate the decision rules, it is necessary to assume that the tank characteristics are known. Under this assumption of no uncertainty, the outputs from the previous DQO steps are integrated into an unambiguous "If...then..." statement that outlines the conditions under which alternative actions will be chosen. Action limits or decision thresholds have been defined to produce the decision rules shown in Table 6-1.

Table 6-1. Decision Rules

Decision	IF (Decision Threshold)	THEN
1.	No organic complexant waste was transferred to tank	Tank is not organic complexant. Stop.
2.	TOC concentration < 3 wt%	Waste cannot support a propagating reaction. Waste categorized as <i>safe</i> , stop.
	TOC concentration $\geq$ 3 wt%	Perform moisture analysis.
3.	Moisture concentration $\geq$ 17 wt%	Measure temperature and examine dry out models.
	Moisture concentration < 17 wt%	Waste categorized as <i>unsafe</i> , implement controls and consider mitigation.
4.	Waste will not dry out during interim storage	Waste categorized as <i>conditionally safe</i> , monitoring may be required.
	Waste can dry out during interim storage	Waste categorized as <i>unsafe</i> , implement controls and consider mitigation.

The first decision threshold, whether a tank contains organic complexants, is a qualitative input from examinations of waste transfer records (Babad and Turner 1993) and historical sampling data (Webb et al. 1995). That is, based on the available data, a tank either received organic complexant waste or did not.

The TOC decision threshold of 3 wt% is based on the TOC fuel concentration criterion for identifying organic tanks (Fisher 1990). This TOC value has been incorporated into the Interim Safety Basis (WHC 1994) and is the current safety criterion. However, recent experiments and propagation theory indicate at least 4.5 wt% TOC as sodium acetate (1200 J/g energy equivalent) is required to support a propagating reaction (Fauske 1995). Corroboration of

the new criteria with actual waste samples is currently underway (Meacham 1995). This DQO will be revised when the new TOC (fuel) decision threshold is approved.

The moisture decision threshold of 17 wt% is based on empirical data from laboratory experiments. Mixtures of sodium acetate and nitrate/nitrite salts are predicted not to support propagating reactions when the moisture content exceeds 17 wt% moisture (Babad and Turner 1993).

The final decision threshold, whether the waste can dry out, is a function of the waste temperature, heat-load, tank breathing rate, and the chemical, physical, and rheological properties of the waste. The rate of moisture lost for the organic tanks identified in Section 2.0 have been modeled (Webb et al. 1995), and the analyses described in Section 4.0 are important to confirm that actual waste is bounded by the model.

## 7.0 DECISION ERROR TOLERANCES

Decision thresholds (criteria) are stated in Table 6-1 in Section 6.0. Based on the data collected for each analyte, a 95% confidence that the mean concentration is below the threshold limit is required. The upper limit to a one-sided 95% confidence interval on the mean will be computed. If the upper limit is less than the threshold limit, then there is 95% confidence that the mean concentration of the analyte is below the threshold limit. Table 7-1 reviews the decision boundaries, decision thresholds, and desired decision error tolerances.

Table 7-1. Decision Boundaries, Thresholds, and Confidence Limits

Decision Boundary	Decision Threshold	Confidence Limit*
Tank	1. No organic complexant waste was transferred to tank	High (Best Engineering Judgement)
24 cm waste layers (all $\frac{1}{2}$ segments)	2. TOC concentration < 3 wt%	95%
24 cm waste layers (all $\frac{1}{2}$ segments)	3. Moisture concentration $\geq$ 17 wt%	95%
Tank	4. Waste will not dry out during interim storage	High (Best Engineering Judgement)

<sup>1</sup> Confidence limit that the decision threshold is satisfied for the sample defined by the decision boundary.

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## 8.0 DESIGN OPTIMIZATION

### 8.1 TANK CHARACTERIZATION AND SAMPLING ANALYSIS PLANS

Most of the design optimization is performed in the tank specific TCP or SAP. TCPs and SAPs combine and summarize all applicable DQOs, test plans, procedure documents, and quality requirements documents. When a tank is to be sampled, all appropriate documents are reviewed and compared to determine commonality of data quality needs. From this review, the TCP and SAP are prepared. The TCP and SAP are designed to optimize the sampling and analysis effort such that the various requirements are supported in the most effective, cost-efficient manner. From the review, number of samples, type of samples, analytes, procedures, and data quality are optimized.

The appropriate number of profiles for a given tank will be determined at the time the TCP and SAP are prepared. The number of profiles will be based on evaluation of historical data, prior sampling activities, and requirements of program specific DQOs. Comparisons with threshold values will be made using one-sided 95% confidence limits. If valid assay data exist from prior sampling efforts, replication of those assays need not be done.

### 8.2 ANALYTICAL REQUIREMENTS

The decisions rules defined in Section 6.0 allow the data requirements to be separated into two groups, primary and secondary. The primary data requirements are always addressed, while the secondary data requirements are only necessary if specific limits are exceeded. Table 8-1 reviews the primary data requirements.

Table 8-1. Primary Data Requirements for Organic Complexant Tanks

Analyte	Analytical Method <sup>1</sup>	Sample <sup>2</sup>	Decision Threshold	Confidence Limit
TOC	Persulfate Oxidation	$\frac{1}{2}$ Segment	< 3 wt%	95%
Fuel	DSC/AC <sup>3</sup>	$\frac{1}{2}$ Segment	< 480 J/g	95%
Moisture	TGA	$\frac{1}{2}$ Segment	$\geq$ 17 wt%	95%

<sup>1</sup> Other techniques that meet the required uncertainty are also acceptable.

<sup>2</sup> Analyses are conducted on homogenized half segments of waste.

<sup>3</sup> Adiabatic calorimetry is conducted on one homogenized half segment per tank (if the fuel concentration is greater than 480 J/g).

Table 8-2 provides a summary of the secondary data requirements for the organic complexant tanks. TOC analysis by furnace oxidation is necessary if the energy equivalent (based on sodium acetate) TOC is low by 25%. Moisture analysis by gravimetric analysis is required on those quarter segments that violate both the fuel and moisture decision rules. The inductively coupled plasma (ICP) cation analyses are required on those half segments that violate



the fuel decision threshold (see Section 6.0 for decision rules). Waste that exhibits propagation during AC testing will be analyzed for the major organic constituents.

Table 8-2. Secondary Data Requirements for Organic Complexant Tanks

Analyte	Analytical Method	Sample	Decision Threshold	Confidence Limit
Cations (Al, Bi, Ca, Fe, P, Na)	ICP	$\frac{1}{2}$ Segment & Liquid	NA <sup>1</sup>	NA
TOC	Furnace Oxidation	$\frac{1}{2}$ Segment	3 wt%	95%
Moisture	Gravimetric	$\frac{1}{2}$ Segment & Liquid	17 wt%	95%
Organic Speciation	GC/MS <sup>2</sup>	$\frac{1}{2}$ Segment & Liquid	NA	NA

<sup>1</sup> NA = Not Applicable

<sup>2</sup> Other techniques that meet the required uncertainty are also acceptable.

## 9.0 REFERENCES

- Babad, H., and D. A. Turner, 1993, *Interim Criteria For Organic Watch List Tanks at the Hanford Site*, WHC-EP-0681, Westinghouse Hanford Company, Richland, Washington.
- Burger, L. L., 1994, *Reaction Energies: Correlation with Carbon Content* (internal memo, February 10), Pacific Northwest Laboratory, Richland, Washington.
- Camaioni, D. M., W. D. Samuels, B. D. Lenihan, S. A. Clauss, K. L. Wahl, and J. A. Campbell, 1994, *Organic Tanks Safety Program Waste Aging Studies*, PNL-10161, Pacific Northwest Laboratory, Richland, Washington.
- Dukelow, G. T., J. W. Hunt, H. Babad, and J. E. Meacham, 1995, *Tank Safety Screening Data Quality Objective*, WHC-SD-WM-SP-004, Rev. 2, Westinghouse Hanford Company, Richland, Washington.
- Fauske, H. K., 1995, *The Contact-Temperature Ignition (CTI) Criterion for Propagating Chemical Reactions and Application to Hanford Waste*, FAI/94-103, Fauske and Associates, Inc., Burr Ridge, Illinois.
- Fisher, 1990, *The Kyshtym Explosion and Explosion Hazards with Nitrate-Nitrite Bearing Wastes with Acetates and Other Organic Salts*, WHC-SD-CP-LB-003, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Gerber, M. A., 1992, *Assessment of Concentration Mechanisms for Organic Wastes in Underground Storage Tanks at Hanford*, PNL-8339, Pacific Northwest Laboratory, Richland, Washington.
- Grumbly, T. P., 1993, *Strategy for (Ferrocyanide) Safety Issue Resolution* (letter to J. P. Conway, Chairman, Defense Nuclear Facilities Safety Board, August 25), U.S. Department of Energy, Washington, D.C.
- Klem, M. J., 1990, *Inventories of Chemicals Used at Hanford Site Production Plants and Support Operations (1944-1980)*, WHC-EP-0172, Westinghouse Hanford Company, Richland, Washington.
- Meacham, J. E., 1995, *Test Plan for Samples From Hanford Waste Tanks 241-BY-103, BY-104, BY-105, BY-106, BY-108, BY-110, TY-103, U-105, U-107, U-108, and U-109*, WHC-SD-WM-TP-378, Westinghouse Hanford Company, Richland, Washington.
- Webb, A. B., D. M. Camaioni, J. M. Grigsby, P. G. Heasler, B. Malinovic, M. G. Plys, J. L. Stewart, J. J. Toth, and D. A. Turner, 1995, *Preliminary Safety Criteria for Organic Watch List Tanks at the Hanford Site*, WHC-SD-WM-SARR-033, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- WHC, 1994, *Interim Safety Basis - ISB - For the Hanford High Level Waste Storage Tanks*, WHC-SD-WM-ISB-001, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- WHC, 1995, *Operating Specifications for Watch List Tanks*, OSD-T-151-00030, Rev. B-8, Westinghouse Hanford Company, Richland, Washington.

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