# DISTRIBUTION SHEET

| To | From | Page 1 of 1 |
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| Distribution | Data Quality Objectives and Technical Support | Date April 26, 1995 |
| Project Title/Work Order | | EDT No. |
| WHC-SD-WM-DQO-006, Rev. 1 | | ECN No. 189572 |

| Name | MSIN | Text With All Attach. | Text Only | Attach./ Appendix Only | EDT/ECN Only |
|---|---|---|---|---|---|
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MASTER

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# ENGINEERING CHANGE NOTICE



1. ECN 189572

Proj. ECN

| 2. ECN Category (mark one) | 3. Originator's Name, Organization, MSIN, and Telephone No. | 3a. USQ Required? | 4. Date |
|---|---|---|---|
| Supplemental [] <br> Direct Revision [X] <br> Change ECN [] <br> Temporary [] <br> Standby [] <br> Supersedure [] <br> Cancel/Void [] | L. L. Buckley/Data Quality Objectives and Technical Support/71340/373-2157 | [] Yes [X] No | April 26, 1995 |
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| | Data Quality Objective to Support Resolution of the Organic Fuel Rich Tank Safety Issue | N/A | SQ |
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| 11a. Modification Work | 11b. Work Package No. | 11c. Modification Work Complete | 11d. Restored to Original Condition (Temp. or Standby ECN only) |
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12. Description of Change

The baseline document Rev. was changed in it's entirety. There were no changes to the text of the report, however, an attachment was added to reflect the revised safety strategy of the Tank Waste Remediation System. An introduction to the attachment is provided to clarify the differences in strategy between the baseline document and the one presented.

13a. Justification (mark one)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Criteria Change | [X] | Design Improvement | [] | Environmental | [] | Facility Deactivation | [] |
| As-Found | [] | Facilitate Const | [] | Const. Error/Omission | [] | Design Error/Omission | [] |

13b. Justification Details

This document revision was done to reflect the revised safety strategy developed to ensure safe operation of the storage tanks waste over a range of waste material and conditions.

14. Distribution (include name, MSIN, and no. of copies)

See distribution sheet.

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Page 2 of 2

1. ECN (use no. from pg. 1) 189572

| 15. Design Verification Required | 16. Cost Impact | | | | 17. Schedule Impact (days) | |
|---|---|---|---|---|---|---|
| | ENGINEERING | | CONSTRUCTION | | | |
| [] Yes | Additional | [] $ | Additional | [] $ | Improvement | [] |
| [X] No | Savings | [] $ | Savings | [] $ | Delay | [] |

18. Change Impact Review: Indicate the related documents (other than the engineering documents identified on Side 1) that will be affected by the change described in Block 12. Enter the affected document number in Block 19.

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

19. Other Affected Documents: (NOTE: Documents listed below will not be revised by this ECN.) Signatures below indicate that the signing organization has been notified of other affected documents listed below.

| Document Number/Revision | Document Number/Revision | Document Number Revision |
|---|---|---|
| | | |

20. Approvals

| Signature | Date | Signature | Date |
|---|---|---|---|
| OPERATIONS AND ENGINEERING | | ARCHITECT-ENGINEER | |
| Cog. Eng. L. L. Buckley L. L. Buckley | 4/27/95 | PE | |
| Cog. Mgr. D. G. Baide D G Baide | 4/27/95 | QA | |
| QA T.C.Trible per Telecon L. Buckley for | 4/27/95 | Safety | |
| Safety J. A Harvey - per Telecon L. Buckley for | 4/27/95 | Design | |
| Environ. | | Environ. | |
| Other: Program Mgr. D. A. Turner [signature] | 4-28-95 | Other | |
| Manager Process Eng. J. P. Sloughter [signature] | 4/27/95 | | |
| | | DEPARTMENT OF ENERGY | |
| | | Signature or a Control Number that tracks the Approval Signature | |
| | | ADDITIONAL | |

# RELEASE AUTHORIZATION

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| **Document Number:** | WHC-SD-WM-DQO-006, REV 1 |
| **Document Title:** | Data Quality Objective to Support Resolution of the Organic Fuel Rich Tank Safety Issue |
| **Release Date:** | 4/28/95 |

**This document was reviewed following the procedures described in WHC-CM-3-4 and is:**

**APPROVED FOR PUBLIC RELEASE**

**WHC Information Release Administration Specialist:**

Kara M. Broz April 28, 1995



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# SUPPORTING DOCUMENT

1. Total Pages ~~51~~ 92

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|---|---|---|
| Data Quality Objective to Support Resolution of the Organic Fuel Rich Tank Safety Issue | WHC-SD-WM-DQO-006 | 1 |

| 5. Key Words | 6. Author |
|---|---|
| Analytical Uncertainty, Characterization, Data Quality Objective, DQO, Issue Resolution, Organics, Safety Issue, TOC, Total Organic Carbon, Watchlist, Nitrate/Nitrite Moisture Concentration, Propagating Organic Reaction, Interim Stabilization | Name: Luther L. Buckley<br>Signature: Luther L. Buckley<br>Organization/Charge Code 8E000/N4A2K |


7. Abstract

During years of Hanford process history, large quantities of complexants used in waste management operations as well as an unknown quantity of degradation products of the solvents used in fuel reprocessing and metal recovery were added to many of the 149 single-shell tanks. These waste tanks also contain a presumed stoichiometric excess of sodium nitrate/nitrite oxidizers, sufficient to exothermically oxidize the organic compounds if suitably initiated.

This DQO identifies the questions that must be answered to appropriately disposition organic watchlist tanks, identifies a strategy to deal with false positive or negative judgements associated with analytical uncertainty, and list the analytes of concern to support dealing with organic watchlist concerns. Uncertainties associated with both assay limitations and matrix effects complicate selection of analytes. This results in requiring at least two independent measures of potential fuel reactivity.


8. RELEASE STAMP

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# RECORD OF REVISION

| (1) Document Number | Page |
| --- | --- |
| WHC-SD-WM-DQO-006, Rev. 1 | Page 1 |

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Data Quality Objective to Support Resolution of the Organic Fuel Rich Tank Issue

CHANGE CONTROL RECORD

| (3) Revision | (4) Description of Change - Replace, Add, and Delete Pages | Authorized for Release: (5) Cog. Engr. | Authorized for Release: (6) Cog. Mgr. Date |
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# DATA QUALITY OBJECTIVE TO SUPPORT RESOLUTION OF THE ORGANIC FUEL RICH TANK SAFETY ISSUE

H. Babad
S. M. Blacker
K. S. Redus

## ABSTRACT

*The Data Quality Objective to support resolution of the Organic Tank Safety Issue identifies that information needed to:*

- *Remove from the organics Watch List a tank that should not have been placed on the organics Watch List (i.e., the tank is safe)*
- *Classify a tank that cannot be removed from the organics Watch List (i.e., the tank is UNSAFE or CONDITIONALLY SAFE)*
- *If necessary, add tanks to the organics Watch List.*

*Tanks have been placed on the organics Watch List based on an evaluation of fill and transfer history or as a result of the safety screening Data Quality Objective. Determining whether a tank can be removed from the organics Watch List, or determining the appropriate classification for a tank containing elevated levels of organics, is based on analyses that establish if organic carbon and moisture content is above or below an established threshold.*

*In some cases, analyses of individual organic species, type of oxidants, hydroxide level and/or radiochemical species may be needed to resolve observations close to the threshold.*

*This organics Data Quality Objective lays out the logic for analyses that classify a tank containing organics as SAFE, CONDITIONALLY SAFE, or UNSAFE. As a simple, first cut understanding why certain analytical procedures are selected at certain junctures in evaluating a tank containing organics, four questions are presented and discussed. These questions lead to the specific logic of this organics Data Quality Objective.*

## EXECUTIVE SUMMARY

The Data Quality Objective (DQO) to support resolution of the Organic Fuel Rich Tank Safety Issue identifies that information needed to:

- Remove from the organics Watch List tanks that do not meet Watch List criteria (i.e., the tank is Safe)
- Classify tanks that cannot be removed from the organics Watch List (i.e., tanks are UNSAFE or CONDITIONALLY SAFE)
- Verify that additional tanks do not need to be added to the Watch List.

The determination of whether a tank can be removed from the organic Watch List, or in what classification to place a tank containing elevated levels of organics, is based on analyses that establish if organic carbon and moisture content are above or below an established threshold. The primary analyses employed are organic carbon, presence of a free organic liquid phase (floating organic layer), moisture content, and tank temperature. Liquid phase and moisture information are obtained during safety screening. Temperature is obtained directly from tank measurements. If the primary analyses are close to the threshold, individual organic species, presence of certain oxidizing agents, hydroxide level, or radiochemical species analysis may be needed.

These additional measurements are referred to as secondary analytes. When primary analytes give results that are close to the decision threshold, false positive or false negative concerns can arise because (1) the primary analytical methods may not be sufficiently robust; or (2) there is sufficient uncertainty about the chemistry of the tank contents to rely on the primary data. By performing the secondary measurements, the "weight of consistent evidence" among different analytical results becomes the strengthened basis for categorizing organic-containing tanks. This results in narrowing the potential for false positive and false negatives to acceptable levels. This combination of primary and, when needed, secondary measurements is the key to a successful DQO for resolving safety issues related to organic tanks.

The Organic Safety Issue arises due to the waste added to single-shell tanks containing quantities of organic complexants and organic degradation products of solvents used in fuel reprocessing and metal recovery. These waste tanks also contain a presumed stoichiometric excess of sodium nitrite and sodium nitrate oxidizers that is sufficient to exothermically oxidize the organic compounds. Double-shell tanks containing organics are not included because the waste contains large quantities of water.

The primary questions asked in this DQO are as follows.

1. If a tank is not presently on the organic Watch List, but historical information suggests it received appreciable quantities of organic waste, what measurements are needed to resolve the inconsistency?

2. If a tank is presently on the organic Watch List, what information is needed to remove it from the Watch List?

3. Does a tank, contain concentrations of reactive organic chemicals that are UNSAFE?

4. If a tank contains insufficient moisture, what characterization-based information is needed to support mitigation or remediation decisions?

Each of these questions is discussed as a way that serves to introduce the specific organics issue and show how this DQO was designed to address each question.

Several tables have been developed to help implement this DQO. Beginning with Table 6-2, different scenarios representing different combinations of carbon, energetics, and history of organic fill and transfer are presented. Associated with each scenario is an analytical action that should be pursued to establish what safety category the organics tank should be placed in. Table 6-3 contains the quantitative threshold levels for each scenario and the specified analytical tests that should be carried out to reduce to acceptable limits the false positive and the false negative concerns associated with each scenario. Table 7-1 and 7-2 describe the analytical method and identify what segment division that analysis should be run.

The primary analytes to support the decisions are as follows:

- Total organic carbon by persulfate oxidation (the primary decision criterion)
- Moisture content obtained during screening DQO
- Total fuel content (energetics) obtained during screening DQO
- Presence of organic floating layer
- Tank temperature (from tank monitoring).

The secondary analytes are as follows:

- Confirmation of total organic carbon (by furnace oxidation to accommodate persulfate oxidation method limitations)
- Confirmation of moisture content by gravimetric analyses, if close to the decision point

- Equilibrium moisture content, used in conjunction with hydroxide assay to validate safe interim storage conditions

- $Cs^{137}$ and $Sr^{90}$ (to validate tank thermal characteristics in support of thermal modeling)

- Nitrite, nitrate, and hydroxide concentration

- Principal organic species

- Chromium and manganese concentrations and, if needed, chromium and manganese oxidation states.

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# ACKNOWLEDGMENTS

The author would like to express appreciation to Stan Blacker and to Ken Redus of MACTEC for their advice, detailed assistance, and patience in shepherding the author's evolution from a casual user of systems engineering oriented data specification techniques to a DQO advocate and author.

Thanks are also due to Ken Redus for extensive help with this manuscript, particularly in the area of helping maintain a sense of balance under pressures of often asynchronous reviewer guidance.

I also would like to acknowledge the assistance of Bob Cash, whose extensive review of the early draft of this document made it all the better.

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*As a result of the large amount of information exchanged and available among stakeholders during the months-long PNL risk-based study to identify the data requirements for the Organic Program, this DQO did not utilize the traditional meeting format to generate input to this document. As a result of Tom Wood's (the PNL Team Leader) efforts, the authors were able to augment the information needed to write this DQO by talking with only some of the stakeholders, to supplement the information previously available. However, all stakeholders, as well as a number of uninvolved peer reviewers, did participate in a detailed technical review of this document prior to its approval. All technical issues raised by the reviewers (including stakeholders) were addressed to their satisfaction.

**WESTINGHOUSE HANFORD OPERATIONS (continued)**

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# LIST OF TERMS

| | |
|---|---|
| D2EHPA | Di-2-Ethylhexyl phosphoric acid |
| DBBP | Dibutyl-butyl Phosphonate |
| DQO | Data Quality Objective |
| DSC | Differential Scanning Calorimetry |
| EDTA | Ethylenediaminetetraacetic acid |
| FAI | Fauske and Associates |
| HEDTA | Hydroxyethylene(ethylenediamine)triacetic acid |
| HPLC | High Performance Liquid Chromatography |
| ICP/AES | Inductively Coupled Plasma/Atomic Emission Spectroscopy Methods |
| LANL | Los Alamos National Laboratory |
| MDL | Method Detection Limit. The minimum concentration of a substance that can be measured and reported with a 99% confidence that the assay is greater than zero. |
| NPH | Normal Paraffin Hydrocarbons |
| PNL | Pacific Northwest Laboratory |
| PQL | Practical Quantification Limit. Usually taken as 10X the MDL. For this DQO, this term is used to represent the lowest analyte value needed to make defensible safety classifications |
| TBP | Tributyl Phosphate |
| TGA | Thermogravimetric Analysis |
| TOC | Total Organic Carbon |

# DEFINITIONS

"Not Safe" This is a specific term (when used in quotes) coined in the Safety Screening DQO* that is used to designate, a priori, a waste classification for interim storage in single-shell tanks that are either CONDITIONALLY SAFE or UNSAFE. Such tanks would be organic Watch List candidates.

CONDITIONALLY SAFE
A tank is considered CONDITIONALLY SAFE if it contains >5% total Organic Carbon, dry weight basis, and ≥17% water. The specifications associated with a CONDITIONALLY SAFE organic containing tank are listed in Table 6-1.**

SAFE A tank is considered SAFE with respect to the organic Watch List when it contains ≤ 5% total Organic Carbon, dry weight basis. This is a specific (when capitalized) term coined by U.S. Department of Energy-Headquarters that is used to classify waste relative to interim waste storage for which no added operational constraints beyond that called for by existing safety bases are needed. The specifications associated with a SAFE organic containing tank are listed in Table 6-1.**

UNSAFE A tank is considered UNSAFE with respect to the organic Watch List when it contains ≥5% total Organic Carbon, dry weight basis, and <17% water. This is a specific (when capitalized) term, coined by U.S. Department of Energy-Headquarters that is used to classify a waste relative to interim safe storage that requires mitigation or remediation to achieve safety.**

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*Babad, H., and K. A. Redus, 1994, *Tank Safety Screening Data Quality Objectives*, WHC-SD-WM-SP-004, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

**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.

CONTENTS

## LIST OF FIGURES



## LIST OF TABLES

# 1.0 INTRODUCTION

The Organic Safety Issue arises due to wastes added to single-shell tanks (SSTs) containing quantities of complexants used in waste management operations as well as degradation products of these complexants and solvents used in fuel reprocessing and metal recovery operations. These waste tanks also contain a presumed stoichiometric excess of sodium nitrite and sodium nitrate oxidizers that is sufficient to exothermically oxidize the organic compounds.

There are presently 10 organic Watch List tanks, as follows (Hanlon 1994):

- 241-B-103
- 241-C-103
- 241-S-102
- 241-SX-106
- 241-T-111
- 241-TX-105, -118
- 241-U-106, -107, and -111.

Tank 241-C-103 also is on the organic Watch List because of the potential for ignition and combustion of the floating organic layer. Tank 241-TX-118 also is on the ferrocyanide Watch List. Tanks 241-S-102 and 241-SX-106 also are on the hydrogen flammable gas Watch List. It is expected that application of the screening DQO (Babad and Redus 1994) or information obtained from detailed historical review underway at Pacific Northwest Laboratory (PNL) and Los Alamos National Laboratory (LANL) will identify additional tanks that need to be added to the organic Watch List.

Double-shell tanks (DSTs) containing organics are not of concern to the Organic Waste Tank Safety Program they contain large quantities of water. Should concerns arise about the safety of DST organic contents, the concerns can be readily dealt with under existing operating procedures.

If a tank is placed on the organic Watch List (either by result of the Safety Screening DQO or by other organic safety program findings and recommendations*), its categorization into the appropriate safety category is based on the results of this Organics DQO.

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*A study soon to be issued by PNL (Toth 1994) collected and attempted to statistically interpret all available TOC data obtained at the Hanford Site. Findings of that report suggest that a significant number of tanks not presently on the Organic Watch List might need to be added.

The organics Watch List criteria is under review and may be revised in the near future.

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# 2.0 DQO STEP 1: STATE THE PROBLEM

## PROBLEM STATEMENT

The problems addressed by this DQO are:

- Are the right tanks on the organic Watch List
- Are any of the Watch List tanks in the UNSAFE category, and
- Do the Watch List tanks have sufficient moisture.

Selecting the proper action depends explicitly on the characterization data obtained for the key decision variables described in the DQO.

## BACKGROUND

Ensuring the safety of the Hanford Site's SSTs containing organic carbon is the objective of the Organic Tanks Safety Program (Hopkins and Babad 1993; Strachan 1993). Analyses show that propagating organic reactions could occur with sufficient fuel at elevated temperature and reduced moisture levels. Exothermic reactions leading to propagation can only occur if there is sufficient concentration of fuel and oxidizer present in the waste, and if a portion of the waste is dried out and heated to temperatures above 180 °C.

The Organic Tank Safety Issue is limited to SSTs. The well ventilated and more heavily instrumented DSTs contain large quantities of water that prevent a potential for exothermic reaction. Water can be added to DSTs, as part of normal operational considerations, if needed.

To evaluate the risk from organic fuel-waste oxidizer reactions, a test program has been initiated. This involves the following study areas:

- Measuring waste reaction kinetics and energetics
- Measuring moisture equilibrium conditions on actual waste
- Evaluating the rates and completeness of waste aging - defined as the degradation of fuel value of the waste as a result of radiation and chemical hydrolysis and/or oxidation of the original process organics (Babad and Strachan 1993)

- Evaluating potential organic waste concentration mechanisms
- Thermal modeling of organic Watch List tank characteristics.

Because of limited amounts of available waste material and the high dose rates of the samples, initially the research efforts are done with waste simulants defined from limited sampling data and tank transfer records. To close the Organic Safety Issue, data from actual waste samples are needed not only to validate the simulant based studies but to provide proof that tank conditions match those predicted by those studies.

The criteria used for evaluation by the Organic Tank Safety Program exist in interim form (Babad and Turner 1993). The interim criteria will be explicitly discussed as part of the decision criteria later in this document. The interim criteria will be updated as more information becomes available. Stringent operating controls are in place in the tank farms to ensure that initiating events in or around the organic Watch List tanks are prevented, and that actions that would serve to significantly reduce waste moisture levels are controlled. In addition, all of the organic Watch List tanks are monitored for waste temperature, and a corrective action plan is in place if abnormal conditions are detected (Turner 1993).

The quantity of bulk organic chemicals used in chemical processing and/or added to the tanks as part of waste management efforts is summarized in Table 2-1. Water-soluble organic complexants were added to the tanks intentionally, as a means of providing interim storage for the wastes. However, the water-insoluble solvents were to be recycled so their addition to the tanks was unintentional. At the time that the fuel reprocessing and metal recovery plant were operating, the fate of the degradation products resulting from solvent radiolysis was not of concern.

These waste tanks also contain large quantities (presumably a stoichiometric excess) of sodium nitrite and sodium nitrate oxidizers that are sufficient to oxidize the organic compounds, if suitably initiated. The organic materials were added to the SSTs as dilute neutralized moderately alkaline aqueous solutions. Under those conditions a majority of the organic chemicals were likely to be soluble. The only exceptions identified involved entrainment loses of solvents into the aqueous layer or the accidental transfers of an organic solvent to the tank farms.

The acidic waste streams generated by chemical and waste processing (e.g., reduction oxidation [REDOX], plutonium/uranium extraction [PUREX], the uranium recovery campaign, and cesium and strontium removal) were treated, as needed, in the operating facility, to recover the excess nitric acid reagent required by most of the flow sheets. The remaining waste was treated with concentrated caustic (NaOH) to neutralize the wastes and prevent corrosion of the low-carbon single-shell tanks. Neutralization precipitated the iron, aluminum, and other metallic hydroxides in the waste, which settled as sludges in the bottom of the tanks, carrying with them any residual actinides.

Table 2-1. Bulk Organic Chemicals Used in Chemical Processing and Recovery of Spent Fuel and/or Added to the Tanks During Waste Management.

| Process or operation | Organic chemical | Amounts purchased or used (x $10^3$)[1] |
|---|---|---|
| PUREX/B Plant | NPH/TBP | 140 Kg (308 lb)[2] |
| B Plant | TBP-NPH-D2EHPA | 0.06 $m^3$ (12.7 gal) |
| Z Plant | TBP-DBBP bottoms that contained some carbon tetrachloride | 1.8 $m^3$ (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™ brand detergents[3] | Unknown |
| PUREX, B Plant | Ion exchange resins | Unknown |

[1]Quantities derived from Klem (1990) and Gerber (1992).

[2]Extensive solvent recycling in PUREX and other reprocessing plants suggests that only small amounts of the TBP and NPH actually entered the tanks. However, the fact that several tanks do contain these chemicals (e.g., tank C-103), and that these solvents degrade to alkali soluble materials on exposure to high radiation fields and strong nitric acid (as was found in PUREX), suggests that some single-shell tanks might have had significant amounts of hexone or NPH-TBP derived materials added to them.

[3]Turco (a trademark of Turco Products, Inc.) detergents were used both in N-Reactor decontamination and in other plant decontamination procedures. Although their composition is proprietary, they are known to contain an estimated 5-10% organic detergents and/or other surface active agents, characterized by a highly hydrophobic hydrocarbon function. The total amount of these materials used has not been determined.

NPH = Normal Paraffin Hydrocarbons.
PUREX = Plutonium-Uranium Extraction.
TBP = Tributyl Phosphate.

# 3.0 DQO STEP 2: IDENTIFY THE QUESTION TO BE ANSWERED

The DQO to support resolution of the Organic Tank Safety Issue will be used to focus information gathering from tank characterization (sampling) efforts for those tanks that are either on the present organic Watch List, or have become candidates for that Watch List as a result of safety screening or other Organic Safety Program findings and recommendations. The decisions to be made are as follows:

1. Confirm if a tank is SAFE or whether it belongs on the organic Watch List.

2. Confirm if a Watch List tank is CONDITIONALLY SAFE or UNSAFE.

Based on answers to these decisions, actions will be identified and implemented to mitigate (in situ) or remediate (remove waste) the conditions that resulted in the classification of UNSAFE.

The Safety Screening DQO supports the first decision. The Safety Screening DQO (Babad and Redus 1994) determines whether a currently uncategorized tank should or should not be considered a potential organic Watch List tank candidate. The relationship between the screening DQO and this Organic DQO is found in Figure 3-1. To understand Figure 3-1, the reader must remember that the Safety Screening DQO focuses on identifying tanks with potentially high energetics while the Organic Safety Issue DQO requires evaluation of the carbon content of the tank.

The primary questions asked in this DQO are as follows:

1. If a tank is not presently on the organic Watch List, but historical information suggests it received appreciable quantities of organic waste, what measurements are needed to resolve the inconsistency?

2. If a tank is presently on the organic Watch List, what information is needed to remove it from the Watch List?

3. Does a tank, contain concentrations of reactive organic chemicals that are UNSAFE?

4. If a tank contains insufficient moisture, what characterization-based information is needed to support mitigation or remediation decisions?

The relationship of these questions is presented in Table 3-1.

Figure 3-1. The Relationship Between the Safety Screening Data Quality Objective and the Organic Data Quality Objective.

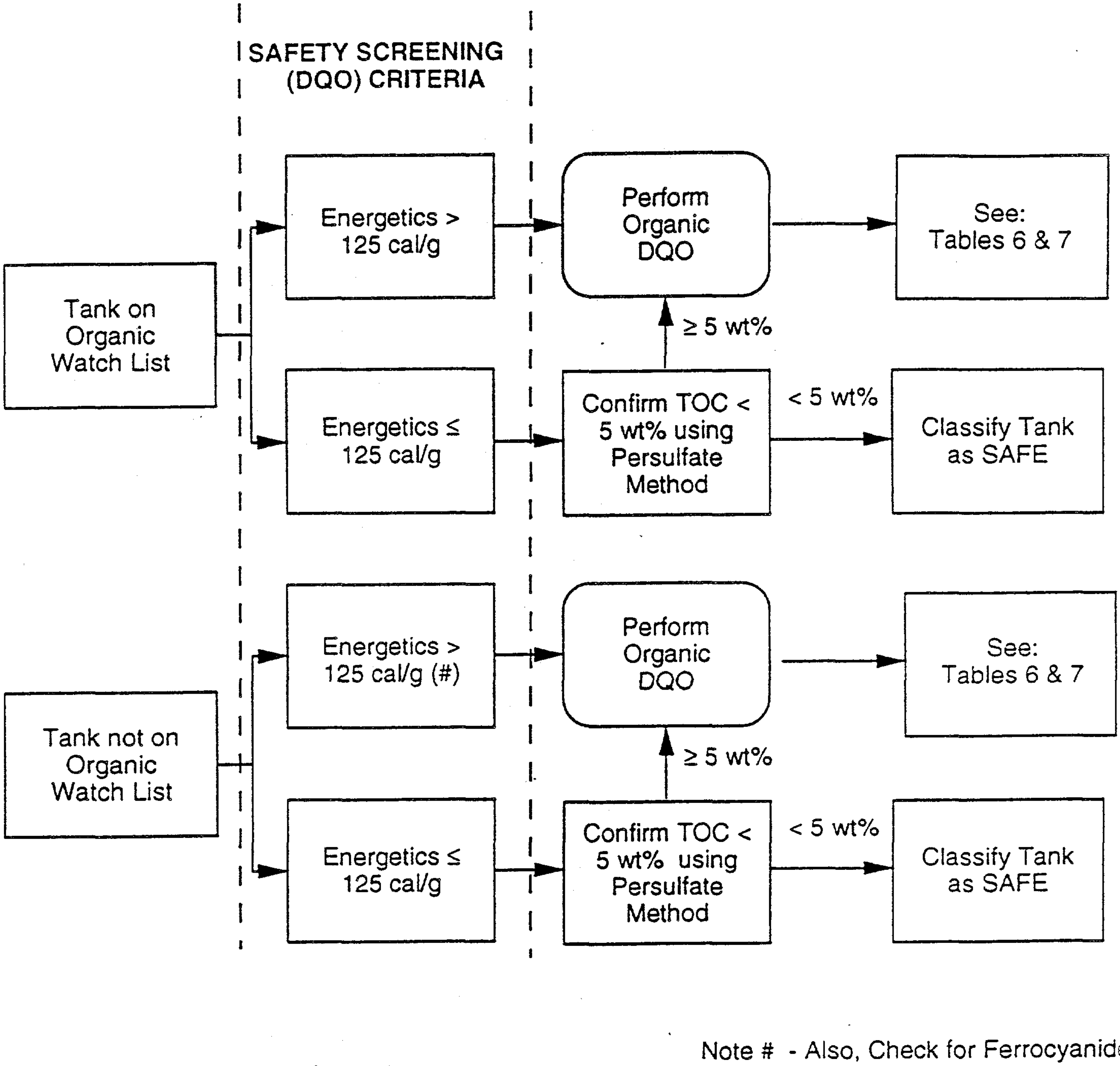

Table 3-1. The Relationship Between Historical Information and Other Prior Knowledge and the Primary Organic DQO Questions.

| Watch List status of tank | Tank on organic Watch List | | Tank not on organic Watch List | |
|---|---|---|---|---|
| Historical information indicates that: | Tank received organic waste | Tank did not receive organic waste | Tank received organic waste | Tank did not receive organic waste |
| Moisture conditions acceptable | Question 1<br>Question 2<br>Question 3 | Question 2<br>Question 3 | Question 2<br>Question 3 | Question 2<br>Question 3 |
| Moisture conditions unacceptable | Question 1<br>Question 4 | Question 4 | Question 4 | |
| Note that questions 1, 2, and 3 address the inclusion or removal of tanks from the Watch List. Question 4 addresses identifying mitigation measures for any tank that exhibits less than threshold moisture content. | | | | |

In summary, this DQO supports resolution of the Organic Safety Issues associated with removal of tanks from organic Watch Lists (e.g., establishing that an individual tank is SAFE), or classification of an individual tank as CONDITIONALLY SAFE or UNSAFE.

The Safety Screening DQO also provides data that allows initial consideration of whether tanks previously added to the organic Watch List based on historical data (e.g., from assessment using the track radionuclide components (TRAC) code (Jungfleisch 1984) do indeed belong on that list. As a result of tank screening, data will be available to allow a more rapid focus on those tanks for which interim safe storage may be of concern.

From Figure 3-1, it is shown that a tank currently on the organics Watch List can be classified as safe by having energetics below 125 cal/g and total organic carbon (TOC) below 5 weight percent, using the persulfate method. These values demonstrate that the tank energetics and the tank carbon fuel content are sufficiently low, so there is no likelihood of a propagating exothermic reaction. To remove concerns about the uncertainty of available information, an evaluation of history records showing fills and transfers needs to be reviewed to confirm the levels of energetics and TOC observed. In some cases there is disagreement within the data sets obtained, and this leads to a requirement for additional assays to resolve analytical or other technical uncertainties.

Tank screening and confirmatory TOC measurement will provide the data to identify those tanks that require further evaluation to ensure interim safe storage of the wastes. The strategy underlying such an evaluation is strongly influenced by the DOE-HQ policy on defining safety classification (Grumbly 1993) that was developed for the Ferrocyanide Tank Safety Program and, according to DOE-HQ guidance, is applicable to the Organic Tank Safety Program. This policy is conservative.

The criteria for establishing the organic Watch List is based on the concentration of TOC present (on a dry weight basis) in the waste. By contrast, the direct measurement of the energetics, as defined in the Waste Tank Safety Screening DQO, is a more direct measurement of chemical reactivity. However, until sufficient data are available from the combined research and characterization efforts, TOC remains the only valid criterion to support decisions about the organic Watch List. These criteria are listed in Table 6-1. They will be used in the discussion of the questions that follow.

If a tank shows high energetics (e.g., ≥ 125 cal/g dry weight basis), that are due to the presence of organic chemicals (e.g., TOC ≥ 5%), the tank needs to be classified into one of three safety groups (e.g., SAFE, CONDITIONALLY SAFE OR UNSAFE). The analyses described in Section 6.0 will provide some of the data for making those decisions.

# 4.0 DQO STEP 3: IDENTIFY THE INPUTS TO THE DECISION OR QUESTIONS

The primary and secondary analytes that will be examined in this DQO are listed in this section. Decision rules that employ these analytes are presented in Section 6.0. Detailed analytical requirements are contained in Section 7.0.

The primary analytes to support the decisions are as follows:

- Total organic carbon by persulfate oxidation (the primary decision criterion)
- Moisture content obtained during screening DQO
- Total fuel content (energetics) obtained during screening DQO
- Presence of organic floating layer.

The secondary analytes are as follows:

- Confirmation of total organic carbon [by furnace oxidation to accommodate persulfate oxidation method limitations]
- Confirmation of moisture content by gravimetric analyses, if close to the decision point
- Equilibrium moisture content, used in conjunction with hydroxide assay to validate safe interim storage conditions
- Cesium-137 and Strontium-90 (to validate tank thermal characteristics in support of thermal modeling)
- Nitrite, nitrate, and hydroxide concentration
- Principal organic species
- Chromium and manganese concentrations and, if needed, chromium and manganese oxidation states.

Section 7.0 presents specific analytical requirements for these primary and secondary analytes.

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# 5.0 DQO STEP 4: DECISION/QUESTION BOUNDARIES

The spatial boundaries to be examined for this DQO are half segment cores of SSTs. Two cores, separated radially to the maximum extent possible by the existing installed risers, at the locations defined in the Safety Screening DQO, are the minimum required by this DQO. If horizontal spatial variability becomes a problem, then additional cores will be needed to characterize the radially central portions of the tank for which riser availability is either limited or presently not available. The temporal boundaries for such sampling is by the end of FY 96.

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# 6.0 DQO STEPS 5 and 6: DECISION RULES AND DECISION ERROR TOLERANCES

## 6.1 DECISION ERROR TOLERANCES AND OTHER UNCERTAINTIES ASSOCIATED WITH THE MEASUREMENT OF ENERGETICS AND TOC

The techniques for measuring energetics and TOC, although well documented, can result in significant uncertainties associated with their application to the diversity of organic compounds expected in the Hanford Site waste tanks. This, along with the unknown role of waste matrix effects on measurement accuracy and precision, raises uncertainties as to the reliability of any one result. This DQO, therefore, requires agreement between energetics and TOC that is consistent with (1) expectations from tank history; and (2) a general but growing chemical knowledge about organic oxidation chemistry under tank conditions. Described below are some of the concerns that justify this "weight of consistent evidence" approach.

The impact of the analytical, sampling, and spatial uncertainties, from a hypothesis testing perspective, can result in classifying a "Watch List" tank as SAFE (false negative) or incorrectly classifying a SAFE tank as "Watch List" (false positive).

The impact of a false negative risk is omitting a dangerous tank from Watch List coverage. The impact of a false positive appears insignificant in terms of human health and safety; however, operational expense is incurred in applying unneeded operating controls when they are not required. Avoiding a false negative is extremely important and must be avoided if possible. On the other hand, a fairly large false positive error can be tolerated. At this time quantification of error is not possible. To do so one would need (1) a good theoretical and experimental understanding of the energetics and degradation of organics in Hanford Site waste; and (2) a definition of spatial uncertainties based on actual tank data of analytical sampling.

The uncertainties discussed in this section do not change the nature of the questions listed in Section 5.0; they simply make collection of valid data to support safety decisions more difficult. Specific limitations to the present assay methods are described below.

- **Obtaining Valid Energetics Estimates.** Although differential scanning calorimetry (DSC) for energetics measurements are known to be conservative because they inherently neglect heat capacities of the sample, the method uses such small amounts of materials that the sample measured may not be representative of the subsegment. Table 7-1 calls for determination of DSC values on duplicates samples taken from a homogenized half segment. If one of the pair of duplicates does not agree within the limits defined for the assay, then another duplicate pair is run. If there is still inconsistency in the DSC data, then an alternate energetics methods will be used. The industry practice, where the measurement is close to the criterion on which a decision is to be made, is to run adiabatic calorimetry to validate the DSC measurements.

- **Accurately Measuring Total Organic Carbon.** Experience on the Hanford Site with the persulfate oxidation method for determining "whole sample" TOC has found that it is effective and appears accurate when used on complexant containing wastes. However, recent data collected on tank T-111 suggests that there could be tank constituents that are resistant to persulfate oxidation. A broader array of organic materials appears to be readily analyzed by using the furnace-combustion-based TOC method, in particular those bearing long chain hydrocarbon fragments that might be resistant to persulfate oxidation. The analytical staff also is aware that the presence of certain metal carbonates in the sample may cause a bias in the furnace-combustion TOC method. Studies have been initiated at PNL and LANL to identify both the chemical constituents and waste matrices that cause significant understatement of TOC values by persulfate oxidation in some wastes. These studies also will address potential interferences with the furnace combustion method. Prudence dictates that, although the furnace combustion method is both more time consuming and exposes laboratory technicians to a higher radiation dose, it should be used on a limited number of program-designated subsegments to check any anomalous results from persulfate oxidation. The segments to which such analysis is applied will be determined by the Organic Program Manager on a tank-by-tank basis.

- **Energy Estimate Considerations - The Relationship Between Total Organic Carbon and Energetics.** Present experimental and modeling data (Berger 1994; Samuels 1994) suggest that the most fuel-rich material known to have been added to tanks are HEDTA and related complexants and salts of carboxylic acid derived from NPH and/or the long chain surfactants that are a part of Turco* decontaminating agents. These appear to have energetics of about 1.5 times that of sodium acetate. Organic destruction by waste aging has been quantified for the HEDTA (as well as other complexants) added to tank 101-SY by mechanisms that appear to be generally applicable to all alkaline-high aluminum, sodium nitrate, and nitrate containing tanks (Babad et al. 1993). Direct evidence for aging of long-chain hydrocarbon containing chemicals has not yet been verified under tank conditions (work will be initiated by PNL during the summer of 1994), but appears reasonable based on detailed literature and limited test findings. Assuming aging to be valid for the most reactive constituents, sodium acetate was chosen as the standard for energetics conversion when comparing TOC and energy measurements.

*Turco is a trademark of Turco Products, Inc.

Low-energy measurements inconsistent with TOC values also can occur if a chemical mixture does not contain an excess of oxidizing agent. The energetics of such an incompletely reacted system will be low. Furthermore, it is being demonstrated by L. L. Burger and coworkers at PNL (Berger 1994; Samuels 1994), in accordance with theoretical predictions, that the reaction pathway for organic oxidation is strongly dependent on the hydroxide content of the reaction mixture. The higher the caustic concentration, all other things being equal, the higher the energy produced in the oxidation of an organic waste.

Finally, if it cannot be shown that the chemical reactivity is a result of nitrate and nitrite salts or air, then analysis for other oxidant should be undertaken. Chromium and manganese salts are the only other inorganic chemicals found in the tanks that are capable of oxidizing organic chemicals in an essentially anoxic environment. As these chemicals were used in various flowsheets, tests for an alternate oxidation path is reasonable and prudent when inconsistencies between data sets are found. Because most of the waste tanks contain a large excess of sodium nitrate and large quantities of sodium nitrite, alternative oxidizer pathways are expected to be the exceptions rather than the rule.

To gain sufficient confidence in the decisions supported by this DQO, an agreement is required between the TOC specification (i.e., the principal basis of the organic safety criterion) and energetics. To avoid false positive and negatives, we rely on additional supplementary analysis to deal with the possible uncertainties and/or inconsistencies between energetics and TOC measurements. This allows the Organic Safety Program to challenge, in case of data inconsistency, the assumption concerning the presence and quantities of oxidizing agents made in establishing the organic safety criteria. In reality, constraints on further adding materials to SSTs, other then perhaps water under emergency conditions would prevent adding oxidizer-containing wastes to an oxidizer-lean SST. Logic requires that this circumstance be documented to remove tanks from the Watch List or to establish appropriate operating controls.

In summary, the DSC method used to estimate energetics and the persulfate oxidation method for measuring TOC can provide an underestimate or overestimate of tank reactivity depending on the sample content and waste matrix. Use of the furnace-combustion method as a confirmatory assay can reduce this uncertainty. Choosing sodium acetate as the standard for energetics conversion, when comparing TOC and energy measurements, serves as an additional basis for comparison--one with it own weaknesses dealing with situations in which historical information suggests either a shortage of oxidizing agent or an alternative oxidant. These challenges to our measuring the risk from an organic containing tank, from waste sample analysis, make devising a precise and accurate assay strategy difficult but not impossible. The analytical requirements are designed to accommodate limitation in both present assay methods and sample or tank variability.

## 6.2 DECISION LOGIC

A top-level logic associated with removing a tank from the organic Watch List, based on TOC and moisture measurements, is shown in Figure 6-1. Temperature is considered a secondary criterion because all Hanford Site SSTs are cooling as their fission product contents decays.

Safety specifications for the Organic Tank Safety Issue are shown in Table 6-1. The rest of this section discusses decision logic associated with each of the four major questions.

### 6.2.1 Question 1

*If a tank is not presently on the organic Watch List, but historical information suggests it received appreciable quantities of organic waste, what measurements are needed to resolve the inconsistency?*

#### Decision Logic

It is assumed that for any tank NOT presently on the organic Watch List, unless there is historical data to the contrary, the tank would be treated as SAFE from the prospective of the Organic Tank Safety Program if both the TOC analysis and the energetics were below the Watch List criteria (see Table 6-1). If the present sample data contradicts historical fill and transfer analysis, further information would be gathered, as is described in Tables 6-2 and 6-3, to ensure that the differences between historical data and present limited core data could be rationalized (e.g., lower energetics were a result of waste aging as predicted from studies on simulants and actual waste samples).

### 6.2.2 Question 2

*If a tank is presently on the organic Watch List, what information is needed to remove it from the Watch List?*

#### Decision Logic

Tanks presently on the organic Watch List were placed there by a combination of the TRAC data base (Jungfleisch 1984) and limited sampling data. Not all tanks on the existing Watch List may belong there. Characterization data on tank TOC contents and energetics will be used to document the conclusion that a present Watch List tank contains a sufficiently low concentration of organics (and therefore energy) to be considered SAFE and allow its removal from the Watch List.

Figure 6-1. The Logic For Removing A Tank From the Organic Watch List.

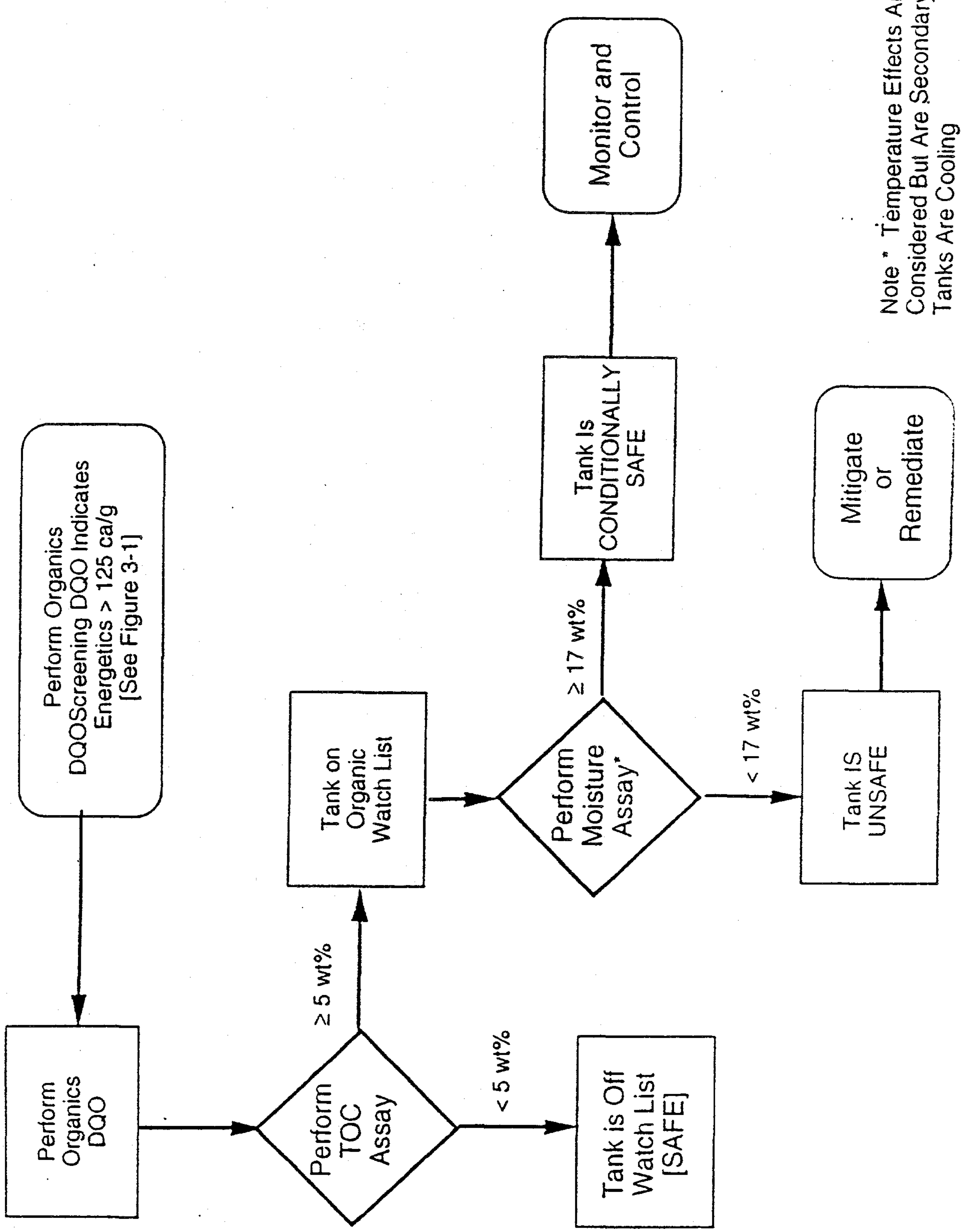

Table 6-1. Safety Specifications for Organic Tank Safety Issue Determination[1].

| Criteria based analyte of concern[2] | Decision threshold for placing tank on Watch List |
|---|---|
| Total organic carbon | >5 wt %[3] |
| Total fuel content (energetics) | ≥125 cal/g[4] |
| Moisture content in tank | <17 wt %[5] |
| Tank temperature | ≥149 °C (300 °F)[6]<br>>90 °C (194 °F)[7] |

[1]Conditions defined by U.S. Department of Energy-Headquarters and concurred with by the Congressionally appointed Defense Nuclear Facilities Safety Board require a conservative approach to Watch List tank classification. To classify a tank as SAFE, in this agreement no credit is taken for the presence of moisture or for the fact that the tank waste temperature is low, often 100 °C or more below the temperature at which significant exothermic reaction (e.g., the initiation temperature) can occur. Furthermore, it is assumed that there is and will always be an excess of oxidizer in the tank. Therefore, only the concentration of organic fuel need be taken into consideration. These and other aspects of criteria associated with organic Watch List tanks are documented in *Interim Criteria For Organic Watch List Tanks at the Hanford Site*[2].

[2]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.

[3]This is the primary analyte of concern when making a determination of whether a tank is SAFE. It is defined on a dry weight basis.

[4]This energy value is a conservatively derived number based on findings that 5% total organic carbon as sodium acetate which in actual experimental screening studies shows an energetics of 151 cal/g (dry weight basis). That information coupled with the fact that a sodium acetate concentration (e.g., dry sodium acetate equivalent to 5% total organic carbon) does not propagate in an excess of sodium nitrate and nitrite while 7% does; making the designated value of 125 cal/g used in the Screening DQO conservative. It is defined on a dry weight basis.

[5]The percent water is initially defined by TGA, as part of the Safety Screening DQO.

[6]Although this is the maximum temperature criteria for a tank to be considered SAFE, operating specification which control tank farm operations would require evaluation and probable corrective action if the temperature of a tank rose by 10 °F/month for no obvious reason. The present policy of monitoring tanks for changes in temperature is an important safety consideration because all Hanford Site SSTs are cooling as the fission products in the waste continues to decay.

[7]This is the temperature criteria for tanks that are considered CONDITIONALLY SAFE. It reflects a desire to prevent tanks (most of which have saturated salt wastes that boil at 120 °C) from drying out.

Table 6-2. Actions Resulting From a Comparison of Persulfate Total Organic Carbon, Differential Scanning Calorimetry Based Energetics and Historical Data*.

| Scenario | TOC (PS) | ΔH (DSC) | History | Oxidizer | Action(s) or conclusions |
|---|---|---|---|---|---|
| 1 | Low | Low | No | Yes | Remove from Watch List |
| 2 | Low | Low | Yes | Yes | Measure organic species (aging) |
| 3 | Low | High | Yes | Yes | Run furnace TOC |
| 4 | Low | Equal | No | Yes | Run adiabatic calorimetry |
| 5 | Low | High | No | ??? | Check for alternate oxidizers |
| 6 | Low | High | No | No | Check for alternate oxidizers |
| 7 | High | High | Yes | Yes | Put tank on Watch List classify based on water content |
| 8 | High | Low | Yes | ??? | Check for nitrate-nitrite concentrations |
| 9 | Equal | Equal | Yes | Yes | Measure organic species (aging) |
| 10. | Equal | Low | No | Yes | Rerun persulfate TOC on well homogenized samples, or run furnace TOC |

Low = Measured Value Below Organic Criteria

High = Value Above Organic Criteria

Equal = Value at or Near Organic Criteria

??? = No Information is Available or the information is uncertain.

TOC (PS) = Total Organic Carbon Measured By Persulfate Analysis. The options are High, Equal or Low.

ΔH (DSC) = Energy of Reaction measured by Differential Scanning Calorimetry. The options are High, Equal or Low.

History = Is there a record of transfer of appreciable organics to the subject tank? The options are Yes or No. A Yes implies a high energetics and/or TOC would have been found when the waste was transferred to the tank.

Oxidizer = Is the waste rich in nitrate and/or nitrite salts. This information is readily available from either historical or actual past tank sampling data. The options are: Yes, No or ???.

*This table deals only with inconsistencies between and within primary analytes and historical data. If results from determination of secondary analytes do not defensibly resolve the safety status of a potential organic Watch List tank, the tank will be placed on the Watch List. Furthermore, additional tests and if necessary requests for characterization data will be defined (in a separate test plan) to collect the data to resolve existing analytical ambiguities.

Table 6-3. Strategy for Establishing Weight of Consistent Evidence For Categorizing Tanks Containing Organics.

| Observations from Safety Screening DQO and TOC (Scenarios) | Confirmatory Step[1] | Concern[2] | General Notes |
|---|---|---|---|
| A. If the measured DSC energetics is 125 cal/g ± 20 cal/g (dry weight basis)<br><br>DSC value near the decision point | Run TOC (persulfate method) to confirm energetics<br><br>Run adiabatic calorimetry to bound the DSC value | False positive | Validates the accuracy of the energetics assay |
| B. If the energy equivalent (by calculation) of the TOC (Persulfate Method) is low by 25% of the measured energetics (based on a sodium acetate average energetics standard)<br><br>Standard TOC ≤ energetics | Run TOC by the furnace combustion method | False negative | Validates TOC by use of a supplementary TOC assay |
| C. If the energy equivalent of the TOC (persulfate method) is high by 25% of the measured energetics (based on a sodium acetate), analyze the subsegment for (the expected oxidant concentration and for hydroxide)<br><br>Standard TOC > energetics | 1. Run nitrite, nitrate, and hydroxide analysis<br><br>2. Verify speciation as a check for aging | False negative | Validates TOC by use of additional assays that confirm the quantity of oxidant present and the alkalinity of the sample |
| D. Energetics and TOC agree but historical records indicate a record of organic transfers<br><br>Standard TOC = energetics | Verify speciation as a check for aging | False negative due to inconsistent historical data | Validates both energetics and TOC by identifying the principal organic species in the sample |
| E. If the energy equivalent of the TOC assay (furnace combustion method) is low by 25% of the measured energetics (based on a Sodium Acetate standard), analyze the subsegment for the presence of alternate oxidants<br><br>Furnace oxidation TOC < energetics | Analyze the mixture for manganese and chromium, if they are present in sufficiently large quantities, determine the exact oxidizing species | False negative (The data is inconclusive to reach a decision) | Validates TOC by use of additional assays that confirm the quantity of alternate oxidants in the sample |

[1]See Tables 7-1 and 7-2 for details on the analytical requirements for organic Watch List tanks.
[2]A false positive occurs when a tank is unnecessarily added to the Watch List.

A false negative occurs when a tank is declared SAFE (e.g., not added to the Watch List) therefore not subject to operating controls when it was necessary to do so.

DQO = Data Quality Objective.
DSC = Differential Scanning Calorimetry.
TOC = Total Organic Carbon.

That is, if a tank on the organic Watch List has an energetics of less than 125 cal/g (dry weight basis) during testing in accordance with the Screening DQO, its place on that Watch List is suspect. In compliance with this Organic DQO, the samples would be tested to see if the measured TOC value is in general agreement with the observed energetics. (A general discussion of the relationship of TOC and energetics is found in the previous section of this document).

A review of source and transfer records would then be completed of that tank's history to ascertain whether the records show transfer of appreciable organic waste to that tank. If no transfer occurred, the waste in the tank can be classified as SAFE and removed from the Watch List. If the history reveals significant organic additions, confirmatory assays to identify residual organics would be required to validate the occurrence of waste aging (see Table 7-2).

### 6.2.3 Question 3

*Does a tank contain concentrations of reactive organic chemicals that are UNSAFE?*

#### Decision Logic

If a tank is not considered safe, a tank is either placed in a CONDITIONALLY SAFE or UNSAFE category. These categories are represented by the combined "Not Safe" category coined for the Tank Safety Screening DQO. This question is applicable both to tanks that are on the organic Watch List and to tanks identified for further analysis by the Safety Screening DQO.

If a tank is considered to be CONDITIONALLY SAFE, it will contain concentrations of organics above the "SAFE" limit but the presence of water (greater than 17 percent) and low waste temperature (less than 90 °C) would allow the waste to be safely stored. A tank that is CONDITIONALLY SAFE must be monitored in accordance with operational controls established by the Organic Safety Program. The interim safety criteria require the initiation of tank monitoring in compliance with operating specifications for such Watch List tanks. Such monitoring ensures that no adverse changes in water content or temperature occur during interim storage. (Note that temperature is considered a criteria secondary to water content in dealing with tanks such as those on the ferrocyanide and organic Watch List [Postma 1994].)

### 6.2.4 Question 4

*If a tank contains insufficient moisture, what characterization-based information is needed to support mitigation or remediation decisions?*

**Decision Logic**

The interim safety criteria require first the initiation of tank monitoring in compliance with operating specification for Watch List tanks. Then, WHC must implement near-term safety issue mitigation and/or remediation actions as technically feasible.

The Organic Safety Program is evaluating several alternative mitigation schemes that would allow re-establishment of a CONDITIONALLY SAFE level of moisture in a tank. These vary from the use of humidified air to the bulk addition of water to the tank. The latter is an option of last resort, as by agreement with the regulators DOE has agreed not to add water or wastes to SSTs (many of which are assumed leakers). A program to stabilize SSTs by removing all pumpable (drainable) fluid has been pursued for several years. Fortunately, the nature of the waste makes it difficult to completely remove moisture from either salt cake or sludge to the level of concern specified by the Organic Safety Program.

Temperature control, if needed, could be attained by chilled air or evaporative cooling. If needed, the water content could be maintained by a steady state addition of water using a mister or other sprinkler system.

Should mitigation not be successful or be deemed impractical, early retrieval of the wastes would be pursued. Unfortunately, the most expedient and only readily available means to remove the wastes is by sluicing them from the tank. This method may violate the DOE intent not to add water to SSTs. Details of information needs associated with retrieval of waste will be covered in a future DQO for retrieval of waste from Hanford Site waste tanks. Because no new SSTs are available for a transfer, compatibility issues related to mixing waste need to be addressed before such an action is implemented. Information associated with issues of retrieved waste compatibility with the materials presently stored in DSTs is found in the Compatibility DQO (Carothers 1994).

### 6.2.5 Decision Rules for Primary Concerns

If a tank shows a high energetics (e.g., $\geq$ 125 calories/gram, dry weight basis) that are due to the presence of organic chemicals (e.g., TOC > 5%), that tank will be added to the organic Watch List.

If the Watch List tank has a moisture content greater than 17%, then the tank will be treated as CONDITIONALLY SAFE and all necessary monitoring for moisture and temperature will be performed.

If the Watch List tank has a moisture content less than 17%, then the tank will be treated as UNSAFE and appropriate mitigation or remediation will be pursued.

### 6.2.6 Supporting Decision Logic

As discussed in Sections 6.1.1 through 6.1.4, and as illustrated in Figure 6-1, four endpoints are possible as a result of characterization data obtained from the Organic DQO. (1) Place a tank on the organic Watch List; (2) remove a tank from the organic Watch List; (3) monitor and control a CONDITIONALLY SAFE tank; or (4) mitigate or remediate an UNSAFE tank. Table 6-1 has presented the decision criteria for placing a tank on the organic Watch List.

Table 6-2 supports the decisions associated with Figure 6-1 and Table 6-1 by identifying possible outcomes and related actions to be taken to meet the four endpoints of this DQO. Table 6-2 also identifies additional outcomes and associated confirmatory assays that are required to support the endpoints. Table 6-3 provides a summary description of the manner in which the outcomes support the questions and endpoints of the DQO.

Outcome 1 supports questions 2 and 3 in terms of the endpoint associated with removal of a tank from the organic Watch List.

Outcome 7 supports questions 2, 3, and 4 in terms of the endpoints associated with both removal of a tank from the organic Watch List and the identification of monitoring and control or mitigation or remediation actions based on moisture content.

Outcomes 2, 3, 8, and 9 support question 1 and the endpoint of ensuring that a tank is not added to the organic Watch List when the tank is not on the organic Watch List and received organic waste as determined from historical information.

Outcomes 4, 5, 6, and 10 support questions 2, 3, and 4 in terms of confirmatory assays required to meet the endpoints associated with removing a tank from the organic Watch List and the monitoring and control required for a CONDITIONALLY SAFE tank.

The ten outcomes are transformed to five key scenarios that result from safety screening that supports tank safety classification. The objective of developing these scenarios is to reduce the number of false positives and false negatives by performing secondary analyses to establish the weight of consistent evidence so that tanks are properly classified.

**Scenario A.** If energetics, as measured by DSC, is close to 125 cal/g, then run adiabatic calorimetry to confirm the energetics value. In parallel, TOC is examined using the persulfate method to define the organic carbon content since TOC is the primary determinant for an organic Watch List tank.

The concern under this scenario is calling a tank Watch List when it is really SAFE, i.e., committing a false positive error. These measurements, including the assessment of the history of tank fills and transfers, will establish that the energetics and the TOC agree. This means that a tank can then be called SAFE.

**Scenario B.** If the energy equivalent of persulfate-oxidation based TOC, determined by calculation, is low by more than 25% of the measured energetics, verify TOC content by furnace method*.

The concern under this scenario is that the energetics based on persulfate TOC measurement gives an artificially low value. This means that a high organic tank would not be placed on the Watch List. Thus, a Watch List tank would be called SAFE (i.e., false negative).

**Scenario C.** If the energy equivalent by TOC (using the persulfate method) reports 25% or more TOC energy equivalent than expected using a sodium acetate basis, it is necessary to determine if sufficient oxidizers are present. If the oxidizers are present, this indicates aging. If not, then there is insufficient oxidizer to complete the reaction.

The concern under this scenario is that TOC is predicting more energetics than measured by DSC, so the tank might be labeled SAFE when it really belongs on a Watch List, namely we would commit a false negative error. Confirming the energetics value is correct results in showing that there are either insufficient oxidizers present or that aging has occurred or both.

**Scenario D.** The energetics and the TOC are low and agree, but historical records indicate significant organic transfers. Verification of aging is then required. Energetics are observed slightly below 125 cal/g.

The concern under this scenario is that results to date are not accounting for the significant amount of organics believed to be present, so the tank might be labeled SAFE when it is

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*Note that the scenarios can be rewritten into secondary decision rules. For example, Scenario B becomes:

- If the energy equivalent by TOC (persulfate method) is low by 25% of the measured energetics (sodium acetate), then run TOC by furnace combustion method. Energetics are observed slightly above 125 cal/g.
- If the TOC by furnace combustion method is below 5% wt, dry basis, then the tank is SAFE.
- If the TOC by furnace combustion method is at or above 5% wt, dry basis, then the tank is a CONDITIONALLY SAFE or UNSAFE, depending on the moisture content of the tank contents.

really a Watch List tank (false negative). Confirming that the expected elevated organics have aged to less energetic species. Therefore, the tank is really SAFE in spite of historical fill and transfer records.

Scenario E. If the energy equivalent by TOC using the furnace method reports TOC values low by more than 25% (based on sodium acetate), determine the presence of Mn or Cr. Energetics are observed slightly above 125 cal/g.

The concern under this scenario is that TOC results are showing an insufficient amount of nitrate/nitrite oxidants to support the elevated energetics, so the tank might be placed on a Watch List when it is really SAFE (false negative). Confirming that there are no elevated levels of Mn or Cr will support the conclusion that there are insufficient oxidants present to support an exothermic reaction. Therefore, the data is inconclusive, and the energetics measurements must be re-evaluated or rerun.

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# 7.0 DQO STEP 7: SAMPLING AND ANALYSIS DESIGN OPTIONS

Current knowledge strongly suggests that a tank may have a wide range of vertical heterogeneity (even within segments of a core sample), and that to meet the analytical requirement to have a sufficient sample to complete the required analyses a compromise has been established on how frequently to sample and homogenize vertical samples. These compromises are presented in the third column of Tables 7-1 and 7-2. The listed analytical requirements (Tables 7-1 and 7-2) support resolution of the Organic Safety Issue.

Details of the optimization steps of the DQO process will be performed when each individual tank characterization plan is prepared or when a waste laydown model to describe tank heterogeneity becomes available. Specifically, the type of sampling procedure and number of samples will be based on the individual tank contents. For example, a tank that has hard salt cake will require a different sampling procedure than a tank with liquid. The number of samples will be determined by the expected heterogeneity of the tank contents, which is established initially by prior sampling and historical fill and transfer information.

Efforts are underway to group tanks based on the problem requiring attention (e.g., safety, pretreatment, retrieval, disposal). It is anticipated that each of the problem areas will have its own basis for grouping tanks. This grouping is intended to simplify the number of samples needed to characterize tank contents. The theory behind grouping is that, if tanks with similar laydown patterns and chemical composition can be grouped, then collecting numerous samples from the first tanks in the group can result in a reduced number of samples in those later tanks from the group (if the sampling results match what is expected). The Safety Screening DQO contains a brief write-up on this approach to tank grouping (Babad and Redus 1994) that will form the initial basis of tank laydown modeling.

Table 7-1. Analytical Requirements for Organic Watch List Tanks - Primary Analytes.

| Analyte to be measured | Analytical method | Sample[1] | Decision threshold | Assumed (desired) analytical uncertainty[2] |
|---|---|---|---|---|
| Total organic carbon | Combined solids/entrained liquid sample direct persulfate oxidation[3] | Homogenized Half Segment Using Duplicate Samples. If one of the pair of duplicates exceeds limit, another pair of duplicates should be run | >5 wt% (dry basis)<br><br>PRIMARY SAFETY ANALYTE | ± 10% of decision threshold<br><br>PQL=1% |
| Moisture content in half segment (obtained during screening Data Quality Objective) | Thermogravimetric analysis | Half Segment Using Duplicate Samples. If none of the pair of duplicates exceed limit, another pair of duplicates should be run | <17% wt. | ± 10% of decision threshold<br><br>PQL=2% |

Table 7-1. Analytical Requirements for Organic Watch List Tanks - Primary Analytes.

| Analyte to be measured | Analytical method | Sample[1] | Decision threshold | Assumed (desired) analytical uncertainty[2] |
|---|---|---|---|---|
| Presence of organic floating layer[4] | Visual observation | Top two segments only (by half segment) unless free organics drain from the sample into liquid layer; duplicate sample not required | N/A | N/A |
| Tank temperature (not a laboratory characterization measurement) | Thermocouple or RSTs | N/A | (90 °C) This temperature limit applies only to CONDITIONALLY SAFE tanks | Estimated error assumed to be ± 4 °F |
| Total fuel content (obtained during screening Data Quality Objective) | Differential scanning calorimetry or adiabatic calorimetry[5] | Homogenized half segment using duplicate samples. If None of the pair of duplicates exceeds limit, another pair of duplicates should be run | To be converted to total organic carbon concentration (wt% dry basis) | ± 10% of decision threshold<br><br>PQL= Not known |

[1]If a half segment contains appreciable free drainable liquid run the assays on that liquid.
A Thermogravimetric Analysis analysis should be made on the liquid sample. The sample should be (a) tested for volatiles other then water, vacuum dried, and the remaining assays run on the dry solid.

Half-segments were selected using engineering judgment, on the basis of the likely laydown pattern of organics in waste as discussed in Section 2.0.

[2]This analytical uncertainty is derived using engineering judgment of the engineers and analytical chemists who participated in this DQO.

[3]The furnace based assay to be done, if necessary as explained in narratives and Table 6-2. The furnace oxidation method should be used as a back-up to resolve analytical uncertainties.

[4]The intent of this test is to determine whether there is a drainable organic liquid present in the waste. The presence of solvents in the tank would be detected by vapor space sampling, which is the subject of another DQO. Although not directly related to fuel-oxidizer reactions the presence of a free organic layer would trigger an additional safety assessment to determine whether conditions exist in which the organic layer could support a fuel fire or contribute to vapor flammability concerns. These conditions have been discussed in the C-103 related Data Quality Objectives on liquid (Wood 1993) and vapor analyses (Osborne 1994).

[5]The adiabatic calorimetry method is only used when the DSC result is 125 ± 20 cal/gram dry weight basis.

Table 7-2. Analytical Requirements for Organic Watch List Tanks - Secondary Analytes (See Table 6-2 for Road Map on Secondary Analyte Use).

| Analyte to be measured | Analytical method | Sample[1] | Decision threshold | Assumed (desired) analytical uncertainty[2] |
|---|---|---|---|---|
| Total moisture analysis (back up method[3]) | Gravimetric analysis (oven technique) | Homogenized selected half segment using duplicate samples | 17% wt. | ± 10% of decision threshold<br><br>PQL = 2 |
| Principal organic species | GC/MS add/or derivatization GC/MS[4], and HPLC for low molecular weight organic acids[4] | Homogenized selected half segment using duplicate samples | Not specified | Detection limit of 3% by weight with an absolute error of 10% of sample mass for any single constituent |
| Equilibrium moisture content | Measurement of moisture loss as a function of relative humidity[4,6] | Homogenized selected half segments using duplicate samples | Not specified | Not specified |
| $^{137}Cs$ | Gamma energy analysis-water digestion and fusion | Homogenized selected half segment using duplicate samples | 40,000 BTU (equivalent of 1,000 micro curies/gram) | ± 10% of decision threshold<br><br>PQL = 100 micro curies/gram[5] |
| Chromium and manganese oxidation state | Some oxidation state determination methods need to be developed | Homogenized selected half segments using duplicate samples | Not specified | Not specified[7,8] |
| Chromium and manganese concentration | ICP/AES Methods | Homogenized selected half segment using duplicate samples | Are these species calculated as oxides >5% of dry sludge? | Not specified[7] |
| Nitrite and nitrate concentration | HPLC or equivalent | Homogenized selected half segment using duplicate samples | None specified | Not specified[7] |
| Hydroxide concentration | Acid-base titrimetry | Homogenized selected half segment using duplicate samples | None specified | |

Table 7-2. Analytical Requirements for Organic Watch List Tanks - Secondary Analytes (See Table 6-2 for Road Map on Secondary Analyte Use).

| Analyte to be measured | Analytical method | Sample[1] | Decision threshold | Assumed (desired) analytical uncertainty[2] |
|---|---|---|---|---|
| $^{90}Sr$ | Beta radiochemistry | Homogenized selected half segment using duplicate samples | 40,000 BTU (equivalent of 1,000 micro curies/g) | ± 10% of decision threshold<br>PQL = 100 micro curies/g [5] |

[1]If a half segment contains appreciable free drainable liquid run the assays on that liquid. A Thermogravimetric Analysis analysis should be made on the liquid sample. The sample should be (a) tested for volatiles other then water, vacuum dried, and the remaining assays run on the dry solid.

Half-segments were selected using engineering judgment, on the basis of the likely laydown pattern of organics in waste as discussed in Section 2.0.

[2]This analytical uncertainty is derived using engineering judgment of the engineers and analytical chemists who participated in this DQO.

[3]Assay to be used too verify the moisture content of the sample, if the value measured by total organic carbon lies within a 17 ± 2% moisture specification.

[4]Analytical methods under development.

[5]The purpose of this measurement is to support thermal modeling of the tanks that remain on the organic Watch List.

[6]This analysis will determine the resistance to drying of the tested waste. It is key to assuring CONDITIONAL SAFETY during interim waste storage.

[7]The purpose of this assay is to determine the approximate concentration and nature of the oxidizers present in the sample, and their alkaline environment.

The accuracy desired for this assay should allow the laboratory to detect differences of 0.3 to 0.5 mole/L of sodium hydroxide in the waste.

[8]It should be noted that concentrations of permanganate in the waste are considered very unlikely because this chemical is not stable in either alkali or water for the extended period of time that the waste has been stored in the tank.

Another, perhaps simpler way of dealing with the variables associated with data uncertainty is tabulated in Table 6-2. This table simplifies identifying the actions to be taken when comparison of characterization and historical data shows inconsistency.

GC/MS = gas chromratography/mas spectrometry.
ICP = inductively coupled plasma.

# 8.0 SUMMARY

A tank is put on the organics Watch List if its energetics as measured by differential scanning calorimetry shows values ≥ 125 cal/g, (dry weight and its total organic carbon is about 5 weight per cent dry weight basis). There are other important factors, discussed in this Organics DQO, that if present would either keep a tank off the organics Watch List or determine whether it should be treated as CONDITIONALLY SAFE or UNSAFE. Each of these factors are discussed in Section 3.0, with the logic and decision rule presented. Following the contents of this organics DQO will result in completion of the first five steps of the DQO Process. The remaining two steps dealing with decision errors and sampling and analysis optimization should be addressed, where possible, on a tank specific sampling and analysis event basis. These last two steps are covered in each tank's Tank Characterization Plan.

There are five scenarios that need to be considered in addressing tanks that are either already on the organics Watch List or are considered serious candidates. A strategy for establishing consistent evidence for categorizing tanks containing organics has been presented.

Details associated with the optimization of the sampling and analysis design need to wait until a specific tank sampling event is to be performed. The unique nature of the tank contents makes it inappropriate to quantify (at this time) decision errors. This will impact the determination of the number of samples required. When individual tank characterization plans are prepared, this detail can be carried out on a tank specific basis. Efforts underway now on grouping tanks by problem to be resolved and physical/chemical nature of the contents will assist in defining the number of samples required.

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WHC-SD-WM-DQO-006, Rev. 1

ATTACHMENT 1

**WHC-SD-WM-DQO-006, Rev. 1**
**DATA QUALITY OBJECTIVES FOR RESOLUTION OF THE ORGANIC NITRATE/NITRITE SAFETY ISSUE**

Consisting of 40 pages,
including cover page

## INTRODUCTION

Any strategy describing the overall approach to safe storage and disposal of waste must identify the problems and decisions requiring characterization data. Requirements for obtaining tank characterization information are developed through the use of the Data Quality Objectives (DQO) Process. The DQO Process addresses each decision or group of related decisions to specify data needs.

The initial attempt at performing the DQO Process to address safety issues revealed points where significant assumptions would be required to proceed. Although the problems and decisions were identified, details of the error tolerances and confidence levels were difficult to develop. Attempts to optimize the data collection for each tank were affected by the limited locations from which samples could be obtained and concerns that samples did not represent overall waste contents. The complexity of sampling made it impossible to design a high-confidence data acquisition scheme based solely on multiple samples, and necessitated review of the overall strategy for obtaining data and resolving issues.

A revised safety strategy was developed for the storage of tank waste, focused on ensuring safe operations over a range of waste materials rather than on characterizing waste in great detail. The revised safety strategy includes several assumptions about the nature of the waste which require verification through additional sample analysis. Should these assumptions be shown to be well founded, the approach to screening the waste for safety issues and resolving those issues is considerably simplified. The following draft of the data requirements, based on the revised safety strategy, has been prepared.

Clearly any assumptions must be addressed before proceeding with the revised safety strategy. The preceding minor revisions to the baseline DQO document were found to be adequate to perform safety analyses in the near term, while specific additional information needs are pursued to verify the assumptions in the revised safety strategy. In addition to resolving the assumptions, the near-term sampling events will obtain information that will support the determination of error tolerances, confidence levels, and optimization schemes in the finalized version of the revised safety strategy DQO. The approach taken in the revised baseline DQO document, simply requesting multiple samples per tank, is the appropriate first step to finalizing the optimization requirements.

The DQO Process is iterative in nature. It is anticipated that the data collected in the near term, based on the revised baseline DQO document, will provide the added information needed to provide complete DQO requirements for longer term characterization. As such, the following revised safety strategy DQO may continue to undergo further development and revision as this added information becomes available. At the appropriate time after the revised safety strategy DQO is completed, the necessary reviews and approvals will be conducted and the document will become the new baseline.

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# DATA QUALITY OBJECTIVES FOR RESOLUTION OF THE ORGANIC NITRATE/NITRITE SAFETY ISSUE

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## EXECUTIVE SUMMARY

This document records the organic nitrate/nitrite Data Quality Objective (DQO) Process which will be used to assist in determining the potential for an unwanted propagating organic nitrate/nitrite reaction in single-shell tanks for fuel/moisture concentrations, given an initiator. The document includes decision statements used to define if a situation is present with the potential to initiate a propagating reaction in the waste tanks. In addition, many of the decision inputs (process knowledge, data, and boundaries) needed to address the decision are briefly described.

The recommended number of core samples is discussed in Section 7.0 of this report. The primary consideration for defining sampling requirements is the desired level of protection from making incorrect decisions, and the expected spatial, sampling, and analytical variations.

The recommendations and decision presented in this report will be used to develop tank-specific characterization plans for the organic nitrate/nitrite Watch List tanks. All available sources of characterization information will be studied to create the most efficient tank characterization plans. To fully optimize the DQO Process, the DQO outlined in this report needs to be applied to each of the Hanford Site organic tanks on an individual basis. Tank-specific optimization of the DQO Process will not be performed in this report but will be included in the tank characterization plans. This report is a living document, and the assumptions contained within will be refined as more data from reports, verification of models, and characterization become available.

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# CONTENTS

## LIST OF FIGURES



## LIST OF TABLES

# DATA QUALITY OBJECTIVES FOR RESOLUTION OF THE ORGANIC NITRATE/NITRITE SAFETY ISSUE

## 1.0 INTRODUCTION

### 1.1 PURPOSE OF DATA QUALITY OBJECTIVE (DQO) PROCESS

The DQO Process was developed by the U.S. Environmental Protection Agency (EPA 1993) to provide decision makers with a tool for determining data requirements and their acceptable levels of confidence before sampling occurs. This process assists in documenting the procedure used to determine the data needs, making the request for data more defensible. The DQO Process can be applied to problems involving the collection and use of data and has been extended to the different issues associated with Hanford Site tank waste. The DQO Process helps identify and define the type, quantity, and quality of data required. The process consists of seven steps:

- Step 1: State the problem
- Step 2: Identify the decision
- Step 3: Identify the inputs to the decision
- Step 4: Define the study boundaries
- Step 5: Develop a decision rule
- Step 6: Specify acceptable limits on decision errors
- Step 7: Optimize the design.

A more detailed description of what each step entails is provided in the Appendix.

This DQO Process applies to the safety issue related to the organic nitrate/nitrite fuel content in the waste tanks.

### 1.2 SCOPE OF ORGANIC NITRATE/NITRITE DQO PROCESS

The primary scope of the organic nitrate/nitrite DQO Process is to assist in determining the potential for an unwanted propagating organic nitrate/ nitrite reaction in single-shell tanks for fuel/moisture concentration, given an initiator. The organic DQO Process helps to determine what data, if any, may be required to categorize the waste in each of the single-shell tanks as "safe" or "unsafe." Using safety categories permits the use of a waste management approach to ensure that the hazard is controlled. At one extreme (safe), where waste is nonreactive through inherent properties (e.g., low fuel content, low oxidizer content, high retained moisture), no fuel nitrate/ nitrite, hazard-related monitoring or controls would be required. At the other (unsafe) end, reactive waste (if any exists) would require mitigative actions. Some waste in the unsafe category will require a set of waste management approaches ranging from monitoring to active controls applied to ensure that fuel nitrate/nitrite hazards are controlled.

### 1.3 STATEMENT OF PROBLEM

The primary safety objective in this process is to maintain the fuel nitrate/nitrite waste in a state that prevents chemical reactions. The result of that reaction may be one of the following:

1. Radiation doses or toxic exposure either onsite or offsite more than the applicable limits or guidelines stated in WHC-SD-WM-ISB-001, *Hanford Site Tank Farm Facilities Interim Safety Basis*, Chapter 2 (Sherwood 1994)

2. Damage to the structure of the tank so as to compromise its ability to store waste safely.

This primary safety objective can be met by imposing a more stringent secondary objective that no sustainable, rapid, exothermic fuel nitrate/nitrite reaction can be possible. A sustainable reaction is one that generates heat faster than it can be removed by conduction; it excludes the slow aging (degradation) reactions believed to be occurring over a period of years.

## 2.0 ORGANIC NITRATE/NITRITE SAFETY PROGRAM BACKGROUND

Radioactive waste from defense operations has been accumulating in underground waste tanks at the Hanford Site since the early 1940's. There are 177 waste tanks: 149 single-shell tanks and 28 double-shell tanks. Over the years, waste has been systematically disposed of among the various tanks. In this process, the two primary objectives were to segregate different types of waste and to reduce the need for additional tanks by concentrating the waste. In addition to the fission products created by the processing of irradiated fuel, the major constituents of the waste are sodium nitrate; sodium nitrite; metal silicates; aluminates; hydroxides, phosphates, sulfates, carbonates of iron, calcium, and other metals; a variety of organic materials; ferrocyanide; and uranium salts.

The presence of organic chemicals in the Hanford Site waste tanks became an issue needing reevaluation when information became available on the deflagration of a waste tank on September 29, 1957 in Kyshtym, Union of Soviet Socialist Republics (Fisher 1990). This event occurred because cooling was disrupted, the aqueous salts evaporated to dryness, and the mixture of oxidizing salts and organic chemical waste self-heated to reaction temperature. The constituents in the tank that caused this incident were sodium nitrate and sodium nitrite mixed with sodium acetate.

The potential for reactions of nitrate with organic constituents stored in Hanford Site waste tanks has been studied. For example, a paper published in April 1976 described some combustion screening studies with sodium nitrate (Beitel 1976). However, in keeping with the concerns at that time, this work was directed toward the oxidative power of sodium nitrate rather than the reactivity of specific organic tank waste chemicals.

A screening study was conducted at the Hanford Site in 1989 (Fisher 1990). Twenty-six tests were performed to study the reactivity of mixtures containing various proportions of sodium acetate, sodium nitrate/sodium nitrite, and diluents. The results were used to define an upper limit for organic carbon constituents in the waste. The limit was defined as 10 wt% organic calculated as sodium acetate on a dry basis. This corresponds to 3 wt% total organic carbon (TOC) on a dry basis. This figure represents the original Waste Tank Organic Safety Program safety criterion. This safety criterion was updated in 1993 based on the results of a limited laboratory test program (Babad and Turner 1993).

In the minimally intrusive waste moisture measurement, an attempt is made to demonstrate continued safe interim waste storage by verifying that the moisture content of the waste solids situated within approximately 14 cm of the surface is >-20 wt%, and will remain at this level for a period of 50 years. The rationale is as follows:

- The safety concern is focused on waste solids situated near the surface. External accident initiators (energy sources capable of heating a small quantity of waste in its reaction initiation temperature and thereby initiating a propagating chemical reaction) are most likely to be encountered at the waste surface. Credible initiators deep in the waste are very unlikely and thus not risk significant.

- A 14 cm depth is specified because credible external accident initiators are shown by analysis to be incapable of adversely affecting waste conditions beyond this depth in a reasonable period of time (approximately 1 hour).

- A limiting waste moisture content of 20 wt% is specified. For a waste matrix aqueous interstitial liquid in equilibrium with precipitated solids (sludge or salt cake), where sodium nitrate is the predominant chemical species in solution, liquid becomes the continuous phase at a moisture content of about 20 wt%. Condensed-phase propagating chemical reactions are physically impossible under this condition. This observation is verified by laboratory test results (FAI 1995).

The 28 double-shell tanks are considered well ventilated, contain large amounts of water (>20% moisture), and are more heavily instrumented; therefore, they will not be addressed in this DQO.

Public Law 101-510, Section 3137, "Safety Measures for Waste Tanks at Hanford Nuclear Reservation," required the U.S. Department of Energy to identify Hanford Site radioactive waste storage tanks with the potential for release of high-level waste resulting from uncontrolled increases in temperature or pressure, and to develop plans to resolve the associated safety issues. These tanks, designated Watch List tanks, are identified in (Hanlon 1995). At the present time, 20 single-shell tanks are included on the Watch List because they are believed to contain relatively high concentrations of organic chemicals (Payne 1994).

# 3.0 KEY DECISIONS

This section completes the second step of the DQO Process: identify the decisions. The five primary decisions listed in this section require information to answer part of the Problem Statement: Is there a situation present with the potential to initiate a propagating reaction in the waste tanks? The five decisions to be addressed, and a discussion on each, are as follows.

1. Is the moisture concentration high enough to prevent an unwanted propagating reaction?

2. Is the fuel concentration low enough to prevent an unwanted propagating reaction?

3. Does the tank waste have the potential to bulk heat to reaction initiation temperature?

4. Is there a potential point source initiator?

5. Does interim stabilization of the tank pose a risk of creating a propagating reaction condition?

1-2. Is the moisture concentration high enough or the fuel concentration low enough to prevent an unwanted propagating reaction?

Two types of experimental apparatus, an adiabatic calorimeter and a propagation tube, were used to explore the potential for propagation reactions in waste surrogate. The results of these experiments suggest a criterion for the combination of fuel and moisture defined the propagation boundary. The criterion line is: % TOC = 4.5 + 0.17 (% $H_2O$) % $H_2O$ <20, where % TOC and % $H_2O$ are the wet basis TOC and moisture percent, respectively, and no propagating reaction can take place when % $H_2O$ >20.

The criterion line was chosen simply because it bounds data obtained with the most energetic proposed mixture, it is independent of actual waste energy, and there is unquestionably additional margin due to well-known waste degradation process.

3. Does the tank waste have the potential to bulk heat to reaction initiation temperature?

This scenario will explore if bulk heating to reaction initiation temperature is possible if there is sufficient radioactive decay heat load (>32,000 Btu/h) in a tank that the waste temperature could increase from its current temperature to a temperature (around 180 °C) where heat from the chemical reaction between organics and nitrate (Arrhenius-type reaction) starts to contribute significantly to the total heat being generated in the tank. The initial temperature increase must happen because of a loss of cooling (i.e., Once the chemical heat starts kicking-in, the temperature goes up which accelerates the chemical reactions, making more heat and the tank runs away (thermally). This runaway reaction generates reaction gases and heat. If the heat and gas production rate is large enough, the tank can be overpressurized and the tank could collapse.

4. Is there a potential point source initiator?

   The reaction initiation evaluation consists of reviewing tank farm operations and operational upsets for the potential to heat even a small portion of reactive waste to reaction initiation temperatures. The evaluation will identify operations that may need to be controlled to eliminate ignition sources if the waste contained in the tank is sufficiently dry and rich in fuel to support a propagating reaction.

5. Does interim stabilization of the tank pose a risk of creating a propagating reaction condition?

   Interim stabilization refers to the removal of supernatant liquid and the bulk of drainable interstitial liquid from the waste solids present in the tank. The carbon steel liners of a number of single-shell tanks have failed, and radioactive liquid waste has been inadvertently discharged to the soil column beneath the tanks. The liners of other tanks can be expected to fail in the future. As a result, efforts are in progress to remove supernatant and the bulk of drainable interstitial liquids from the tanks at the earliest possible date. Interim stabilization milestones are identified in the *Hanford Federal Facility Agreement and Consent Order* (Ecology et al. 1994).

   Interim stabilization of organic Watch List tanks must be assessed relative to a number of potential safety issues (refer to Table 3-1) because interim stabilization materially alters the physical (and possibly the chemical) configuration of the waste. As shown in Table 3-1, three potential safety issues need to be addressed.

   Condensed-phase propagating chemical reactions might occur if the organic chemicals in the tanks, admixed with sodium nitrate/nitrite salts, are dried and heated to approximately 200 °C. The heat and pressure associated with the resultant deflagration could conceivably compromise tank integrity and release radioactive material to the environment. Safety criteria to prevent condensed-phase propagating chemical reactions have been issued (Fisher 1990; Babad and Turner 1993). Updated criteria have recently been issued (Webb et al. 1995).

Table 3-1. Waste Tank Organic Safety Program Safety Issues.

| Potential hazard | Phenomneology | Organic chemicals of concern | Safety issue |
|---|---|---|---|
| Condensed-phase propagating chemical reaction | Nonvolatile organic nitrate/ nitrite mixtures, if dry and heated to ≈200°C, could deflagrate | Complexants (salt cake) | Deflagration in dry salt cake waste caused by external initiator |
| Vapor phase combustion | Semivolatile organics, if heated to their flashpoint, could ignite and burn | Process solvents (immiscible, floating organic layer) | Pool fire caused by external initiator |
| Vapor phase combustion followed by condensed-phase propagating chemical reaction | Semivolatile organics, if heated to their flashpoint, could ignite and burn | Process solvents (entrained in salt cake) | Wick-stabilized fire caused by external initiator<br><br>Deflagration caused by heat from wick stabilization |

A floating, immiscible organic layer (such as that present in tank 241-C-103) might ignite and burn if heated to its flashpoint (≈119°C). The heat and pressure associated with the resultant "pool fire" could conceivably compromise tank integrity and release radioactive material to the environment. A safety analysis for the tank 241-C-103 pool fire scenario has been issued as WHC-SD-WM-SARR-001, *Safety Analysis of Exothermic Reaction Hazards Associated with the Organic Liquid Layer in Tank 241-C-103* (Postma et al. 1994). A key conclusion of the safety analysis is that the organic pool would be difficult to ignite, requiring about 1.2 MJ of energy.

A floating, immiscible organic layer might become entrained in waste solids if it comes into intimate contact with the solids during interim stabilization pumping operations. The safety concern is that the organic might be ignited more readily in this configuration, requiring perhaps only 1,000 J of energy to create a wick-stabilized flame. The fire might then spread from this point to engulf a major portion of the waste surface. The heat and pressure associated with the fire could conceivably compromise tank integrity and release radioactive material to the environment. A safety analysis that addresses the potential hazard of organic entrained in waste solids (sludge and salt cake) is to be completed in September 1995.

These three safety issues must be assessed to ensure that, following interim stabilization, controls are in place to ensure continued safe interim waste storage.

# 4.0 DECISION INPUTS

## 4.1 INPUTS REQUIRED TO RESOLVE DECISION

This section completes the third section of the DQO Process: identify inputs to the decision. The decision inputs that are needed to make the decision are summarized in Table 4-1.

The decisions that form the basis of the organic nitrate/nitrite DQO are outlined in Section 3.0. Decision inputs consist of the information or data that are needed to make the decision. At this point, it is important to distinguish the difference between decision inputs and sample measurements. Decision inputs may consist of any piece of information or data that can help make the decision. It does not necessarily need to be from sampling and analysis. In Table 4-1, the decision input is listed along with the reason the decision input is needed. Each of the decision inputs listed are connected to one of the five decisions listed in Section 3.0. These decisions are also summarized in the first column of Table 4-1 for each of the decision inputs. The limits for the decision inputs are summarized in Section 6.0.

## 4.2 POTENTIAL SOURCES OF DECISION INPUTS

It has been stressed throughout this DQO Process that decision input sources need not consider only sampling and analysis. The characterization program has access to many other sources of characterization information other than future sampling and analysis work. These other sources are listed throughout the rest of this section.

To optimize the DQO Process such that all resources have been considered and that the cost of characterization is truly reduced, the DQO Process needs to consider available data before it considers sampling and analysis. Sources of data other than from sampling and analysis (i.e., process knowledge) need to be validated before they are acceptable for use as input sources. Validation of process knowledge in this context implies that it will be a "qualitative" decision always subject to interpretation.

Table 4-2 lists possible sources of characterization information and data that need to be considered in the organic nitrate/nitrite DQO. This table lists input sources for each of the decision inputs within the scope of this DQO. Only the known input sources are listed. If another input source of any decision input is discovered, it can be added to the list.

The possible input sources listed in Table 4-2 actually come from several characterization information and data sources. These sources will be covered throughout the rest of this section.

There are several sources of previous sampling information. Liquid (and some solid) samples were taken in the early 1970's. A limited amount of core sampling has been done since the early 1980's. Recently, extensive core samples, as well as supernate and auger samples, have been taken. While there are many sources of previous sampling results, all sources known to the characterization program have been collected in the Tank Characterization

Table 4-1. Summary of Decision Inputs.

| Decision input | Decision | Reason for requesting decision input |
|---|---|---|
| Temperature | 1, 2, 3, 4, and 5 | Waste temperature control and monitoring are important in the assurance of safety for organic nitrate/nitrite reaction. |
| wt % water | 1, 2, 3, 4, and 5 | A high moisture content indicates that the tank is safe for storage. |
| Fuel | 1, 2, 3, 4, and 5 | Low fuel content indicates that the tank is safe for storage. |
| Interim stabilization status | 1, 2, 3, 4, and 5 | Interim stabilization materially alters the physical and configuration of the waste. |

Table 4-2. Possible Decision Input Sources.

| Decision input | Possible input sources |
|---|---|
| Temperature | • Thermocouple trees<br>• Psychrometer measurements<br>• Active/passive ventilation |
| Moisture | • Process knowledge<br>• Field monitoring<br>• Tank photos/video<br>• PNL TOC/moisture statistical model<br>• Confirmed with gravimetric analysis if close to decision point |
| Fuel | • Process knowledge<br>• Tank photos/video<br>• Surrogate/stimulant data<br>• PNL TOC/moisture statistical data<br>• Fuel value, surface sample if close to decision point |
| Interim stabilization | • Process knowledge of fuel content |

PNL = Pacific Northwest Laboratory
TOC = Total organic carbon

Resource Center. A listing of these samples may be found in Sathyanarayana (1994). Other useful sources of previous sampling information include the Tank Characterization Reports, and the Supporting Documents for the Historical Tank Content Estimate Reports (Brevick 1994a, 1994b, and 1995). Note that previous sampling data do not generally have the same quality assurance requirements as current laboratory data.

The next source listed is tank grouping models. Currently, tank grouping models (Pacific Northwest Laboratory TOC/moisture statistical data) are being developed but none have been completed. A tank grouping model is a model that groups tanks of similar waste type together. This will provide an effective characterization tool because tanks that are in the same group as another tank that has been well characterized may require less sampling. Other sources of historical model estimates include the Historical Tank Content Estimate Reports (Brevick 1994a, 1994b, and 1995), the Waste Status and Transaction Record Summaries (Agnew 1994a, 1994b, 1994c, and 1995) and the Hanford Defined Waste document (Agnew 1994d). Again, for these models to be of use as input sources, validation of the models is necessary. Without validation, these models can be used as support of sampling data.

Surveillance data used to provide inputs for the organic nitrate/ nitrite DQO Process consist of thermocouple data from the solids layers of the tank and photographs of the waste surface. This information can be obtained from the Tank Waste Remediation Systems surveillance group. These data have also been summarized in the Historical Tank Content Estimate Reports (Brevick 1994a, 1994b, and 1995). Surveillance information may not be valid if transfer activity has occurred since the time of surveillance. This needs to be checked before surveillance information is used.

After all other characterization sources have been considered, sampling plans will be made if information is still missing.

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# 5.0 DECISION BOUNDARIES

Data collection design must incorporate the area or "population" of the study and the time period in which data must be collected or time frame in which the data can be used to make the decision. These decision boundaries need to be identified before data collection to help ensure that the data are timely and representative for decision-making purposes.

The organic fuel DQO requires that temporal and tank population boundaries be defined for sample prioritization and interior tank sampling boundaries be established before sampling activities.

## 5.1 SPATIAL AND TEMPORAL BOUNDARIES FOR TANK SAMPLING PRIORITIZATION

Tank sampling prioritization will be scheduled based on a review of the tank process record inventory and interim stabilization schedule. The removal of liquids from tanks for the purpose of interim stabilization may create an unsafe condition in single-shell tanks that contain salt cake and organic fuels. These tanks will receive a high-priority listing. Tanks that may have received organic fuels will be evaluated to determine if sampling should be required before interim stabilization activities. Tanks that have the potential to become unsafe if pumped for interim stabilization will be removed from the interim stabilization schedule.

Tank populations need to be sorted using process knowledge and existing data to separate tanks into one of the following categories:

- Tanks that have received organic fuels
- Tanks that have low moisture content
- Tanks that are classified as "high-heat" tanks.

## 5.2 SPATIAL BOUNDARIES AND CONSTRAINTS FOR INDIVIDUAL TANKS

The sampling of each tank for organic fuel content and percentage of weight moisture will be limited to the first 14 cm of the waste. At this time, the number of samples that will be taken within an individual tank will be limited to the number of available risers.

Monitoring of the temperature of the waste for "high-heat" tanks will be conducted within the waste using a single thermocouple tree.

## 5.3 TEMPORAL BOUNDARIES FOR INDIVIDUAL TANK DECISIONS

Tanks that contain salt cake and organic fuels that have been sampled and found to have sufficient moisture may be considered safe for a duration of time. This "safe" period is based on the drying rate of the salt cake. A waste drying rate model will be used to determine the length of time the data are considered valid before resampling is required to determine potential changes in tank conditions. The waste drying rate model will establish tank resampling frequency.

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# 6.0 DECISION RULE

Decision rules define the information that needs to be applied in a logical manner and summarize the tank population attributes that the decision maker needs to know to determine a course of action. This section describes the decision process for determining how tanks will be prioritized for evaluation and the information required to determine if the potential exists for the waste in any given tank to propagate a rapid exothermic reaction.

Waste conditions that exist within the tank can either enhance or suppress a propagating reaction. Rapid exothermic reactions in tank wastes require an oxygen source, a combustible fuel, and an initiating condition. A low moisture content in the waste suppresses the potential for a propagating reaction. Therefore, obtaining information concerning these waste components will help the decision makers determine appropriate courses of action for any given tank.

Process knowledge indicates that nitrates and nitrites were used extensively throughout the processes at the Hanford Site, so it is assumed that all single-shell tanks have an adequate oxygen source. As a result, measurement for oxygen sources within the waste is not necessary for decision-making purposes.

Process knowledge will be used to identify tanks that have received organic fuel wastes.

Additionally, Tank Waste Remediation System operations have established an interim stabilization schedule for single-shell tanks to help eliminate potential soil contamination from leaking tanks. This process, as described in Section 3.0, may contribute to establishing a fuel-rich/low-moisture condition that may support a propagating reaction.

Consequently, the tank interim stabilization schedule along with process knowledge will be evaluated to prioritize tank evaluations.

## 6.1 INDIVIDUAL TANK DECISION RULES

The following decision rules have been established to define the conditions that will choose an action for an individual tank.

If mean fuel concentrations in the waste are <4.5%, the waste is considered safe.

If the mean moisture content of the waste is >20 wt%, the waste drying rate model will be used to determine the length of time the tank can be considered safe.

If the mean moisture content of the waste is <20 wt% and the mean fuel content is >4.5 wt%, the safety criterion calculation* will be used to determine if the waste is potentially "unsafe."

If the mean moisture content of the waste is <20 wt%, the mean fuel content is >4.5 wt% and the mean temperature, calculated by the <u>thermal model</u>, is >180 °C, measures will be taken to mitigate the tank.

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*The safety criterion calculation is determined by: % total organic carbon = 4.5 + 0.17 (% free $H_2O$).

## 7.0 NUMBER OF CORE SAMPLES FOR PERCENT WATER AND TOC

The number of core samples (a) is determined by four parameters ($\alpha$, $\beta$, $\sigma$, and $\delta$). The first parameter $\alpha$ is the probability of a Type I error, $\beta$ is the probability of a Type II error, $\delta$ is the magnitude of the shift in the mean to be detected, and $\sigma$ is one standard deviation. The equation for the number of core samples is as follows:

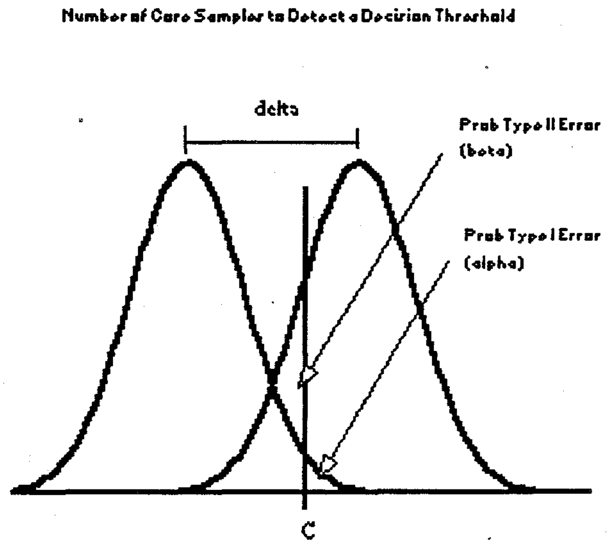
$$a = (Z_{(1-\alpha)} + Z_{(\beta)})^2 \left[\frac{\sigma}{\delta}\right]^2 \qquad (1)$$

where $Z_{(1-\alpha)}$ and $Z_{(\beta)}$ are the quantiles from the standard normal distribution. If, for example, $\alpha = 0.05$ and $\beta = 0.2$, then $Z_{(0.95)} = 1.64$ and $Z_{(0.2)} = 0.84$.

The details associated with the derivation of Equation 1 can be found in standard statistical methods books; for example, see Chapter 17 of *Statistics in Research* (Ostel and Malone 1988). Figure 7-1 gives the definitions of the four parameters based on the normal distribution.

In Equation 1, the standard deviation ($\sigma$) is assumed to be known without error. This means that Equation 1 can give an answer of a = 1 core samples. If uncertainty in the estimate of $\sigma$ is to be incorporated into the number of core samples problem, a more complicated version of Equation 1 is appropriate.

Figure 7-1. Definitions of $\alpha$, $\beta$, $\delta$ and $\sigma$ Based on the Normal Distribution.



## 7.1 DEFINITION OF TYPE I AND TYPE II ERRORS

The analytes of interest are percent water and TOC. Total organic carbon is the fuel in the waste. The threshold values of interest are 20% for percent water and 5% for TOC.

Table 7-1 gives the definition of the Type I and Type II errors for percent water.

The Type II error is making the decision, based on percent water, that the tank is not safe when it is safe. The Type I error is making the decision, based on percent water, that the tank is safe when it is not safe.

The consequence of a Type II error is that the tank, based on percent water measurements, will be unnecessarily mitigated. The consequence of a Type I error is the tank is not placed on a Watch List when it should be. *The costs associated with these two errors are needed before this analysis can be completed.*

Table 7-2 gives the definition of the Type I and Type II errors for TOC.

Table 7-1. Definition of Type I and Type II Errors for Percent Water.

| Null hypothesis: mean percent water <20% | | | |
|---|---|---|---|
| | | Percent water in tank is | |
| | | <20% | >20% |
| Based on data, percent water is | <20% | No error | Type II error |
| | >20% | Type I error | No error |

Table 7-2. Definition of Type I and Type II Errors for Fuel (Total Organic Carbon).

| Null hypothesis: mean fuel (TOC) >5% | | | |
|---|---|---|---|
| | | Fuel (TOC) in tank is | |
| | | <5% | >5% |
| Based on data, fuel (TOC) is | <5% | No error | Type I error |
| | >5% | Type II error | No error |

TOC = Total organic carbon

The Type I error is making the decision, based on TOC, that the tank is safe when it is not safe. The Type II error is making the decision, based on TOC, that the tank is not safe when it is safe.

The consequence of a Type II error is that the tank, based on TOC measurements, will be unnecessarily mitigated. The consequence of a Type I error is that it will not be placed on a safety Watch List when it should be. *The costs associated with these two errors are needed before this analysis can be completed.*

## 7.2 NUMBER OF CORE SAMPLES

To determine the number of core samples, the four parameters ($\alpha$, $\beta$, $\sigma$, and $\delta$) need to be specified. The probability of a Type I error was fixed at 0.05 and the probability of a Type II error was fixed at 0.20.

Percent water data, by thermogravimetric analysis (TGA), is available from core composite samples for six different single-shell tanks (B110, BX107, C109, C110, S104, and T104). The standard deviation and mean percent water concentrations are given in Table 7-3. This table also gives the number of core samples for a value of $\delta$ between 5% and 25%.

An example of the interpretation of the results in this table is as follows. If, for a tank to be sampled, the standard deviation of percent water (TGA) is like that found in tank C109, five core samples are needed to detect a deviation of 10% from the threshold value of 20%. This number is from Equation 1 with $\alpha$ = 0.05 and $\beta$ = 0.20.

Table 7-3. Number of Core Samples for Percent Water by Thermogravimetric Analysis, Various Values of $\delta$ and $\sigma$, $\alpha$ = 0.05 and $\beta$ = 0.20.

| Tank | B110 | BX107 | C109 | C110 | S104 | T104 |
|---|---|---|---|---|---|---|
| Mean | 46.0% | 59.0% | 20.7% | 56.7% | 30.0% | 67.6% |
| $\sigma$ | 3.0% | 3.5% | 8.3% | 5.5% | 2.5% | 1.8% |
| $\delta$ + 20% | Number of core samples | | | | | |
| 25% | 3 | 4 | 17 | 8 | 2 | 1 |
| 30% | 1 | 1 | 5 | 2 | 1 | 1 |
| 35% | 1 | 1 | 2 | 1 | 1 | 1 |
| 40% | 1 | 1 | 2 | 1 | 1 | 1 |
| 45% | 1 | 1 | 1 | 1 | 1 | 1 |

Three observations regarding the numbers in Table 7-3 need to be emphasized. They are as follows.

- The results are based on core composite data, not segment level data representing the surface material in a tank.

- The standard deviation for percent water (TGA) is not constant. This means that the estimated number of core samples is tank dependent.

- The number of core samples may be equal to 1. This is a consequence of the assumption that the standard deviation is known.

Total organic carbon data are available from core composite samples for five different single-shell tanks (T111, C109, C112, T105, and T107). The TOC concentrations and standard deviations are so small compared to the threshold of 5% that Equation 1 always gives an answer of one core sample.

## 7.3 BIASES

The number of core samples given in Section 7.2 are based on tank concentration estimates that may be biased. The core sample data used to give the results in Table 7-3 may contain two sources of bias. They are as follows.

- The core samples were obtained from existing risers within a tank, i.e., the sample locations were not randomly selected.

- The core samples were not a complete sample of waste from the top to the bottom of the tank, i.e., there was incomplete core sample recovery.

At present, the magnitude of the bias in analyte concentrations results, due to these two difficulties, is unknown. If appropriate experiments are designed, it will be possible to determine whether or not these biases are significant.

## 8.0 OPTIMIZATION OF THE DQO PROCESS

This chapter initiates the final step of the DQO Process: optimization of the DQO Process. Optimization of the DQO Process consists of researching the decision inputs and optimizing the sampling needs for the DQO. This second step is performed on a tank-by-tank basis and will be included in the separate Tank Characterization Plans. It must be understood that the optimization must consider all the information that is included in the previous sections of the DQO Process and this uncertainty is a large issue that has very drastic implications on the optimization process.

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# APPENDIX

# DESCRIPTION OF DATA QUALITY OBJECTIVE PROCESS

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# APPENDIX

## DESCRIPTION OF DATA QUALITY OBJECTIVE PROCESS

The basic structure of the Data Quality Objective (DQO) Process consists of seven steps. The steps are sequential, and each step is dependent on the previous step. The seven steps are as follows.

- Step 1: State the problem
- Step 2: Identify the decision
- Step 3: Identify the inputs to the decision
- Step 4: Define the study boundaries
- Step 5: Develop a decision rule
- Step 6: Specify acceptable limits on decision errors
- Step 7: Optimize the design.

### STEP 1: STATE THE PROBLEM

The context of the problem is established by reviewing and summarizing existing information and describing the approach(es) under consideration to address the problem. During this step, participants who should be involved in planning are identified and any practical constraints (measurement technology limits, budgetary or time constraints) that might limit the approaches to problem resolution are recognized.

### STEP 2: IDENTIFY THE DECISION

A statement of the decision(s) that must be resolved based on data, including the possible decision outcomes (alternative courses of action), is identified. In addition, secondary data uses are specified.

### STEP 3: IDENTIFY THE INPUTS TO THE DECISION

The information needed to make the decision is specified and the measurements that must be made to generate this information are specified. Measurements needed to support secondary data uses should also be specified during this step. Typically the planning team iterates back to this step after attempting to specify the decision rule. At that point further focusing of the inputs to the decision frequently occurs. Any variables that are not included in the decision rule come under closer scrutiny. If a convincing argument cannot be made for its inclusion, the variable is dropped from the list of required measurements.

### STEP 4: DEFINE THE STUDY BOUNDARIES

The spatial area or volume to which a decision will apply and within which data should be collected are defined. The planning team should consider whether representative (random) sampling is required or practical, and should define what population the data may represent and the decisions to which the data can be applied. The smallest sub-population of tank waste or tank atmosphere for which a separate decision might be made should be specified. For example, if a separate decision will be made for each layer of material in the tank, data representative of each layer must be collected. Finally, some phenomena are variable over time within the tanks. The time frame for which a decision will be made should be specified. Also, for some measurements the time period over which samples or measurements should be taken in support of decision making should be specified.

## STEP 5: DEVELOP A DECISION RULE

The outputs from previous steps are integrated during this step into one or more statements that describe how data will be summarized and combined to form a result (mean, median, maximum, etc.) that will be used to determine the decision outcome. This step defines how the data generated from the study will be used. Typically the decision rule is stated as an "if... then..." statement that defines the conditions that would cause the decision maker to choose among alternative courses of action. The decision rule ignores the possibility of uncertainty in the data results (uncertainty is considered in Step 6).

## STEP 6: SPECIFY ACCEPTABLE LIMITS ON DECISION ERRORS

The decision maker's (key data user's) acceptable decision error rates are defined in this step based on a careful consideration of the consequences of making incorrect decisions. By specifying decision error tolerances, the decision maker (data user) is accepting the fact that some probability of making an incorrect decision is inevitable because data can never perfectly reflect truth. The limits on decision errors drive many aspects of the design, including the number of samples and required precision and accuracy of the measurements. Iteration back to this step frequently occurs in order to balance the cost of collecting data against the uncertainty that can be accepted in the decision. Note that although decision errors may be affected by analytical uncertainties, decision error tolerances are not the same as analytical error tolerances.

## STEP 7: OPTIMIZE THE DESIGN

This step requires that the DQOs generated in the previous steps be carefully reviewed. The design team then translates the problem into a statistical framework, uses existing data and knowledge to specify the form of the underlying distribution and to estimate other key design parameters (e.g., the mean and variance of the underlying distribution and the cost of obtaining data), and generates alternative sampling designs. The most resource-efficient design that ensures an acceptable probability of making incorrect decisions is usually selected. If no design can be developed that meets all of the constraints specified (e.g., uncertainty limits and cost limits), the planning team iterates back to earlier steps. Either a decision to relax or alter earlier DQO outputs is made, or a different approach may be selected (e.g., a decision may be made without data or with a different set of data).

The DQO Process is meant to be iterative in nature. If measurements or decision error tolerances are deemed to be unattainable as one progresses through the DQO steps, reevaluating requirements outlined in earlier steps may be necessary. For some applications, sufficient progress through the first few steps may have been accomplished previously such that only documentation of the previous thought process cast in the context of the DQO logic may be needed before progressing through the remainder of the DQO steps.

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