

ENGINEERING CHANGE NOTICE

1. ECN **653804**

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Proj. ECN

2. ECN Category (mark one) Supplemental <input type="checkbox"/> Direct Revision <input checked="" type="checkbox"/> Change ECN <input type="checkbox"/> Temporary <input type="checkbox"/> Standby <input type="checkbox"/> Supersedure <input type="checkbox"/> Cancel/Void <input type="checkbox"/>	3. Originator's Name, Organization, MSIN, and Telephone No. Andrew M. Templeton, Data Assessment and Interpretation, R2-12, 373-5589		4. USQ Required? <input type="checkbox"/> Yes <input checked="" type="checkbox"/> No	5. Date 05/26/99
	6. Project Title/No./Work Order No. Tank 241-U-108		7. Bldg./Sys./Fac. No. 241-U-108	8. Approval Designator N/A
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12a. Modification Work <input type="checkbox"/> Yes (fill out Blk. 12b) <input checked="" type="checkbox"/> No (NA Blks. 12b, 12c, 12d)	12b. Work Package No. N/A	12c. Modification Work Complete N/A	12d. Restored to Original Condition (Temp. or Standby ECN only) N/A	
		Design Authority/Cog. Engineer Signature & Date	Design Authority/Cog. Engineer Signature & Date	

13a. Description of Change
 This ECN has been generated in order to update the document to reflect results of recent data/information evaluation.

Replace pages:
 2-1 through 2-4, 4-1, 4-2, 5-3, and 5-4



14a. Justification (mark one)

Criteria Change <input checked="" type="checkbox"/>	Design Improvement <input type="checkbox"/>	Environmental <input type="checkbox"/>	Facility Deactivation <input type="checkbox"/>
As-Found <input type="checkbox"/>	Facilitate Const <input type="checkbox"/>	Const. Error/Omission <input type="checkbox"/>	Design Error/Omission <input type="checkbox"/>

14b. Justification Details
 A tank characterization report page change revision is required to reflect the results of recent evaluation of data/information pertaining to adequacy of tank sampling for safety screening purposes (Reynolds et al. 1999, Evaluation of Tank Data for Safety Screening, HNF-4217, Rev. 0, Lockheed Martin Hanford Corporation, Richland, Washington).

15. Distribution (include name, MSIN, and no. of copies)
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Tank Characterization Report for Single-Shell Tank 241-U-108

Andrew M. Templeton

Lockheed Martin Hanford Corp., Richland, WA 99352
U.S. Department of Energy Contract 8023764-9-K001

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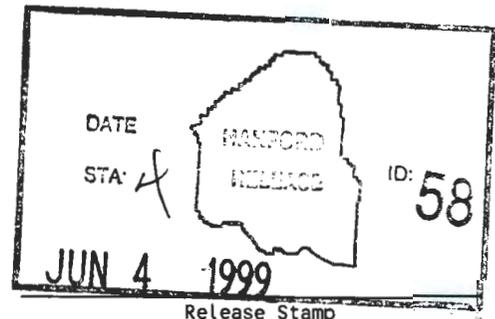
Key Words: Waste Characterization, Single-Shell Tank, SST, Tank 241-U-108, Tank U-108, U-108, U Farm, Tank Characterization Report, TCR, Waste Inventory, TPA Milestone M-44

Abstract: N/A

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2.0 RESPONSE TO TECHNICAL ISSUES

The following five technical issues have been identified for tank 241-U-108 (Brown et al. 1996). They are:

- Safety screening: Does the waste pose or contribute to any recognized potential safety problems?
- Organic complexants: Does the potential exist for exothermic organic complexant reactions in the waste to produce a radioactive release?
- Vapor screening: 1) Does the tank headspace exceed 25 percent of the lower flammability limit (LFL), and if so, what are the principal fuel components?
2) Is there an organic solvent pool in excess of 1 m² (10.76 ft²) in area that may cause an organic solvent pool fire or ignition of organic solvents entrained in the waste?
- Historical model evaluation: Is the waste inventory generated by a model based on process knowledge and historical information (Agnew et al. 1996a) representative of the current tank waste inventory?
- Compatibility: Do safety or operational problems exist with waste in tank 241-U-108 that could inhibit the transfer of pumpable liquid from the tank into a double-shell receiver tank?

The tank 241-U-108 TCP (Winkelman 1996) provides the types of sampling and analysis used to address the above issues. Data from the recent analysis of three core samples, a grab sample, and tank headspace samples, as well as available historical information, provided the means to respond to these issues. This response is detailed in the following sections. See Appendix B for sample and analysis data for tank 241-U-108.

The 1996 core sampling events took place to satisfy sampling and analysis requirements of the safety screening, organic, and historical DQO documents, and the organic test plan. The 1995 grab samples were taken and analyzed to satisfy the requirements of the compatibility DQO. The 1995 vapor samples were taken and analyzed to satisfy the requirements of the generic vapor and rotary core vapor DQOs. The 1996 and 1995 sampling events will be treated separately in the sections below.

The 1995 vapor samples were taken to address the issues listed in the first revision of the tank 241-U-108 TCP (Winkelman 1996). Since the 1995 vapor sampling, the generic vapor and rotary core vapor DQOs have been superseded by the health and safety vapor DQO listed in the latest revision of the tank 241-U-108 TCP (Hewitt 1996).

2.1 SAFETY SCREENING AND ORGANIC COMPLEXANT EVALUATION

The data needed to screen the waste in tank 241-U-108 for potential safety problems are documented in *Tank Safety Screening Data Quality Objective* (Dukelow et al. 1995). The potential safety problems are exothermic conditions in the waste, flammable gases in the waste and/or tank headspace, and criticality conditions in the waste. The safety screening DQO was not the only safety-related DQO associated with the sampling effort. Tank 241-U-108 is not on the Organic Watch List; however, reviews of waste transfer records indicate that it may contain greater than 3 percent total organic carbon (TOC) on a dry weight basis. The data needed to determine if the waste in tank 241-U-108 poses a potential safety concern with respect to a fuel (organic compounds) and oxidizer (nitrate or nitrite) propagating reaction are documented in *Data Quality Objective to Support Resolution of the Organic Complexant Safety Issue* (Turner et al. 1995), and *Test Plan for Samples From Hanford Waste Tanks 241-BY-103, BY-104, BY-105, BY-106, BY-108, BY-110, TY-103, U-105, U-107, U-108, and U-109* (Meacham 1995). In addition, organic solvent screening requirements as required in DOE (1996) have been added to all passively ventilated tanks per Cash (1996). Cash (1996) requires that tank 241-U-108 be vapor sampled for total non-methane hydrocarbons as part of the organic DQO (Turner et al. 1995).

2.1.1 Sampling and Analysis Requirements

The safety screening DQO documents suggest an optimum of two vertical profiles of the waste in tank 241-U-108 be obtained and analyzed at the half-segment level. Even though the upper and lower half subsegments from segment 2 were obtained only from core 146, the tank was sufficiently sampled to satisfy the requirements of safety screening (Reynolds et al. 1999). There was no bulk density determination on the upper half of segment 9 from core 141. Analysis for total non-methane hydrocarbons was performed on the 1995 vapor samples, satisfying the requirement in Cash (1996).

The organic test plan's sampling requirements are not clear. It appears that performing the analyses requested on one sample would meet the sampling requirement of the test plan. Most of the analytical requirements of the test plan were not met, including adiabatic calorimetry and tube propagation tests and analysis for diethylenediamine tetracetic acid, hydroxyethylenediamine tetraacetic acid, nitrilotriacetic acid, citrate, acetate, formate, and dibutyl phosphate. The missing analyses may be performed on archived samples at a later date.

2.1.2 Exothermic Conditions (Energetics)

The first analytical requirement outlined in the safety screening and organic DQO documents and the organic test plan is to ensure that not enough exothermic constituents (organic compounds, ferrocyanide, or cyanide) are present in tank 241-U-108 to cause a safety hazard. Because of this requirement, energetics in the tank 241-U-108 waste were evaluated using differential scanning calorimetry (DSC). The safety screening and organic DQO documents required that the waste sample profile be tested for energetics every 24 cm (9.5 in.) to determine if the energetics exceed the DQO notification limit. The threshold for energetics in the DQO documents is 480 J/g on a dry-weight basis and 1,200 J/g (dry) for the test plan.

Results obtained using DSC indicated that exotherms were apparent in most samples. Analyses were performed on all subsegments and drainable liquids from tank 241-U-108. One sample from the upper half of segment 4 from core 141 had an average DSC result of 496 J/g on a dry-weight basis, thus exceeding the DSC notification limit specified in the core sampling and analysis plan (SAP) (Homi 1996). A re-run of a second sample did not exceed the notification limit at 82.6 J/g (dry). The mean water content of the sample was 32.8 percent. Two other samples exceeded the DSC notification limit at the one-sided 95 percent upper confidence limit of the mean, although the individual measurements did not exceed the 480 J/g notification limit. The one-sided 95 percent lower confidence limits of the means for the respective water content of these two samples were 39.75 and 33.42 percent. Hence, adequate moisture is present to mediate the exothermic reactions.

Waste in tank 241-U-108 was expected to contain organic complexants (Agnew et al. 1996b); therefore, it is reasonable to expect exothermic behavior in the liquid and solid tank waste. The energy equivalent conversion for TOC (based on a sodium acetate average energetics standard) is calculated by converting the analytical results from $\mu\text{g/g}$ to weight percent (dividing by 10,000). The equation (Meacham 1995) is:

$$\left[\frac{-1,200 \text{ J/g}}{4.5\% \text{ TOC}} \right] * \text{measured TOC (\% dry)} = \text{energetics (J/g dry)}.$$

The average tank TOC concentration is 0.63 percent (dry). According to the above equation, the TOC would be expected to yield an average exotherm of 168 J/g (dry). The actual average of the DSC results was 64.4 J/g (dry). The discrepancy may result from the assumption that the TOC is in the form of acetate. Radiolysis and chemical degradation convert higher-energy organic species to lower-energy organic species. The core composite data show that oxalate accounts for 28 percent of the carbon. The amount of TOC present as other low-energy species such as formate was not determined. The TOC measurement may also be low because all the TOC is not being oxidized. However, the data suggest that this is not the case (Section B3.3.5). A third possibility is that some of the TOC has been degraded through chemical or radiological decarboxylation (loss of carbon dioxide and, thus, measured organic carbon).

2.1.3 Flammable Gas

Tank vapor samples, taken in the tank headspace in August 1995 and vacuum pumped from the tank from June 1995 to May 1996, and tank headspace flammability measurements taken prior to and during core sampling in April/May 1996, indicated that little flammable gases were present (highest reading was 6 percent of the LFL). Data from these vapor phase measurements are presented in Appendix B, Section B2.7.

2.1.4 Criticality

The safety screening total alpha notification limit is 1 g/L. However, total alpha is measured in $\mu\text{Ci/g}$ rather than in g/L. To convert the notification limit for total alpha into a practical number, it was assumed that all alpha activity originated from Pu-239. Using the average measured tank bulk density of 1.74 g/mL (Table B3-7), 1 g/L of Pu-239 is equivalent to 35.3 $\mu\text{Ci/g}$ of alpha activity.

Each core subsegment and drainable liquid was analyzed for total alpha activity. The total alpha activity in all core samples was well below the notification limit; the highest activity found at the one-sided 95 percent upper confidence limit of the mean was 0.37 $\mu\text{Ci/g}$. Therefore, no criticality concern exists for tank 241-U-108.

2.1.5 Total Organic Carbon Content

Total organic carbon is a primary analyte for the organic DQO, but not for the safety screening DQO. The TOC decision threshold is 3 percent TOC (dry weight). The highest TOC concentration found at the one-sided 95 percent upper confidence limit of the mean was 1.86 percent; thus, no samples exceeded the 3 percent threshold at the 95 percent confidence limit.

2.1.6 Moisture Content

Moisture content by thermogravimetric analysis (TGA) is another primary analyte for the organic DQO, but not for the safety screening DQO. The percent moisture decision threshold is ≤ 17 percent. One sample was below this threshold, and 18 samples were below the threshold at the lower 95 percent confidence limit of the mean (Table C1-3). This is not necessarily a safety concern according to the organic DQO, because none of the "dry" subsegments contained greater than 3 percent TOC.

4.0 RECOMMENDATIONS

Three subsamples from the 1996 core sampling of tank 241-U-108 exceeded the DSC safety decision threshold limit of 480 J/g at the 95 percent upper confidence interval on the mean; however, in each case adequate moisture was present to mediate the exothermic behavior. Nineteen samples were below the organic DQO moisture decision threshold of 17 percent at the lower 95 percent confidence limit on the mean, but the low moisture was mediated by the low TOC content of the samples. Despite high DSC and low moisture results on specific samples, the tank is classified as conditionally safe. This tank was sufficiently sampled to satisfy the requirements of safety screening (Reynolds et al. 1999).

The sampling and analysis requirements of the vapor DQO document were not met. Analyses for 1,3-butadiene, butanal, and tributyl phosphate were not performed, possibly because no sample was sent to ORNL for organic analysis. One vapor sample exceeded the notification limit for ammonia. Since the 1995 vapor sampling, tank vapors are no longer being evaluated as a health concern (Hewitt 1996).

The requirements of the historical DQO document were satisfied by the sampling and analysis of the three 1996 core samples. The requirements of the compatibility DQO document were satisfied by the 1995 liquid grab sample. Analysis of the core samples allowed for development of a characterization best-basis inventory.

Table 4-1 summarizes the status of the Project Hanford Management Contract (PHMC) TWRS Program review and acceptance of the sampling and analysis results reported in this tank characterization report. All DQO issues required to be addressed by sampling and analysis are listed in column one of Table 4-1. The second column indicates whether the requirements of the DQO were met by the sampling and analysis activities performed and is answered with "Yes," "No," or "Partially." The third column indicates concurrence and acceptance by the program in TWRS that is responsible for the DQO that the sampling and analysis activities performed adequately meet the needs of the DQO. A "Yes" or "No" in column three indicates acceptance or disapproval of the sampling and analysis information presented in the TCR. The waste was sampled and analyzed in accordance with the safety screening DQO and accepted by the responsible TWRS program.

Table 4-2 summarizes the status of PHMC TWRS Program review and acceptance of the evaluations and other characterization information contained in this report. The evaluations specifically outlined in this report are the best-basis inventory evaluation, the historical evaluation, and the evaluation to determine whether the tank is safe, conditionally safe, or unsafe. Column one lists the different evaluations performed in this report. Columns two and three are in the same format as Table 4-1. The manner in which concurrence and acceptance are summarized is also the same as that in Table 4-1. None of the analyses performed on the 1996 core samples indicate any safety problems.

Table 4-1. Acceptance of Tank 241-U-108 Sampling and Analysis.

Issue	Sampling and Analysis Performed	PHMC TWRS Program Office Acceptance
Safety screening DQO	Yes	Yes
Organic complexant DQO ³	Yes	No
Organic solvent screening ¹	Yes	Yes
Historical evaluation DQO	Yes	Yes
Waste compatibility DQO	Yes	Yes
Generic in-tank health & safety DQO	Partially	Yes ²
Organic test plan	Partially	No

Notes:

¹Considered part of the Organic DQO (Cash 1996)

²Tank vapors are no longer being evaluated as a health concern (Hewitt 1996)

³Organic complexant issue was closed in December 1998 (Owendoff 1998).

Table 4-2. Acceptance of Evaluation of Characterization Data and Information for Tank 241-U-108.

Issue	Evaluation Performed	PHMC TWRS Program Office Acceptance
Historical evaluation	Yes	Yes
Safety categorization (Tank is safe)	Yes	Yes

Analysis of 1996 core material for adiabatic calorimetry, tube propagation, diethylenediamine tetracetic acid, hydroxyethylenediamine tetraacetic acid, nitrilotriacetic acid, citrate, acetate, formate, and dibutyl phosphate is recommended to satisfy the analytical requirements of the organic test plan.

- Owendoff, J. M., 1998, *Approval to Close the Organic Complexant Safety Issue and Remove 18 Organic Complexant Tanks from the Watchlist*, (memorandum to J. Wagoner, December 9), U.S. Department of Energy, Washington D.C.
- Price, O. N., 1994, *Rotary Core Vapor Sampling Data Quality Objectives*, WHC-S-WM-SP-003, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Public Law 101-510, 1990, "Safety Measures for Waste Tanks at Hanford Nuclear Reservation," Section 3137 of *National Defense Authorization Act for Fiscal Year 1991*.
- Reynolds, D. A., W. T. Cowley, J. A. Lechelt, B. C. Simpson, and C. DeFig-Price, 1999, *Evaluation of Tank Data for Safety Screening*, HNF-4217, Rev. 0, Lockheed Martin Hanford Corporation, Richland, Washington.
- Schreiber, R. D., 1995, *Compatibility Grab Sampling and Analysis Plan*, WHC-SD-WM-TP-330, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
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- Smith, D. A., 1986, *Single-Shell Tank Isolation Safety Analysis Report*, WHC-SD-WM-SAR-006, Rev. 2, Westinghouse Hanford Company, Richland, Washington.
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- Thomas, B. L., T. W. Clauss, J. C. Evana, B. D. McVeety, K. H. Pool, K. B. Olsen, J. S. Fruchter, and M. W. Ligothke, 1996, *Headspace Vapor Characterization of Hanford Waste Tank 241-U-108: Results from Samples Collected on 08/29/95*, PNNL-10961, Pacific Northwest National Laboratory, Richland, Washington.
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