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Title/Desc:

TANK 241U106 HEADSPACE GAS & VAPOR
CHARACTERIZATION RESULTS FOR SAMPLES COLLECTED IN
3/1995

COMPLETE

ENGINEERING CHANGE NOTICE

Page 1 of 2

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ECN

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13b. Justification Details Complete rewrite which includes all vapor sampling events to date and data qualification.			
14. Distribution (include name, MSIN, and no. of copies) See attached Distribution Sheet			RELEASE STAMP OFFICIAL RELEASE BY WHC DATE SEP 27 1995 <i>Steel</i>

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Page 2 of 2

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

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15. Design Verification Required

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☒ No

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ENGINEERING

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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	☐
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APPROVED FOR PUBLIC RELEASE

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7. Abstract

Significant changes have been made to all of the original vapor characterization reports. This report documents specific headspace gas and vapor characterization results for all vapor sampling events to date. In addition, changes have been made to the original vapor reports to qualify the data based on quality assurance issues associated with the performing laboratories.

8. RELEASE STAMP

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Tank 241-U-106 Headspace Gas and Vapor Characterization Results for Samples Collected in March 1995

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Acronyms and Abbreviations

CES	consensus exposure standard
EPA	Environmental Protection Agency
GC	gas chromatograph
GC/MS	gas chromatograph/mass spectrometer
ISS	<i>in situ</i> sampling
LFL	lower flammability limit
MS	mass spectrometer
NFPA	National Fire Protection Association
NPH	normal paraffinic hydrocarbon
ORNL	Oak Ridge National Laboratory
PNL	Pacific Northwest Laboratory
ppmv	parts per million by volume, 1 ppmv = 10 ⁻⁴ vol%
TST	triple sorbent trap
Vol%	percent by volume, 1 vol% = 10,000 ppmv
VSS	vapor sampling system
WHC	Westinghouse Hanford Company

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Tank 241-U-106 Headspace Gas and Vapor Characterization Results

for Samples collected in March 1995

1.0 INTRODUCTION

1.1 Characterization Objectives

Tank U-106 headspace gas and vapor samples were collected and analyzed to help determine the potential risks of fugitive emissions to tank farm workers. The drivers and objectives of waste tank headspace sampling and analysis are discussed in *Program Plan for the Resolution of Tank Vapor Issues* (Osborne and Huckaby 1994). Tank U-106 was vapor sampled in accordance with *Data Quality Objectives for Generic In-Tank Health and Safety Issue Resolution* (Osborne et al. 1994).

1.2 Characterization Data Criteria

Data Quality Objectives for Generic In-Tank Health and Safety Issue Resolution describes parameters for data collection to ensure appropriate conclusions can be drawn from the data. Tank headspace characterization data was collected to help in the evaluation of 1) headspace flammability, and 2) identification and quantification of compounds of toxicological concern.

Single Shell Tank Interim Operational Safety Requirements (Dougherty 1995) specifies that combustible constituents in tank headspaces be maintained below 25 % of the lower flammability limit (LFL). This essentially agrees with National Fire Protection Association requirements that combustible concentrations be maintained at or below 25 % of the LFL (NFPA 1994). However, current governing operating specifications for single shell waste tanks, such as tank U-107 specify that combustible constituents be maintained at or below 20 % of the LFL (WHC 1995a).

Headspace characterization data is used by Westinghouse Hanford Company (WHC) Tank Waste Remediation Systems Industrial Hygiene as source term data in the industrial hygiene strategy to protect workers from tank fugitive emissions. Because selection of worker protective equipment must be based on industrial hygiene monitoring of the work place and not on source term data (29 CFR 1910.120), tank headspace characterization data can not be used for this purpose. Furthermore, because there are mechanisms by which headspace constituents can be either diluted or concentrated as they are released to the atmosphere, the headspace characterization data should not be considered to be representative of emissions at the point of emission.

These statements notwithstanding, the data quality objectives document specifies that the industrial hygiene group be advised if constituents with toxicological properties exceed 50 % of the appropriate consensus exposure standard (CES) for non-carcinogens, or 10 % of the appropriate CES for carcinogens. A CES is defined as the most stringent of known regulatory or recommended toxicological values for the workplace (Osborne et al. 1994).

1.3 Sampling Overview

Gas and vapor samples were collected from tank U-106 on August 25, 1994 using the *in situ* sampling (ISS) method (Pingel 1994), and again on March 7, 1995 using the more robust vapor sampling system (VSS) method (WHC 1995b). Analytical results from the 2 sampling events are similar but not identical

(Klinger et al. 1995a, Ligothke et al. 1995a; Jenkins et al. 1995a, 1995b). Differences in the results may be attributed to the less accurate sample air flow measurement of the ISS equipment, and various differences in the sampling methods. Because the VSS method has been more thoroughly tested and its limitations are better understood, all of results presented here are from the March 7, 1995 VSS sampling event.

One of the organic vapor samples from the August 25, 1994 ISS event was determined to have trace levels of methyl isocyanate (Jenkins et al. 1995b). This compound would not be expected to be stable in the high-ammonia, high-humidity headspace of tank U-106, and may actually have been an artifact of the analytical method. Nevertheless, extra samples were collected on March 7, 1995 to address the possible existence of methyl isocyanate in tank U-106. A discussion of the identification of methyl isocyanate in tank U-106 is given by Huckaby and Babad (1995).

Samples collected are thought to have been representative of tank U-106 headspace when the tank was sampled (Meacham et al. 1995), and samples analyses were designed to provide a reasonably accurate and complete characterization of the significant headspace constituents. No assessment has been made as to how the tank U-107 headspace composition changes with time, though studies of tank C-103 suggest that composition changes probably occur very slowly in the passively ventilated tanks (Huckaby and Story 1994).

1.4 Tank Headspace Dynamics

Tank U-106 is the third tank in a 3-tank cascade with tanks U-104 and U-105. It is connected to tank U-105 via a 7.4-cm (2.9-in.) inside diameter, 7.6-m (25-ft) long underground cascade line. A similar line connects tanks U-104 and U-105. Since these cascade lines connect the headspaces of these tanks, gases and vapors originating from the wastes in tank U-104 or tank U-105 may be transferred to tank U-106 (unless the cascade lines are obstructed). Sections 3.4 and 4.3 briefly compare the headspace constituents of tanks U-105 and U-106 and discusses the potential transfer of gases and vapors to tank U-106.

The cascade of tanks U-104, U-105, and U-106 is passively ventilated, which means that the tanks are allowed to exhale air, waste gases, and vapors as the barometric pressure falls, and inhale ambient air as the barometric pressure rises. Each of these tanks has its own filtered breather riser. Barometric pressure typically rises and falls on a diurnal cycle, producing an average daily exchange of air equal to about 0.46 % of each tank headspace (Huckaby 1994). Changes in the concentrations of tank headspace constituents due to barometric pressure changes are consequently very slow.

2.0 SAMPLING EVENT

Headspace gas and vapor samples were collected from tank U-106 using the VSS on March 7, 1995 by WHC Sampling and Mobile Laboratories (WHC 1995b). Sample collection and analysis were performed as directed by *Tank 241-U-106 Tank Characterization Plan* (Homi 1995). The tank headspace temperature was determined to be 21.9 °C. Air from the U-106 headspace was withdrawn from a single elevation via a 7.3-m long heated sampling probe mounted in riser 2, and transferred via heated tubing to the VSS sampling manifold. All heated zones of the VSS were maintained at approximately 50°C. All tank air samples were collected between 10:27 a.m. and 3:47 p.m., with no anomalies noted.

Sampling media were prepared and analyzed by WHC, Oak Ridge National Laboratories (ORNL), and Pacific Northwest Laboratories (PNL). The 46 tank air samples and 2 ambient air control samples collected are listed in Table 2-1 by analytical laboratory. Table 2-1 also lists the 14 trip blanks and 2 field blanks provided by the laboratories.

A general description of vapor sampling and sample analysis methods is given by Huckaby et al. (1995). The sampling equipment, sample collection sequence, sorbent trap sample air flow rates and flow times, chain of custody information, and a discussion of the sampling event itself are given in WHC 1995b.

3.0 INORGANIC GASES AND VAPORS

Analytical results of sorbent trap and SUMMA^{TM,1} canister tank air samples for selected inorganic gases and vapors are given in Table 3-1 in parts per million by volume (ppmv) in dry air. The concentration of water vapor given in Table 3-1 has been adjusted to tank conditions as given in Section 3.3. Inorganic analyte sorbent traps and SUMMATM canisters were prepared and analyzed by PNL, with analyses performed within 10 days and 6 days, respectively, of sample collection (Ligotke 1995). This satisfied the 60-day maximum holding time requirement of the WHC quality assurance project plan (Keller 1994). It should be noted that these inorganic compounds (i.e., the permanent gases) would be expected to be very stable in the SUMMATM canisters, and the results may not have been affected even if the 60-day holding time requirements had been exceeded. PNL results were produced at PNL quality assurance impact level 2.

3.1 Ammonia, Hydrogen, and Nitrous Oxide

The reported ammonia concentration, 988 ppmv, is the second highest measured in any waste tank to date. Ammonia has been observed in virtually all of the passively ventilated waste tanks sampled to date, at concentrations ranging from about 3 ppmv in tank C-108 (Lucke et al. 1995), to 1040 ppmv in BY-108 (McVeety et al. 1995). Given the LFL of ammonia in air is about 15 % by volume (vol%), the measured 988 ppmv corresponds to less than 0.7 % of the LFL, and does not contribute appreciably to the flammability of the headspace.

The concentration of hydrogen in tank U-106 was determined to be 210 ppmv. Hydrogen in the waste tanks is of concern as a fuel. Given that the LFL for hydrogen in air is about 4 % by volume, 210 ppmv hydrogen concentration in tank U-106 corresponds to about 0.5 % of its LFL. At this level, hydrogen is not a flammability concern in tank U-106.

The nitrous oxide concentration in tank U-106, 559 ppmv, is the among highest measured in any waste tank to date. Nitrous oxide has been detected in other passively ventilated waste tanks at average concentrations as low as about 12 ppmv in tank TX-105 (Klinger 1995b), and as high as 878 ppmv in tank U-103 (Ligotke et al. 1995b). Under proper conditions, nitrous oxide can serve as an oxidizer to support combustion. However, Cashdollar et al. (1992) found that nitrous oxide had no significant effect on the flammability of hydrogen and air mixtures for hydrogen concentrations less than 20 vol%, and that "small amounts of nitrous oxide (relative to air) do not appear to have much effect on the flammability". Their results suggest the measured nitrous oxide concentration is much too low to have a significant effect on the flammability of the tank U-106 headspace.

3.2 Carbon Monoxide and Carbon Dioxide

Carbon monoxide in the tank U-106 headspace was measured as < 12 ppmv. In ambient air it typically ranges from 0.05 to 0.15 ppmv. Because different analytical methods have been used to measure carbon monoxide in the waste tanks sampled to date, the information on carbon monoxide has varied from tank to tank. However, elevated waste tank headspace carbon monoxide concentrations are common, and are thought to be due to the decomposition of organic waste in the tanks. Carbon monoxide has not been

¹ SUMMA is a trademark of Molectrics, Inc., Cleveland, Ohio.

measured at very high levels in any of the waste tanks, the highest level measured to date was [26.7 ppmv] in tank C-103² (Huckaby and Story 1994).

The average carbon dioxide concentration in the tank U-106 headspace, 46.5 ppmv, is significantly lower than it is in ambient air. Carbon dioxide is normally present in the ambient air at a concentration of 350 to 400 ppmv, and is typically lower than ambient in the waste tank headspaces. Carbon dioxide introduced by air exchange with the atmosphere is readily absorbed by caustic supernatant and interstitial liquids of the waste tanks, and converted to carbonate in solution. The 46.5 ppmv of carbon dioxide measured in tank U-106 is within the range of typical values for the waste tanks sampled to date.

3.3 Nitric Oxide, Nitrogen Dioxide, Water and Tritium

Nitric oxide and nitrogen dioxide concentrations in the tank U-106 headspace were both determined to be ≤ 0.04 ppmv. These are acid gases that would have very low equilibrium concentrations above the high pH sludge in tank U-106. The measurable presence of nitric oxide is not uncommon in the waste tank headspaces, and may be due to its formation from oxygen and nitrogen in the radiation field of the headspace. These constituents could potentially serve as oxidizers to support combustion, but at the measured concentrations would have a negligible effect on the flammability of the tank U-106 headspace.

The water vapor concentration of tank U-106 was determined to be about 12.9 mg/L, at the measured tank headspace temperature of 21.9 °C and pressure of 995.5 mbar (746.8 torr), (WHC 1995b). This corresponds to a water vapor partial pressure of 17.5 mbar (13.2 torr), to a dew point of 15.4 °C, and to a relative humidity of 67 %.

Silica gel sorbent traps were used to test for tritium. It is assumed that tritium produced by the waste combines with hydroxide ions to form tritium-substituted water. Evaporation of the tritium-substituted water would then result in airborne radioactive contamination. Silica gel sorbent traps adsorb virtually all (normal and tritium-substituted) water vapor from the sampled tank air, and are analyzed at the WHC 222-S laboratory. Radiochemical analysis of the silica gel trap indicated the total activity of the headspace to be less than 50 pCi/L (WHC 1995b).

3.4 Discussion of Inorganic Gases and Vapors

Aside from water vapor, the most abundant waste constituents in the tank U-106 headspace are ammonia, nitrous oxide, and hydrogen. These have been detected in most tank headspaces sampled to date, and are usually the dominate waste species. Ammonia in tank U-106 is particularly high compared to other waste tanks.

The relative standard deviations of the inorganic gas and vapor results given in the last column in Table 3-1 are excellent for the methods used. Relative standard deviations range from about 1.1 % for water vapor to 3 % for ammonia and hydrogen results. Because the precision reported depends both on sampling parameters (e.g., sample flow rate and flow time for sorbent traps) and analytical parameters (e.g., sample preparation, dilutions, etc.), small relative standard deviations suggest proper control was maintained both in the field and in the laboratories.

² The carbon monoxide measurement in tank C-103 was made by Oregon Graduate Institute of Science and Technology, and have been placed in brackets to indicate it should be considered secondary data.

As discussed in Section 1.4, the headspaces of tanks U-105 and U-106 are connected by an underground cascade line. To examine the possibility that constituents of the tank U-106 headspace originate elsewhere in the cascade and are transported to tank U-106 via the cascade from tank U-105, selected gas and vapor results from the headspace characterization of tanks U-105 and U-106 are given in Table 3-2. From Table 3-2 it can be concluded (assuming all results presented are valid) that the primary source of ammonia, hydrogen, and nitrous oxide in the tank U-106 headspace is the waste in tank U-106.

4.0 ORGANIC VAPORS

Organic vapors in the tank U-106 headspace were sampled using SUMMA™ canisters, which were analyzed by PNL, and triple sorbent traps (TSTs), which were analyzed by ORNL. Gas chromatography (GC) and mass spectroscopy (MS) were used by PNL and ORNL to separate, identify, and quantitate the analytes. Descriptions of sample device cleaning, sample preparations, and analyses are given by Jenkins et al. (1995a) and Klinger et al. (1995a).

SUMMA™ sample results should be considered to be the primary organic vapor data for tank U-106. These results were produced at PNL quality assurance impact level 2. All analyses were completed 9 days after sample collection, well within the administratively chosen 60-day holding time (Keller 1994). No holding time study has been performed to address the stability of organic compounds in SUMMA™ canisters in the chemical matrix of the waste tank samples.

ORNL analyses of TST samples from this and other waste tanks generally agree with, support, and augment the SUMMA™ sample results. However, because certain WHC quality assurance requirements were not satisfied by ORNL, the quality assurance assessment of ORNL by Hendrickson (1995) should be reviewed before results unique to the TST samples are used for decision making.

ORNL analyzed 6 of the 12 TST tank samples, 1 of the 2 TST field blanks, and 1 of the 2 TST trip blanks. ORNL reported average analyte concentrations based on 4 of the 6 TSTs analyzed, because 2 of the TSTs were analyzed under different GC and/or MS conditions. Instrumental conditions were altered to enhance separation and identification of methyl isocyanate.

All TSTs prepared by ORNL had 3 surrogate compounds added to evaluate sample matrix effects, potential handling, storage, and shipment problems, and analytical instrumentation performance (Jenkins et al. 1995a). ORNL evaluated the surrogate recoveries using a statistical approach similar to that prescribed by SW 846 Method 8260A *Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) Capillary Column Technique* (EPA 1992). Using this approach, ORNL reported that surrogate recovery standard deviation values were within the 95 % confidence interval for variance, indicating that no bias was introduced in the measurement of analyte quantities (Jenkins 1995a).

4.1 Positively Identified Organic Compounds

Positive identification of organic analytes using the methods employed by PNL and ORNL involves matching the GC retention times and MS data from a sample with that obtained from the analysis of standards. The concentration of an analyte in the sample is said to be quantitatively measured if the response of the GC/MS has been established at several known concentrations of that analyte (i.e., the GC/MS has been calibrated for that analyte), and the MS response to the analyte in the sample is between the lowest and highest responses to the known concentrations (i.e., the analyte is within the calibration range).

ORNL and PNL were assigned different lists of organic compounds, or target analytes, to positively identify and measure quantitatively. The ORNL target analyte list was derived from a review of the tank C-103 headspace constituents by a panel of toxicology experts (Mahlum et al. 1994). The PNL target analyte list included 39 compounds from the Environmental Protection Agency (EPA) task order 14 (TO-14) method, which are primarily halocarbons and common industrial solvents (EPA 1988), plus 14 analytes selected mainly from the toxicology panel's review of vapor data from tank C-103. In addition to these customary target analytes, positive identification of methyl isocyanate in both SUMMA™ and TST samples was sought.

Both PNL and ORNL report target analyte concentrations in ppmv of analyte in dry air. To correct for the measured water vapor content of tank U-106 and obtain concentration in ppmv of analyte in moist tank air, multiply by 0.983.

Table 4-1 lists the organic compounds positively identified and quantitated in SUMMA™ samples. SUMMA™ analyses were performed according to the TO-14 methodology, except for methane analysis, which was analyzed with the inorganic gases (Klinger et al. 1995a). Only 2 of the 39 TO-14 target analytes and 3 of the 15 additional target analytes were measured to be above the 0.005 ppmv detection limit of the analyses. Averages reported are from analyses of 3 SUMMA™ canister samples.

Jenkins et al. (1995a) report the positive identification of 22 of 27 target analytes in TST samples. 1,1-Dichloroethene, dichloromethane, butanal, dibutyl butylphosphonate, and tributyl phosphate were the only TST target analytes not detected. The average concentrations of the positively identified organic analytes, from the analysis of 4 TSTs, are given in Tables 4-2 and 4-3. Table 4-2 lists the quantitated compounds and their average measured concentrations, and Table 4-3 lists those compounds for which at least 1 sample result was outside the instrument calibration range, and consequently not quantitatively measured.

All the TST analyses by ORNL were completed within 15 days of sample collection, and none of the analytes positively identified in TSTs by ORNL exceeded their practical holding times (Jenkins 1995b). The practical holding time is defined as the holding time for which there is a 15 % risk that the concentration of an analyte in the sample will be below its initial concentration (Jenkins et al. 1995c). One of the target compounds that was not detected, specifically butanal, may not have been detected because the sample holding time of 15 days exceeded the practical holding time for this compound. It should be noted that the contractual holding time for the TST samples was 60 days.

Eleven target analytes were common to both TST and SUMMA™ analyses. Table 4-4 lists these, and their reported average concentrations in TST and SUMMA™ samples. Results from these 2 sampling and analytical methods are in fairly good agreement for propanone and toluene. As indicated in Table 4-4, the reported concentrations of propanenitrile, benzene, n-hexane, and n-heptane in TST samples are moderately higher than the SUMMA™ sample analytical detection limit, yet were not reported as being present in the SUMMA™ samples.

The largest discrepancy between the target analyte results from the 2 methods is for ethanenitrile, which was determined to be present at 0.10 ppmv in TST samples, and < 0.005 ppmv in SUMMA™ samples. None of these compounds, however, even assuming the higher concentrations to be correct, are at or above levels of concern.

The most abundant analytes in Tables 4-1, 4-2, and 4-3 are 1-butanol, n-tridecane, propanone, and n-dodecane, each of which was measured to be above 1 ppmv. At the reported concentrations, the target analytes do not individually or collectively represent a flammability hazard.

4.2 Tentatively Identified Organic Compounds

In addition to the target analytes, the ORNL and PNL analytical procedures allow the tentative identification of other organic compounds. Tentative identification of analytes was performed by comparing the MS molecular fragmentation patterns with a library of known MS fragmentation patterns. This method allows an organic analyte to be identified (with reasonable certainty) as an alkane, a ketone, an aldehyde, etc., and may also determine its molecular weight. The method usually does not, however, allow the unambiguous identification of structural isomers, and this ambiguity increases with analyte molecular weight. Using this method, many analytes can be tentatively identified with reasonable confidence without having to inject standards of each into the GC/MS to determine their GC retention times or specific MS patterns.

By the nature of the sampling devices, virtually all organic vapors present in the tank headspace are collected by both TST and SUMMA™ samples. Analyses of the samples are designed to recover, separate, identify, and quantify the organic vapors in the samples. TSTs are not good for collecting highly volatile compounds (i.e., molecules more volatile than propane), but are quite good for most others. In contrast, the recovery of very low volatility compounds (e.g., molecules with more than about 15 carbon atoms) and some polar compounds with moderate volatility (e.g., butanal) from SUMMA™ samples has been problematic.

The list of tentatively identified compounds recovered from SUMMA™ samples, with estimated concentrations, is given in Table 4-5. Compounds are listed in Table 4-5 in the order by which they eluted chromatographically, and only non-zero results are included in the reported averages. The list of tentatively identified compounds detected in TST samples, and their estimated concentrations, is given in Table 4-6. Compounds are listed in Table 4-6 according to the order by which they eluted chromatographically. The averages reported by ORNL in Table 4-6 are all 3-sample averages, and if an analyte was not detected in a sample, its concentration in that sample was considered to be zero for averaging purposes. Estimated concentrations are in mg/m³, based on dry air at 0 °C and 1.01 bar.

Because the list of tentatively identified organic compounds in TST samples is rather long and finding a given compound may be difficult, the list has been sorted both alphanumerically by compound name in Table 4-7, and also in order of decreasing estimated concentrations in Table 4-8. Numbers in the first columns of Tables 4-7 and 4-8 (Cmpd #) identify the location of the compound in Table 4-6.

The ORNL and PNL methods used to tentatively identify and estimate concentrations are described by Jenkins et al. (1995a) and Klinger et al. (1995a), respectively, and should be reviewed before this data is used for decision making. Concentrations given in Tables 4-5 through 4-8 should be considered rough estimates. Furthermore, results in Tables 4-5 through 4-8 are presented in terms of observed chromatographic peaks, and are not adjusted for the occurrence of split peaks or the assignment of the same identity to different peaks (e.g., Cmpd # 25 and 26 in Table 4-6). In these instances, the estimated concentration of a compound appearing in more than 1 peak is simply the sum of the individual peak estimates.

4.3 Discussion of Organic Compounds

A convenient way to consider the organic compounds listed in Tables 4-1 through 4-6 is to separate them into 2 categories: 1) Organic compounds added to tank U-106 as waste that are still evaporating; and 2) organic compounds that have been generated by reactions of the original waste.

Organic vapors in the first category (those that were placed into the tank as waste) include the semivolatile straight-chain alkanes, which were used as diluents of tributyl phosphate in various plutonium extraction processes. These alkanes (i.e., n-undecane, n-dodecane, n-tridecane, n-tetradecane, and n-pentadecane) are often referred to in Hanford site literature as the normal paraffinic hydrocarbons (NPHs). Though NPHs are positively identified in tank U-106, their concentrations are very low compared to other NPH-rich tanks.

The tentatively identified cyclosiloxanes (i.e., Cmpd # 21 and 33 in Table 4-6) are also in this category. Small quantities of siloxanes may have been introduced to the waste tank through their use as defoaming agents, but they may also be present in the headspace due to their use in liquid traps at the tank's breather riser. Siloxanes are frequently detected in laboratory and field blanks, and their appearance in TST tank samples may be due to column bleed in the GC.

Organic vapors in the second category, those that are thought to have been generated via radiolytic and chemical reactions of the waste, constitute the majority of compounds listed in Tables 4-1 through 4-8.

Included in this category are the alcohols, aldehydes, ketones, nitriles, alkenes, and volatile alkanes, all of which have been associated with the degradation of the NPHs. While both larger and smaller molecules are generated from the waste, the most abundant of these in the headspace of tank U-106 are the smaller, short-chain volatile compounds.

The absence of tributyl phosphate in the tank U-106 samples does not necessarily indicate it is not present in the tank headspace or the waste. The identification of the tributyl phosphate diluents and their degradation products is reason to expect tributyl phosphate may be present in the tank waste. 1-Butanol, which is one of the more abundant organic compounds in tank U-106 samples, is known to be a product of the hydrolysis of tributyl phosphate. Furthermore, informal tests by ORNL indicate that tributyl phosphate is adsorbed by the glass fiber filters used during sampling to protect the samples from radiolytic particulate contamination. Based on these considerations, the lack of tributyl phosphate in the tank U-106 headspace samples should not be taken as proof it is not present in the headspace or the waste.

On the basis of concentrations, alcohols are the dominate type of organic compound in the tank U-106 headspace. Methanol, ethanol, 1-propanol, and 1-butanol account for about 89 % of the total estimated concentration of organic compounds in SUMMA™ samples. Similarly, about 64 % of the total estimated organic compound concentration in TST samples is due to the 12 alcohols identified. In contrast to tanks having higher NPH concentrations, tank U-106 has relatively few aldehydes and ketones.

Though not present in high concentrations, 8 straight-chain alkyl nitriles were identified in TST samples. A relatively large number of nitrogen-containing cyclic compounds were also detected in TST samples from tank U-106, including pyridines, pyrazines, pyrazoles, oxazoles, and a piperidine.

The total organic vapor concentration of tank U-106 was estimated by ORNL to be about 10.1 mg/m³ from the analysis of the 3 TST samples by GC/MS. A similar summation of positively and tentatively identified organic compounds measured in SUMMA™ samples gives a total organic vapor concentration of 12.4 mg/m³. This is typical of other passively ventilated waste tanks, though organic vapor concentrations have been measured to range roughly 2 orders of magnitude to either side of this value.

Ambient air SUMMA™ samples collected during the tank U-106 sampling event suggest the VSS manifold may have been contaminated with trace amounts of propanone. Specifically, analysis of an ambient air sample collect upwind of the VSS (not through the VSS manifold) indicated propanone to be present at < 0.005 ppmv, while an ambient air sample collected through the VSS (to check system cleanliness) was determined to have about 0.012 ppmv of propanone. Residual amounts of propanone, used as a cleaning solvent, may have been present in the VSS transfer tubing.

In summary, the organic vapor concentrations in tank U-106 are moderately low compared to other waste tanks. The organic vapors in tank U-106 clearly indicate the presence of the semivolatile NPHs and their degradation products in the tank waste. Short-chain alcohols are more prominent in tank U-106 and there are fewer ketones and aldehydes than in NPH-rich waste tanks. Though tributyl phosphate was not detected in any of the headspace samples, there is strong evidence that it is also present in the waste. The majority of organic vapors in the tank U-106 headspace appear to originate from the waste stored in the tank, and are not transferred in from tank U-105 via the cascade line, based on the comparison given in Table 3-2.

5.0 SUMMARY

The tank U-106 headspace was sampled in August 1994 and March 1995 for gases and vapors to address flammability and industrial hygiene concerns. Results unique to the August 1994 event and essentially all results from the March 1995 event have been reported. It was determined that no headspace constituents exceeded the flammability notification limits, but that ammonia, measured to be 988 ppmv, exceeded the 150 ppmv industrial hygiene notification limits specified in the current *Vapor Sampling and Analysis Plan* (Homi 1995).

6.0 REFERENCES

- 29 CFR 1910.120, 1993, "Hazardous Waste Operations and Emergency Response", *Code of Federal Regulations*.
- Cashdollar, K. L., M. Hertzberg, I. A. Zlochower, C. E. Lucci, G. M. Green, and R. A. Thomas, 1992, *Laboratory Flammability Studies of Mixtures of Hydrogen, Nitrous Oxide, and Air*, WHC-SD-WM-ES-219 Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Dougherty, L. F., 1995, *Single Shell Tank Interim Operational Safety Requirements*, WHC-SD-WM-OSR-005 Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- EPA 1988, *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, PB90-127374, U.S. Environmental Protection Agency, Washington, D.C.
- Hendrickson, R. W., 1995, *Tank Vapor Characterization Oak Ridge National Laboratories Quality Assurance Assessment*, TWRSQA-95-0012, Westinghouse Hanford Company, Richland, Washington.
- Homi, C. S., 1995, *Tank 241-U-106 Tank Characterization Plan*, WHC-SD-WM-TP-245 Rev. 0B, Westinghouse Hanford Company, Richland, Washington.
- Homi, C. S., 1995, *Vapor Sampling and Analysis Plan*, WHC-SD-WM-TP-335 Rev. 0G, Westinghouse Hanford Company, Richland, Washington.
- Huckaby, J. L., 1994, *Tank 241-C-103 Headspace Flammability*, WHC-EP-0734 Rev. 1, Westinghouse Hanford Company, Richland, Washington.
- Huckaby, J. L., H. Babad, and D. R. Bratzel, 1995, *Headspace Gas and Vapor Characterization Summary for the 43 Vapor Program Suspect Tanks*, WHC-SD-WM-ER-514, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Huckaby, J. L., and M. S. Story, 1994, *Vapor Characterization of Tank 241-C-103*, WHC-EP-0780 Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Huckaby, J. L., and D. R. Bratzel, 1995, *Tank 241-U-105 Headspace Gas and Vapor Characterization Results for Samples Collected in February 1995*, WHC-SD-WM-ER-511, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Jenkins, R. A., 1995a, (letter to J. W. Osborne, Westinghouse Hanford Company, June 7), Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- Jenkins, R. A., 1995b, *Untitled*, (Letter 091495A to D. Bratzel, September 14), Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- Jenkins, R. A., A. B. Dindal, C. Y. Ma, M. A. Palausky, J. T. Skeen, and C. K. Bayne, 1995a, *Analysis of Tank 241-U-106 Headspace Components*, ORNL-CASD-FR-241U106.95 Rev. 1, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

- Jenkins, R. A, A. B. Dindal, C. Y. Ma, M. A. Palausky, J. T. Skeen, and C. K. Bayne, 1995b, *Analysis of Tank 241-U-106 Headspace Components Collected via In-Situ Sampling*, ORNL-CASD-FR-241U106ISS.95 Rev. 0, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- Jenkins, R. A, A. B. Dindal, C. Y. Ma, M. A. Palausky, J. T. Skeen, and C. K. Bayne, 1995c, *Analysis of Tank 241-TY-104 Headspace Components*, ORNL-CASD-FR-241TY104.95 Rev. 1, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- Keller, K.K., 1994, *Quality Assurance Project Plan for Tank Vapor Characterization*, WHC-SD-WM-QAPP-013 Rev. 2, Westinghouse Hanford Company, Richland, Washington.
- Klinger, G. S., R. B. Lucke, B. D. McVeety, T. W. Clauss, M. W. Ligothke, K. H. Pool, K. B. Olsen, O. P. Bredt, J. S. Fruchter, and S. C. Goheen, 1995a, *Vapor Space Characterization of Waste Tank 241-U-106: Results from Samples Collected on 3/7/95*, PNL-10593 UC-606, Pacific Northwest Laboratory, Richland, Washington.
- Klinger, G. S., T. W. Clauss, M. W. Ligothke, K. H. Pool, R. B. Lucke, B. D. McVeety, O. P. Bredt, J. S. Young, M. McCulloch, J. S. Fruchter, and S. C. Goheen, 1995b, *Vapor Space Characterization of Waste Tank 241-TX-105: Results from Samples Collected Through the Vapor Sampling System on 12/20/94*, PNL-10594 UC-606, Pacific Northwest Laboratory, Richland, Washington.
- Ligothke, M. W., 1995, *PNL Vapor Project Analytical Holding Times*, (Letter to D. R. Bratzel, September 23, 1995) Pacific Northwest Laboratory, Richland, Washington.
- Ligothke, M. W., R. B. Lucke, K. H. Pool, B. D. McVeety, G. S. Klinger, T. W. Clauss, J. S. Young, M. McCulloch, J. S. Fruchter, and S. C. Goheen, 1995a, *Vapor Space Characterization of Waste Tank 241-U-106 (In Situ): Results from Samples Collected on 8/25/94*, PNL-10730 UC-606, Pacific Northwest Laboratory, Richland, Washington.
- Ligothke, M. W., K. H. Pool, T. W. Clauss, B. D. McVeety, G. S. Klinger, K. B. Olsen, O. P. Bredt, J. S. Fruchter, and S. C. Goheen, 1995, *Vapor Space Characterization of Waste Tank 241-U-103: Results from Samples Collected on 2/15/95*, PNL-10813 UC-606, Pacific Northwest Laboratory, Richland, Washington.
- Lucke, R. B., M. W. Ligothke, K. H. Pool, T. W. Clauss, A. K. Sharma, B. D. McVeety, M. McCulloch, J. S. Fruchter, and S. C. Goheen, 1995, *Vapor Space Characterization of Waste Tank 241-C-108: Results from Samples Collected Through the Vapor Sampling System on 8/5/94*, PNL-10351 UC-606, Pacific Northwest Laboratory, Richland, Washington.
- Mahlum, D. D., J. Y. Young, and R. E. Weller, 1994, *Toxicologic Evaluation of Analytes from Tank 231-C-103*, PNL-10189, Pacific Northwest Laboratory, Richland, Washington.
- McVeety, B. D., T. W. Clauss, M. W. Ligothke, K. H. Pool, R. B. Lucke, G. S. Klinger, J. S. Young, M. McCulloch, J. S. Fruchter, and S. C. Goheen, 1995, *Vapor Space Characterization of Waste Tank 241-BY-108: Results from Samples Collected on 10/27/94*, PNL-10495 UC-606, Pacific Northwest Laboratory, Richland, Washington.
- Meacham, J. E., H. Babad, R. J. Cash, G. T. Dukelow, S. J. Eberlein, D. W. Hamilton, G. D. Johnson, J. W. Osborne, M. A. Payne, D. J. Sherwood, D. A. Turner, and J. L. Huckaby, 1995, *Approach for Tank Safety Characterization of Hanford Site Waste*, WHC-EP-0843 Rev. 0, UC-2070, Westinghouse Hanford Company, Richland, Washington.

NFPA 1992, *Standard on Explosion Prevention Systems*, NFPA 69, National Fire Protection Association, Quincy, Massachusetts.

Osborne, J. W., and J. L. Huckaby, 1994, *Program Plan for the Resolution of Tank Vapor Issues*, WHC-EP-0562 Rev. 1, Westinghouse Hanford Company, Richland, Washington.

Osborne, J. W., J. L. Huckaby, T. P. Rudolph, E. R. Hewitt, D. D. Mahlum, J. Y. Young, and C. M. Anderson, 1994, *Data Quality Objectives for Generic In-Tank Health and Safety Issue Resolution*, WHC-SD-WM-DQO-002, Westinghouse Hanford Company, Richland, Washington.

Pingel, L. A., 1994, *Draft Report from the In-Situ Vapor Sampling of Waste Tank U-106*, (Internal memorandum 8E920-SAS94-10730, September 12), Westinghouse Hanford Company, Richland, Washington.

WHC 1995a, *Operating Specifications for Watchlist Tanks*, OSD-T-151-00030, Rev. B-9, Westinghouse Hanford Company, Richland, Washington.

WHC 1995b, *Vapor and Gas Sampling of Single-Shell Tank 241-U-106 Using the Vapor Sampling System*, WHC-SD-WM-RPT-151, Westinghouse Hanford Company, Richland, Washington.

Table 2-1
Tank U-106 Gas and Vapor Sample Type and Number

Laboratory	Sampling Device	Nominal Sample Volume (L)	Target Analytes	Number of Samples
Oak Ridge National Laboratories	Triple Sorbent Trap	2.0	Organic vapors	6 tank air samples
		6.0	Organic vapors	6 tank air samples + 2 trip blanks + 2 field blanks
Pacific Northwest Laboratories	Acidified Carbon Sorbent Trap	3.0	Ammonia	6 tank air samples + 3 trip blank
	Triethanolamine Sorbent Trap	3.0	Nitrogen Dioxide	6 tank air samples + 3 trip blank
	Oxidation Bed + Triethanolamine Sorbent Trap	3.0	Nitric Oxide	6 tank air samples + 3 trip blank
	Silica Gel Sorbent Trap	3.0	Water vapor	6 tank air samples + 3 trip blanks
	SUMMA™ canister	6.0	Carbon Dioxide, Carbon Monoxide, Hydrogen, Methane, Nitrous Oxide, Organic vapors	9 tank air samples + 2 ambient air samples
WHC 222-S Laboratory	Silica Gel Sorbent Trap	1.0	Tritium-Substituted Water Vapor	1 tank air sample

Table 3-1
Tank U-106 Inorganic Gas and Vapor Concentrations --
Analyses by Pacific Northwest Laboratory

Compound	CAS ¹ Number	Sample Type	Number of samples	Average (ppmv)	Standard Deviation (ppmv)	RSD ² (%)
Ammonia, NH ₃	7664-41-7	Sorbent Trap	6	988	29	3
Carbon Dioxide, CO ₂	124-38-9	SUMMA TM	3	46.5	1.2	2
Carbon Monoxide, CO	630-08-0	SUMMA TM	3	< 12	—	—
Hydrogen, H ₂	1333-74-0	SUMMA TM	3	210	6	3
Nitric Oxide, NO	10102-43-9	Sorbent Trap	6	≤ 0.04	—	—
Nitrogen Dioxide, NO ₂	10102-44-0	Sorbent Trap	6	≤ 0.04	—	—
Nitrous Oxide, N ₂ O	10024-97-2	SUMMA TM	3	559	8	1.4
Water Vapor, H ₂ O	7732-18-5	Sorbent Trap	6	17,600 (12.9 mg/L)	200 (0.15 mg/L)	1.1

1 CAS = Chemical Abstracts Service.

2 RSD = relative standard deviation. Burnum (1995) specifies the RSD should be less than 25 %.

Table 3-2
Comparison of Tank U-105 and U-106 Headspace Constituents --
Inorganic Analyses by Pacific Northwest Laboratory
and Organic Analyses by Oak Ridge National Laboratory¹

Tank:	U-105 ²	U-106
Date sampled, (mo/day/yr)	2/24/95	3/7/95
Headspace temperature, (°C)	42.6	21.9
Ammonia, (ppmv)	325	988
Hydrogen, (ppmv)	< 49	210
Carbon dioxide, (ppmv)	< 23	46.5
Carbon monoxide, (ppmv)	< 23	< 12
Nitric oxide, (ppmv)	± 0.03	± 0.04
Nitrogen dioxide, (ppmv)	± 0.002	± 0.04
Nitrous oxide, (ppmv)	154	559
Water vapor, (mg/m ³)	11.9	12.9
Water vapor, (% relative humidity)	20	67
Ethanenitrile (acetonitrile), (ppmv)	0.037	(0.10)
Propanone (acetone), (ppmv)	0.033	0.064
1-Butanol, (ppmv)	(0.096)	(0.51)
n-Dodecane, (ppmv)	(0.0012)	0.0022
n-Tridecane, (ppmv)	(0.0046)	0.0046
Total estimated organic vapor ³ (mg/m ³)	(4.4)	(10.1)

1 Organic vapor results are from ORNL, with non-quantitated values in parentheses and quantitative values not in parentheses.

2 Data are from Huckaby and Bratzel 1995.

3 This value is the summation of quantitated and estimated organic vapor concentrations in ORNL TST samples.

Table 4-1
Tank U-106 Quantitatively Measured Organic Compounds in SUMMA™ Samples --
Analyses by Pacific Northwest Laboratory

Cmpd #	Compound	CAS ¹ Number	Average ² (ppmv)	Standard Deviation (ppmv)	RSD ³ (%)
1	Trichlorofluoromethane	75-69-4	0.040	0.002	4
2	Toluene	108-88-3	0.039	0.002	6
3	Propanone (acetone)	67-64-1	0.044	0.004	10
4	Tetrahydrofuran	109-99-9	0.024	0.002	10
5	1-Propanol	71-23-8	0.34	0.002	1
6	Pyridine ⁴	110-86-1	0.068	--	--
7	Methane	74-82-8	< 61	--	--
Sum of positively identified compounds:			1.75	mg/m ³	

1 CAS = Chemical Abstract Service.

2 Average of 3 samples.

3 RSD = relative standard deviation. Burnum (1995) specifies the RSD should be less than 25 %.

4 Detected in only 1 sample.

Table 4-2
 Tank U-106 Quantitatively Measured Organic Compounds in TST Samples --
 Analyses by Oak Ridge National Laboratory¹

Cmpd #	Compound	CAS ² Number	Average ³ (ppmv)	Standard Deviation (ppmv)	RSD ⁴ (%)
1	Propanone (acetone)	67-64-1	0.064	0.021	33
2	Propanenitrile	107-12-0	0.012	0.002	14
3	n-Hexane	110-54-3	0.0075	0.0020	26
4	Benzene	71-43-2	0.0076	0.0006	8
5	n-Heptane	142-82-5	0.011	0.002	19
6	Toluene	108-88-3	0.036	0.008	22
7	2-Hexanone	591-78-6	0.0028	0.0001	4
8	n-Octane	111-65-9	0.0026	0.0002	8
9	n-Undecane	1120-21-4	0.0016	0.00005	3
10	n-Dodecane	112-40-3	0.0022	0.0001	6
11	n-Tridecane	629-50-5	0.0046	0.0002	5

1 Results in this table are quantitative (as defined in Section 4.1).

2 CAS = Chemical Abstract Service.

3 Average of 4 TST samples: 3 were 2-L and 1 was 6-L.

4 RSD = relative standard deviation. Burnum (1995) specifies the RSD should be less than 25 %.

Table 4-3
Tank U-106 Positively Identified Organic Compounds in TST Samples --
Analyses by Oak Ridge National Laboratory¹

Cmpd #	Compound	CAS ² Number	Average ³ (ppmv)	Standard Deviation (ppmv)	RSD ⁴ (%)
1	Ethanenitrile (acetonitrile)	75-05-8	0.10	0.03	27
2	1-Butanol	71-36-3	0.51	0.13	26
3	n-Butanenitrile	109-74-0	0.0036	0.0003	9
4	2-Pentanone	107-87-9	0.0031	0.0002	8
5	n-Pentanenitrile	110-59-8	0.0015	0.0002	12
6	n-Hexanenitrile	628-73-9	0.00047	0.00009	19
7	2-Heptanone	110-43-0	0.0024	0.0002	9
8	n-Nonane	111-84-2	0.0016	0.0002	10
9	n-Heptanenitrile	629-08-3	0.00061	0.00006	10
10	2-Octanone	111-13-7	0.00065	0.00008	12
11	n-Decane	124-18-5	0.00093	0.00005	5

1 Results in this table are not quantitative (as defined in Section 4.1) because measured values in at least 1 of the samples are outside instrument calibration limits.

2 CAS = Chemical Abstract Service.

3 Average of 4 TST samples: 3 were 2-L and 1 was 6-L.

4 RSD = relative standard deviation. Burnum (1995) specifies the RSD should be less than 25 %.

Table 4-4
 Tank U-106 Comparison of Organic Compounds in TST and SUMMA™ Samples --
 Analyses conducted by Pacific Northwest Laboratory
 and Oak Ridge National Laboratory

Compound	CAS ¹ Number	TST Average ² (ppmv)	SUMMA™ Average ³ (ppmv)	PRD ⁴ (%)
1,1-Dichloroethene (vinylidene chloride)	75-35-4	< 0.00039	< 0.005	—
Dichloromethane (methylene chloride)	75-09-2	< 0.00089	< 0.005	—
Propanone (acetone)	67-64-1	0.064	0.044	37
Ethanenitrile (acetonitrile)	75-05-8	0.10	< 0.005	> 181
Propanenitrile	107-12-0	0.012	< 0.005	> 82
n-Butanenitrile	109-74-0	0.0036	< 0.005	—
Benzene	71-43-2	0.0076	< 0.005	> 41
Toluene	108-88-3	0.036	0.039	8
n-Hexane	110-54-3	0.0075	< 0.005	> 40
n-Heptane	142-82-5	0.011	< 0.005	> 75
n-Decane	124-18-5	0.000933	< 0.005	—

1 CAS = Chemical Abstract Service.

2 Average of 4 TST samples: 3 were 2-L and 1 was 6-L.

3 Average of 3 sample analyses.

4 PRD = percent relative difference. Keller (1994) requires the PRD to be less than 20 %.

Table 4-5
 Tank U-106 Tentatively Identified Organic Compounds in SUMMA™ Samples --
 Analyses by Pacific Northwest Laboratory

Cmpd #	Compound	CAS ¹ Number	Average ² (mg/m ³)	Standard Deviation ³ (mg/m ³)
1	Propene	115-07-1	0.11	0.02
2	Unknown ⁴		0.067	--
3	Dimethyl ether	115-10-6	0.085	0.008
4	Cyclopropane ⁴	75-19-4	0.064	--
5	Methanol	67-56-1	4.67	0.63
6	1-Propene, 2-methyl-	115-11-7	0.38	0.04
7	n-Butane	106-97-8	0.18	0.02
8	Propane, 2-methyl-2-nitro-	594-70-7	0.062	0.007
9	Ethanol	64-17-5	3.75	0.59
10	Propanone ⁴ (acetone)	67-64-1	0.33	--
11	n-Pentane ⁴	109-66-0	0.076	--
12	2-Propanol, 2-Methyl	75-65-0	< 0.03	--
13	2-Propanal, 2-Methyl	78-85-3	< 0.03	--
14	1-Butanol	71-36-3	1.16	0.17
15	Unknown C7 Alkane		0.10	0.01
16	N-Nitrosodimethylamine	62-75-9	0.059	0.003
17	Pyrazine ⁵	290-37-9	0.055	0.005
Sum of tentatively identified compounds:			10.62	

1 CAS = Chemical Abstract Service.

2 Based on analyses of 3 samples, values listed are estimates.

3 When the analyte was detected in only 2 samples, the entry is the relative difference (i.e., their difference divided by 2).

4 Detected in only 1 sample.

5 Detected in only 2 samples.

Table 4-6
 Tank U-106 Tentatively Identified Organic Compounds in TST Samples
 in Order of Chromatographic Elution --
 Analyses by Oak Ridge National Laboratory

Cmpd #	Compound	CAS ¹ Number	Average ² (mg/m ³)	Standard Deviation (mg/m ³)
1	Methanol	67-56-1	2.24	0.24
2	Ethanol	64-17-5	3.25	0.77
3	2-Propanol	67-63-0	0.15	0.05
4	2-Propanol, 2-methyl-	75-65-0	0.010	0.017
5	1-Propanol	71-23-8	0.15	0.04
6	Ethanal (acetaldehyde)	75-07-0	0.018	0.031
7	Furan, tetrahydro-	109-99-9	0.13	0.04
8	1-Propanol, 2-methyl-	78-83-1	0.0094	0.0162
9	3-Hexanol	623-37-0	0.037	0.006
10	1,2,3,6-Tetrahydropyridine	694-05-3	0.075	0.089
11	Pyrazine	290-37-9	0.10	0.09
12	1-Butanol, 2-methyl-, (S)-	1565-80-6	0.0089	0.0154
13	N-Nitrosodimethylamine	62-75-9	0.13	0.01
14	Pyridine	110-86-1	0.023	0.026
15	Heptane, 3-methyl-	589-81-1	0.020	0.017
16	Cyanamide, dimethyl-	1467-79-4	0.13	0.11
17	1-Butene, 3,3-dimethyl-	558-37-2	0.021	0.019
18	1H-Pyrazole, 4,5-dihydro-5-methyl-	1568-20-3	0.040	0.012
19	1-Butanamine, N-ethylidene-	6898-74-4	0.012	0.020
20	1H-Pyrazole, 4,5-dihydro-4, 5-dimethyl-	28019-94-5	0.016	0.014
21	Cyclotrisiloxane, hexamethyl	541-05-9	0.081	0.038
22	Pyrazine, methyl-	109-08-0	0.0064	0.0111
23	1H-Pyrazole, 4,5-dihydro-5-methyl-	1568-20-3	0.027	0.010
24	1H-Pyrazole, 4,5-dihydro-5-methyl & others		0.031	0.010
25	Oxazole, 4,5-dihydro-2-methyl-	1120-64-5	0.053	0.009
26	Oxazole, 4,5-dihydro-2-methyl-	1120-64-5	0.0091	0.0158
27	Benzene, 1,3-dimethyl-	108-38-3	0.079	0.013

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Cmpd #	Compound	CAS ¹ Number	Average ² (mg/m ³)	Standard Deviation (mg/m ³)
28	3-Heptanone	106-35-4	0.046	0.010
29	p-Xylene	106-42-3	0.019	0.017
30	2-Hexene, 4,4,5-trimethyl-	55702-61-9	0.034	0.004
31	2-Heptanone, 6-methyl-	928-68-7	0.017	0.015
32	2-Nonen-4-one	32064-72-5	0.063	0.008
33	Cyclotetrasiloxane, octamethyl-	556-67-2	0.038	0.008
34	1-Nonanol	143-08-8	0.0037	0.0064
35	2-Undecene, 4,5-dimethyl- [R*,R*-(E)]-	55170-92-8	0.0037	0.0064
36	1-Hexanol, 2-ethyl-	104-76-7	0.029	0.003
37	Benzyl Alcohol	100-51-6	0.049	0.002
38	Aniline, N-methyl- & others		0.0056	0.0097
39	Nonanenitrile	2243-27-8	0.011	0.010
40	Decanenitrile	1975-78-6	0.0037	0.0064
41	2(3H)-Furanone, 5-ethyldihydro-	695-06-7	0.089	0.009
42	2-Oxazolidinone, 5-methyl-3-(2-propenyl)-	55956-20-2	0.067	0.006
43	1,4-Cyclohexanedione	637-88-7	0.017	0.002
44	Mixture		0.022	0.021
45	4-Piperidinemethanol, 1-methyl-	20691-89-8	0.014	0.025
46	n-Tetradecane	629-59-4	0.029	0.004
47	Tetradecanoic acid	544-63-8	0.023	0.008
48	Benzenesulfonamide, N-butyl-	3622-84-2	0.043	0.011
49	Pentadecanoic acid	1002-84-2	0.0053	0.0091
50	9-Hexadecenoic acid	2091-29-4	0.016	0.027
51	Hexadecanoic acid	57-10-3	0.059	0.024
52	Isopropyl Palmitate	142-91-6	0.0056	0.0097
Sum of Tentatively Identified Compounds:			7.6	

1 CAS = Chemical Abstract Service.

2 Average of 4 TST samples: 3 were 2-L and 1 was 6-L, values listed are estimates.

Table 4-7
Tank U-106 Tentatively Identified Organic Compounds in TST Samples
Sorted Alphanumerically --
Analyses by Oak Ridge National Laboratory

Cmpd #	Compound	CAS ¹ Number	Average ² (mg/m ³)	Standard Deviation (mg/m ³)
17	1-Butene, 3,3-dimethyl-	558-37-2	0.021	0.019
8	1-Propanol, 2-methyl-	78-83-1	0.0094	0.0162
34	1-Nonanol	143-08-8	0.0037	0.0064
12	1-Butanol, 2-methyl-, (S)-	1565-80-6	0.0089	0.0154
5	1-Propanol	71-23-8	0.15	0.04
36	1-Hexanol, 2-ethyl-	104-76-7	0.029	0.003
19	1-Butanamine, N-ethylidene-	6898-74-4	0.012	0.020
43	1,4-Cyclohexanedione	637-88-7	0.017	0.002
10	1,2,3,6-Tetrahydropyridine	694-05-3	0.075	0.089
20	1H-Pyrazole, 4,5-dihydro-4, 5-dimethyl-	28019-94-5	0.016	0.014
23	1H-Pyrazole, 4,5-dihydro-5-methyl-	1568-20-3	0.027	0.010
24	1H-Pyrazole, 4,5-dihydro-5-methyl & others		0.031	0.010
18	1H-Pyrazole, 4,5-dihydro-5-methyl-	1568-20-3	0.040	0.012
35	2-Undecene, 4,5-dimethyl- [R*,R*-(E)]-	55170-92-8	0.0037	0.0064
4	2-Propanol, 2-methyl-	75-65-0	0.010	0.017
31	2-Heptanone, 6-methyl-	928-68-7	0.017	0.015
30	2-Hexene, 4,4,5-trimethyl-	55702-61-9	0.034	0.004
32	2-Nonen-4-one	32064-72-5	0.063	0.008
42	2-Oxazolidinone, 5-methyl-3-(2-propenyl)-	55956-20-2	0.067	0.006
41	2(3H)-Furanone, 5-ethyldihydro-	695-06-7	0.089	0.009
3	2-Propanol	67-63-0	0.15	0.05
28	3-Heptanone	106-35-4	0.046	0.010
9	3-Hexanol	623-37-0	0.037	0.006
45	4-Piperidinemethanol, 1-methyl-	20691-89-8	0.014	0.025
50	9-Hexadecenoic acid	2091-29-4	0.016	0.027
38	Aniline, N-methyl- & others		0.0056	0.0097

Cmpd #	Compound	CAS ¹ Number	Average ² (mg/m ³)	Standard Deviation (mg/m ³)
27	Benzene, 1,3-dimethyl-	108-38-3	0.079	0.013
48	Benzenesulfonamide, N-butyl-	3622-84-2	0.043	0.011
37	Benzyl Alcohol	100-51-6	0.049	0.002
16	Cyanamide, dimethyl-	1467-79-4	0.13	0.11
33	Cyclotetrasiloxane, octamethyl-	556-67-2	0.038	0.008
21	Cyclotrisiloxane, hexamethyl	541-05-9	0.081	0.038
40	Decanenitrile	1975-78-6	0.0037	0.0064
6	Ethanal (acetaldehyde)	75-07-0	0.018	0.031
2	Ethanol	64-17-5	3.25	0.77
7	Furan, tetrahydro-	109-99-9	0.13	0.04
15	Heptane, 3-methyl-	589-81-1	0.020	0.017
51	Hexadecanoic acid	57-10-3	0.059	0.024
52	Isopropyl Palmitate	142-91-6	0.0056	0.0097
1	Methanol	67-56-1	2.24	0.24
44	Mixture		0.022	0.021
13	N-Nitrosodimethylamine	62-75-9	0.13	0.01
46	n-Tetradecane	629-59-4	0.029	0.004
39	Nonanenitrile	2243-27-8	0.011	0.010
25	Oxazole, 4,5-dihydro-2-methyl-	1120-64-5	0.053	0.009
26	Oxazole, 4,5-dihydro-2-methyl-	1120-64-5	0.0091	0.0158
29	p-Xylene	106-42-3	0.019	0.017
49	Pentadecanoic acid	1002-84-2	0.0053	0.0091
11	Pyrazine	290-37-9	0.10	0.09
22	Pyrazine, methyl-	109-08-0	0.0064	0.0111
14	Pyridine	110-86-1	0.023	0.026
47	Tetradecanoic acid	544-63-8	0.023	0.008

¹ CAS = Chemical Abstract Service.

² Average of 4 TST samples: 3 were 2-L and 1 was 6-L, values listed are estimates

Table 4-8
Tank U-106 Tentatively Identified Organic Compounds in TST Samples
Sorted by Estimated Concentration --
Analyses by Oak Ridge National Laboratory

Cmpd #	Compound	CAS ¹ Number	Average ² (mg/m ³)	Standard Deviation (mg/m ³)
2	Ethanol	64-17-5	3.25	0.77
1	Methanol	67-56-1	2.24	0.24
3	2-Propanol	67-63-0	0.15	0.05
5	1-Propanol	71-23-8	0.15	0.04
13	N-Nitrosodimethylamine	62-75-9	0.13	0.01
16	Cyanamide, dimethyl-	1467-79-4	0.13	0.11
7	Furan, tetrahydro-	109-99-9	0.13	0.04
11	Pyrazine	290-37-9	0.10	0.09
41	2(3H)-Furanone, 5-ethylidihydro-	695-06-7	0.089	0.009
21	Cyclotrisiloxane, hexamethyl	541-05-9	0.081	0.038
27	Benzene, 1,3-dimethyl-	108-38-3	0.079	0.013
10	1,2,3,6-Tetrahydropyridine	694-05-3	0.075	0.089
42	2-Oxazolidinone, 5-methyl-3-(2-propenyl)-	55956-20-2	0.067	0.006
32	2-Nonen-4-one	32064-72-5	0.063	0.008
51	Hexadecanoic acid	57-10-3	0.059	0.024
25	Oxazole, 4,5-dihydro-2-methyl-	1120-64-5	0.053	0.009
37	Benzyl Alcohol	100-51-6	0.049	0.002
28	3-Heptanone	106-35-4	0.046	0.010
48	Benzenesulfonamide, N-butyl-	3622-84-2	0.043	0.011
18	1H-Pyrazole, 4,5-dihydro-5-methyl-	1568-20-3	0.040	0.012
33	Cyclotetrasiloxane, octamethyl-	556-67-2	0.038	0.008
9	3-Hexanol	623-37-0	0.037	0.006
30	2-Hexene, 4,4,5-trimethyl-	55702-61-9	0.034	0.004
36	1-Hexanol, 2-ethyl-	104-76-7	0.029	0.003
46	n-Tetradecane	629-59-4	0.029	0.004
23	1H-Pyrazole, 4,5-dihydro-5-methyl-	1568-20-3	0.027	0.010
47	Tetradecanoic acid	544-63-8	0.023	0.008

WHC-SD-WM-ER-450 REV. 1

Cmpd #	Compound	CAS ¹ Number	Average ² (mg/m ³)	Standard Deviation (mg/m ³)
14	Pyridine	110-86-1	0.023	0.026
44	Mixture		0.022	0.021
17	1-Butene, 3,3-dimethyl-	558-37-2	0.021	0.019
15	Heptane, 3-methyl-	589-81-1	0.020	0.017
29	p-Xylene	106-42-3	0.019	0.017
6	Ethanal (acetaldehyde)	75-07-0	0.018	0.031
43	1,4-Cyclohexanedione	637-88-7	0.017	0.002
31	2-Heptanone, 6-methyl-	928-68-7	0.017	0.015
50	9-Hexadecenoic acid	2091-29-4	0.016	0.027
20	1H-Pyrazole, 4,5-dihydro-4, 5-dimethyl-	28019-94-5	0.016	0.014
45	4-Piperidinemethanol, 1-methyl-	20691-89-8	0.014	0.025
19	1-Butanamine, N-ethylidene-	6898-74-4	0.012	0.020
39	Nonanenitrile	2243-27-8	0.011	0.010
24	1H-Pyrazole, 4,5-dihydro-5-methyl & others		0.031	0.010
4	2-Propanol, 2-methyl-	75-65-0	0.010	0.017
8	1-Propanol, 2-methyl-	78-83-1	0.0094	0.0162
26	Oxazole, 4,5-dihydro-2-methyl-	1120-64-5	0.0091	0.0158
12	1-Butanol, 2-methyl-, (S)-	1565-80-6	0.0089	0.0154
22	Pyrazine, methyl-	109-08-0	0.0064	0.0111
38	Aniline, N-methyl- & others		0.0056	0.0097
52	Isopropyl Palmitate	142-91-6	0.0056	0.0097
49	Pentadecanoic acid	1002-84-2	0.0053	0.0091
34	1-Nonanol	143-08-8	0.0037	0.0064
35	2-Undecene, 4,5-dimethyl- [R*,R*-(E)]-	55170-92-8	0.0037	0.0064
40	Decanenitrile	1975-78-6	0.0037	0.0064

1 CAS = Chemical Abstract Service.

2 Average of 4 TST samples: 3 were 2-L and 1 was 6-L, values listed are estimates.