RMIS View/Print Document Cover Sheet

This document was retrieved from the Boeing ISEARCH System.

Accession #: D196054421

Document #: SD-WM-ER-420

Title/Desc:

TANK 241BY106 HEADSPACE GAS & VAPOR
CHARACTERIZATION RESULTS FOR SAMPLES COLLECTED
IN 5/1994 & 7 1994

COMPLETE

ENGINEERING CHANGE NOTICE

Page 1 of 21. ECN **No 625440**Proj.
ECN

2. ECN Category (mark one) Supplemental ☒ Direct Revision ☐ Change ECN ☐ Temporary ☐ Standby ☐ Supersedure ☐ Cancel/Void ☐	3. Originator's Name, Organization, MSIN, and Telephone No. D. R. BRATZEL, 75640, S7-21, 373-3579		3a. USQ Required? ☐ Yes ☒ No	4. Date 09/27/95
	5. Project Title/No./Work Order No. TANK 241-BY-106 HEADSPACE GAS AND VAPOR CHARACTERIZATION RESULTS FOR SAMPLES COLLECTED IN MAY 1994 AND JULY 1994		6. Bldg./Sys./Fac. No. 2704HV/200E	7. Approval Designator N/A
11a. Modification Work ☐ Yes (fill out Blk. 11b) ☒ No (NA Blks. 11b, 11c, 11d)	11b. Work Package No. N/A	11c. Modification Work Complete N/A Cog. Engineer Signature & Date	11d. Restored to Original Condition (Temp. or Standby ECN only) N/A Cog. Engineer Signature & Date	
12. Description of Change Title change and complete rewrite.				
13a. Justification (mark one) Criteria Change ☒ Design Improvement ☐ Environmental ☐ Facility Deactivation ☐ As-Found ☐ Facilitate Const ☐ Const. Error/Omission ☐ Design Error/Omission ☐				
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 28 1995 <i>Sta. 4</i>	

625440

RELEASE AUTHORIZATION

Document Number: WHC-SD-WM-ER-420, REV 2

Document Title: Tank 241-BY-106 Headspace Gas and Vapor
Characterization Results for Samples Collected in
May 1994 and July 1994

Release Date: 9/28/95

**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 Broz

TRADEMARK DISCLAIMER. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors.

This report has been reproduced from the best available copy. Available in paper copy. Printed in the United States of America. To obtain copies of this report, contact:

Westinghouse Hanford Company - Document Control Services
P.O. Box 1970, Mailstop H6-08, Richland, WA 99352
Telephone: (509) 372-2420; Fax: (509) 376-4989

THIS PAGE INTENTIONALLY LEFT BLANK

SUPPORTING DOCUMENT

1. Total Pages 38

2. Title

TANK 241-BY-106 HEADSPACE GAS AND VAPOR
CHARACTERIZATION RESULTS FOR SAMPLES COLLECTED IN
MAY 1994 AND JULY 1994

3. Number

WHC-SD-WM-ER-420

4. Rev No.

2

5. Key Words

CHARACTERIZATION OBJECTIVES, TANK HEADSPACE,
SAMPLING EVENT, INORGANIC GASES, ORGANIC VAPORS

6. Author

Name: D. R. BRATZEL

DRB 9/25/95
Signature

Organization/Charge Code 75640/N4AB1

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

OFFICIAL RELEASE
BY WHC
DATE SEP 28 1995

3

Sta 4

THIS PAGE INTENTIONALLY LEFT BLANK

THIS PAGE INTENTIONALLY LEFT BLANK

Tank 241-BY-106 Headspace Gas and Vapor Characterization Results for Samples Collected in May 1994 and July 1994

J. L. Huckaby
Pacific Northwest Laboratories

D. R. Bratzel
Westinghouse Hanford Company

Date Published
September 1995

Prepared for the U.S. Department of Energy
Office of Environmental Restoration and
Waste Management

Westinghouse
Hanford Company

P.O. Box 1970
Richland, Washington

Management and Operations Contractor for the
U.S. Department of Energy under Contract DE-AC06-87RL10930

Approved for Public Release

THIS PAGE INTENTIONALLY LEFT BLANK

Contents

1.0 INTRODUCTION	1
1.1 Characterization Objectives	1
1.2 Characterization Data Criteria	1
1.3 Sampling Overview	2
1.4 Tank Headspace Dynamics	2
2.0 SAMPLING EVENT	3
2.1 May 1994 <i>In Situ</i> Sampling Event	3
2.2 July 1994 Vapor Sampling System Sampling Event	3
3.0 INORGANIC GASES AND VAPORS	4
3.1 Ammonia, Hydrogen, and Nitrous Oxide	4
3.2 Carbon Dioxide and Carbon Monoxide	5
3.3 Nitric Oxide, Nitrogen Dioxide, Water and Tritium	5
3.4 Hydrogen Cyanide	5
3.5 Discussion of Inorganic Analytes	6
4.0 ORGANIC VAPORS	7
4.1 Positively Identified Organic Analytes	7
4.2 Tentatively Identified Organic Analytes	8
4.3 Total Nonmethane Organic Carbon	9
4.4 Discussion of Organic Analytes	9
5.0 SUMMARY	11
6.0 REFERENCES	12

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
OGIST	Oregon Graduate Institute of Science and Technology
ORNL	Oak Ridge National Laboratory
PNL	Pacific Northwest Laboratory
ppmv	parts per million by volume, 1 ppmv = 10 ⁻⁴ vol%
TNMOC	total nonmethane organic carbon
TST	triple sorbent trap
Vol%	percent by volume, 1 vol% = 10,000 ppmv
VSS	vapor sampling system
WHC	Westinghouse Hanford Company

Acknowledgements

The author wishes to thank Chris Simonen for her work verifying data and generating tables, and Shas Mattigod for his help with the construction and reviews of this document.

Tank 241-BY-106 Headspace Gas and Vapor Characterization Results
for Samples Collected in May 1994 and July 1994

1.0 INTRODUCTION

1.1 Characterization Objectives

Tank BY-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). This report primarily discusses results from the July 1994 sampling event, but also includes selected results of the May 1994 sampling event. The tank BY-106 headspace was sampled in May 1994 in accordance with *Safety Assessment for Gas Sampling All Ferrocyanide Tanks* (Farley 1991), and in July 1994 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 1992). Current governing operating specifications for Watchlist tanks, such as tank BY-106, specify that combustible constituents be maintained at or below 20 % of the LFL (WHC 1995a).

Headspace characterization data are 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

Tank BY-106 was vapor sampled in May 1994 using the *in situ* sampling (ISS) method, and again in July 1994 using the more robust vapor sampling system (VSS) method. Because the ISS sample volume flow measurement used during the May 1994 event was inherently less accurate than that of the VSS, the sorbent trap samples from the ISS event are not considered to be equivalent to those from the VSS sampling event (Huckaby and Babad 1995). Furthermore, there are other discrepancies between results from the ISS and VSS methods that are not understood (Huckaby 1994a), and until the ISS method has been validated and the discrepancies resolved, results from early ISS events should be considered suspect.

Nevertheless, a brief description of the ISS event and hydrogen cyanide sampling results from the May 1994 ISS event are presented below, because this analyte was not sampled for during the VSS event. Huckaby and Babad (1995) describe the bases for using the ISS method for hydrogen cyanide, and why it was not sampled for during the VSS event. All other results presented here are from the July 1994 VSS sampling event.

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

1.4 Tank Headspace Dynamics

Tank BY-106 is the third tank in a 3-tank cascade with tanks BY-104 and BY-105. It is connected to tank BY-105 via a 7.4-cm (2.9-in.) inside diameter, 7.6-m (25-ft) long underground cascade line. Tanks BY-104 and BY-105 are connected by a similar line. Since these cascade lines connect the headspaces of these tanks, gases and vapors originating from the wastes in tank BY-104 or BY-105 may be transferred to tank BY-106 (unless the cascade lines are obstructed).

The cascade of tanks BY-104, BY-105, and BY-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 1994b). Changes in the concentrations of tank headspace constituents due to barometric pressure changes are consequently very slow.

2.0 SAMPLING EVENT

2.1 May 1994 *In Situ* Sampling Event

Tank BY-106 was sampled using ISS methods on May 4, 1994 by WHC Sampling and Mobile Laboratories. This sampling was conducted to satisfy requirements of *Safety Assessment for Gas Sampling All Ferrocyanide Tanks* (Farley 1991). Samples for hydrogen cyanide were collected from a point approximately 7.9 m below the top of the flange on riser 3, between 9:45 a.m. and 10:45 a.m.

Huckaby et al. (1995) give a general description of the ISS method and equipment. Pingel (1994) provides field sampling information for the tank BY-106 May 1994 ISS event, and Mahon (1995) provides revised sample volume measurements. In addition to the hydrogen cyanide results presented below, Pool et al. (1995) provide sample preparation and analysis results for selected organic and inorganic vapors. SUMMA™ canister samples collected during the May 1994 ISS event were prepared and analyzed Oregon Graduate Institute of Science and Technology (OGIST) and these results are reported by Rasmussen (1994a).

2.2 July 1994 Vapor Sampling System Sampling Event

Headspace gas and vapor samples were collected from tank BY-106 using the vapor sampling system (VSS) on July 8, 1994 by WHC Sampling and Mobile Laboratories (WHC 1995b). Sample collection and analysis were performed as directed by the sample and analysis plan¹ (WHC 1995b, Appendix A). The tank headspace temperature was determined to be 27 °C. Air from the tank BY-106 headspace was withdrawn via a heated sampling probe mounted in riser 10B, and transferred via heated tubing to the VSS sampling manifold. All heated zones of the VSS were maintained at approximately 65 °C.

Sampling media were prepared and analyzed by WHC, Oak Ridge National Laboratories (ORNL), Pacific Northwest Laboratories (PNL), and OGIST through a contract with Sandia National Laboratories. 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 10 trip 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 and references therein.

¹ The current requirement that sampling and analysis parameters be specified by a tank characterization plan was not in effect for gas and vapor sampling until October 1, 1994.

3.0 INORGANIC GASES AND VAPORS

Analytical results of sorbent trap and SUMMA^{TM,2} 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 were prepared and analyzed by PNL, and SUMMATM canisters were analyzed for inorganic analytes by OGIST. Lucke et al. (1994) and Rasmussen (1994b) describe sample preparation and analyses.

Analyses of the VSS event inorganic vapor sorbent traps were performed within 20 days of sample collection, analyses of VSS event SUMMATM canisters for inorganic compounds were performed 66 days after sample collection, and analyses of the ISS event hydrogen cyanide sorbent traps were performed 58 days after sample collection (Ligotke 1995). The solvent trap analyses satisfied the 60-day holding time requirement of the WHC quality assurance project plan (Keller 1994), but SUMMATM analyses did not. Though no holding time study has been performed to address the stability of compounds in SUMMATM canisters in the chemical matrix of the tank samples, 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 though the 60 day holding time requirement had been exceeded.

PNL results were produced at PNL quality assurance impact level 3. OGIST did not have a WHC-approved quality assurance project plan in place when performing analyses, so OGIST data have been placed in square brackets both in Table 3-1 and elsewhere in this report to indicate that they represent secondary results.

3.1 Ammonia, Hydrogen, and Nitrous Oxide

Ammonia concentration in the headspace of tank BY-106 was measured to be 74 ppmv. Ammonia concentrations at this level are not uncommon in the waste tank headspaces, and are known to as high as about 1040 ppmv in tank BY-108 (McVeety et al. 1995). Given the LFL of ammonia in air is about 15 % by volume (vol%), the measured 74 ppmv corresponds to less than 0.05 % of the LFL, and does not contribute appreciably to the flammability of the headspace.

The concentration of hydrogen was determined to be an average of [45.5 ppmv] in 3 SUMMATM canister samples from the May 1994 ISS event by OGIST (Rasmussen 1994a). Analysis by OGIST of the SUMMATM canister samples from the July 1994 VSS sampling event was problematic (Rasmussen 1994b). In general, hydrogen is of concern as a fuel. Given that the LFL for hydrogen in air is about 4 vol%, the measured 45.5 ppmv of hydrogen in tank BY-106, corresponds to only about 0.1 % of the LFL. At this concentration, the hydrogen in tank BY-106 is not a flammability concern.

The nitrous oxide concentration in tank BY-106 was determined to be [70.6 ppmv] by OGIST. This is a typical concentration for nitrous oxide in the waste tanks that have been sampled. 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 BY-106 headspace.

² SUMMA is a trademark of Molectrics, Inc., Cleveland, Ohio.

3.2 Carbon Dioxide and Carbon Monoxide

The average measured headspace carbon dioxide concentration, [47.6 ppmv], is markedly lower than normal ambient air concentrations of about 350 to 400 ppmv. 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. Though some tanks have sufficient waste carbonate concentrations to warrant above-ambient carbon dioxide concentrations, most do not, and consequently have below-ambient carbon dioxide concentrations in their headspaces.

Carbon monoxide in the tank BY-106 headspace, at about [0.45 ppmv], is more concentrated than in ambient air, where it typically is about 0.05 to 0.15 ppmv. 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 measured at very high levels in any of the waste tanks, the highest level measured to date was [26.7 ppmv] in tank C-103³ (Huckaby and Story 1994).

3.3 Nitric Oxide, Nitrogen Dioxide, Water and Tritium

Nitric oxide and nitrogen dioxide concentrations in the tank BY-106 headspace were determined to be 0.13 ppmv and 0.05 ppmv, respectively. These are both acid gases that would have very low equilibrium concentrations above the high pH interstitial liquid in tank BY-106. The measurable presence of nitric oxide is not uncommon in 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 BY-106 headspace.

The water vapor concentration of tank BY-106 was determined to be about 14.7 mg/L, at the tank headspace temperature of 27 °C and pressure of 984 mbar (740 torr), (WHC 1995b). This corresponds to water vapor partial pressure of 20.4 mbar (15.3 torr), to a dew point of 17.8 °C, and to a relative humidity of 57 %.

Tritium was tested for using silica gel sorbent traps. 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. Analysis of the silica gel, which would have trapped approximately 34 mg of water vapor, indicated the total activity of the sample to be below the method detection limit of 50 pCi (WHC 1995b).

3.4 Hydrogen Cyanide

Analysis of the hydrogen cyanide specific sorbent traps indicated the concentration of this analyte to be $\leq$ 0.01 ppmv in all 3 samples. The absence of hydrogen cyanide at measurable concentrations is consistent with the expectation that an acid gas, such as hydrogen cyanide, would not exist at significant concentrations above the caustic waste in tank BY-106. No hydrogen cyanide has been detected in any of the 10 waste tank headspaces sampled for this analyte.

³ The carbon monoxide measurement in tank C-103 was made by Oregon Graduate Institute of Science and Technology, and placed in brackets to emphasize it should be considered secondary data.

3.5 Discussion of Inorganic Analytes

Aside from water and carbon dioxide, the most abundant waste constituents in the tank BY-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. The concentrations of each of these is about average for the passively ventilated tanks that have been sampled, with other values ranging roughly 1 order of magnitude higher and lower than those in tank BY-106. For comparison, inorganic compound results for tanks BY-104, BY-105, and BY-106 are given in Table 3-2.

The small relative standard deviations of the results, given in the last column in Table 3-1, indicate the precision of reported results is very good. Relative standard deviations range from 1 % for nitrous oxide results, to 28 % for nitric oxide results. The larger relative standard deviation of the nitric oxide results is due to the fact that it is very near the analytical method's limit of quantitation. 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.), and the small relative standard deviations suggest a high degree of control was maintained both in the field and in the laboratories.

As discussed briefly in Section 1.4, it is possible that gases and vapors generated by the waste in tanks BY-104 and BY-105 could be transferred to tank BY-106 via the cascade lines. If significant exchange of selected inorganic gases and vapors were taking place between adjacent tanks, either their headspace compositions would be very similar (if the exchange was mutual), or all constituents detected in one tank would be at or equal or higher concentrations in the other tank (if air flowed predominantly from 1 tank to the other). Consideration of data in Table 3-2 suggests that tanks BY-105 and BY-106 have similar headspace compositions, and the potential transfer of air, gases, and vapors from tank BY-105 to tank BY-106 can neither be proven nor ruled out.

4.0 ORGANIC VAPORS

Organic vapors in the tank BY-106 headspace were sampled using SUMMA™ canisters, which were analyzed at PNL, and triple sorbent traps (TSTs), which were analyzed by ORNL. None of the positively or tentatively identified organic analytes were at or above levels of concern. Both laboratories used a gas chromatograph (GC) equipped with a mass spectrometer (MS) detector to separate, identify, and quantitate the analytes. A quantitative measurement of the methane concentration and the total nonmethane organic carbon (TNMOC) concentration by the U.S. Environmental Protection Agency (EPA) task order 12 (TO-12) method was also performed by OGIST. Descriptions of sample device cleaning, sample preparations, and analyses are given by Jenkins et al. (1994), Lucke et al. (1994), and Rasmussen (1994b). No holding time study has been performed to determine the stability of analytes in SUMMA™ canisters in the chemical matrix of the tank samples.

SUMMA™ sample results should be considered to be the primary organic vapor data for tank BY-106. These results were produced at PNL quality assurance impact level 3, and all PNL analyses were completed 20 days after sample collection, well below the specified 60 day holding time (Keller 1994).

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.

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 all surrogates had standard deviation values within the 95 % confidence interval for variance, indicating that no bias was introduced in the measurement of analyte quantities (Jenkins 1995).

4.1 Positively Identified Organic Analytes

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 by 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 40 compounds in the Environmental Protection Agency (EPA) task order 14 (TO-14) method, which are primarily halocarbons and common industrial solvents (EPA 1988).

Table 4-1 lists the organic compounds positively identified and quantitated in SUMMA™ samples. Analysis for methane was performed by OGIST, all other analyses were performed by PNL. Only 7 of the 40 TO-14 analytes were observed to be above the 0.002 ppmv quantitation limit of the analyses. Averages reported are from analyses of 3 SUMMA™ canister samples except where noted.

Jenkins et al. (1994) report the positive identification of 26 of 27 analytes selected by WHC, (only 1 analyte, 1,1-dichloroethene, was below detection limits). Despite calibration of the instrument over about a 20-fold concentration range, 18 of the 24 compounds were outside of the calibration range in at least 1 of the 4 TST samples (i.e., these were not quantitated). The average concentrations of the positively identified compounds are given in Tables 4-2, 4-3, and 4-4. Table 4-2 lists the positively identified, quantitated analytes, Table 4-3 lists the positively identified analytes which were not quantitated, and Table 4-3 lists the positively identified analytes which exceeded their practical holding times. Tables 4-2, 4-3, and 4-4 are mutually exclusive, so that no analyte appears in more than 1 of these tables. Results in Tables 4-3 and 4-4 may not be accurate to within $\pm 30\%$, as specified by Burnum (1995).

The ORNL 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. As indicated in Table 4-4, butanal and 1-butanol exceeded their practical holding times, and may have been affected by the 25 day period between sample collection and analysis (Jenkins 1995b). Jenkins et al. (1995) describe the ORNL practical holding time study, and report the practical holding times of butanal and 1-butanol are 1 and 17 days, respectively. It should be noted that the contractual holding time for the TST samples was 60 days.

Three analytes, dichloromethane, benzene, and toluene, were common to both the ORNL and PNL target lists. A comparison of the ORNL and PNL results for these analytes is given in Table 4-5. The ORNL and PNL results are in excellent agreement for dichloromethane and toluene, but differ by more than a factor of 3 for benzene.

The 3 most abundant organic compounds in the tank BY-106 headspace are methane, propanone, and 1-butanol. At [3.6 ppmv], the methane concentration is about 2 times higher than its normal ambient air concentration. Methane is probably formed during the chemical and radiolytic degradation of organic wastes in the tank. Methane is not a constituent of toxicological concern, and its LFL in air is about 5 vol%. The [3.6 ppmv] of methane in tank BY-106 consequently corresponds to about 0.007 % of its LFL. Propanone, at 0.37 ppmv, and 1-butanol, at 0.34 ppmv, similarly present virtually no flammable or toxicological risks.

4.2 Tentatively Identified Organic Analytes

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 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 SUMMATM samples. Analyses of the samples are designed to recover, separate, and identify 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 SUMMATM samples has been problematic.

The organic compounds tentatively identified in SUMMATM canister samples by PNL are listed, with their estimated concentrations, in Table 4-6. Compounds are listed in Table 4-6 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 4-7. Compounds are listed in Table 4-7 according to the order by which the eluted chromatographically. The averages reported by ORNL in Table 4-7 are all 4-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 $\mu\text{g}/\text{m}^3$, based on dry air at 0 °C and 1.01 bar.

Because the list of tentatively identified organic compounds in TST samples is particularly long and locating any given compound may be difficult, the list has been sorted alphanumerically by compound name in Table 4-8. Table 4-9 gives the same list, sorted in order of decreasing estimated concentration. Numbers in the first columns of Tables 4-8 and 4-9 (Cmpd #) identify the location of the compound in Table 4-7.

The ORNL and PNL methods used to tentatively identify and estimate concentrations are described by Jenkins et al. (1994) and Pool et al. (1995), respectively, and should be reviewed before this data is used for decision making. Concentrations given in Tables 4-6 through 4-9 should be considered rough estimates. Results in these tables are presented in terms of observed peaks, and are not adjusted for the occurrence of split chromatographic peaks (e.g., Cmpd # 2, 3, and 4 in Table 4-7). In these instances, the estimated concentration of a compound appearing as a doublet or triplet is simply the sum of the individual peak estimates.

4.3 Total Nonmethane Organic Carbon

OGIST measured the TNMOC concentration in 3 SUMMA™ canister samples using the EPA TO-12 method (Rasmussen 1994b). The sample mean was $[9,900 \mu\text{g}/\text{m}^3]$, with a standard deviation of $[350 \mu\text{g}/\text{m}^3]$. This value is neither high nor low compared to most other waste tanks sampled to date.

4.4 Discussion of Organic Analytes

Some of the compounds listed in Tables 4-1 through 4-9 were introduced to the tank with process waste streams, and are detected in the headspace because the original inventory has not been completely evaporated or degraded. Examples of these are tributyl phosphate, which was used as an extractant in several Hanford processes; dibutyl butylphosphonate, which was a contaminant of tributyl phosphate; and the semivolatile normal paraffinic hydrocarbons (NPHs), (i.e., n-undecane, n-dodecane, n-tridecane, n-tetradecane, and n-pentadecane) and branched and cyclic alkanes (e.g., methylated decahydronaphthalenes, cyclopentanes, and cyclohexanes) with similar boiling points that were used as diluents for tributyl phosphate. The specific presence of the decahydronaphthalenes and cyclohexanes, which are not observed in all tanks with high NPH concentrations, is an indication of their different waste histories.

Most of the compounds in Tables 4-1 through 4-9, however, are believed to be chemical reaction and radiolytic reaction products of the semivolatile or nonvolatile organic waste stored in the tank. Specifically, 1-butanol is known to be formed by the hydrolysis of tributyl phosphate, and it thought that the alcohols, aldehydes, ketones, nitriles, alkenes, and short chain alkanes are all degradation products of NPHs.

Examination of the compounds listed in Tables 4-1 through 4-9 suggests many of the volatile species (presumed to be degradation products of the NPHs) have functional groups on the molecule's first or second carbon atom. For example, most alkenes listed have their double bond between the first and second carbon atoms, and ketones generally have the double bonded oxygen atom on the second carbon atom.

WHC-SD-WM-ER-420 REV. 2

As observed in other NPH-containing waste tanks, there are many small cyclic compounds, specifically cyclopropanes, cyclopentanes, and furans. The presence of these suggest that organic radicals, formed in the radiation field of the tank, play a role in the degradation of the semivolatile compounds.

5.0 SUMMARY

The tank BY-106 headspace was sampled in May 1994 and July 1994 for gases and vapors to address flammability and industrial hygiene concerns. Results unique to the May 1994 event and essentially all results from the July 1994 event have been reported. It was determined that no headspace constituents exceeded the flammability or 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*.
- Burnum, S. T., 1995, *Qualification of Reported WHC Vapor Program Data*, (letter 95-CHD-065 to president, Westinghouse Hanford Company, August 18), Department of Energy, Richland Operations Office, Richland, Washington.
- 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.
- EPA 1992, *Test Methods for Evaluating Solid Waste*, SW-846 Rev. 1, U.S. Environmental Protection Agency, Washington, D.C.
- Farley, W. G., 1991, *Safety Assessment for Gas Sampling All Ferrocyanide Tanks*, WHC-SD-WM-SAD-009 Rev. 2, Westinghouse Hanford Company, Richland, Washington.
- 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, *Vapor Sampling and Analysis Plan*, WHC-SD-WM-TP-335 Rev. 0G, Westinghouse Hanford Company, Richland, Washington.
- Huckaby, J. L., 1994a, *Vapor Sampling System (VSS) and In Situ Sampling (ISS) Method Comparison*, WHC-SD-WM-RPT-101 Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Huckaby, J. L., 1994b, *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 D. R. Bratzel, 1995a, *Tank 241-BY-104 Headspace Gas and Vapor Characterization Results for Samples Collected in April 1994 and June 1994*, WHC-SD-WM-ER-418, Rev. 1, Westinghouse Hanford Company, Richland, Washington.
- Huckaby, J. L., and D. R. Bratzel, 1995b, *Tank 241-BY-105 Headspace Gas and Vapor Characterization Results for Samples Collected in May 1994 and July 1994*, WHC-SD-WM-ER-419, Rev. 1, 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.
- Jenkins, R. A., 1995a, *Untitled*, (Letter 090195A to D. Bratzel, September 1), 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. E. Higgins, C. Y. Ma, and J. T. Skeen, 1994, *Analysis of Tank 241-BY-106 Headspace Components*, 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-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.
- Ligotke, M. W., 1995, *PNL Vapor Project Analytical Holding Times*, (Letter to D. R. Bratzel, September 23, 1995) Pacific Northwest Laboratory, Richland, Washington.
- Lucke, R. B., K. H. Pool, M. W. Ligotke, T. W. Clauss, B. D. McVeety, J. S. Fruchter, and S. C. Goheen, 1994, *Vapor Space Characterization of Waste Tank 241-BY-106: Results from Samples Collected Through the Vapor Sampling System on 7/8/94*, PNL-10248 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.
- Mahon, R., 1995, *FY 1994 In-Situ Sampling System Summary Report*, (Letter OM624-95-055 to Bratzel), Westinghouse Hanford Company, Richland, Washington.
- McVeety, B. D., T. W. Clauss, M. W. Ligotke, K. H. Pool, R. B. Lucke, G. S. Klinger, J. S. Young, M. McCulloch, J. S. Fruchter, and S. C. Goheen, 1994, *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.

WHC-SD-WM-ER-420 REV. 2

- 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, *Results from the In-Situ Vapor Sampling of Waste Tank BY-106*, (Internal memorandum 8E920-SAS94-090 to J. L. Huckaby, May 25), Westinghouse Hanford Company, Richland, Washington.
- Pool, K. H., M. W. Ligothe, T. W. Clauss, R. B. Lucke, B. D. McVeety, M. McCulloch, J. S. Fruchter, and S. C. Goheen, 1995, *Vapor Space Characterization of Waste Tank 241-BY-106 (In Situ): Results from Samples Collected on 5/4/94 and 5/5/94*, PNL-10284 UC-606, Pacific Northwest Laboratory, Richland, Washington.
- Rasmussen, R. A., 1994a, *Air Samples Collected at Waste Tanks: BY-103, BY-104, BY-105, BY-106, BY-111 by Westinghouse Hanford in 6-L SS SUMMA® Canisters*, Oregon Graduate Institute of Science and Technology, Beaverton, Oregon.
- Rasmussen, R. A., 1994b, *Air Samples Collected at Waste Tank 241-BY-106 on July 8, 1994 by Westinghouse Hanford in 6-L SS SUMMA® Canisters*, Oregon Graduate Institute of Science and Technology, Beaverton, Oregon.
- WHC 1995a, *Operating Specifications for Watchlist Tanks*, OSD-T-151-00030, Rev. B-9, Westinghouse Hanford Company, Richland, Washington
- WHC 1995b, *Sampling Report for the Vapor and Gas Sampling of Tank 241-BY-106 Using the Vapor Sampling System*, WHC-SD-WM-RPT-109, Westinghouse Hanford Company, Richland, Washington.

Table 2-1
Tank BY-106 Gas and Vapor Sample Type and Number for the July 1994 Sampling Event

Laboratory	Sampling Device	Nominal Sample Volume (L)	Target Analytes	Number of Samples
Oak Ridge National Laboratories	Triple Sorbent Trap	5.0	Organic vapors	4 tank air samples + 2 trip blanks
Oregon Graduate Institute of Science and Technology	SUMMA™ canister	6.0	Hydrogen, Nitrous Oxide, Carbon Dioxide, Carbon Monoxide	3 tank air samples
Pacific Northwest Laboratories	Acidified Carbon Sorbent Trap	3.0	Ammonia	5 tank air samples + 2 trip blanks
	Triethanolamine Sorbent Trap	3.0	Nitrogen Dioxide	10 tank air samples + 2 trip blanks
	Oxidation bed + Triethanolamine Sorbent Trap	3.0	Nitric Oxide	10 tank air samples + 2 trip blanks
	Silica Gel Sorbent Trap	3.0	Water vapor	10 tank air samples + 2 trip blanks
	SUMMA™ canister	6.0	Organic vapors	3 tank air samples + 2 ambient air samples
WHC 222-S Laboratory	Silica Gel Sorbent Trap	2.0	Tritium-Substituted Water Vapor	1 tank air sample

Table 3-1
 Tank BY-106 Inorganic Gas and Vapor Concentrations
 Analyses Conducted by Oregon Graduate Institute of Science and Technology and Pacific Northwest Laboratory

Compound	CAS ¹ Number	Sample Type	Number of samples	Average ² (ppmv)	Standard Deviation (ppmv)	RSD ³ (%)
Ammonia, NH ₃	7664-41-7	Sorbent Trap	5	74	2	3
Carbon Dioxide, CO ₂	124-38-9	SUMMA TM	3	[47.6]	[1.4]	[3]
Carbon Monoxide, CO	630-08-0	SUMMA TM	3	[0.45]	[.03]	[7]
Hydrogen, H ₂	1333-74-0	SUMMA ^{TM,4}	3	[45.5]	[2.5]	[5]
Hydrogen Cyanide ⁵ , HCN	74-90-8	Sorbent Trap	3	< 0.0xx	--	--
Nitric Oxide, NO	10102-43-9	Sorbent Trap	10	0.13	0.04	28
Nitrogen Dioxide, NO ₂	10102-44-0	Sorbent Trap ^{TM,6}	5	0.05	0.006	13
Nitrous Oxide, N ₂ O	10024-97-2	SUMMA TM	3	[70.6]	[0.6]	[1]
Water Vapor, H ₂ O	7732-18-5	Sorbent Trap	10	20,700 (14.7 mg/L)	1,200 (0.8 mg/L)	6

1 CAS = Chemical Abstract Service.

2 Bracketed values are from OGIST and should be considered secondary results, non-bracketed values are from PNL and should be considered primary results.

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

4 Hydrogen analysis of 7/8/94 samples problematic, average given is for 3 SUMMATM canister samples collected 5/4/94 (Rasmussen 1994a).

5 Results for hydrogen cyanide are from the July 1993 ISS event.

6 Only 5 of the 10 samples were statistically above blank NO₂ levels.

Table 3-2
Comparison of Tank BY-104, BY-105, and BY-106 Headspace Constituents --
Inorganic Analyses by Oregon Graduate Institute of Science and Technology,
and Organic Analyses by Oak Ridge National Laboratory¹

Tank:	BY-104 ²	BY-105 ³	BY-106
Date sampled, (mo/day/yr)	6/24/94	7/7/94	7/8/94
Headspace temperature, (°C)	26	26	27
Ammonia, (ppmv)	248	43	74
Hydrogen, (ppmv)	[295]	[47.9]	[45.5]
Carbon dioxide, (ppmv)	[10.5]	[94]	[47.6]
Carbon monoxide, (ppmv)	[1.0]	[0.38]	[0.45]
Nitric oxide, (ppmv)	0.29	0.10	0.13
Nitrogen dioxide, (ppmv)	≤ 0.07	≤ 0.02	0.05
Nitrous oxide, (ppmv)	[201]	[49.5]	[70.6]
Water vapor, (mg/m ³)	14.1	14.9	14.7
Water vapor, (% relative humidity)	58	76	57
Ethanenitrile (acetonitrile), (ppmv)	(0.33)	(0.081)	(0.12)
Propanone (acetone), (ppmv)	(1.2)	(0.25)	(0.37)
1-Butanol, (ppmv)	(1.0)	(0.70)	(0.34)
n-Dodecane, (ppmv)	(0.058)	(0.0081)	(0.0065)
n-Tridecane, (ppmv)	(0.084)	(0.010)	(0.0069)
Total nonmethane organic carbon, (mg/m ³)	[60.8]	[12.7]	[9.9]

¹ Where PNL inorganic gas or vapor data was unavailable, OGIST results are given. OGIST results are in brackets to indicate the data should be considered secondary results. Organic vapor results are from ORNL, with non-quantitative values in parentheses and quantitative values not in parentheses.

² Data are from Huckaby and Bratzel 1995a.

³ Data are from Huckaby and Bratzel 1995b.

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

Cmpd #	Compound	CAS ⁴ Number	Average ⁵ (ppmv)	Standard Deviation (ppmv)	RSD ⁶ (%)
1	Methane ⁷	74-82-8	[3.6]	[<0.1]	[4]
2	Dichlorodifluoromethane	75-71-8	0.011	0.002	18
3	Chloromethane (Methyl chloride)	74-87-3	0.0028	0.0006	20
4	Trichlorofluoromethane	75-69-4	0.19	0.02	9
5	Dichloromethane (Methylene chloride)	75-09-2	<0.002	—	—
6	Benzene	71-43-2	0.0022	0.0004	19
7	Toluene	108-88-3	0.0071	0.0003	5
8	Tetrachloroethene	127-18-4	0.003	0.001	34
9	Ethylbenzene	100-41-4	0.0013 ⁸	—	—
10	1,3-Dimethylbenzene (m-xylene) + 1,4-Dimethylbenzene (p-xylene)	108-38-3 106-42-3	0.0031	0.0004	13

4 CAS = Chemical Abstract Service.

5 Average of 3 samples.

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

7 Methane analyses were performed by OGIST and should be considered a secondary result (Ramussen 1994a).

8 Result of single sample, other samples <0.002 ppmv.

Table 4-2
Tank BY-106 Quantitatively Measured Organic Compound Average Concentrations –
Analyses by Oak Ridge National Laboratory¹

Cmpd #	Compound	CAS ² Number	Average ³ (ppmv)	Standard Deviation (ppmv)	RSD ⁴ (%)
1	Propanenitrile	107-12-0	0.0043	0.0002	5
2	Benzene	71-43-2	0.0073	0.0008	11
3	Toluene	108-88-3	0.0083	0.0011	13
4	2-Hexanone	591-78-6	0.0042	0.0005	13
5	2-Heptanone	110-43-0	0.0032	0.0007	23
6	n-Nonane	111-84-2	0.0046	0.0006	14

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

2 CAS = Chemical Abstract Service.

3 Average of 4, 5-L TST samples.

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

Table 4-3
Tank BY-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	Dichloromethane (methylene chloride)	75-09-2	0.00047	0.00017	36
2	Ethanenitrile (acetonitrile)	75-05-8	0.12	0.02	16
3	Propanone (acetone)	67-64-1	0.37	0.08	23
4	n-Hexane	110-54-3	0.085	0.011	13
5	n-Butanenitrile	109-74-0	0.0015	0.00009	6
6	2-Pentanone	107-87-9	0.011	0.0009	9
7	n-Heptane	142-82-5	0.031	0.002	6
8	n-Pentanenitrile	110-59-8	0.0010	0.0001	11
9	n-Octane	111-65-9	0.012	0.001	11
10	n-Hexanenitrile	628-73-9	0.00072	0.00011	15
11	n-Heptanenitrile	629-08-3	0.00034	0.00003	9
12	2-Octanone	111-13-7	0.00094	0.00029	31
13	n-Octanenitrile	124-12-9	0.00018	0.00002	9
14	n-Nonanenitrile	2243-27-8	0.00019	0.00003	15
15	n-Dodecane	112-40-3	0.0065	0.0014	22
16	n-Tridecane	629-50-5	0.0069	0.0019	28
17	Tributyl phosphate	126-73-8	0.000044	0.000009	20
18	Dibutyl butylphosphonate	78-46-6	0.0000064	0.0000030	47

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, 5-L TST samples.

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

Table 4-4
Tank BY-106 Positively Identified Compounds in TST Samples
for which Practical Holding Times were Exceeded --
Analyses by Oak Ridge National Laboratory¹

Cmpd #	Compound	CAS ² Number	Average ³ (ppmv)	Standard Deviation (ppmv)	RSD ⁴ (%)
1	Butanal ⁵	123-72-8	0.061	0.013	21
2	1-Butanol ⁵	71-36-3	0.34	0.03	8

1 Practical holding times are defined and discussed in Section 4.1.

2 CAS = Chemical Abstract Service.

3 Average of 4, 5-L TST samples.

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

5 The concentration of this analyte was not quantitatively measured (as defined in Section 4.1), because the measured concentration was outside of the instrumental calibration limits.

Table 4-5
Tank BY-106 Comparison of Organic Compounds in TST and SUMMA™ Samples –
Analyses by Pacific Northwest Laboratory
and Oak Ridge National Laboratory

Cmpd #	Compound	CAS ¹ Number	TST Average ² (ppmv)	SUMMA™ Average ³ (ppmv)	PRD ⁴ (%)
1	Dichloromethane (Methylene chloride)	75-09-2	0.00047	<0.002	—
2	Benzene	71-43-2	0.0073	0.0022	107
3	Toluene	108-88-3	0.0083	0.0071	16

1 CAS = Chemical Abstract Service.

2 Average of 4, 5-L TST samples analyses.

3 Average of 3 samples analyses.

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

Table 4-6
Tank BY-106 Tentatively Identified Organic Compounds in SUMMA™ Samples –
Analyses by Pacific Northwest Laboratory

Cmpd #	Compound	CAS ¹ Number	Average ⁵ (mg/m ³)	Standard ² Deviation (mg/m ³)
1	Propene	115-07-1	1.04	0.18
2	Propane	74-98-6	0.68	0.14
3	Propyne	74-99-7	0.06	0.01
4	Cyclopropane	75-19-4	0.17	0.04
5	2-Methylpropane	75-28-5	0.56	0.24
6	2-Methylpropene	115-11-7	0.73	0.27
7	n-Butane	106-97-8	0.86	0.35
8	2-Butene	107-01-7	0.16	0.07
9	Ethanol ³	64-17-5	0.11	—
10	C4 Alkene		0.09	0.04
11	Acetone	67-64-1	0.88	0.46
12	C5 Alkane ⁴		0.40	0.24
13	1-Pentene	109-67-1	0.25	0.11
14	n-Pentane	109-66-0	0.75	0.44
15	C5 Alkene ³		0.06	—
16	C6 Alkene ³		0.08	—
17	1-Pentanol ³	71-41-0	0.07	—
18	2-Methylpentane	107-83-5	0.71	0.06
19	Butanal	123-72-8	0.17	0.04
20	2-Butanone (MEK)	78-93-3	0.17	0.03
21	3-Methylpentane	96-14-0	0.14	0.01
22	1-Hexene	592-41-6	0.15	0.02
23	n-Hexane	110-54-3	0.54	0.08
24	Tetrahydrofuran	109-99-9	0.17	0.02
25	2-Methyl-1-pentene	763-29-1	0.07	0.01
26	1-Butanol	71-36-3	0.99	0.13
27	2-Pentanone	107-87-9	0.13	0.02

WHC-SD-WM-ER-420 REV. 2

Cmpd #	Compound	CAS ¹ Number	Average ⁵ (mg/m ³)	Standard ² Deviation (mg/m ³)
28	C7 Alkane		0.24	0.05
29	1-Heptene	592-76-7	0.06	0.01
30	n-Heptane	142-82-5	0.33	0.04
31	C7 Alkene		0.06	0.01
32	C8 Alkane		0.12	0.02
33	Hexanal ³	66-25-1	0.07	--
34	n-Octane	111-65-9	0.11	0.02
35	2-Butoxyethanol ³	111-76-2	0.06	--
36	C10 Alkane		0.06	0.01
37	C10 Alkane ³		0.05	--
38	Phenol ³	108-95-2	0.05	--
39	C11 Alkane ³		0.05	--
40	n-Undecane	1120-21-4	0.06	0.00
41	n-Dodecane	112-40-3	0.09	0.01
42	C12 Alkane		0.07	0.01
43	Benzothiazole ³ (impurity)	95-16-9	0.06	--
44	C7 Cyclohexane ³		0.06	--
45	C13 Alkane		0.06	0.01
46	n-Tridecane	629-50-5	0.09	0.01
47	C13 Alkane		0.06	0.01
48	C13 Alkane ⁴		0.06	0.01

1 CAS = Chemical Abstract Service.

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

3 Detected in only 1 sample.

4 Detected in only 2 samples.

5 Average of 3 samples.

Table 4-7
 Tank BY-106 Tentatively Identified Organic Compounds in TST Samples
 in Order of Chromatographic Elution --
 Analyses Conducted by Oak Ridge National Laboratory

Cmpd #	Compound	CAS ¹ Number	Average ² (mg/m ³)
1	2-Butene, (Z)-	107-01-7	0.527
2	1-Propene, 2-methyl-	115-11-7	0.040
3	1-Propene, 2-methyl-	115-11-7	0.125
4	1-Propene, 2-methyl-	115-11-7	0.035
5	1-Butene, 3-methyl-	563-45-1	0.053
6	Methyl ether	115-10-6	0.133
7	Butane, 2-methyl-	78-78-4	0.298
8	Methane, trichlorofluoro-	75-69-4	0.265
9	1-Pentene	109-67-1	0.297
10	1-Butyne and others	107-00-6	0.004
11	Propane, 2-methyl-	75-28-5	1.685
12	Furan	110-00-9	0.028
13	1,3-Pentadiene, (E)- and C5-Alkene	2004-70-8	0.017
14	2-Propanol	67-63-0	0.276
15	2-Pentene, (Z)-	627-20-3	0.016
16	Cyclopentane	287-92-3	0.076
17	Cyclopropane, 1,1-dimethyl-	1630-94-0	0.026
18	1-Pentyne and C4-alkene	627-19-0	0.018
19	1,3-Pentadiene, (Z)-	504-60-9	0.027
20	Butane, 2,2-dimethyl-	75-83-2	0.005
21	2-Propenenitrile and others	107-13-1	0.007
22	1-Pentene, 4-methyl-	691-37-2	0.109
23	Cyclopentane	287-92-3	0.048
24	Pentane, 2-methyl-	107-83-5	0.699
25	C3-cyclopropane		0.045
26	2,3-Dihydrofuran	1191-99-7	0.035
27	Cyclopropane, propyl-	2415-72-7	0.004
28	1-Butene	106-98-9	0.005
29	Pentane, 3-methyl-	96-14-0	0.152
30	Propanenitrile	107-12-0	0.006
31	1-Pentene, 2-methyl-	763-29-1	0.068

WHC-SD-WM-ER-420 REV. 2

Cmpd #	Compound	CAS ¹ Number	Average ² (mg/m ³)
32	C6-alkene		0.169
33	3-Buten-2-one	78-94-4	0.036
34	2-Butanone	78-93-3	0.212
35	2-Hexene, (Z)-	7688-21-3	0.023
36	2-Pentene, 4-methyl-, (E)-	674-76-0	0.029
37	Alkanol		0.032
38	Cyclopropane, propyl-	2415-72-7	0.116
39	C6-alkene		0.025
40	Cyclopentane, methyl-	96-37-7	0.096
41	Alkenol		0.158
42	Furan, tetrahydro-	109-99-9	0.302
43	1,3-Butadiene, 2,3-dimethyl-	513-81-5	0.048
44	1,4-Hexadiene	592-45-0	0.033
45	1H-Pyrrole and others	109-97-7	0.008
46	Mixture		0.007
47	1-Hexene, 5-methyl-	3524-73-0	0.028
48	2-Butenal	4170-30-3	0.015
49	Furan, 2,5-dihydro-	1708-29-8	0.029
50	3-Butenenitrile	109-75-1	0.016
51	Hexane, 2-methyl-	591-76-4	0.044
52	1-Hexene, 3,4-dimethyl-	16745-94-1	0.003
53	Pentane, 2,3-dimethyl-	565-59-3	0.001
54	Furan, 2-propyl-	4229-91-8	0.340
55	Cyclopentane, 1,3-dimethyl-, cis-	2532-58-3	0.002
56	C3-Cyclopentane		0.002
57	C6-alkenone		0.008
58	Cyclopentane, 1,2-dimethyl-	2452-99-5	0.010
59	C2-cyclopentane		0.066
60	2-Pentanol	6032-29-7	0.009
61	2-Heptene, (E)-	14686-13-6	0.005
62	2-Pentanone, 4-methyl-	108-10-1	0.010
63	2-Heptene	592-77-8	0.001
64	Cyclohexane, methyl-	108-87-2	0.041
65	1-Hexene, 2-methyl-	6094-02-6	0.001

Cmpd #	Compound	CAS ¹ Number	Average ² (mg/m ³)
66	Hexane, 2,4-dimethyl-	589-43-5	0.001
67	C7-alkene		0.010
68	2-Pentanol, 2-methyl-	590-36-3	0.013
69	C6-Alkenone		0.001
70	C8-Alkene		0.002
71	2-Pentanone, 4-methyl-	108-10-1	0.010
72	Alkane		0.006
73	Mixture		0.001
74	Mixture		0.005
75	Cyclopropane, 1-heptyl-2methyl-	74663-91-5	0.015
76	C8-Alkene		0.001
77	Pentane, 3-ethyl-2-methyl-	609-26-7	0.024
78	Heptane, 3-methyl-	589-81-1	0.055
79	1-Octen-3-one	4312-99-6	0.017
80	Cyclohexane, 1,3-dimethyl-, cis-	638-04-0	0.007
81	C2-cyclohexane		0.001
82	1,4-Hexadiene, 4-methyl- and others	1116-90-1	0.001
83	3-Hexanone	589-38-8	0.016
84	1-Hexene, 4,5-dimethyl-	16106-59-5	0.001
85	Hexanal	66-25-1	0.010
86	Formamide, N-(2-methylpropyl)-	6281-96-5	0.007
87	Alkanol		0.003
88	1-Pentanol, 5-methoxy-	4799-62-6	0.003
89	Cyclopentane, 1,1,3-trimethyl-	4516-69-2	0.005
90	Hexanal	66-25-1	0.003
91	Ethene, tetrachloro-	127-18-4	0.023
92	Acetic acid, butyl ester	123-86-4	0.007
93	Hexamethylcyclotrisiloxane	541-05-9	0.006
94	Pyridine, 4-methyl-	108-89-4	0.007
95	Nitric acid, butyl ester	928-45-0	0.000
96	Heptane, 2,6-dimethyl-	1072-05-5	0.022
97	2-Pentanol, 2,3-dimethyl-	4911-70-0	0.005
98	4-Heptenal, (Z)-	6728-31-0	0.002
99	Cyclohexane, ethyl-	1678-91-7	0.011

WHC-SD-WM-ER-420 REV. 2

Cmpd #	Compound	CAS ¹ Number	Average ² (mg/m ³)
100	Cyclohexane, 1,1,3-trimethyl-	3073-66-3	0.019
101	Hexane, 3-methoxy-	54658-01-4	0.009
102	7-Octen-2-one	3664-60-6	0.007
103	Cyclobutanone, 2,3,3-trimethyl-	28290-01-9	0.011
104	Cyclohexane, 1,3,5-trimethyl-	1839-63-0	0.006
105	Heptane, 2,3-dimethyl-	3074-71-3	0.012
106	Octane, 2-methyl-	3221-61-2	0.020
107	Nitro-Compound		0.001
108	Octane, 3-methyl-	2216-33-3	0.024
109	Benzene, 1,3-dimethyl-	108-38-3	0.020
110	4-Octen-3-one	14129-48-7	0.001
111	Cyclohexane, 1,2,3-trimethyl-	1678-97-3	0.001
112	Alkane		0.015
113	C3-cyclohexane and others		0.004
114	Acetamide, N,N-dimethyl- and others	127-19-5	0.001
115	3-Heptanone	106-35-4	0.028
116	Styrene	100-42-5	0.005
117	Benzene, 1,4-dimethyl-	106-42-3	0.008
118	Heptanal	111-71-7	0.007
119	Cyclohexane, 1,1,3,5-tetramethyl-, trans-	50876-31-8	0.001
120	C3-Cyclohexane		0.001
121	Cyclohexane, 1-ethyl-4-methyl-, cis	4926-78-7	0.004
122	C7-alkanone		0.005
123	Mixture		0.002
124	Cyclopropene, 1-butyle-2-ethyl-	50915-91-8	0.016
125	Cyclohexanol, 3-methyl- and others	591-23-1	0.001
126	2-Heptanol, 2-methyl-	625-25-2	0.003
127	Octane, 2,6-dimethyl-	2051-30-1	0.022
128	Cyclohexane, (1-methylethyl)-	696-29-7	0.002
129	Pyridine, 3,5-dimethyl- and others	591-22-0	0.004
130	Furan and others	110-00-9	0.001
131	Heptane, 3-ethyl-2-methyl-	14676-29-0	0.006
132	Mixture		0.003
133	2-Heptanone, 6-methyl-	928-68-7	0.031

Cmpd #	Compound	CAS ¹ Number	Average ² (mg/m ³)
134	Benzene, propyl-	103-65-1	0.003
135	Nonane, 4-methyl-	17301-94-9	0.012
136	1,1,2,3-tetramethylcyclohexane	6783-92-2	0.024
137	Alkenol		0.034
138	Alkene		0.010
139	C3-cyclohexene		0.003
140	3-Penten-2-ol and others		0.002
141	4-Octanone and others		0.002
142	Cyclopentane, 1-methyl-3-(2-methylpropyl)-	29053-04-1	0.006
143	C3-Cyclohexene		0.001
144	Cyclohexane, 1-methyl-4-(-methylethyl)-, cis-	6069-98-3	0.006
145	Phenol	108-95-2	0.010
146	Cyclotetrasiloxane, octamethyl-	556-67-2	0.024
147	Butanoic acid, butyl ester	109-21-7	0.005
148	Decane	124-18-5	0.049
149	4-Nonene, 5-methyl-	15918-07-7	0.001
150	(Z)-2,3,4,5-tetramethyl-3-hexene		0.005
151	C5-cyclopentane		0.002
152	C4-Cyclohexane		0.001
153	Cyclopentane, 1-methyl-3-(2-methylpropyl)-	29053-04-1	0.004
154	Heptane, 2,3,6-trimethyl-	4032-93-3	0.004
155	3-Hexane, 2,2,5,5-tetramethyl-, (A)- and others		0.006
156	Nonane, 2,6-dimethyl-	17302-28-2	0.034
157	Cyclohexanol, 4-(1,1,3,3-tetramethylbutyl)-	4631-98-5	0.004
158	1-Hexanol, 2-ethyl	104-76-7	0.001
159	Undecane	1120-21-4	0.005
160	Cyclohexane, (1-methylpropyl)-	7058-01-7	0.014
161	Cyclopentane, 1-hexyl-3-methyl-	61142-68-5	0.001
162	1,1,2,3-Tetramethylcyclohexane	6783-92-2	0.001
163	C5-cyclohexane		0.004
164	C4-cyclohexane		0.008
165	1-Undecene	821-95-4	0.001
166	Mixture		0.001
167	Cyclohexanone, 2,6-diethyl-	16519-68-9	0.001

WHC-SD-WM-ER-420 REV. 2

Cmpd #	Compound	CAS ¹ Number	Average ² (mg/m ³)
168	1,1-dimethyl-2-propylcyclohexane		0.017
169	Decane, 4-methyl-	2847-72-5	0.006
170	Decane, 2,6,7-trimethyl-	62108-25-2	0.016
171	Naphthalene, decahydro-, trans-	493-02-7	0.024
172	Mixture		0.001
173	Ethanone, 1-phenyl-	98-86-2	0.010
174	1-Naphthalenol, decahydro-4a-methyl-8-methylene-2-(1-met) and others	30951-17-8	0.007
175	C5-cyclohexane		0.007
176	Cyclohexane, 1,2-diethyl-1-methyl-Zinc, bis[2-(1,1-dimethylethyl)-3,3-dimethylcyclopro	61141-79-5	0.005
177	C5-cyclohexane		0.016
178	2-Nonanone	821-55-6	0.004
179	C6-cyclohexane		0.005
180	Undecane	1120-21-4	0.071
181	5-Undecene	4941-53-1	0.005
182	C11-alkene		0.006
183	Cyclopropane, octyl-	1472-09-9	0.004
184	Undecane, 5-methyl-	1632-70-8	0.012
185	Cyclohexene, 1-pentyl-	15232-85-6	0.006
186	Naphthalene, decahydro-2-methyl-	2958-76-1	0.030
187	C6-Alkenyl-cyclopentane		0.001
188	5-Dodecene, (Z)-	7206-28-2	0.006
189	Benzoic acid, 2-[(trimethylsilyl)oxyl-, trimethylsilyl ester	3789-85-3	0.004
190	Cyclohexane, pentyl-	4292-92-6	0.014
191	Naphthalene, decahydro-2-methyl-	2958-76-1	0.025
192	Decane, 2,4-dimethyl-	2801-84-5	0.003
193	6-Methylundecane	17302-33-9	0.023
194	Undecane, 4-methyl-	2980-69-0	0.012
195	Undecane, 2-methyl-	7045-71-8	0.019
196	C6-cyclohexane		0.006
197	Undecane, 3-,methyl-	1002-43-3	0.009
198	2-Cyclohexen-1-one, 4-ethyl-3,4-dimethyl-	17622-46-7	0.003
199	2-Propyl-1,1,3-trimethylcyclohexane		0.005

WHC-SD-WM-ER-420 REV. 2

Cmpd #	Compound	CAS ¹ Number	Average ² (mg/m ³)
200	Naphthalene, decahydro-2,3-dimethyl-	1008-80-6	0.007
201	Decane, 2,3,6-trimethyl-	62238-12-4	0.007
202	Mixture		0.001
203	Cyclohexane, 1,-methyl-3-pentyl-	54411-02-8	0.002
204	Cyclopentane, 2-isopropyl-1,3-dimethyl-	32281-85-9	0.006
205	Naphthalene, decahydro-1,6-dimethyl-	1750-51-2	0.001
206	Cyclohexane, 1-ethyl-2-methyl-, cis-	4923-77-7	0.016
207	Undecane, 2,6-dimethyl-	17301-23-4	0.027
208	C2-Decahydronaphthalene		0.005
209	Undecane, 4,8-dimethyl-	17301-33-6	0.006
210	C2-Decahydronaphthalene		0.003
211	Naphthalene, decahydro-1,5-dimethyl-	66552-62-3	0.010
212	4-Nonene, 5-butyl-	7367-38-6	0.019
213	(E,E)(3S,8S),3,8-dimethyldeca-4,6-diene		0.015
214	C7-Cyclohexane		0.002
215	Naphthalene, decahydro-1,6-dimethyl-	1750-51-2	0.001
216	C7-Cyclohexane		0.009
217	Undecane, 2,10-dimethyl-	17301-27-8	0.019
218	Tridecane, 7-methyl-	26730-14-3	0.049
219	Cyclohexane, 1,2-diethyl-3-methyl-	61141-80-8	0.007
220	2(3H)-Benzofuranone, 3a,4,5,6-tetrahydro-3a,6,6-trimethyl-	16778-26-0	0.010
221	6-Tridecene, 7-methyl-	24949-42-6	0.022
222	Phenol, 4-(1,1-dimethylethyl)- and others		0.004
223	Cyclohexane, (2-ethyl-1-methyl-1-butenyl)-	74810-42-7	0.002
224	Undecane, 6-ethyl-	17312-60-6	0.001
225	Dodecane, 2,5-dimethyl-	56292-65-0	0.010
226	C8-Cyclohexane		0.004
227	C8-Cyclohexane		0.006
228	7-Tetradecene	10374-74-0	0.004
229	2-Octylfuran	4179-38-8	0.006
230	Cyclohexane, octyl-	1795-15-9	0.012
231	Tridecane, 4-methyl-	26730-12-1	0.005
232	Tridecane, 2-methyl-	1560-969	0.006
233	C1-acridine and others		0.021

Cmpd #	Compound	CAS ¹ Number	Average ² (mg/m ³)
234	Dodecane, 2,6,10-trimethyl-	3891-98-3	0.061
235	Tetradecane	629-59-4	0.045
236	Tridecane, 4,8-dimethyl-	55030-62-1	0.012
237	1,1,2,3-tetramethylcyclohexane	6783-92-2	0.019
238	Cyclopentane, (1-methylbutyl)-	4737-43-3	0.007
239	Cyclohexane, 1,1,3,5-tetramethyl-, cis-	50876-32-9	0.001
240	1-Pentadecene	13360-61-7	0.001
241	Alkane		0.001
242	C16-Alkane		0.006
243	Dodecane, 2-methyl-8-propyl-	55045-07-3	0.057
245	Pentadecane, 2-methyl-	1560-93-6	0.003
246	Alkane		0.004
247	3-tert-butyl-4-methoxyphenol	88-32-4	0.000
248	Phenol, (1,1-dimethylethyl)-4-methoxy-	25013-16-5	0.001
249	7-Hexadecene, (Z)-	35507-09-6	0.010
250	Pentadecane	629-62-9	0.043
251	3,4-Undecadiene-2,10-dione, 6,6-dimethyl-	52588-78-0	0.000
252	C9-Cyclohexane		0.000
253	Tridecane, 2-methyl-	1560-96-9	0.005
254	Alkane		0.004
255	Alkane		0.005
256	Alkane		0.000
257	Hexadecane, 3-methyl-	6418-43-5	0.001
258	5-Undecanone, 2-methyl-	50639-02-6	0.001
259	Hexadecane	544-76-3	0.015
260	1,2-Benzenedicarboxylic acid, diethyl ester	84-66-2	0.038
261	Pentadecane, 2,6,10-trimethyl-	3892-00-0	0.006
262	1-Hexadecanol	36653-82-4	0.003
263	Heptadecane	629-78-7	0.003
264	Pentadecane, 2,6,10,14-tetramethyl-	1921-70-6	0.004
265	Alkane		0.004
266	1,1'-Biphenyl, 2,2'-diethyl-	13049-35-9	0.000
267	Tetradecanoic acid	544-63-8	0.008
268	Benzenesulfonamide, N-butyl-	3622-84-2	0.034

WHC-SD-WM-ER-420 REV. 2

Cmpd #	Compound	CAS ¹ Number	Average ² (mg/m ³)
269	Pentadecanoic acid	1002-84-2	0.002
270	1-Hexadecanol	36653-82-4	0.003
271	Alkene and others		0.004
272	Hexadecanoic acid	57-10-3	0.013
273	Pthalate		0.001
274	Hexadecanoic acid	57-10-3	0.003

1 CAS = Chemical Abstract Service.

2 Average includes samples with zero concentration, values listed are estimates.

THIS PAGE INTENTIONALLY LEFT BLANK