DISTRIBUTION SHEET

To	From	Page 1 of 1
Distribution	J. W. Osborne	Date May 31, 1995
Project Title/Work Order		EDT No. 612345
Tank 241-C-101 Vapor Sampling and Analysis Tank Characterization Report (WHC-SD-WM-ER-458)		ECN No.

Name	MSIN	Text With All Attach.	Text Only	Attach./Appendix Only	EDT/ECN Only
<u>RL</u>					
S. O. Branch	S7-54	X			
C. R. Briggs	A5-55	X			
P. R. Hernandez	S7-54	X			
M. F. Jarvis	S7-54	X			
T. Noble	S7-54	X			
C. O. Olaiya	S7-54	X			
J. F. Thompson	S7-54	X			
<u>ECOLOGY</u>					
A. B. Stone	B5-18	X			
<u>MACTEC</u>					
J. P. Haney	S7-73	X			
S. T. Murff	S7-73	X			
<u>PNL</u>					
J. S. Fruchter	K6-96	X			
S. C. Goheen	P8-08	X			
J. L. Huckaby	K6-80	X			
M. W. Ligothke	P7-59	X			
<u>WHC</u>					
Central Files	L8-04	X			
H. Babad	S7-30	X			
D. R. Bratzel	S7-31	X			
D. R. Carls	R3-01	X			
R. J. Cash	S7-15	X			
G. T. Dukelow	S7-15	X			
S. J. Eberlein	R2-12	X			
L. F. Ermold	S7-84	X			
E. R. Hewitt	R3-01	X			
G. D. Johnson	S7-15	X			
T. J. Kelley	S7-30	X			
N. W. Kirch	R2-11	X			
J. G. Kristofzski	T6-06	X			
J. W. Lentsch	S7-15	X			
E. J. Lipke	S7-15	X			
N. G. McDuffie	S7-15	X			
J. E. Meacham	S7-15	X			
R. D. Mitchell	R3-01	X			
M. A. Payne	S7-84	X			
D. A. Turner	S7-15	X			
O.S.T.I. (2)	L8-07	X			

RECEIVED
JUN 19 1995
OSTI

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

15
MAY 31 1995

ENGINEERING DATA TRANSMITTAL

Page 1 of 1
1. EDT No 612345

2. To: (Receiving Organization) Distribution		3. From: (Originating Organization) Tank Vapor Characterization Program		4. Related EDT No.: N/A					
5. Proj./Prog./Dept./Div.: Characterization		6. Cog. Engr.: J. W. Osborne		7. Purchase Order No.: N/A					
8. Originator Remarks: N/A				9. Equip./Component No.: N/A					
				10. System/Bldg./Facility: N/A					
11. Receiver Remarks: N/A				12. Major Assm. Dwg. No.: N/A					
				13. Permit/Permit Application No.: N/A					
				14. Required Response Date: N/A					
15. DATA TRANSMITTED									
(A) Item No.	(B) Document/Drawing No.	(C) Sheet No.	(D) Rev. No.	(E) Title or Description of Data Transmitted	(F) Approval Designator	(G) Reason for Transmittal	(H) Originator Disposition	(I) Receiver Disposition	
1	WHC-SD-WM-ER-458	N/A	0	Tank 241-C-101 Vapor Sampling and Analysis Tank Characterization Report	N/A	2	1	1	
16. KEY									
Approval Designator (F)		Reason for Transmittal (G)			Disposition (H) & (I)				
E, S, Q, D or N/A (see WHC-CM-3-5, Sec.12.7)		1. Approval 4. Review 2. Release 5. Post-Review 3. Information 6. Dist. (Receipt Acknow. Required)			1. Approved 4. Reviewed no/comment 2. Approved w/comment 5. Reviewed w/comment 3. Disapproved w/comment 6. Receipt acknowledged				
(G)	(H)	17. SIGNATURE/DISTRIBUTION (See Approval Designator for required signatures)						(G)	(H)
Reason	Disp.	(J) Name	(K) Signature	(L) Date	(M) MSIN	(J) Name	(K) Signature	(L) Date	(M) MSIN
1	/	Cog. Eng. J. W. Osborne		5-31-95					
1	/	Cog. Mgr. T. J. Kelley		5/31/95					
		QA							
		Safety							
		Env.							
18. J. W. Osborne Signature of EDT Originator		19. T. J. Kelley Authorized Representative for Receiving Organization		20. T. J. Kelley Cognizant Manager		21. DOE APPROVAL (if required) Ctrl. No. ☐ Approved ☐ Approved w/comments ☐ Disapproved w/comments			

RELEASE AUTHORIZATION

Document Number: WHC-SD-WM-ER-458, REV 0

Document Title: Tank 241-C-101 Vapor Sampling and Analysis Tank
Characterization Report

Release Date: 5/31/95

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

APPROVED FOR PUBLIC RELEASE

WHC Information Release Administration Specialist:

Kara M. Broz

May 31, 1995

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 and microfiche. Printed in the United States of America. Available to the U.S. Department of Energy and its contractors from:

U.S. Department of Energy
Office of Scientific and Technical Information (OSTI)
P.O. Box 62
Oak Ridge, TN 37831
Telephone: (615) 576-8401

Available to the public from:

U.S. Department of Commerce
National Technical Information Service (NTIS)
5285 Port Royal Road
Springfield, VA 22161
Telephone: (703) 487-4650

SUPPORTING DOCUMENT		1. Total Pages 31
2. Title Tank 241-C-101 Vapor Sampling and Analysis Tank Characterization Report	3. Number WHC-SD-WM-ER-458	4. Rev No. 0
5. Key Words 241-C-101, Headspace vapor samples, organic analytes, VSS, SUMMA™, inorganic gases and vapors	6. Author Name: J. L. Huckaby Signature <u>J. L. Huckaby</u> Organization/Charge Code 75600/N4AB1	
7. Abstract Tank 241-C-101 headspace gas and vapor samples were collected and analyzed to help determine the potential risks to tank farm workers due to fugitive emissions from the tank. 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 241-C-101 was vapor sampled in accordance with "Data Quality Objectives for Generic In-Tank Health and Safety Issue Resolution (Osborne et al., 1994).		
<p>DISCLAIMER</p> <p>This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. 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. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.</p>		
<p>MASTER</p>		<p>8. RELEASE STAMP</p> <div style="border: 1px solid black; padding: 5px; text-align: center;"> <p>OFFICIAL RELEASE BY WHC DATE MAY 31 1995 <i>Sta. 4</i></p> </div>

Tank 241-C-101 Vapor Sampling and Analysis Tank Characterization Report

X.0 INTRODUCTION

Tank C-101 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 C-101 was vapor sampled in accordance with *Data Quality Objectives for Generic In-Tank Health and Safety Issue Resolution* (Osborne et al. 1994).

Gas and vapor samples from the tank C-101 headspace were collected on July 7, 1994 using the *in situ* sampling (ISS) method (Pingel 1994), and again on September 1, 1994 using the more robust vapor sampling system (VSS), (WHC 1995). Because sorbent trap samples from the July 7, 1994 event were radiologically contaminated, only the SUMMA^{TM,1} samples from this event were analyzed. SUMMATM samples from the July 7 and September 1 sampling events provide contradictory results, and indicate the July 7 SUMMATM canisters were filled primarily with ambient air. This is discussed briefly in Section X.3.2. Results presented below represent the best available data on the headspace constituents of tank C-101.

X.1 VENTILATION SYSTEM CONSIDERATIONS

Gas and vapor concentrations in tank C-101 are influenced by its connections to other tanks and its ventilation pathways. Tank C-101 is the first tank in a 3-tank cascade with tanks C-102 and C-103, and is connected to tank C-102 via a 7.4-cm (2.9-in.) inside diameter, 7.6-m (25-ft) long cascade line. Tanks C-102 and C-103 are connected by a similar cascade line. These 3 waste tanks are passively ventilated, which means that they are allowed to exhale air, waste gases, and vapors as the barometric pressure falls, and inhale ambient air as the barometric pressure rises.

Barometric pressure typically rises and falls on a diurnal cycle, with an average daily exchange of air equal to about 0.46 % of each tank headspace (Huckaby 1994). During the period when headspace samples were collected from these tanks, tanks C-102 and C-103 also received small streams of dry ambient air to protect waste surface level instruments from condensation of water vapor. The flowrate of this instrument air varied from about 1.4 to 1.7 m³/hr (50 to 60 ft³/hr), (Huckaby 1994).

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

The breather riser on tank C-101 was valved shut in December 1989, so that any air exchange with the atmosphere would occur via the cascade line to tank C-102. Furthermore, since December 1989 the cascade of tanks C-101, C-102, and C-103 has had only 1 breather riser open (either on tank C-102 or tank C-103). In the period before headspace samples were collected from tank C-101 (specifically, since March 1993), the breather riser on tank C-103 had been valved shut, and the intended pathway for all air exchange between tanks C-101, C-102, and C-103 and the atmosphere was via the breather riser on tank C-102 (Conrad 1994).

Constituents detected in the headspace of tank C-101, because it may be breathing via tank C-102, may actually have originated from the waste in tanks C-102 or C-103. Therefore, to determine the origin of gases and vapors in tank C-102, the extent to which tank C-101 breathes through tank C-102 must be known. This is particularly important because tanks C-101, C-102, and C-103 are all known to have high concentrations of organic vapors, and at issue is whether the organic vapors in tank C-101 are from the waste in that tank, or from tanks C-102 or C-103².

Anderson (1990) notes that the cascade line between tanks C-101 and C-102 was partially plugged in 1954. Sections X.3.4 and X.4.4 discuss what the available headspace data from tanks C-101 and C-102 indicate about whether tank C-101 is breathing freely via the cascade line to tank C-102. The inorganic gas and vapor data from tanks C-101 and C-102 is consistent with the premise that tank C-101 does exchange gases and vapors via the cascade with tank C-102, but does not constitute proof that this is indeed happens. However, the semivolatile organic vapor data suggests that little of the semivolatile organic vapors are being exchanged between tanks C-101 and C-102. On this basis, the organic vapor data does provide a reasonably compelling argument that the cascade line between tanks C-101 and C-102 is essentially closed.

X.2 SAMPLING EVENT

Headspace gas and vapor samples were collected from tank C-101 using the VSS on September 1, 1994 by WHC Sampling and Mobile Laboratories (WHC 1995). Sample collection and analysis were performed as directed by the sample and analysis plan (WHC 1995, Appendix A). Air from the tank C-101 headspace was withdrawn via a 7.9-m long heated sampling probe mounted in riser 8, and transferred via heated tubing to the VSS sampling manifold. The tank headspace temperature was determined to be 34.0 °C, and all heated zones of

² Tank C-103 is known to have a layer of semivolatile organic liquid floating on the aqueous waste (Pool and Bean 1994), and the highest total concentration of organic vapors of any waste tank known (Huckaby and Story 1994). Tank C-102 is known to have contained bulk quantities of the same semivolatile organic liquid (Carothers 1988), and its presence is still evident in auger samples (Campbell et al. 1995).

the VSS were maintained at approximately 50 °C. All samples were collected between 8:26 a.m. and 11:49 a.m.

Sampling media were prepared and analyzed by WHC, Oak Ridge National Laboratories (ORNL), Pacific Northwest Laboratories (PNL), and Oregon Graduate Institute of Science and Technology (OGIST) through a contract with Sandia National Laboratories. The 39 tank air samples and 2 ambient air control samples collected are listed in Table X-1 by analytical laboratory. Table X-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 (1995a). Descriptions of the sampling equipment, sample collection sequence, sorbent trap sample air flow rates and flow times, chain of custody information, and the sampling event itself are given in WHC 1995 and references therein.

One anomaly was reported for the tank C-101 headspace sampling event. After the installation of the heated sampling probe into tank C-101 on August 19, 1994, a WHC industrial hygienist using a combustible gas meter observed a reading of 100 % of the lower flammability limit (LFL) at the probe's opening. A significant reduction in the reading was observed as the probe was purged with air from the tank headspace. A subsequent investigation concluded that a damaged valve had trapped solvents used to clean the probe, specifically acetone and methanol, and prevented their complete removal during the cleaning process (Mahon 1995). Though the damaged valve was replaced, residual amounts of the cleaning solvents may have been present at the start of the September 1, 1994 tank C-101 sampling event.

However, residual cleaning solvents should have been removed during the standard procedure of heating the probe to 50 °C and purging with air from the tank headspace for 30 min at 5.4 L/min before any samples were collected. Comparison of ambient air SUMMATM samples collected upwind of tank C-101 and via the heated VSS manifold (after being purged with ambient air) indicated no significant contamination of the manifold.

X.3 INORGANIC GASES AND VAPORS

Analytical results of sorbent trap and SUMMA^{TM,3} canister tank air samples for selected inorganic gases and vapors are given in Table X-2 in parts per million by volume (ppmv) in dry air. Inorganic analyte sorbent traps were prepared and analyzed by PNL (Lucke et al. 1995a), and SUMMATM canisters were analyzed for inorganic analytes by OGIST (Rasmussen 1994a).

³ SUMMA is a trademark of Moleetrics, Inc., Cleveland, Ohio.

X.3.1 Ammonia, Hydrogen, and Nitrous Oxide

The reported ammonia concentration, 98 ppmv, is about 4 times the National Institute of Occupational Safety and Health (NIOSH) 8-hr recommended exposure limit (REL) of 25 ppmv for ammonia (NIOSH 1995). Ammonia has been observed in virtually all of the waste tanks sampled to date, at concentrations ranging from about 3 ppmv in tank C-108 (Lucke et al. 1995b), to 1040 ppmv in BY-108 (McVeety et al. 1995).

The concentration of hydrogen in tank C-101 was determined to be 436 ppmv. Hydrogen in the waste tanks is of concern as a fuel. Given that the lower flammability limit (LFL) for hydrogen in air is about 4 % by volume, the 436 ppmv hydrogen concentration in tank C-101 corresponds to about 1 % of its LFL, and indicates hydrogen is not a flammability concern in tank C-101.

The nitrous oxide concentration in tank C-101, 642 ppmv, is over 25 times the NIOSH 8-hr REL of 25 ppmv for nitrous oxide (NIOSH 1995). Nitrous oxide, also known as laughing gas, has been detected in other passively ventilated waste tanks at average concentrations as low as about 12 ppmv in tank TX-105 (Klinger 1995a), and as high as 763 ppmv in tank C-103 (Huckaby and Story 1994).

X.3.2 Carbon Monoxide and Carbon Dioxide

Carbon monoxide in the tank C-101 headspace, measured to be 15.5 ppmv, is much higher than in ambient air, where it typically ranges from 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. The 15.5 ppmv of carbon monoxide in tank C-101 is the second highest measured in any waste tank to date, the highest being 26.7 ppmv measured in tank C-103 (Huckaby and Story 1994). The 15.5 ppmv of carbon monoxide in tank C-101 is less than the NIOSH 8-hr REL of 35 ppmv.

The average carbon dioxide concentration in the tank C-101 headspace, 1426 ppmv, is the highest measured in any waste tank to date. Carbon dioxide is normally present in the ambient air at a concentration of 350 to 400 ppmv, and is typically 10 to 250 ppmv 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. Higher than ambient concentrations of carbon dioxide have also been observed in tank C-107, where it was present at an average 725 ppmv in 3 SUMMATM samples (Rasmussen 1994b).

Because the reported carbon dioxide concentration was unexpectedly high, OGIST was asked to re-examine the analyses. Though the tank C-101 SUMMATM samples sent to OGIST had been disposed of, precluding reanalysis, review of laboratory records and analyses provided no reason to doubt the reported results. A discussion of the issue with the laboratory director, R. A. Rasmussen, confirmed that the instrument had been properly calibrated prior to sample analyses and had responded properly to gas standards, and that blank

runs performed between the analyses of the 3 tank C-101 samples were satisfactory. The analytical method used is relatively robust, and well-accepted amongst air analysis chemists.

The carbon dioxide concentrations in other SUMMATM samples from tank C-101 have been measured by PNL. An archived SUMMATM sample from the September 1, 1994 sampling event⁴ was analyzed by PNL, using significantly different analytical methods, and found to have 1401 ppmv of carbon dioxide. This essentially confirms the results reported by OGIST.

Three other SUMMATM samples from the July 7, 1994 ISS event were also analyzed by PNL by special request to confirm the high carbon dioxide result. Analyses indicated levels of carbon dioxide in these samples to be an average 414 ppmv, with a relative standard deviation of 0.4 % (PNL 1995). This average value is very different from the 1426 ppmv average found by OGIST for the 3 SUMMATM samples from the September 1, 1994 event. Other analyses indicate the July 7 SUMMATM samples have similarly much lower concentrations for hydrogen, nitrous oxide, and organic vapors (PNL 1995). These data suggest that the SUMMATM samples collected on July 7, 1994 were not representative of tank C-101, and that the SUMMATM canisters were actually filled with about an 80:1 ratio of ambient air to headspace sample. It is suspected that a fitting or valve on the sampling manifold used to collect the July 7, 1994 SUMMATM samples was inadvertently left open. Consequently, all SUMMATM sample data from the July 7, 1994 event is deemed invalid in this report.

X.3.3 Nitric Oxide, Nitrogen Dioxide, Water and Tritium

Nitric oxide and nitrogen dioxide concentrations in the tank C-101 headspace were determined to be 1.5 ppmv and ≤ 0.04 ppmv, respectively. These are both acid gases that would have very low equilibrium concentrations above the high pH sludge in tank C-101. The measurable presence of nitric oxide may be due to its formation from oxygen and nitrogen in the radiation field of the headspace. The NIOSH 8-hr REL is 25 ppmv for nitric oxide, and the 15-minute short term exposure limit (STEL) for nitrogen dioxide is 1 ppmv.

The water vapor concentration of tank C-101 was determined to be about 30.1 mg/L, at the tank headspace temperature of 34.0 °C and pressure of 986 mbar (739.7 torr), (WHC 1995). This corresponds to a water vapor partial pressure of 42.6 mbar (32.0 torr), to a dew point of 30.1 °C, and to a relative humidity of 80 %.

Silica gel sorbent traps were used to sample 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

⁴ PNL was not originally tasked to analyze the SUMMATM samples for carbon dioxide, and 2 of the 3 SUMMATM samples collected for PNL during the VSS sampling event had been disposed of prior to the request for these special analyses.

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 1995).

X.3.4 Discussion of Inorganic Gases and Vapors

Aside from water vapor, the most abundant waste constituents in the tank C-101 headspace are carbon dioxide, nitrous oxide, hydrogen, and ammonia. Nitrous oxide, hydrogen, and ammonia have been detected in most tanks sampled to date, and are usually the dominate waste species in the tank headspaces.

The elevated carbon dioxide concentration in tank C-101 is unusual, and not completely understood. Because it is readily absorbed by high pH aqueous wastes (and generally measured to be at lower than ambient concentrations in other tanks), its high concentration in tank C-101 may indicate that the pH of waste in that tank is relatively low. Further examination of data is planned, as is the collection of more samples.

The relative standard deviations of the inorganic gas and vapor results given in the last column in Table X-2 are excellent. Relative standard deviations range from 0.6 % for hydrogen and carbon monoxide, to 6.7 % for nitric oxide results. 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 good control was maintained both in the field and in the laboratories.

The inorganic gases and vapors in tanks C-101 and C-102 are at concentrations that support the premise that tank C-101 breathes primarily via its cascade line with tank C-102. To understand this, suppose that tank C-101 did breathe only via its cascade line to tank C-102 (as per the intended ventilation configuration). Then all the air inhaled by tank C-101 would have the composition of air in tank C-102, so that at steady state (neglecting any losses of constituents in transit), every headspace constituent in tank C-102 would be present in tank C-101 at a concentration at least as high as it is in tank C-102. Furthermore, any gases or vapors generated or released by the waste in tank C-101 would raise the concentration of these constituents in tank C-101 above the level in tank C-102. As indicated in Table X-3, the concentrations of hydrogen, carbon dioxide, carbon monoxide, nitric oxide, and nitrous oxide are all significantly higher in tank C-101 than they are in tank C-102.

Amongst the inorganic analytes listed in Table X-3, only ammonia is at a higher concentration in tank C-102 than it is in tank C-101. This exceptional relationship of ammonia, if indeed tank C-101 breathed primarily via the cascade line with tank C-102, may be reasonable given its solubility in water. Aqueous condensate forming in the cascade line (recall the dewpoint of tank C-101 is about 30 °C) might absorb enough of the ammonia vapor in transit to

tank C-101 to cause this constituent to be lower in tank C-101 than in tank C-102.

Though the data from tanks C-101 and C-102, with special allowance for ammonia, are consistent with the premise that tank C-101 breathes primarily via the cascade line with tank C-102, they do not prove that this is happening. The selected gas and vapor concentrations may be higher in tank C-101 than in tank C-102 simply because their generation rates are higher in tank C-101.

X.4 ORGANIC VAPORS

Organic vapors in the tank C-101 headspace were sampled using SUMMATM canisters, which were analyzed by OGIST and PNL, and triple sorbent traps (TSTs), which were analyzed by ORNL. ORNL and PNL used gas chromatographs (GCs) equipped with mass spectrometer (MS) detectors to separate, identify, and quantitate the analytes. A quantitative measurement of the total organic vapor concentration by the U.S. Environmental Protection Agency (EPA) task order 12 (TO-12) method was also performed by OGIST (EPA 1988, Rasmussen 1994a). Descriptions of sample device cleaning, sample preparations, and analyses are given by Jenkins et al. (1994a), Rasmussen (1994a), and Lucke et al. (1995a).

SUMMATM sample results should be considered to be the primary organic vapor data for tank C-101. ORNL analyses of TST samples from this and other waste tanks generally agree with, support, and augment the SUMMATM 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.

X.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 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 the 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 X-4 lists the organic compounds positively identified and quantitated in SUMMATM samples. Analysis for methane was performed by OGIST (Rasmussen 1994a), and other SUMMATM analyses were performed according to the EPA TO-14 methodology by PNL (EPA 1988, Lucke et al. 1995a). Toluene, trichlorofluoromethane, and tetrachloroethene were the only analytes of the 40 TO-14 target analytes measured to be above the 0.002 ppmv quantitation limit of the analyses. Averages reported are from analyses of 3 SUMMATM canister samples.

Jenkins et al. (1994a) report the positive identification of 26 of 27 target analytes in TST samples. 1,1-Dichloroethene was the only TST target analyte not detected in the TST samples. The average concentrations of the target analytes, from the analysis of 3 TSTs, are given in Table X-5. The concentrations of tributyl phosphate and dibutyl butylphosphonate reported in Table X-5 probably underestimate the actual concentrations in the tank headspace. These compounds have very low volatility, and are thought to be adsorbed by glass fiber filters used during sampling to protect samples from radiolytic particulates.

Both PNL and ORNL report target analyte concentrations in ppmv of analyte in dry air. The results given may be corrected for the measured water vapor content of tank C-101 to obtain concentration in ppmv of analyte in moist tank air by multiplying the dry-air ppmv concentrations by 0.959.

1,1-Dichloroethene, dichloromethane, benzene, and toluene were target analytes for both the TST and SUMMATM analyses. 1,1-Dichloroethene was not detected in either type of sample. The reported average concentrations of dichloromethane, 0.21 ppmv, benzene, 0.28 ppmv, and toluene, 0.071 ppmv, in TST samples, are much higher than their concentrations in the SUMMATM samples (i.e., < 0.002 ppmv, < 0.002 ppmv, and 0.011 ppmv, respectively). The TST sample average 0.071 ppmv of toluene is well below the 100 ppmv NIOSH 8-hr REL for toluene. However, NIOSH identifies dichloromethane as a potential carcinogen, and "usually recommends that occupational exposures to carcinogens be limited to the lowest feasible concentration" (NIOSH 1995). Also, the 0.28 ppmv average benzene concentration found in TST samples is higher than the 0.1 ppmv NIOSH 8-hr REL for benzene.

The most abundant analytes in Tables X-4 and X-5 are methane, acetone, n-dodecane, acetonitrile, n-tridecane, 1-butanol, and n-undecane. At the reported concentrations, the target analytes do not individually or collectively represent a flammability hazard.

X.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. 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 SUMMATM 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 (i.e., molecules with more than about 15 carbon atoms) and some polar compounds with moderate volatility (i.e., butanal) from SUMMATM samples has been problematic.

The list of tentatively identified compounds recovered from SUMMATM samples, with estimated concentrations, is given in Table X-6. Compounds are listed in Table X-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 X-7. Compounds are listed in Table X-7 according to the order by which they eluted chromatographically. The averages reported by ORNL in Table X-7 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.

The ORNL and PNL methods used to tentatively identify and estimate concentrations are described by Jenkins et al. (1994a) and Lucke et al. (1995a), respectively, and should be reviewed before this data is used for decision making. Concentrations given in Tables X-6 and X-7 should be considered rough estimates. Results in Tables X-6 and X-7 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 # 19 and 21 in Table X-7). In these instances, the estimated concentration of a compound appearing in more than 1 peak is simply the sum of the individual peak estimates.

X.4.3 Total Nonmethane Organic Compounds

OGIST measured the total nonmethane organic compound (TNMOC) concentration in 3 SUMMATM canister samples using the EPA TO-12 method (Rasmussen 1994a). The sample mean was 256 mg/m³, with a standard deviation of 9 mg/m³. A comparable analysis of 1 TST sample by gas chromatography with flame ionization detection indicated the organic vapor concentration to be 272 mg/m³ (Jenkins et al. 1994a). This is in excellent agreement with the EPA TO-12 result.

For comparison, Table X-3 lists the measured TNMOC concentration of tanks C-102 and C-103. Among the waste tanks sampled to date, tank C-103 has the

highest measured TNMOC concentration, tank BY-108 has the next highest TNMOC concentration (594 mg/m^3 , McVeety et al. 1995), and tanks C-102 and C-101 have the next highest TNMOC concentrations. EPA TO-12 method TNMOC measurements of other waste tanks are generally much lower, with 5 to 30 mg/m^3 being typical, and lower values common, such as 0.18 mg/m^3 in tank C-111 (Rasmussen 1994c). For comparison, the TNMOC concentration of clean ambient air ranges from about 0.03 to 0.1 mg/m^3 .

X.4.4 Discussion of Organic Gases and Vapors

The organic vapors identified in the tank C-101 headspace are typical of other waste tanks in the 241-C and 241-BY farms. It is useful to consider the organic vapors in the waste tanks in terms of their origin. Some organic compounds, particularly semivolatile compounds, were constituents of the waste sent to the tanks, and are present in the tank headspaces because they are still evaporating from the waste. Other organic compounds present in the tanks have been produced via chemical and radiolytic reactions of the original organic waste. The most abundant of these degradation products in the tank headspaces are volatile, and most contain functional groups. Among the most common degradation products are the alcohols, aldehydes, alkenes, ketones, nitriles, and short-chain alkanes. In tank C-101, semivolatile alkanes tend to dominate the organic vapors, and their associated degradation products represent the majority of other organic compounds.

Comparisons of organic vapor analyses of tanks C-101 and C-102 suggest that most of the organic vapors present in tank C-101 are evolved from the waste in tank C-101, and not transferred via the cascade line from tank C-102. Though many organic compounds are common to both tanks, and there are even many with similar concentrations, the distributions of the semivolatile compounds in tanks C-101 and C-102 are quite different. Specifically, in the headspace of tank C-101 the semivolatile branched alkanes, cyclic alkanes, and alkenes represent a significant fraction of the total semivolatile vapors. In the headspace of tank C-102, however, the normal paraffinic hydrocarbons (NPHs) are overwhelmingly the dominant semivolatile organic species, and there are relatively few non-NPH semivolatile organic species.

The differences between the distributions of semivolatile compounds in tanks C-101 and C-102 are well illustrated in Figure X-1. Here the total ion chromatogram from a tank C-102 SUMMATM sample is provided in the upper half of the figure (Klinger et al. 1995b), and that from a tank C-101 SUMMATM sample is provided in the lower half of the figure (Lucke et al. 1995a). The abscissa of both chromatograms is elution time, and the ordinate is instrumental response. The mixture of organic compounds in each sample has been separated chromatographically so that, inasmuch as the separation is complete, individual analytes elute at different times and appear as individual peaks. Each peak height is roughly proportional to the concentration of the associated analyte present in the sample. Though there is a slight shift of retention times (peaks in the upper chromatogram are shifted slightly to the right), the instrumental settings were identical for the 2 analyses. Also, the ordinate scales in the 2 chromatograms are

different, as are the amounts of sample analyzed, but the peak height-to-concentration relationships are similar; for comparison, the tallest peak in the tank C-101 (lower) chromatogram, at about 44 min, has an estimated concentration of 15.2 mg/m^3 , while the corresponding peak in the tank C-102 (upper) chromatogram (also at about 44 min), has an estimated concentration of 13.5 mg/m^3 .

The tallest peak in the tank C-102 (upper) chromatogram of Figure X-1, at about 18 min, is due to 1-butanol. The 5 next tallest peaks in the tank C-102 chromatogram are n-decane (at 36 min), n-undecane (at 40 min), n-dodecane (at 44 min), n-tridecane (at 48 min), and n-tetradecane (at 52 min). These are the semivolatile NPHs. Their presence in the tank C-102 sample can be traced to waste received from the Plutonium Uranium Extraction (PUREX) process (Carothers 1988). The peaks amongst the NPH peaks in the 40 to 52 min region, tentatively identified as cyclic and branched alkanes, are at relatively low concentrations.

By contrast, as indicated by the tank C-101 (lower) chromatogram in Figure 1, the concentrations of non-NPH semivolatile organic vapors are so high in the 40 to 52 min region that they are no longer separated by the GC. Table X-6 lists the analytes in this region (i.e., Cmpd # 75 through Cmpd # 109). The semivolatile compounds in the headspace of tank C-101 are also from a process diluent of tributyl phosphate, but there is much higher concentration of the non-NPH semivolatile organic vapors in tank C-101 than in tank C-102.

Though TST sample results presented in Table X-7 do not reveal the same variety of semivolatile branched and cyclic alkanes as found in SUMMATM samples, this is largely due to the difficulty of identifying individual analytes in that region of the chromatogram. Visual comparison of TST sample chromatograms from tanks C-101 and C-102 (Jenkins et al. 1994a, 1994b), indicates the same relation as discussed above for SUMMATM analyses.

Because the concentrations of semivolatile non-NPH compounds are much higher in tank C-101 than in tank C-102, it is very likely that these, as well as the majority of other organic vapors present in the headspace of tank C-101, are evolved from the waste in tank C-101. Though some organic vapors may be removed by condensation or absorption within the cascade line as tanks C-101 and C-102 exchange air, it does not seem reasonable to assume tank C-101 is breathing freely with tank C-102. Given the contrasting character of the semivolatile organics in tanks C-101 and C-102, it appears that the cascade line between them is essentially closed, and that if tank C-101 is breathing with barometric fluctuations at all, it must be via leak paths directly to the atmosphere.

Careful examination of Figure 1 indicates there are strong similarities between tanks C-101 and C-102 in the 3 to 40 min region of the chromatograms. Indeed, MS data indicate that many peaks present in both chromatograms are tentatively identified to be the same compounds. The fact that many of these compounds appear in both tanks C-101 and C-102 does not, however, indicate the tank headspaces are connected. These compounds (with certain exceptions) are

products of the chemical and radiolytic degradation of the semivolatile organic compounds. Whether the initial reactants are primarily the straight-chain alkanes (the NPHs), as in tank C-102, or branched and cyclic alkanes, as in tank C-101, many of the same short-chain reaction products are formed. Just as ammonia, hydrogen, and nitrous oxide appear ubiquitously with the Hanford high-level waste, many of these volatile degradation products are observed wherever semivolatile alkanes are present in the waste tanks.

Supporting the premise that the volatile organic vapors are reaction products of the semivolatiles is the fact that several compounds of a homologous series are commonly found in this as well as other waste tanks. Specifically, the following homologous series of straight-chain compounds are found in tank C-101:

- 2-ketones, from 2-propanone (acetone) through 2-octanone;
- aldehydes, with the exception of propanal, from acetaldehyde (ethanal) through octanal;
- nitriles, from acetonitrile (ethanenitrile) through heptanenitrile;
- alkanes, with the exception of ethane (which would not be detected) from methane through nonane; and
- 1-alkenes, from propene through 1-hexene.

Given that the total organic vapor concentrations of tanks C-101 and C-102 (by the EPA TO-12 measurement) are both relatively high compared to most other waste tanks (see Section X.4.3), and that auger samples of the waste in tank C-102 indicate significant condensed phase concentrations of the NPHs and tributyl phosphate (Campbell et al. 1995), it is reasonable to assume that tank C-101 also contains semivolatile organic compounds in the condensed phase.

Table X-1
Tank C-101 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	0.2 and 1.0	Organic vapors	8 tank air samples, + 2 trip blanks + 2 field blanks
Oregon Graduate Institute of Science and Technology	SUMMA TM canister	6.0	Hydrogen, Nitrous Oxide, Carbon Dioxide, Carbon Monoxide, Methane, TNMOC ¹	3 tank air samples
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 TM canister	6.0	Organic vapors	3 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

1. TNMOC = total nonmethane organic compound[s].

Table X-2
Tank C-101 Inorganic Gas and Vapor Concentrations

Compound	CAS ² number	Sample Type	Number of samples	Average (ppmv)	Standard Deviation (ppmv)	RSD ³ (%)
Ammonia, NH ₃	7664-41-7	Sorbent Trap	6	98	1	1.0
Carbon Dioxide, CO ₂	124-38-9	SUMMA TM	3	1426	11.8	0.8
Carbon Monoxide, CO	630-08-0	SUMMA TM	3	15.5	0.1	0.6
Hydrogen, H ₂	1333-74-0	SUMMA TM	3	436	2.5	0.6
Nitric Oxide, NO	10102-43-9	Sorbent Trap	6	1.5	0.1	6.7
Nitrogen Dioxide, NO ₂	10102-44-0	Sorbent Trap	6	≤ 0.04	--	--
Nitrous Oxide, N ₂ O	10024-97-2	SUMMA TM	3	642	6.4	1.0
Water Vapor, H ₂ O	7732-18-5	Sorbent Trap	6	43,200 (30.1 mg/L)	640 (0.4 mg/L)	1.5

2. CAS = Chemical Abstracts Service.

3. RSD = relative standard deviation.

Table X-3
Comparison of Tank C-101, C-102, and C-103 Headspace Constituents¹

Tank:	C-101	C-102 ²	C-103 ³
Date sampled, (mo/day/yr)	9/1/94	8/23/94	4/7/94 - 5/25/94
Headspace temperature, (°C)	34	25.8	38
Ammonia, (ppmv)	98	189	304
Hydrogen, (ppmv)	436	133	782
Carbon dioxide, (ppmv)	1426	8.2	--
Carbon monoxide, (ppmv)	15.5	4.0	26.7
Nitric oxide, (ppmv)	1.5	0.24	1.5
Nitrogen dioxide, (ppmv)	≤ 0.04	≤ 0.05	≤ 0.04
Nitrous oxide, (ppmv)	642	154	763
Water vapor, (mg/m ³)	30.1	20.4	42.2
Water vapor, (% relative humidity)	80	85	91
Ethanenitrile (acetonitrile), (ppmv)	0.69	0.34	9.1
Propanone (acetone), (ppmv)	1.0	2.2	8.8
1-Butanol, (ppmv)	0.46	7.6	28.4
n-Dodecane, (ppmv)	0.94	0.91	40.3
n-Tridecane, (ppmv)	0.61	0.81	52.0
Total nonmethane organic compounds, (mg/m ³)	256	313	3,000 - 5,000 ⁴

1. For consistency in this table, individual organic analyte results are all from TST samples.

2. Data are from Huckaby 1995b.

3. Tank C-103 was sampled on various dates; data are from Huckaby and Story 1994.

4. TNMOC concentrations were too high for precise measurement; this range is from Rasmussen and Einfeld 1994.

Table X-4
Tank C-101 Positively Identified Organic Compounds in SUMMA™ Samples

Cmpd #	Compound	CAS ¹ Number	Average (ppmv)	Standard Deviation (ppmv)	RSD ² (%)
1	Methane ³	74-82-8	12.0	< 0.06	< 0.5
2	Methyl Benzene (toluene)	108-88-3	0.011	0.0005	5
3	Trichlorofluoromethane	75-69-4	0.12	0.04	30
4	Tetrachloroethene (Perchloroethylene)	127-18-4	0.0039	0.0010	25
Sum of positively identified compounds:			9.4	mg/m ³	

1. CAS = Chemical Abstract Service.
2. RSD = relative standard deviation.
3. Methane results are from Rasmussen 1994a.

Table X-5
Tank C-101 Positively Identified Organic Compounds in TST Samples

Cmpd #	Compound	CAS ¹ Number	Average (ppmv)	Standard Deviation (ppmv)	RSD ² (%)
1	Ethanenitrile (acetonitrile)	75-05-8	0.69	0.17	24
2	Propanone (acetone)	67-64-1	1.0	0.2	16
3	Dichloromethane (methylene chloride)	75-09-2	0.21	0.07	32
4	Propanenitrile	107-12-0	0.086	0.014	17
5	Butanal	123-72-8	0.065	0.14	22
6	n-Hexane	110-54-3	0.28	0.02	9
7	Benzene	71-43-2	0.28	0.08	27
8	1-Butanol	71-36-3	0.46	0.02	3
9	Butanenitrile	109-74-0	0.052	0.002	5
10	2-Pentanone	107-87-9	0.12	0.02	13
11	n-Heptane	142-82-5	0.24	0.04	19
12	Toluene	108-88-3	0.071	0.011	16
13	Pentanenitrile ³	110-59-8	0.022	0.003	15
14	2-Hexanone	591-78-6	0.05	0.01	26
15	n-Octane	111-65-9	0.14	0.023	17
16	Hexanenitrile ³	628-73-9	0.016	0.003	19
17	2-Heptanone	110-43-0	0.057	0.019	34
18	n-Nonane	111-84-2	0.079	0.007	8
19	Heptanenitrile	629-08-3	0.011	0.001	7
20	2-Octanone	111-13-7	0.015	0.001	6
21	n-Decane	124-18-5	0.12	0.01	4
22	n-Undecane ³	1120-21-4	0.46	0.04	8
23	n-Dodecane ³	112-40-3	0.94	0.06	6
24	n-Tridecane ³	629-50-5	0.61	0.18	29
25	Dibutyl butylphosphonate ³	78-46-6	0.00051	0.0001	19

26	Tributyl phosphate ³	126-73-8	0.0088	0.0013	15
Sum of positively identified compounds:			30.6 mg/m ³		

1. CAS = Chemical Abstract Service.
2. RSD = relative standard deviation.
3. Two or more samples were outside calibration range.

Table X-6
Tank C-101 Tentatively Identified Compounds in SUMMA™ Samples

Cmpd #	Compound	CAS ¹ Number	Average (mg/m ³)	Standard Deviation ² (mg/m ³)
1	Propene	115-07-1	0.28	0.01
2	Propane	74-98-6	0.49	0.01
3	Propyne	74-99-7	0.56	0.01
4	Cyclopropane	75-19-4	0.26	0.00
5	Ethanal (acetaldehyde) ³	75-07-0	0.07	--
6	Isobutane	75-28-5	0.06	0.00
7	1-Butene	106-98-9	0.17	0.00
8	n-Butane	106-97-8	0.67	0.02
9	2-Methyl-1-propene	115-11-7	0.14	0.01
10	Ethanenitrile (acetonitrile)	75-05-8	0.24	0.00
11	Propanone (acetone)	67-64-1	0.91	0.01
12	1-Pentene ⁴	109-67-1	0.07	< 0.01
13	n-Pentane	109-66-0	0.36	0.00
14	Methyl nitrate	598-58-3	0.08	0.00
15	Propanenitrile ³	107-12-0	0.08	--
16	3-Butanone	78-94-4	< 0.03	--
17	2-Pentene ³	109-68-2	0.07	--
18	2-Pentanone	107-87-9	< 0.04	--
19	2-Methylpentane	107-83-5	0.24	< 0.01
20	Butanal	123-72-8	0.22	0.00
21	2-Butanone	78-93-3	0.35	0.01
22	1-Hexene	592-41-6	0.08	0.00
23	Tetrahydrofuran	109-99-9	0.36	0.10
24	2-Methyl-2-propanenitrile ³	126-98-7	0.11	--
25	Butanenitrile ⁴	109-74-0	0.13	0.005
26	3-Methyl-2-butanone ⁴	563-80-4	0.13	0.005
27	2-Pentanone ³	107-87-9	0.11	--

Cmpd #	Compound	CAS ¹ Number	Average (mg/m ³)	Standard Deviation ² (mg/m ³)
28	3-Methyl-2-butanone ⁴	563-80-4	0.13	0.005
29	1-Butanol	71-36-3	0.75	0.13
30	1-Methylethyl nitrate	1712-64-7	0.15	0.01
31	2-Pentanone	107-87-9	0.60	0.06
32	Pentanal	110-62-3	0.92	0.09
33	n-Heptane	142-82-5	2.01	0.17
34	Unknown C7 Alkane		0.25	0.02
35	Methylcyclohexane	108-87-2	0.13	0.01
36	2-Methyl-1-butanol ³	137-32-6	0.16	--
37	Unknown C7 Alkene/Cycloalkane ⁴		0.17	0.03
38	Unknown C3 Nitrate		0.09	0.00
39	Unknown C8 Alkane		0.30	0.00
40	2-Hexanone	591-78-6	0.27	0.01
41	Hexanal	66-25-1	0.37	0.03
42	n-Octane	111-65-9	1.22	0.05
43	Hexamethylcyclotrisiloxane ³	541-05-9	0.99	--
44	3-Methylcyclopentanone	1757-42-2	0.10	0.00
45	Unknown C9 Alkane		0.16	0.00
46	Methylpyridine ⁴	108-99-6	0.15	0.02
47	Unknown C9 Alkane ³		0.09	--
48	2-Heptanone	110-43-0	0.29	0.01
49	Cyclohexanone	108-94-1	0.17	0.04
50	Heptanal	111-71-7	0.31	0.01
51	n-Nonane	111-84-2	0.59	0.02
52	Penstet Nitrate	1002-16-0	0.12	0.00
53	6-Methyl-2-heptanone	928-68-7	0.60	0.03
54	Unknown C9 Alkane ³		0.09	--
55	Unknown C9 Ketone ⁴		0.09	0.005

Cmpd #	Compound	CAS ¹ Number	Average (mg/m ³)	Standard Deviation ² (mg/m ³)
56	2-Octanone	111-13-7	0.16	0.00
57	Unknown C10 Alkene/Cycloalkane ⁴		0.09	0.005
58	Octanal ⁴	124-13-0	0.22	0.015
59	Octamethylcyclotetrasiloxane ³	556-67-2	0.39	--
60	Unknown Alkene/Cycloalkane		0.10	0.00
61	n-Decane	124-18-5	1.46	0.05
62	Hexane Nitrate	20633-11-8	0.09	0.00
63	4-Methyldecane	2847-72-5	0.51	0.01
64	Unknown C10 Alkene/Cycloalkane		0.10	0.00
65	Unknown C10 Alkene/Cycloalkane		0.19	0.00
66	Unknown C11 Alkene/Cycloalkane		0.10	0.01
67	Unknown C11 Alkane		0.09	0.01
68	Unknown C12 Alkane		0.11	0.00
69	Unknown C11 Alkene/Cycloalkane		0.11	0.00
70	Unknown C11 Alkane		0.15	0.01
71	trans-Decahydronaphthalene	493-02-7	0.14	0.01
72	Unknown C12 Alkene/Cycloalkane		0.16	0.02
73	Unknown C11 Alkene/Cycloalkane		0.17	0.02
74	Undecane	1120-21-4	6.45	0.53
75	Unknown Alkene/Cycloalkane		0.31	0.01
76	Unknown C12 Alkane		0.36	0.02
77	Unknown C12 Alkane		0.47	0.03
78	2-Methyldecahydronaphthalene	2958-76-1	0.33	0.05
79	Pentylcyclohexane	4292-92-6	0.57	0.12
80	Unknown C12 Alkane		1.26	0.37
81	Unknown C12 Alkane		0.57	0.14
82	Unknown C13 Alkane		1.30	0.14
83	Unknown C12 Alkane		0.84	0.08

Cmpd #	Compound	CAS ¹ Number	Average (mg/m ³)	Standard Deviation ² (mg/m ³)
84	Unknown C12 Alkene/Cycloalkane		0.21	0.01
85	Unknown C12 Alkene/Cycloalkane		0.17	0.02
86	Unknown C13 Alkane		1.38	0.11
87	n-Dodecane	112-40-3	13.61	1.42
88	Unknown C12 Alkene/Cycloalkane ⁴		0.55	0.07
89	2,6-Dimethyldecahydronaphthalene	1618-22-0	0.83	0.03
90	Unknown C13 Alkane		5.70	0.81
91	Unknown C13 Alkane		1.01	0.06
92	Unknown C13 Alkane		0.22	0.04
93	Unknown		0.23	0.02
94	Unknown C2 Decahydronaphthalene		1.21	0.08
95	Unknown C3 Alkene/Cycloalkane		4.05	0.33
96	Unknown C2 Alkyl Decahydronaphthalene		1.46	0.16
97	Unknown C13 Alkane		1.42	0.22
98	Unknown C2 Decahydronaphthalene ⁴		0.38	0.04
99	Unknown Alkane		0.94	0.09
100	7-Methyltridecane	26730-14-3	5.28	0.47
101	Unknown Alkene/Cycloalkane		1.00	0.13
102	n-Tridecane	629-50-5	7.04	0.60
103	Unknown Alkene/Cycloalkane		1.87	0.13
104	Unknown Alkane		0.61	0.05
105	Unknown Alkene/Cycloalkane ³		0.44	--
106	Unknown C12 Ketone		1.14	0.47
107	3-Dodecanone	1534-27-6	0.13	0.01
108	Unknown Alkane		0.56	0.08
109	Unknown		0.42	0.02
110	n-Tetradecane	629-59-4	0.17	0.08
111	Unknown Alkene/Cycloalkane		0.16	0.02

Cmpd #	Compound	CAS ¹ Number	Average (mg/m ³)	Standard Deviation ² (mg/m ³)
Sum of tentatively identified compounds:			86.5	

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).
3. Detected in only 1 sample.
4. Detected in only 2 samples.

Table X-7
Tank C-101 Tentatively Identified Organic Compounds in TST Samples

Cmpd #	Compound	CAS ¹ Number	Average (mg/m ³)	Standard Deviation (mg/m ³)
1	Methane, trichlorofluoro	75-69-4	2.4	0.6
2	Pentane, 2-methyl	107-83-5	0.23	0.39
3	Cyclopropane, propyl	107-01-7	0.16	0.27
4	2-Butanone	78-93-3	0.17	0.29
5	Furan, tetrahydro	109-99-9	0.75	0.77
6	Hexane, 3-methyl	589-34-4	0.11	0.20
7	2-Hexenal	505-57-7	0.098	0.169
8	Nitrile acid, propyl ester	627-13-4	0.08	0.14
9	Alkane		0.056	0.096
10	Hexane, 3-methyl	589-34-4	0.70	1.00
11	C8-Alkane		0.21	0.18
12	Octane, 4-methyl	2216-34-4	0.38	0.07
13	3-Hexanone	589-38-8	0.061	0.106
14	2-Pentanone, 4-methyl	108-10-1	0.68	0.10
15	Hexanal	66-25-1	0.34	0.31
16	Cyclobutane, 1,2-diethyl	19341-98-1	0.10	0.18
17	Alkyl ester of nitric acid		0.089	0.154
18	2-Hexenal, (E)	6728-26-3	0.20	0.18
19	Benzene, ethyl	100-41-4	0.22	0.05
20	Benzene, 1,2-dimethyl	95-47-6	0.26	0.23
21	Benzene, ethyl	100-41-4	0.082	0.143
22	Butane, 2-bromo	78-76-2	0.048	0.083
23	3-Heptanone	106-35-4	0.044	0.077
24	Bicyclo[4.2.0]octa-1,3,5-triene	694-87-1	0.046	0.08
25	Heptanal	111-71-7	0.31	0.05
26	1-Octanol	111-87-5	0.051	0.088

Cmpd #	Compound	CAS ¹ Number	Average (mg/m ³)	Standard Deviation (mg/m ³)
27	2-Heptanone, 6-methyl	928-68-7	0.32	0.28
28	2-Pentanone, 3-methyl	565-61-7	0.036	0.062
29	1,1,2,3-tetramethyl- cyclohexane		0.19	0.18
30	2-Buten-1-ol	4088-60-2	0.041	0.071
31	1-Heptanol	111-70-6	0.044	0.077
32	Cyclotetrasiloxane, octamethyl	556-67-2	0.13	0.22
33	Cycloheptane, methoxy	42604-04-6	0.036	0.062
34	Phenol and ethanone, 1-phenyl-		0.037	0.065
35	Cyclohexane,1-methyl- 3-propyl	4294-80-9	0.054	0.094
36	3-Decene, cis-trans		0.049	0.086
37	Octanal	124-13-0	0.96	0.87
38	3-Heptene, 2,2,3,5,5,6,6-heptamethyl	54845-26-0	0.072	0.124
39	Nonane, 2,6-dimethyl	17302-28-2	0.63	0.03
40	Benzene, 2-propenyl-	300-57-2	0.289	0.077
41	Nonane, 3,7-dimethyl	17302-32-8	0.32	0.10
42	Cyclohexanone, 2,2,6-trimethyl	2408-37-9	0.12	0.11
43	Cyclohexanone, 3,3,5-trimethyl	873-94-9	0.20	0.03
44	1-ethyl-2,2,6-trimethyl- cyclohexane		0.15	0.17
45	Octane, 5-ethyl-2-methyl	62016-18-6	0.18	0.05
46	Decane, 4-methyl	2847-72-5	0.034	0.059
47	Benzene, butyl and C11-alkane		0.48	0.11
48	Naphthalene, decahydro-, trans-	493-02-7	0.25	0.05

Cmpd #	Compound	CAS ¹ Number	Average (mg/m ³)	Standard Deviation (mg/m ³)
49	Decane, 3-methyl	13151-34-3	0.28	0.06
50	1-Propanone, 1-phenyl	93-55-0	0.28	0.004
Sum of tentatively identified compounds:			31.6	

1. CAS = Chemical Abstract Service.

WHC-SD-WM-ER-458 REV. 0

Figure X-1
Total Ion Chromatograms for SUMMATM Samples from Tanks C-101 and C-102

SUMMA sample total ion chromatogram for tank C-102 (Klinger et al. 1995b).

SUMMA sample total ion chromatogram for tank C-101 (Lucke et al. 1995a).

X.4 REFERENCES

- Anderson, J. D., 1990, *A History of the 200 Area Tank Farms*, WHC-MR-0132, Westinghouse Hanford Company, Richland, Washington.
- Campbell, J. A., R. M. Bean, K. L. Wahl, G. M. Wong, K. E. Bell, K. B. Wehner, A. D. Rice, R. J. Ray, D. B. Bechtold, B. R. Wels, R. W. Schroeder, J. W. Ball, B. D. Valenzuela, J. M. Frye, S. L. Fitzgerald, P. P. Bachelor, B. Griffin, R. K. Fuller, A. B. Benally, and S. M. Parong, 1995, *Analysis of Samples from Hanford Waste Tanks 241-C-102, 241-BY-108, and 241-C-103*, PNL-10531, UC-601, Pacific Northwest Laboratory, Richland, Washington.
- Carothers, K. G., 1988, *Tank C-103 Transaction History - Post January 1976*, (internal memorandum 13331-88-600 to D. A. Dodd, G. L. Dunford, G. N. Hanson, A. W. Lilly and R. E. Van der Cook, September 22), Westinghouse Hanford Company, Richland, Washington.
- Conrad, R. B., 1994, *Engineering Evaluation of Alternatives for Treatment of Tank 241-C-103 Vapor Space*, WHC-SD-WM-ES-281, 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.
- Huckaby, J. L., 1994, *Tank 241-C-103 Headspace Flammability*, WHC-EP-0734 Rev. 1, Westinghouse Hanford Company, Richland, Washington.
- Huckaby, J. L., 1995a, *Waste Tank Headspace Gas and Vapor Characterization Reference Guide*, WHC-SD-WM-ER-430 Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Huckaby, J. L., 1995b, *Tank 241-C-102 Vapor Sampling and Analysis Tank Characterization Report*, WHC-SD-WM-ER-459, 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., A. B. Dindal, C. E. Higgins, C. Y. Ma, M. A. Palausky, and J. T. Skeen, 1994a, *Analysis of Tank 241-C-101 Headspace Components*, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

- Jenkins, R. A., A. B. Dindal, C. E. Higgins, C. Y. Ma, M. A. Palausky, and J. T. Skeen, 1994b, *Analysis of Tank 241-C-102 Headspace Components*, ORNL-CASD-FR-241C102.95 Rev. 0, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- 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, 1995a, *Vapor Space Characterization of Waste Tank 241-TX-105: Results from Samples Collected Through the Vapor Sampling System on 12/20/94*, PNL-xxxxx 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, K. B. Olsen, O. P. Bredt, J. S. Fruchter, and S. C. Goheen, 1995b, *Vapor Space Characterization of Waste Tank 241-C-102: Results from Samples Collected on 8/23/94*, PNL-xxxxx UC-606, Pacific Northwest Laboratory, Richland, Washington.
- Lucke, R. B., T. W. Clauss, M. W. Ligothke, K. H. Pool, B. D. McVeety, J. S. Young, M. McCulloch, J. S. Fruchter, and S. C. Goheen, 1995a, *Vapor Space Characterization of Waste Tank 241-C-101: Results from Samples Collected Through the Vapor Sampling System on 9/1/94*, PNL-xxxxx 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, 1995b, *Vapor Space Characterization of Waste Tank 241-C-108: Results from Samples Collected Through the Vapor Sampling System on 8/5/94*, PNL-xxxxx 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. D., 1995, *C-101 Probe Cleaning Resolution*, (Internal memorandum to J. W. Osborne, OM612-SML95-015, May), Westinghouse Hanford Company, 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-xxxxx UC-606, Pacific Northwest Laboratory, Richland, Washington.
- NIOSH 1995, *NIOSH Pocket Guide to Chemical Hazards*, U.S. Department of Health and Human Resources, National Institute for Occupational Safety and Health, Cincinnati, Ohio.

- 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, 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 C-101*, (Internal memorandum 8E920-SAS94-XXX, September 9), Westinghouse Hanford Company, Richland, Washington.
- PNL, 1995, (Draft) *Vapor Space Characterization of Waste Tank 241-C-101 (In Situ): Results from Samples Collected on 7/7/94*, PNL-xxxxx, UC-606, Pacific Northwest Laboratories, Richland, Washington.
- Pool, K. H., and R. M. Bean, 1994, *Analysis of Liquid Samples from Hanford Waste Tank 241-C-103*, PNL-9403 UC-601, Pacific Northwest Laboratory, Richland, Washington.
- Rasmussen, R. A., 1994a, *Air Samples Collected at Waste Tank 241-C-101 on September 1, 1994 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-C-107 on September 29, 1994 by Westinghouse Hanford in 6-L SS SUMMA® Canisters*, Oregon Graduate Institute of Science and Technology, Beaverton, Oregon.
- Rasmussen, R. A., 1994c, *Air Samples Collected at Waste Tank 241-C-111 on September 13, 1994 by Westinghouse Hanford in 6-L SS SUMMA® Canisters*, Oregon Graduate Institute of Science and Technology, Beaverton, Oregon.
- WHC 1995, *Vapor and Gas Sampling of Single-Shell Tank 241-C-101 Using the Vapor Sampling System*, WHC-SD-WM-RPT-128, Westinghouse Hanford Company, Richland, Washington.