

## DISTRIBUTION SHEET

To	From	Page 1 of 1
Distribution	J. W. Osborne	Date May 31, 1995
Project Title/Work Order		EDT No. 612338
Tank 241-S-102 Vapor Sampling and Analysis Tank Characterization Report (WHC-SD-WM-ER-446)		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			

## **DISCLAIMER**

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

13  
 MAY 31 1995

ENGINEERING DATA TRANSMITTAL

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					(F)	(G)	(H)	(I)
(A) Item No.	(B) Document/Drawing No.	(C) Sheet No.	(D) Rev. No.	(E) Title or Description of Data Transmitted	Approval Designator	Reason for Transmittal	Originator Disposition	Receiver Disposition
1	WHC-SD-WM-ER-446	N/A	0	Tank 241-S-102 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	1. Approved	4. Reviewed no/comment
		2. Release	5. Post-Review	2. Approved w/comment	5. Reviewed w/comment
		3. Information	6. Dist. (Receipt Acknow. Required)	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	Reason	Disp.
1	/	Cog.Eng. J. W. Osborne	<i>J. Osborne</i>	5-31-95							
1	/	Cog. Mgr. T. J. Kelley	<i>T. Kelley</i>	5/31/95							
		QA									
		Safety									
		Env.									

18. <i>J. Osborne</i> Signature of EDT Originator Date 5-31-95	19. _____ Authorized Representative for Receiving Organization Date _____	20. <i>T. Kelley</i> Cognizant Manager Date 5/31/95	21. DOE APPROVAL (if required) Ctrl. No. _____ <input type="checkbox"/> Approved <input type="checkbox"/> Approved w/comments <input type="checkbox"/> Disapproved w/comments
--	---	---	---

## RELEASE AUTHORIZATION

**Document Number:** WHC-SD-WM-ER-446, REV 0

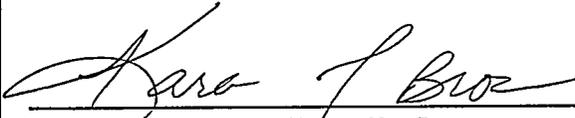
**Document Title:** Tank 241-S-102 Vapor Sampling and Analysis Tank  
Characterization Report

**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 **20**

## 2. Title

Tank 241-S-102 Vapor Sampling and Analysis Tank  
Characterization Report

## 3. Number

WHC-SD-WM-ER-446

## 4. Rev No.

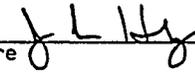
0

## 5. Key Words

241-S-102, headspace vapor samples, organic  
analytes, VSS, SUMMA™, inorganic gases and vapors

## 6. Author

Name: J. L. Huckaby

Signature Organization/Charge Code  
75600/N4AB1

## 7. Abstract

Tank 241-S-102 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-S-102 was vapor sampled in accordance with "Data Quality Objectives for Generic In-Tank Health and Safety Issue Resolution (Osborne et al., 1994).

**MASTER****DISCLAIMER**

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.

## 8. RELEASE STAMP

OFFICIAL RELEASE  
BY WHC  
DATE MAY 31 1995

SA 4

## Tank 241-S-102 Vapor Sampling and Analysis Tank Characterization Report

### X.0 INTRODUCTION

Tank S-102 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). The tank S-102 headspace was sampled in accordance with *Data Quality Objectives for Generic In-Tank Health and Safety Issue Resolution* (Osborne et al. 1994).

### X.1 SAMPLING EVENT

Headspace gas and vapor samples were collected from tank S-102 using the vapor sampling system (VSS) on March 14, 1995 by WHC Sampling and Mobile Laboratories (WHC 1995). Sample collection and analysis were performed as directed by *Tank 241-S-102 Tank Characterization Plan* (Homi 1995). The tank headspace temperature was determined to be 24.3 °C. Air from the tank S-102 headspace was withdrawn from a single elevation via a 6.1-m long heated sampling probe mounted in riser 1, and transferred via heated tubing to the VSS sampling manifold. All heated zones of the VSS were maintained at approximately 50 °C. All tank air samples were collected between 11:26 a.m. and 2:47 p.m., with no anomalies noted.

Sampling media were prepared and analyzed by WHC, Oak Ridge National Laboratories (ORNL), and Pacific Northwest Laboratories (PNL). The 40 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 (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 1995 and references therein.

### X.2 INORGANIC GASES AND VAPORS

Analytical results of sorbent trap and SUMMA<sup>TM,1</sup> canister tank air samples for selected inorganic gases and vapors are given in Table X-2 in parts per

---

<sup>1</sup> SUMMA is a trademark of Moleetrics, Inc., Cleveland, Ohio.

MASTER

million by volume (ppmv). Inorganic analyte sorbent traps and SUMMA™ canisters were prepared and analyzed by PNL (Pool et al. 1995).

### X.2.1 Ammonia, Hydrogen, and Nitrous Oxide

The reported ammonia concentration, 412 ppmv, is relatively high compared to other waste tanks sampled to date. It is over 16 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 passively ventilated waste tanks sampled to date, at concentrations ranging from about 3 ppmv in tank C-108 (Lucke et al. 1995), to 1040 ppmv in BY-108 (McVeety et al. 1995).

The concentration of hydrogen in tank S-102 was determined to be 669 ppmv, and is among the highest measured in any of the passively ventilated waste tanks. 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 669 ppmv hydrogen concentration in tank S-102 corresponds to about 1.7 % of its LFL. At this level, hydrogen is not a flammability concern in tank S-102.

The nitrous oxide concentration in tank S-102, 509 ppmv, is also relatively high compared to other waste tanks sampled to date. It is over 20 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 1995), and as high as 763 ppmv in tank C-103 (Huckaby and Story 1994).

### X.2.2 Carbon Monoxide and Carbon Dioxide

Carbon monoxide in the tank S-102 headspace, characterized as < 12 ppmv, is below the NIOSH 8-hr REL of 35 ppmv for carbon monoxide. In ambient air it typically ranges from 0.05 to 0.15 ppmv. Because different analytical methods have been used to measure carbon monoxide in the waste tanks sampled to date, the information on carbon monoxide has varied from tank to tank. However, elevated waste tank headspace carbon monoxide concentrations are common, and are thought to be due to the decomposition of organic waste in the tanks. Carbon monoxide has not been measured at very high levels in any of the waste tanks, the highest level measured to date was 26.7 ppmv in tank C-103 (Huckaby and Story 1994).

The carbon dioxide concentration in the tank S-102 headspace, reported as < 64 ppmv, is significantly lower than it is in ambient air. Carbon dioxide is normally present in the ambient air at a concentration of 350 to 400 ppmv, and is typically lower than ambient in the waste tank headspaces. The 2 ambient air samples collected at the start of the tank S-102 gas and vapor sampling event, for example, were measured to have an average 360 ppmv of carbon dioxide.

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. Like the carbon monoxide measurements, because different analytical methods have been used to measure carbon dioxide in the waste tank samples, the information on waste tank carbon dioxide varies. The < 64 ppmv of carbon dioxide characterization of the tank S-102 headspace is consistent with typical values for the waste tanks sampled to date.

### **X.2.3 Nitric Oxide, Nitrogen Dioxide, Water and Tritium**

Nitric oxide and nitrogen dioxide concentrations in the tank S-102 headspace were determined to be  $\leq 0.04$  and  $\leq 0.02$  ppmv, respectively. These are acid gases that would have very low equilibrium concentrations above the high pH sludge in tank S-102. A measurable presence of nitric oxide is not uncommon in the waste tank headspaces, and may be due to its formation from oxygen and nitrogen in the radiation field of the headspace. 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 S-102 was determined to be about 14.1 mg/L, at the measured tank headspace temperature of 24.3 °C and pressure of 988.0 mbar (741.2 torr), (WHC 1995). This corresponds to a water vapor partial pressure of 19.3 mbar (14.5 torr), to a dew point of 16.9 °C, and to a relative humidity of 63 %.

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

### **X.2.4 Discussion of Inorganic Gases and Vapors**

Aside from water vapor, the most abundant waste constituents in the tank S-102 headspace are hydrogen, nitrous oxide, and ammonia. These have been detected in most tank headspaces sampled to date, and are usually the dominate waste species. The concentrations of these 3 constituents in tank S-102 are well above the average measured in passively ventilated waste tanks.

The relative standard deviations of the inorganic gas and vapor results given in the last column in Table X-2 are excellent for the methods used. Relative standard deviations range from less than 1 % for hydrogen to about 7 % for nitrous oxide results. Because the precision reported depends both on sampling parameters (e.g., sample flow rate and flow time for sorbent traps) and analytical parameters (e.g., sample preparation, dilutions, etc.), small

relative standard deviations suggest proper control was maintained both in the field and in the laboratories.

### X.3 ORGANIC VAPORS

Organic vapors in the tank S-102 headspace were sampled using SUMMA™ canisters, which were analyzed by PNL, and triple sorbent traps (TSTs), which were analyzed by ORNL. Gas chromatography (GC) and mass spectroscopy (MS) were used by PNL and ORNL to separate, identify, and quantitate the analytes. Descriptions of sample device cleaning, sample preparations, and analyses are given by Jenkins et al. (1995) and Pool et al. (1995).

SUMMA™ sample results should be considered to be the primary organic vapor data for tank S-102. 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.

#### X.3.1 Positively Identified Organic Compounds

Positive identification of organic analytes using the methods employed by PNL and ORNL involves matching the GC retention times and MS data from a sample with that obtained 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 39 compounds in the Environmental Protection Agency (EPA) task order 14 (TO-14) method, which are primarily halocarbons and common industrial solvents (EPA 1988), plus 14 analytes selected mainly from the toxicology panel's review of tank C-103.

Table X-3 lists the organic compounds positively identified and quantitated in SUMMA™ samples. SUMMA™ analyses were performed according to the TO-14 methodology, except for methane analysis, which was analyzed with the inorganic gases (Pool et al. 1995). Only 5 of the 39 TO-14 target analytes and 7 of the 14 additional target analytes were measured to be above the 0.005 ppmv detection limit of the analyses. Averages reported are from analyses of 3 SUMMA™ canister samples.

Jenkins et al. (1995) report the positive identification of 24 of 27 target analytes in TST samples. Dichloromethane, dibutyl butylphosphonate, and tributyl phosphate were the only TST target analytes not detected. The average concentrations of the detected target analytes, from the analysis of 3 TSTs, are given in Table X-4. Despite calibration of the instrument over about a 20-fold concentration range, 11 of the compounds listed in Table X-4 were outside of the calibration range in at least 2 of the TST samples.

Both PNL and ORNL report target analyte concentrations in ppmv of analyte in dry air. To correct for the measured water vapor content of tank S-102 and obtain concentration in ppmv of analyte in moist tank air, multiply the dry-air ppmv concentrations by 0.981.

Eleven target analytes were common to both TST and SUMMA™ analyses. Table X-5 lists these, and their reported average concentrations in TST and SUMMA™ samples. Results from these 2 sampling and analytical methods are in fairly good agreement for benzene and n-heptane. As indicated in Table X-5, the reported concentrations of propanenitrile, butanenitrile, and n-hexane in TST samples are moderately higher than the SUMMA™ sample analytical detection limit, yet were not reported as being present in the SUMMA™ samples.

The largest discrepancy between the target analyte results from the 2 methods is for acetone, which was determined to be present at 0.10 ppmv in TST samples, and 0.56 ppmv in SUMMA™ samples. Acetonitrile and toluene measurements from the 2 types of samples differ by about a factor of 2. None of these compounds, however, even assuming the higher concentrations to be correct, are at or above levels of concern. Benzene, propanenitrile, and acetonitrile have the lowest NIOSH RELs of the identified compounds in Table X-5, being 0.1, 6, and 20 ppmv, respectively.

The most abundant analytes in Tables X-3 and X-4 are acetone, 1-butanol, 1-propanol, and toluene, each of which was measured to between 0.1 and 1 ppmv. At the reported concentrations, the target analytes do not individually or collectively represent a flammability hazard.

### **X.3.2 Tentatively Identified Organic Compounds**

In addition to the target analytes, the ORNL and PNL analytical procedures allow the tentative identification of other organic compounds. Tentative identification of analytes was performed by comparing the MS molecular fragmentation patterns with a library of known MS fragmentation patterns. This method allows an organic analyte to be identified (with reasonable certainty) as an alkane, a ketone, an aldehyde, etc., and may also determine its molecular weight. The method usually does not, however, allow the unambiguous identification of structural isomers, and this ambiguity increases with analyte molecular weight. 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 SUMMA™ 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 (i.e., molecules with more than about 15 carbon atoms) and some polar compounds with moderate volatility (i.e., butanal) from SUMMA™ samples has been problematic.

The list of tentatively identified compounds recovered from SUMMA™ 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/m<sup>3</sup>, 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. (1995) and Pool et al. (1995), 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.

#### X.3.4 Discussion of Organic Compounds

A convenient way to consider the organic compounds listed in Tables X-3 through X-7 is to separate them into 2 categories: 1) Organic compounds added to tank S-102 as waste that are still evaporating; and 2) organic compounds that have been generated by reactions of the original waste.

The first category encompasses all organic compounds that were placed into the tank as waste. It includes the semivolatile straight-chain alkanes, which were used as diluents of tributyl phosphate in various plutonium extraction processes. These alkanes (i.e., n-undecane, n-dodecane, n-tridecane, n-tetradecane, and n-pentadecane) are often referred to in Hanford site literature as the normal paraffinic hydrocarbons (NPHs). Though NPHs are positively identified in tank S-102, their concentrations are very low compared to other NPH-rich tanks in the 241-BY and 241-C farms.

The tentatively identified cyclosiloxanes (i.e., Cmpd # 15 and 18 in Table X-7), and other silicon-containing compounds (i.e., Cmpd # 9, 16, and 22 in Table X-7) are also in this category. Small quantities of organosilicon compounds may have been introduced to the waste tank through their use as defoaming agents, but they may also be present in the headspace due to their use in liquid traps at the tank's breather riser.

The absence of tributyl phosphate in the tank S-102 samples does not necessarily indicate it is not present in the waste. The identification of the tributyl phosphate diluents and their degradation products is reason to expect tributyl phosphate may be present in the tank waste. 1-Butanol, which is one of the more abundant compounds in tank S-102 samples, is known to be a product of the hydrolysis of tributyl phosphate. Furthermore, informal tests by ORNL indicate that tributyl phosphate is adsorbed by the glass fiber filters used during sampling to protect the samples from radiolytic particulate contamination. Based on these considerations, the lack of tributyl phosphate in the tank S-102 headspace samples should not be taken as proof it is not present in the headspace.

The second category includes all organic compounds that have been generated via radiolytic and chemical reactions of the waste. The majority of compounds listed in Tables X-3 through X-7 fall into this category, including the alcohols, ketones, nitriles, alkenes, and volatile alkanes, all of which have been associated with the degradation of the NPHs.

On the basis of concentration, alcohols are the dominate type of organic compound in the tank S-102 headspace. Methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol account for about 76 % of the total estimated concentration of organic compounds in SUMMA™ samples. Similarly, about 65 % of the total estimated organic compound concentration in TST samples is due to the same 6 alcohols. By contrast, the NPH-rich waste tanks in 241-BY and 241-C farms have few alcohols other than 1-butanol. Also in contrast to tanks having higher NPH concentrations, tank S-102 has relatively few ketones, and no aldehydes were detected.

The total organic vapor concentration of tank S-102 was estimated by Jenkins et al. to be about  $9.4 \text{ mg/m}^3$  from the analysis of 3 TST samples by GC/MS. A similar summation of organic compounds measured in SUMMA™ samples from tank S-102 provides an estimated total organic vapor concentration of  $20.6 \text{ mg/m}^3$ . This disagreement is largely due to the different estimated concentrations of the dominant alcohols in the 2 sample types.

Though these estimated total organic vapor concentrations are not completely equivalent to the total nonmethane organic compound (TNMOC) concentration obtained using the EPA task order 12 (TO-12) method, they are comparable. TNMOC measurements of other waste tanks have ranged from as high as about  $5,000 \text{ mg/m}^3$  in tank C-103 (Rasmussen and Einfeld 1994), to as low as  $0.18 \text{ mg/m}^3$  in tank C-111 (Rasmussen 1994), while the TNMOC concentration of clean ambient air ranges from about 0.03 to  $0.1 \text{ mg/m}^3$ .

The organic vapor concentrations in tank S-102 are moderately low. The organic vapors in tank S-102 clearly indicate the presence of the semivolatile NPHs and their degradation products in the tank waste, though the NPHs are at trace levels. Tributyl phosphate was not detected in any of the headspace samples, but there is strong evidence that it is also present in the waste. Tank S-102 is the only 241-S farm tank to be sampled to date. Its headspace organic vapor composition is quite similar to the 241-U farm tanks U-106, U-

WHC-SD-WM-ER-446 REV. 0

107, and U-111, in that NPH vapors are present but only in trace amounts, and the short-chain alcohols are the most abundant organic compounds.

**Table X-1  
Tank S-102 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, 1.0, and 4.0	Organic vapors	12 tank air samples, + 2 trip blanks + 2 field blanks
Pacific Northwest Laboratories	Acidified Carbon Sorbent Trap	3.0	Ammonia	6 tank air samples + 3 trip blank
	Triethanolamine Sorbent Trap	3.0	Nitrogen Dioxide	6 tank air samples + 3 trip blank
	Oxidation Bed + Triethanolamine Sorbent Trap	3.0	Nitric Oxide	6 tank air samples + 3 trip blank
	Silica Gel Sorbent Trap	3.0	Water vapor	6 tank air samples + 3 trip blanks
	SUMMA™ canister	6.0	Carbon Dioxide, Carbon Monoxide, Hydrogen, Methane, Nitrous Oxide, Organic vapors	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

Table X-2  
 Tank S-102 Inorganic Gas and Vapor Concentrations

Compound	CAS <sup>1</sup> Number	Sample Type	Number of samples	Average (ppmv)	Standard Deviation (ppmv)	RSD <sup>2</sup> (%)
Ammonia, NH <sub>3</sub>	7664-41-7	Sorbent Trap	6	412	5	1.2
Carbon Dioxide, CO <sub>2</sub>	124-38-9	SUMMA <sup>TM</sup>	3	< 64	--	--
Carbon Monoxide, CO	630-08-0	SUMMA <sup>TM</sup>	3	< 12	--	--
Hydrogen, H <sub>2</sub>	1333-74-0	SUMMA <sup>TM</sup>	3	669	1	0.2
Nitric Oxide, NO	10102-43-9	Sorbent Trap	6	≤ 0.04	--	--
Nitrogen Dioxide, NO <sub>2</sub>	10102-44-0	Sorbent Trap	6	≤ 0.02	--	--
Nitrous Oxide, N <sub>2</sub> O	10024-97-2	SUMMA <sup>TM</sup>	3	509	35	7
Water Vapor, H <sub>2</sub> O	7732-18-5	Sorbent Trap	6	19,500 (14.1 mg/L)	400 (0.3 mg/L)	2

1. CAS = Chemical Abstracts Service.

2. RSD = relative standard deviation.

**Table X-3**  
**Tank S-102 Positively Identified Organic Compounds in SUMMA™ Samples**

Cmpd #	Compound	CAS <sup>1</sup> Number	Average (ppmv)	Standard Deviation (ppmv)	RSD <sup>2</sup> (%)
1	Ethanenitrile (acetonitrile)	75-05-8	0.039	0.004	12
2	Propanone (acetone)	67-64-1	0.56	0.01	1
3	Trichlorofluoromethane	75-69-4	0.034	0.002	5
4	Propanol	71-23-8	0.20	0.22	113
5	2-Butanone	78-93-3	0.080	0.018	22
6	Tetrahydrofuran	109-99-9	0.052	0.002	3
7	Benzene	71-43-2	0.019	0.0005	3
8	n-Heptane	142-82-5	0.012	0.0003	2
9	Pyridine	110-86-1	0.023	0.018	77
10	Toluene	108-88-3	0.20	0.004	2
11 & 12	p-Xylene and m-Xylene <sup>3</sup>	106-42-3 108-38-3	0.006	0.0002	3
13	Methane	74-82-8	< 12	--	--
Sum of positively identified compounds:			3.76	mg/m <sup>3</sup>	

1. CAS = Chemical Abstract Service.

2. RSD = relative standard deviation.

3. m-xylene and p-xylene coelute and the reported value represents the sum of their concentrations.

**Table X-4**  
**Tank S-102 Positively Identified Organic Compounds in TST Samples**

Cmpd #	Compound	CAS <sup>1</sup> Number	Average (ppmv)	Standard Deviation (ppmv)	RSD <sup>2</sup> (%)
1	Ethanenitrile (acetonitrile)	75-05-8	0.081	0.014	18
2	Propanone (acetone)	67-64-1	0.10	0.02	23
3	1,1-Dichloroethene <sup>3</sup> (vinylidene chloride)	75-35-4	0.0022	0.0003	15
4	Propanenitrile <sup>3</sup>	107-12-0	0.0063	0.0016	25
5	Butanal	123-72-8	0.059	0.002	3
6	n-Hexane	110-54-3	0.0071	0.0004	5
7	Benzene	71-43-2	0.015	0.001	6
8	1-Butanol <sup>4</sup>	71-36-3	0.39	0.02	5
9	Butanenitrile	109-74-0	0.018	0.001	3
10	2-Pentanone	107-87-9	0.0066	0.0003	4
11	n-Heptane	142-82-5	0.0084	0.0009	10
12	Toluene	108-88-3	0.094	0.002	2
13	Pentanenitrile <sup>3</sup>	110-59-8	0.00080	0.00005	7
14	2-Hexanone <sup>3</sup>	591-78-6	0.0034	0.0007	21
15	n-Octane	111-65-9	0.0094	0.0007	8
16	Hexanenitrile <sup>3</sup>	628-73-9	0.00026	0.00002	9
17	2-Heptanone <sup>3</sup>	110-43-0	0.0024	0.0003	12
18	n-Nonane	111-84-2	0.0042	0.0001	2
19	Heptanenitrile <sup>3</sup>	629-08-3	0.00024	0.00005	20
20	2-Octanone <sup>3</sup>	111-13-7	0.00077	0.00016	20
21	n-Decane <sup>3</sup>	124-18-5	0.0027	0.0001	4
22	n-Undecane <sup>3</sup>	1120-21-4	0.0026	0.0001	4
23	n-Dodecane	112-40-3	0.0032	0.0003	8
24	n-Tridecane	629-50-5	0.0066	0.0005	8
Sum of positively identified compounds:			2.7 mg/m <sup>3</sup>		

1. CAS = Chemical Abstract Service.
2. RSD = relative standard deviation.
3. Results from 2 or more samples were below lower calibration limit.
4. Results from 2 or more samples were above upper calibration limit.

**Table X-5**  
**Tank S-102 Comparison of Organic Compounds in TST and SUMMA™ Samples**

Compound	CAS <sup>1</sup> Number	TST Average (ppmv)	SUMMA™ Average (ppmv)
1,1-Dichloroethene (vinylidene chloride)	75-35-4	0.0022	< 0.005
Dichloromethane (methylene chloride)	75-09-2	< 0.0053	< 0.005
Propanone (acetone)	67-64-1	0.10	0.56
Ethanenitrile (acetonitrile)	75-05-8	0.081	0.039
Propanenitrile	107-12-0	0.0063	< 0.005
Butanenitrile	109-74-0	0.018	< 0.005
Benzene	71-43-2	0.015	0.019
Toluene	108-88-3	0.094	0.20
n-Hexane	110-54-3	0.0071	< 0.005
n-Heptane	142-82-5	0.0084	0.012
n-Decane	124-18-5	0.0027	< 0.005

1. CAS = Chemical Abstract Service.

**Table X-6  
Tank S-102 Tentatively Identified Organic Compounds in SUMMA™ Samples**

Cmpd #	Compound	CAS <sup>1</sup> Number	Average (mg/m <sup>3</sup> )	Standard <sup>2</sup> Deviation (mg/m <sup>3</sup> )
1	Propene <sup>3</sup>	115-07-1	0.43	< 0.35
2	Propane <sup>3</sup>	74-98-6	0.34	< 0.21
3	Cyclopropane <sup>3</sup>	75-19-4	0.10	< 0.005
3	Methanol (methyl alcohol)	67-56-1	4.49	0.70
4	1-Butene	106-98-9	0.40	0.06
5	n-Butane	106-97-8	0.24	0.01
6	1-Propene, 2-methyl- <sup>3</sup>	115-11-7	0.06	< 0.005
7	Ethanol	64-17-5	9.44	0.30
8	2-Propanol <sup>4</sup> (isopropyl alcohol)	67-63-0	0.24	--
9	n-Pentane <sup>4</sup>	109-66-0	0.07	--
10	2-Butanol	78-92-2	0.14	0.02
11	1-Butanol	71-36-3	1.18	0.19
12	N-Nitrosodimethylamine <sup>4</sup>	62-75-9	0.03	--
13	Pyrazine <sup>3</sup>	290-37-9	0.05	< 0.01
Sum of tentatively identified compounds:			16.87	

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 two samples.

4. Detected in only one sample.

**Table X-7**  
**Tank S-102 Tentatively Identified Organic Compounds in TST Samples**

Cmpd #	Compounds	CAS <sup>1</sup> Number	Average (mg/m <sup>3</sup> )	Standard Deviation (mg/m <sup>3</sup> )
1	1-Propene, 2-methyl-	115-11-7	0.047	0.041
2	Methanol (methyl alcohol)	67-56-1	1.55	0.14
3	Ethanol	64-17-5	3.91	0.37
4	Trichlorofluoromethane	75-69-4	0.043	0.074
5	2-Propanol (isopropyl alcohol)	67-63-0	0.16	0.01
6	1-Propanol	71-23-8	0.078	0.009
7	2-Butanol, (R)-	14898-79-4	0.015	0.026
8	Furan, tetrahydro-	109-99-9	0.056	0.010
9	Silane, dimethoxydimethyl-	1112-39-6	0.019	0.033
10	1,4-Dioxane	123-91-1	0.040	0.035
11	1,4-Dioxane and others		0.027	0.046
12	Pyrazine	290-37-9	0.13	0.01
13	Aziridine, 2-methyl	75-55-8	0.046	0.080
14	N-Nitrosodimethylamine	62-75-9	0.10	0.01
15	Cyclotrisiloxane, hexamethyl	541-05-9	0.14	0.09
16	1-Propanone, 1-[4-(tri-methylsilyl)oxyphenyl]	33342-89-1	0.013	0.023
17	2-Heptanone, 6-methyl and others		0.010	0.018
18	Cyclotetrasiloxane, octamethyl	556-67-2	0.066	0.028
19	Alkyl nitrile		0.037	0.005
20	Oxazole, 4,5-dimethyl-2-propyl-	53833-32-2	0.047	0.014
21	Benzyl Alcohol	100-51-6	0.0077	0.0134
22	Benzoic acid, 2-[(trimethylsilyloxy)- trimethylsilyl ester	3789-85-3	0.010	0.018
23	Isopropyl Palmitate	142-91-6	0.054	0.094
24	Benzenesulfonamide, n-butyl	3622-84-2	0.054	0.011
Sum of Tentatively Identified Compounds:			6.66	

1. CAS = Chemical Abstract Service.

#### X.4 REFERENCES

- EPA 1988, *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, PB90-127374, U.S. Environmental Protection Agency, Washington, D.C.
- Hendrickson, R. W., 1995, *Tank Vapor Characterization Oak Ridge National Laboratories Quality Assurance Assessment*, TWRSQA-95-0012, Westinghouse Hanford Company, Richland, Washington.
- Homi, C. S., 1995, *Tank 241-S-102 Tank Characterization Plan*, WHC-SD-WM-TP-238 Rev. 0A, Westinghouse Hanford Company, Richland, Washington.
- Huckaby, J. L., 1995, *Waste Tank Headspace Gas and Vapor Characterization Reference Guide*, WHC-SD-WM-ER-430 Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Huckaby, J. L., and M. S. Story, 1994, *Vapor Characterization of Tank 241-C-103*, WHC-EP-0780 Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Jenkins, R. A, A. B. Dindal, C. Y. Ma, M. A. Palausky, J. T. Skeen, and C. K. Bayne, 1995, *Analysis of Tank 241-S-102 Headspace Components*, ORNL-CASD-FR-241S102.95 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, 1995, *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.
- Lucke, R. B., M. W. Ligothke, K. H. Pool, T. W. Clauss, A. K. Sharma, B. D. McVeety, M. McCulloch, J. S. Fruchter, and S. C. Goheen, 1995, *Vapor Space Characterization of Waste Tank 241-C-108: Results from Samples Collected Through the Vapor Sampling System on 8/5/94*, PNL-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.
- 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.

WHC-SD-WM-ER-446 REV. 0

- 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.
- Pool, K. H., R. B. Lucke, B. D. McVeety, G. S. Klinger, T. W. Clauss, M. W. Ligothe, K. B. Olsen, O. P. Bredt, J. S. Fruchter, and S. C. Goheen, 1995, *Vapor Space Characterization of Waste Tank 241-S-102: Results from Samples Collected on 3/14/95*, PNL-xxxxx UC-606, Pacific Northwest Laboratory, Richland, Washington.
- Rasmussen, R. A., 1994, *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.
- Rasmussen, R. A., and W. Einfeld, 1994, *Hanford Tank 103-C Analyses and Method Validation Development Phase*, SAND94-1807, Sandia National Laboratories, Albuquerque, New Mexico.
- WHC 1995, *Vapor and Gas Sampling of Single-Shell Tank 241-S-102 Using the Vapor Sampling System*, WHC-SD-WM-RPT-142, Westinghouse Hanford Company, Richland, Washington.