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7. Abstract <p>Tank 241-U-111 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-U-111 was vapor sampled in accordance with "Data Quality Objectives for Generic In-Tank Health and Safety Issue Resolution (Osborne et al., 1994).</p>		

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Tank 241-U-111 Vapor Sampling and Analysis Tank Characterization Report

X.0 INTRODUCTION

Tank U-111 headspace gas and vapor samples were collected and analyzed to help determine the potential risks of fugitive emissions to tank farm workers. The drivers and objectives of waste tank headspace sampling and analysis are discussed in *Program Plan for the Resolution of Tank Vapor Issues* (Osborne and Huckaby 1994). Tank U-111 was vapor 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 U-111 using the vapor sampling system (VSS) on February 28, 1995 by WHC Sampling and Mobile Laboratories (WHC 1995). Sample collection and analysis were performed as directed by *Tank 241-U-111 Tank Characterization Plan* (Carpenter 1995). The tank headspace temperature was determined to be 20 °C. Air from the U-111 headspace was withdrawn from a single elevation via a 6.1-m long heated sampling probe mounted in riser 4, and transferred via heated tubing to the VSS sampling manifold. All heated zones of the VSS were maintained at approximately 60 °C. All tank air samples were collected between 10:45 a.m. and 2:07 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^{TM,1} canister tank air samples for selected inorganic gases and vapors are given in Table X-2 in parts per

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

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

X.2.1 Ammonia, Hydrogen, and Nitrous Oxide

The reported ammonia concentration, 676 ppmv, is relatively high compared to other waste tanks sampled to date. It is about 27 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 U-111 was determined to be 247 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, 247 ppmv hydrogen concentration in tank U-111 corresponds to about 0.6 % of its LFL. At this level, hydrogen is not a flammability concern in tank U-111.

The nitrous oxide concentration in tank U-111, 327 ppmv, is also relatively high compared to other waste tanks sampled to date. It is about 13 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 U-111 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 U-111 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 U-111 gas and vapor sampling event, for example, were measured to have an average 368 ppmv of carbon dioxide.

Carbon dioxide introduced by air exchange with the atmosphere is readily absorbed by caustic supernatant and interstitial liquids in 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 U-111 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 U-111 headspace were determined to be ≤ 0.04 and ≤ 0.01 ppmv, respectively. These are acid gases that would have very low equilibrium concentrations above the high pH sludge in tank U-111. The measurable presence of nitric oxide is not uncommon in the waste tank headspaces, and may be due to its formation from oxygen and nitrogen in the radiation field of the headspace. 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 U-111 was determined to be about 11.3 mg/L, at the measured tank headspace temperature of 20 °C and pressure of 1004 mbar (753.0 torr), (WHC 1995). This corresponds to a water vapor partial pressure of 15.2 mbar (11.4 torr), to a dew point of 13.2 °C, and to a relative humidity of 65 %.

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 U-111 headspace are ammonia, nitrous oxide, and hydrogen. These have been detected in most tank headspaces sampled to date, and are usually the dominate waste species.

The 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 ammonia vapor to about 3 % for nitrous oxide and water vapor 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 U-111 headspace were sampled using SUMMATM 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 Clauss et al. (1995).

SUMMATM sample results should be considered to be the primary organic vapor data for tank U-111. 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.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 from the analysis of standards. The concentration of an analyte in the sample is said to be quantitatively measured if the response of the GC/MS has been established at several known concentrations of that analyte (i.e., the GC/MS has been calibrated for that analyte), and the MS response to the analyte in the sample is between the lowest and highest responses to the known concentrations (i.e., the analyte is within the calibration range).

ORNL and PNL were assigned different lists of organic compounds, or target analytes, to positively identify and measure quantitatively. The ORNL target analyte list was derived from a review of the tank C-103 headspace constituents by a panel of toxicology experts (Mahlum et al. 1994). The PNL target analyte list included 39 compounds 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 SUMMATM samples. SUMMATM analyses were performed according to the TO-14 methodology, except for methane analysis, which was analyzed with the inorganic gases (Clauss et al. 1995). Only 2 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 SUMMATM canister samples.

Jenkins et al. (1995) report the positive identification of 24 of 27 target analytes in TST samples. 1,1-Dichloroethene, dichloromethane, and dibutyl butylphosphonate 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, the 1-butanol concentration was determined to be above the upper calibration limit, and 16 other compounds were determined to be below the lower calibration limit of the analyses 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 U-111 and obtain concentration in ppmv of analyte in moist tank air, multiply the dry-air ppmv concentrations by 0.985.

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 acetone, and in very good agreement for toluene. As indicated in Table X-5, the reported concentrations of propanenitrile, butanenitrile, benzene, n-hexane, n-heptane, and n-decane 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 acetonitrile, which was determined to be present at 0.20 ppmv in TST samples, and < 0.005 ppmv in SUMMA™ samples. None of these compounds, however, even assuming the higher concentrations to be correct, are at or above levels of concern. 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 1-butanol, acetonitrile, and acetone, each of which was measured to have an average concentration of between 0.1 and 1 ppmv in TST samples. 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 standards of each into the GC/MS to determine their GC retention times or specific MS patterns.

By the nature of the sampling devices, virtually all organic vapors present in the tank headspace are collected by both TST and SUMMA™ samples. Analyses of the samples are designed to recover, separate, 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 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. (1995) and Clauss 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 U-111 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 U-111, their concentrations are very low compared to other NPH-rich tanks.

Tributyl phosphate was also added to the tank as waste. The measured concentration of tributyl phosphate in the tank U-111 samples may not be representative of its headspace concentration. 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. This would result in loss of tributyl phosphate from the sampled air, and an underestimation of its actual concentration in the tank headspace.

The tentatively identified cyclosiloxanes (i.e., Cmpd # 11 and 16 in Table X-7) are also in this category. Small quantities of siloxanes may have been introduced to the waste tank through their use as defoaming agents, but they may also be present in the headspace due to their use in liquid traps at the tank's breather riser.

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, aldehydes, ketones, nitriles, and volatile alkanes, all of which have been associated with the degradation of the NPHs. 1-Butanol is known to be a product of the hydrolysis of tributyl phosphate.

Though not present in high concentrations, 6 straight-chain alkyl nitriles were identified in TST samples. Nitrogen-containing cyclic compounds were also detected in both SUMMATM and TST samples, including pyridine, pyrazine, and 2 oxazoles. Of toxicological interest is the tentative identification of 1,4-dioxane in TST samples. However, the average estimated 1,4-dioxane concentration of 0.048 mg/m³ is well below the NIOSH 30-min ceiling REL of 3.6 mg/m³ (NIOSH 1995).

On the basis of concentrations, alcohols are the dominate type of organic compounds in the tank U-111 headspace. Methanol, ethanol, 1-propanol, 2-propanol, and 1-butanol account for about 79 % of the total estimated concentration of organic compounds in TST samples. Similarly, about 76 % of the total estimated organic compound concentration in SUMMATM samples is due to methanol, 1-propanol, 2-propanol, and 1-butanol. Ethanol was not detected in the SUMMATM samples from tank U-111. The abundance of volatile alcohols is common to tanks U-106, U-107, and U-111. Also similar to tanks U-106 and U-107, and in contrast to tanks having higher NPH concentrations, tank U-111 has relatively few ketones.

The total organic vapor concentration of tank U-111 was estimated by Jenkins et al. to be about 9.1 mg/m³ from the analysis of 3 TST samples by GC/MS. A similar summation of organic compounds measured in SUMMATM samples from tank U-111 provides an estimated total organic vapor concentration of 4.3 mg/m³. This disagreement is largely due to the different estimated concentrations of the dominant alcohols in the 2 sample types.

While the estimated total organic vapor concentrations by GC/MS 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 mg/m³ in tank C-103 (Rasmussen and Einfeld 1994), to as low as 0.18 mg/m³ in tank C-111 (Rasmussen 1994), while the TNMOC concentration of clean ambient air ranges from about 0.03 to 0.1 mg/m³.

Ambient air SUMMATM samples collected during the tank U-111 sampling event suggest the VSS manifold may have been contaminated with trace amounts of acetone. Specifically, analysis of an ambient air sample collect upwind of

the VSS (not through the VSS manifold) indicated acetone to be present at < 0.005 ppmv, while an ambient air sample collected through the VSS (to check system cleanliness) was determined to have about 0.0077 ppmv of acetone. Residual amounts of acetone, used as a cleaning solvent, may have been present in the VSS transfer tubing.

In summary, the organic vapor concentrations in tank U-111 are relatively low. The organic vapors in tank U-111 clearly indicate the presence of tributyl phosphate, the semivolatile NPHs and their degradation products in the tank waste. As with the other 241-U farm tanks sampled to date, the concentrations of short-chain alcohols are higher in tank U-111 than in waste tanks with higher NPH vapor concentrations. Conversely, ketones and aldehydes are less abundant in tank U-111 than in NPH-rich waste tanks.

Table X-1
Tank U-111 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 U-111 Inorganic Gas and Vapor Concentrations

Compound	CAS ¹ number	Sample Type	Number of samples	Average (ppmv)	Standard Deviation (ppmv)	RSD ² (%)
Ammonia, NH ₃	7664-41-7	Sorbent Trap	6	676	6	0.9
Carbon Dioxide, CO ₂	124-38-9	SUMMA TM	3	< 64	--	--
Carbon Monoxide, CO	630-08-0	SUMMA TM	3	< 12	--	--
Hydrogen, H ₂	1333-74-0	SUMMA TM	3	247	3	1.2
Nitric Oxide, NO	10102-43-9	Sorbent Trap	6	≤ 0.04	--	--
Nitrogen Dioxide, NO ₂	10102-44-0	Sorbent Trap	6	≤ 0.01	--	--
Nitrous Oxide, N ₂ O	10024-97-2	SUMMA TM	3	327	10	2.9
Water Vapor, H ₂ O	7732-18-5	Sorbent Trap	6	15,100 (11.3 mg/L)	440 (0.3 mg/L)	2.9

1. CAS = Chemical Abstracts Service.

2. RSD = relative standard deviation.

Table X-3
Tank U-111 Positively Identified Organic Compounds in SUMMA™ Samples

Cmpd #	Compound	CAS ¹ Number	Average (ppmv)	Standard Deviation (ppmv)	RSD ² (%)
1	Ethanenitrile (acetonitrile)	75-05-8	0.023	0.003	13
2	Propanone (acetone)	67-64-1	0.076	0.007	10
3	Trichlorofluoromethane	75-69-4	0.014	0.001	10
4	Propanol	71-23-8	0.020	0.005	27
5	2-Butanone	78-93-3	0.019	0.0002	1.5
6	Tetrahydrofuran	109-99-9	0.020	0.0003	1.5
7	Cyclohexane	110-82-7	0.020	0.0003	1.5
8	Pyridine	110-86-1	0.0069	0.0008	11
9	Toluene	108-88-3	0.030	0.0004	1.3
10	Methane	74-82-8	< 12	--	--
Sum of positively identified compounds:			0.71	mg/m ³	

1. CAS = Chemical Abstract Service.

2. RSD = relative standard deviation.

Table X-4
Tank U-111 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	0.20	0.03	17
2	Propanone (acetone)	67-64-1	0.11	0.03	25
3	Propanenitrile ³	107-12-0	0.0073	0.0008	11
4	Butanal	123-72-8	0.016	0.0004	3
5	Hexane ³	110-54-3	0.004	0.0001	3
6	Benzene ³	71-43-2	0.0057	0.0017	29
7	1-Butanol ³	71-36-3	0.26	0.01	4
8	Butanenitrile	109-74-0	0.0093	0.0006	7
9	2-Pentanone ³	107-87-9	0.0022	0.0004	16
10	n-Heptane ³	142-82-5	0.0040	0.0001	3
11	Toluene	108-88-3	0.026	0.002	8
12	Pentanenitrile ³	110-59-8	0.00083	0.00011	14
13	2-Hexanone ³	591-78-6	0.0014	0.0001	8
14	n-Octane ³	111-65-9	0.0018	0.0001	6
15	Hexanenitrile ³	628-73-9	0.00070	0.00013	20
16	2-Heptanone ³	110-43-0	0.0013	0.0002	11
17	n-Nonane ³	111-84-2	0.0010	0.00004	4
18	Heptanenitrile ³	629-08-3	0.00038	0.00006	15
19	2-Octanone ³	111-13-7	0.00057	0.00005	8
20	n-Decane ³	124-18-5	0.0012	0.00001	1
21	n-Undecane ³	1120-21-4	0.0013	0.0001	5
22	n-Dodecane	112-40-3	0.0042	0.0001	3
23	n-Tridecane	629-50-5	0.0086	0.0005	6
24	Tributyl phosphate ³	126-73-8	0.00040	0.00060	151
Sum of positively identified compounds:			1.9 mg/m ³		

1. CAS = Chemical Abstract Service.

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2. RSD = relative standard deviation.
3. Two or more samples were outside calibration range.

Table X-5
Tank U-111 Comparison of Organic Compounds in TST and SUMMA™ Samples

Compound	CAS ¹ Number	TST Average (ppmv)	SUMMA™ Average (ppmv)
1,1-Dichloroethene (vinylidene chloride)	75-35-4	< 0.0023	< 0.005
Dichloromethane (methylene chloride)	75-09-2	< 0.0053	< 0.005
Propanone (acetone)	67-64-1	0.11	0.076
Ethanenitrile (acetonitrile)	75-05-8	0.20	0.023
Propanenitrile	107-12-0	0.0073	< 0.005
Butanenitrile	109-74-0	0.0094	< 0.005
Benzene	71-43-2	0.0057	< 0.005
Toluene	108-88-3	0.026	0.030
n-Hexane	110-54-3	0.0042	< 0.005
n-Heptane	142-82-5	0.0040	< 0.005
n-Decane	124-18-5	0.0013	< 0.005

1. CAS = Chemical Abstract Service.

Table X-6
Tank U-111 Tentatively Identified Organic Compounds in SUMMA™ Samples

Cmpd #	Compound	CAS ¹ Number	Average (mg/m ³)	Standard Deviation (mg/m ³)
1	Propane	74-98-6	0.20	0.01
2	Methanol (methyl alcohol)	67-56-1	2.98	0.20
3	n-Butane	106-97-8	0.070	0.007
4	2-Propanol (isopropyl alcohol)	67-63-0	0.19	0.01
5	2-Butanol	78-92-2	0.072	0.002
6	N-Nitrosodimethylamine	62-75-9	0.042	0.007
7	Pyrazine	290-37-9	0.035	0.004
Sum of tentatively identified compounds:			3.59	

1. CAS = Chemical Abstract Service.

Table X-7
Tank U-111 Tentatively Identified Organic Compounds in TST Samples

Cmpd #	Compounds	CAS ¹ Number	Average (mg/m ³)	Standard Deviation (mg/m ³)
1	Methanol (methyl alcohol)	67-56-1	2.49	0.49
2	Ethanol	64-17-5	3.55	0.34
3	2-Propanol (isopropyl alcohol)	67-63-0	0.17	0.02
4	1-Propanol	71-23-8	0.072	0.002
5	Furan, tetrahydro-	109-99-9	0.043	0.046
6	1,4-Dioxane	123-91-1	0.048	0.011
7	Pyrazine	290-37-9	0.15	0.06
8	N-Nitrosodimethylamine	62-75-9	0.14	0.03
9	Propylene Glycol	57-55-6	0.020	0.034
10	Pentanal, 3-methyl	15877-57-3	0.19	0.05
11	Cyclotrisiloxane, hexamethyl	541-05-9	0.044	0.019
12	Oxazole, 4,5-dihydro-2-methyl & C2 Benzene		0.011	0.019
13	Ethylbenzene	100-41-4	0.011	0.018
14	p-Xylene	106-42-3	0.0079	0.0137
15	Octanal	124-13-0	0.0095	0.0165
16	Cyclotetrasiloxane, octamethyl	556-67-2	0.036	0.010
17	1-Hexanol, 2-ethyl-	104-76-7	0.031	0.002
18	Oxazole, 4,5-dimethyl-2-propyl	53833-32-2	0.019	0.016
19	Benzyl Alcohol	100-51-6	0.016	0.014
20	n-Tetradecane	629-59-4	0.052	0.005
21	Benzenesulfonamide, n-butyl	3622-84-2	0.094	0.019
22	Isopropyl Palmitate	142-91-6	0.012	0.021
Sum of tentatively identified compounds:			7.21	

1. CAS = Chemical Abstract Service.

X.4 REFERENCES

- Carpenter, B. C., 1995, *Tank 241-U-111 Tank Characterization Plan*, WHC-SD-WM-TP-249, Westinghouse Hanford Company, Richland, Washington.
- Clauss, T. W., M. W. Ligothke, K. H. Pool, R. B. Lucke, B. D. McVeety, G. S. Klinger, K. B. Olsen, O. P. Bredt, J. S. Fruchter, and S. C. Goheen, 1995, *Vapor Space Characterization of Waste Tank 241-U-111: Results from Samples Collected on 2/28/95*, PNL-xxxxx UC-606, Pacific Northwest Laboratory, 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., 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-U-111 Headspace Components*, ORNL-CASD-FR-241U111.95 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.

WHC-SD-WM-ER-452 REV. 0

- 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, and C. M. Anderson, 1994, *Data Quality Objectives for Generic In-Tank Health and Safety Issue Resolution*, WHC-SD-WM-DQO-002, Westinghouse Hanford Company, Richland, Washington.
- 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-U-111 Using the Vapor Sampling System*, WHC-SD-WM-RPT-153, Westinghouse Hanford Company, Richland, Washington.