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Tank 241-SX-106 Vapor Sampling and Analysis Tank Characterization Report (WHC-SD-WM-ER-460)	ECN No.			
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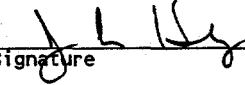
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7. Abstract <p>Tank 241-SX-106 headspace gas and vapor samples were collected and analyzed to help determine the potential risks to tank farm workers due to fugitive emissions from the tank. The drivers and objectives of waste tank headspace sampling and analysis are discussed in "Program Plan for the Resolution of Tank Vapor Issues" (Osborne and Huckaby 1994). Tank 241-SX-106 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-SX-106 Vapor Sampling and Analysis Tank Characterization Report

X.0 INTRODUCTION

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

The tank SX-106 headspace composition is affected by the use of forced ventilation. The headspace of tank SX-106 is connected via an underground ventilation pipe to tank SX-109, and tank SX-109 is actively exhausted via a vent header to the 241-SX farm exhauster. In 1992 the 241-SX farm ventilation system was surveyed, and the air entering tank SX-106 via its filtered breather riser was estimated to be 1.8 m³/min (64 ft³/min), (WHC 1992).

X.1 SAMPLING EVENT

Headspace gas and vapor samples were collected from tank SX-106 using the vapor sampling system (VSS) on March 24, 1995 by WHC Sampling and Mobile Laboratories (WHC 1995). Sample collection and analysis were performed as directed by *Tank 241-SX-106 Tank Characterization Plan* (Homi 1995). The tank headspace temperature was determined to be 30 °C. Air from the tank SX-106 headspace was withdrawn from a single elevation via a 6.7-m long heated sampling probe mounted in riser 14, 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 9:24 a.m. and 1:00 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 SUMMATM,¹ canister tank air samples for selected inorganic gases and vapors are given in Table X-2 in parts per million by volume (ppmv). Inorganic analyte sorbent traps and SUMMATM canisters were prepared and analyzed by PNL (Klinger et al. 1995a).

X.2.1 Ammonia, Hydrogen, and Nitrous Oxide

The reported ammonia concentration, 179 ppmv, is over 7 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 SX-106 was determined to be < 98 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, a 98 ppmv hydrogen concentration in tank SX-106 would correspond to about 0.24 % of its LFL. At this level, hydrogen is not a flammability concern in tank SX-106.

The reported nitrous oxide concentration, 14 ppmv, is very near the analytical method detection limit, and in 2 of the 3 SUMMATM samples, nitrous oxide was measured to be < 12.6 ppmv. It is less than the NIOSH 8-hr REL of 25 ppmv for nitrous oxide (NIOSH 1995). It is relatively low compared to most passively ventilated waste tanks sampled to date. Nitrous oxide has been detected in passively ventilated waste tanks at average concentrations as low as about 12 ppmv in tank TX-105 (Klinger 1995b), 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 SX-106 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 SX-106 headspace, measured at an average 107 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

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

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 SX-106 gas and vapor sampling event, for example, were measured to have an average 359 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. The 107 ppmv of carbon dioxide in the tank SX-106 headspace is typical of values for the passively ventilated waste tanks sampled to date.

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

Nitric oxide and nitrogen dioxide concentrations in the tank SX-106 headspace were both determined to be \leq 0.02 ppmv. These are acid gases that would have very low equilibrium concentrations above the high pH sludge in tank SX-106. 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 SX-106 was determined to be about 14.3 mg/L, at the measured tank headspace temperature of 30 °C and pressure of 990 mbar (742.3 torr), (WHC 1995). This corresponds to a water vapor partial pressure of 19.9 mbar (14.9 torr), to a dew point of 17.5 °C, and to a relative humidity of 47 %.

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 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 SX-106 headspace are ammonia and nitrous oxide. These have been detected in most tank headspaces sampled to date and, along with hydrogen, are usually the dominate waste species. The concentration of ammonia is relatively high given that tank SX-106 is actively ventilated. If the 1992 measurement indicating that tank SX-106 is ventilated at a rate of 1.8 m³/min is correct, and it is assumed that the concentration of ammonia in the exhaust is 179 ppmv, then the generation rate of ammonia within tank SX-106 would be estimated to be about 310 g/day.

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 water vapor to about 3 % for ammonia and carbon dioxide 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 SX-106 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 Klinger et al. (1995a).

SUMMATM sample results should be considered to be the primary organic vapor data for tank SX-106. 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 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 (T0-14) 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 T0-14 methodology, except for methane analysis, which was analyzed with the

inorganic gases (Klinger et al. 1995a). None of the 39 T0-14 target analytes and only 4 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 20 of 27 target analytes in TST samples. Dichloromethane, pentanenitrile, octane, hexanenitrile, heptanenitrile, 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 4 TSTs, are given in Table X-4. Despite calibration of the instrument over about a 20-fold concentration range, 16 of the 20 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 SX-106 and obtain concentration in ppmv of analyte in moist tank air, multiply the dry-air ppmv concentrations by 0.980.

Eleven target analytes were common to both TST and SUMMATM analyses. Table X-5 lists these, and their reported average concentrations in TST and SUMMATM samples. Results from these 2 sampling and analytical methods are in fairly good agreement. As indicated in Table X-5, the reported concentrations of vinylidene chloride and acetonitrile in TST samples are higher than in SUMMATM samples, and the reported concentration of acetone is higher in SUMMATM samples than in TST samples. The target analytes are generally only present at very low concentrations, however, and none are near levels of concern. Benzene, propanenitrile, and acetonitrile have the lowest NIOSH RELs of the 11 compounds in Table X-5, being 0.1, 6, and 20 ppmv, respectively.

The only analyte in either Tables X-3 or X-4 above 0.1 ppmv is 1-butanol, measured to be about 0.13 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 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. Only non-zero results are included in the reported averages. The tentatively identified compounds detected in TST samples, and their estimated concentrations, are listed in Table X-7. Compounds are listed in Table X-7 according to the order by which the eluted chromatographically. The averages reported by ORNL in Table X-7 are all 4-sample averages, and if an analyte was not detected in a sample, its concentration in that sample was considered to be zero for averaging purposes. Estimated concentrations are in 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 Klinger 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.

X.3.4 Discussion of Organic Compounds

The organic compounds listed in Tables X-3 through X-7 may be classified as either 1) organic compounds added to tank SX-106 as waste that are still evaporating, or 2) organic compounds that have been generated by reactions of the original waste.

The first class 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, and n-tetradecane) are often referred to in Hanford site literature as the normal paraffinic hydrocarbons (NPHs). Though NPHs are positively identified in tank SX-106, 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 # 24, and the split peak of Cmpd # 39 and 40 in Table X-7), and other silicon-containing compounds (e.g., Cmpd # 10 and 14 in Table X-7) may also have been sent to tank SX-106 with other wastes. Small quantities of organo-silicon compounds may have been introduced to the waste tank through their use as defoaming agents, and they may also be present in the headspace due to their use in liquid traps at the tank's breather riser. Several of these have been observed in TST blanks, however, and they may be present as artifacts of the gas chromatography process. Chlorotrimethylsilane (Cmpd # 5 in Table X-7) reacts very rapidly

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with water, and it is not reasonable to think it actually exists in the SX-106 headspace.

The absence of tributyl phosphate in the tank SX-106 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 SX-106 samples, is known to be a product of the hydrolysis of tributyl phosphate. Furthermore, informal tests by ORNL indicate that tributyl phosphate is adsorbed by the glass fiber filters used during sampling to protect the samples from radiolytic particulate contamination. Based on these considerations, the lack of tributyl phosphate in the tank SX-106 headspace samples should not be taken as proof it is not present in the headspace or the waste.

The second class 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 SX-106 headspace. Methanol, ethanol, 1-propanol, and 1-butanol account for 92 % of the total estimated concentration of organic compounds in SUMMA™ samples. 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 SX-106 has relatively few nitrile or ketones, and no aldehydes were detected.

A relatively large number of nitrogen-containing cyclic compounds were also detected in TST samples from tank SX-106, including pyridines, pyrazines, pyrroles, an oxazole, a piperidine, and an indole. Because the overall level of organic vapors is low, and relatively large TST sample volumes were collected, these compounds were detectable in the tank SX-106 TST samples. These compounds may be present at similar levels in other waste tanks, but because larger quantities of other organic vapors are usually present, their presence may be obscured.

The total organic vapor concentration of tank SX-106 was estimated by Jenkins et al. to be about 1.5 mg/m³ from the analysis of 4 TST samples by GC/MS. A similar summation of organic compounds measured in SUMMA™ samples from tank SX-106 provides an estimated total organic vapor concentration of 2.4 mg/m³. This disagreement is largely due to the different estimated concentrations of the volatile alcohols in the 2 sample types. Volatile alcohols may not be quantitatively recovered from TST samples.

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 (T0-12) method, they are comparable. TNMOC measurements of passively ventilated waste tanks have ranged from as

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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.

The organic vapor concentrations in tank SX-106 are low compared to the passively ventilated waste tanks that have been sampled. However, if the ventilation rate for the tank SX-106 headspace at the time it was sampled was similar to the 1992 estimated ventilation rate (WHC 1992), then tank SX-106 may actually have a moderately high organic vapor generation rate. The organic vapors in tank SX-106 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 SX-106 is the only 241-SX farm tank to be sampled to date. Its headspace organic vapor composition is quite similar to the 241-U farm tanks U-106, U-107, and U-111, as well as tank S-102 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 SX-106 Gas and Vapor Sample Type and Number

Laboratory	Sampling Device	Nominal Sample Volume (L)	Target Analytes	Number of Samples
Oak Ridge National Laboratories	Triple Sorbent Trap	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 SX-106 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	179	5	3
Carbon Dioxide, CO ₂	124-38-9	SUMMA™	3	107	3	3
Carbon Monoxide, CO	630-08-0	SUMMA™	3	< 12	--	--
Hydrogen, H ₂	1333-74-0	SUMMA™	3	< 98	--	--
Nitric Oxide, NO	10102-43-9	Sorbent Trap	6	≤ 0.02	--	--
Nitrogen Dioxide, NO ₂	10102-44-0	Sorbent Trap	6	≤ 0.02	--	--
Nitrous Oxide ³ , N ₂ O	10024-97-2	SUMMA™	3	14	--	--
Water Vapor, H ₂ O	7732-18-5	Sorbent Trap	6	20,100 (14.9 mg/L) mg/L	90 (0.07)	0.5

1. CAS = Chemical Abstracts Service.

2. RSD = relative standard deviation.

3. Detected in only 1 sample.

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Table X-3
Tank SX-106 Positively Identified Organic Compounds in SUMMA™ Samples

Cmpd #	Compound	CAS ¹ Number	Average (ppmv)	Standard Deviation (ppmv)	RSD ² (%)
1	Acetone	67-64-1	0.021	0.001	6
2	Propanol	71-23-8	0.041	0.036	87
3	Tetrahydrofuran	109-99-9	0.007	0.0003	4
4	Pyridine	110-86-1	0.015	0.012	81
5	Methane	74-82-8	< 12	--	--
Sum of positively identified compounds:			0.23	mg/m ³	

1. CAS = Chemical Abstract Service.

2. RSD = relative standard deviation.

WHC-SD-WM-ER-460 REV. 0

Table X-4
Tank SX-106 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	0.018	0.001	6
2	Propanone (acetone)	67-64-1	0.012	0.002	20
3	1,1-Dichloroethene (vinylidene chloride)	75-35-4	0.0050	0.0036	72
4	Propanenitrile ³	107-12-0	0.0010	0.0001	10
5	Butanal	123-72-8	0.022	0.002	7
6	n-Hexane ³	110-54-3	0.00070	0.00031	44
7	Benzene ³	71-43-2	0.00055	0.00014	25
8	1-Butanol ³	71-36-3	0.13	0.01	7
9	Butanenitrile ³	109-74-0	0.0032	0.0003	10
10	2-Pentanone ³	107-87-9	0.00040	0.00015	36
11	n-Heptane ³	142-82-5	0.00025	0.00005	20
12	Toluene ³	108-88-3	0.00055	0.00015	28
13	2-Hexanone ³	591-78-6	0.00026	0.00009	34
14	2-Heptanone ³	110-43-0	0.00032	0.00013	39
15	n-Nonane ³	111-84-2	0.00020	0.00006	31
16	2-Octanone ³	111-13-7	0.00018	0.00008	43
17	n-Decane ³	124-18-5	0.00019	0.00006	34
18	n-Undecane ³	1120-21-4	0.00052	0.00008	16
19	n-Dodecane ³	112-40-3	0.00045	0.00011	24
20	n-Tridecane ³	629-50-5	0.00062	0.00015	25
Sum of positively identified compounds:			0.63 mg/m ³		

1. CAS = Chemical Abstract Service.

2. RSD = relative standard deviation.

3. Two or more samples were outside the calibration range.

Table X-5
Tank SX-106 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	0.0050	< 0.005
Dichloromethane (methylene chloride)	75-09-2	< 0.0013	< 0.005
Propanone (acetone)	67-64-1	0.012	0.021
Ethanenitrile (acetonitrile)	75-05-8	0.018	< 0.005
Propanenitrile	107-12-0	0.0010	< 0.005
Butanenitrile	109-74-0	0.0032	< 0.005
Benzene	71-43-2	0.00055	< 0.005
Toluene	108-88-3	0.00055	< 0.005
n-Hexane	110-54-3	0.00070	< 0.005
n-Heptane	142-82-5	0.00025	< 0.005
n-Decane	124-18-5	0.00019	< 0.005

1. CAS = Chemical Abstract Service.

Table X-6
Tank SX-106 Tentatively Identified Organic Compounds in SUMMA™ Samples

Cmpd #	Compound	CAS ¹ Number	Average (mg/m ³)	Standard Deviation (mg/m ³)
1	Methanol (methyl alcohol)	67-56-1	1.34	0.05
2	Ethanol	64-17-5	0.38	0.01
3	1-Butanol	71-36-3	0.41	0.01
Sum of tentatively identified compounds:				2.13

1. CAS = Chemical Abstract Service.

Table X-7
Tank SX-106 Tentatively Identified Organic Compounds in TST Samples

Cmpd #	Compounds	CAS ¹ Number	Average (mg/m ³)	Standard Deviation (mg/m ³)
1	1-Propene, 2-methyl-	115-11-7	0.00074	0.00148
2	Methanol (methyl alcohol)	67-56-1	0.18	0.03
3	Ethanol	64-17-5	0.084	0.012
4	Trichlorofluoromethane	75-69-4	0.0088	0.0051
5	Silane, chlorotrimethyl-	75-77-4	0.0054	0.0109
6	2-Propanol (isopropyl alcohol)	67-63-0	0.014	0.004
7	2,3-Dimethyl-1, 4-pentadiene	758-86-1	0.0019	0.0038
8	1-Propanol	71-23-8	0.011	0.007
9	Benzeneacetic acid, .alpha.-hydroxy ethyl	774-40-3	0.0034	0.0068
10	Silanol, trimethyl-	1066-40-6	0.0053	0.0106
11	Mixture		0.0021	0.0042
12	Ester of Acetic Acid		0.0017	0.0034
13	Furan, tetrahydro	109-99-9	0.0076	0.0055
14	Silane, dimethoxydimethyl-	1112-39-6	0.012	0.012
15	1,4-Dioxane	123-91-1	0.0096	0.0003
16	Mixture		0.0017	0.0033
17	Pyrazine	290-37-9	0.014	0.001
18	Propane, 2-methyl-2-nitro-	594-70-7	0.0039	0.0026
19	N-Nitrosodimethylamine	62-75-9	0.025	0.010
20	1-ethyl-6-ethylidene- cyclohexene	61141-57-9	0.0037	0.0073
21	(S)-(+)-1,2-Propanediol	4254-15-3	0.12	0.20
22	Phenol,4-(aminomethyl)- 2-methoxy		0.0053	0.0106
23	Benzothiazole, 2-phenyl	883-93-2	0.016	0.031
24	Cyclotrisiloxane, hexamethyl	541-05-9	0.15	0.25
25	Pyrazine, methyl	109-08-0	0.00059	0.00117

WHC-SD-WM-ER-460 REV. 0

Cmpd #	Compounds	CAS ¹ Number	Average (mg/m ³)	Standard Deviation (mg/m ³)
26	Oxazole, 4,5-dihydro-2-methyl-	1120-64-5	0.0061	0.0041
27	1H-Pyrrole, 2,5-dimethyl	625-84-3	0.0029	0.0057
28	Benzene, 1,3-dimethyl- and others		0.0017	0.0019
29	2-Propen-1-ol	107-18-6	0.0071	0.0049
30	3-Heptanone	106-35-4	0.00080	0.00160
31	Ethanol, 2-butoxy and others		0.0015	0.0018
32	Pyrazine, ethyl	13925-00-3	0.00075	0.00150
33	Pyrazine, ethyl and butyrolactone		0.0010	0.0020
34	1-Pentyn-3-ol, 3,4-dimethyl	1482-15-1	0.00069	0.00137
35	9-Decen-2-one and others		0.00081	0.00163
36	6-Amino-2,3-diphenyl(1H) pyrrolo[2,3-b]pyridine		0.0040	0.0080
37	Benz[a]acridine, 8,10-diethyl and others		0.00073	0.00147
38	2-Buten-1-ol, (Z)-	4088-60-2	0.0039	0.0030
39	Cyclotetrasiloxane, octamethyl	556-67-2	0.055	0.082
40	Cyclotetrasiloxane, octamethyl	556-67-2	0.0023	0.0046
41	1-Hexanol, 2-ethyl-	104-76-7	0.0081	0.0012
42	Benzyl Alcohol	100-51-6	0.0066	0.0045
43	2(3H)-Furanone, 5-ethenyl- dihydro-5-methyl-	1073-11-6	0.00062	0.00124
44	Cyclopentane, 2-ethyl-1,1-dimethyl-	54549-80-3	0.00054	0.00109
45	Benzenemethanol, 4-(1,1-dimethylethyl)- α -methyl and others		0.0061	0.0121
46	Mixture		0.00058	0.00116
47	Benzoic acid, 2-[(trimethylsilyl)oxy]-, trimethylsilyl ester	3789-85-3	0.015	0.022

WHC-SD-WM-ER-460 REV. 0

Cmpd #	Compounds	CAS ¹ Number	Average (mg/m ³)	Standard Deviation (mg/m ³)
48	Octanamide, N-(2-hydroxyethyl)-	7112-02-9	0.0049	0.0033
49	n-Methyl-3-Piperidine carboxamide	5115-98-0	0.0070	0.0050
50	1H-Indole, 2-phenyl-	948-65-2	0.0014	0.0028
51	2-Hexenedioic acid, bis (trimethylsilyl) ester	55494-10-5	0.0023	0.0046
52	Tetradecane	629-59-4	0.0028	0.0023
53	Propanoic acid, 2-methyl-, 1-(1,1-dimethylethyl)	74381-40-1	0.0040	0.0029
54	Mixture		0.0040	0.0047
55	2-Propen-1-one, 3-(2-furanyl)-1-phenyl-	717-21-5	0.0013	0.0026
56	Benzenesulfonamide, n-butyl	3622-84-2	0.055	0.035
57	1-Pentadecene	13360-61-7	0.00098	0.00196
58	Nonadecane	629-92-5	0.00064	0.00129
59	Hexadecanoic acid	57-10-3	0.0063	0.0126
60	Isopropyl Palmitate	142-91-6	0.0028	0.0032
<u>Sum of tentatively identified compounds:</u>				0.91

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*, TWRQA-95-0012, Westinghouse Hanford Company, Richland, Washington.

Homi, C. S., 1995, *Tank 241-SX-106 Tank Characterization Plan*, WHC-SD-WM-TP-314 Rev. 0, 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-SX-106 Headspace Components*, ORNL-CASD-FR-241SX106.95 Rev. 0, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Klinger, G. S., T. W. Clauss, M. W. Ligotke, K. H. Pool, R. B. Lucke, B. D. McVeety, K. B. Olsen, O. P. Bredt, J. S. Fruchter, and S. C. Goheen, 1995a, *Vapor Space Characterization of Waste Tank 241-SX-106: Results from Samples Collected on 3/24/95*, PNL-xxxxx UC-606, Pacific Northwest Laboratory, Richland, Washington.

Klinger, G. S., T. W. Clauss, M. W. Ligotke, K. H. Pool, R. B. Lucke, B. D. McVeety, O. P. Bredt, J. S. Young, M. McCulloch, J. S. Fruchter, and S. C. Goheen, 1995b, *Vapor Space Characterization of Waste Tank 241-TX-105: Results from Samples Collected Through the Vapor Sampling System on 12/20/94*, PNL-xxxxx UC-606, Pacific Northwest Laboratory, Richland, Washington.

Lucke, R. B., M. W. Ligotke, 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-460 REV. 0

McVeety, B. D., T. W. Clauss, M. W. Ligotke, K. H. Pool, R. B. Lucke, G. S. Klinger, J. S. Young, M. McCulloch, J. S. Fruchter, and S. C. Goheen, 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.

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 1992, *241-SX Breather 101-106*, 2W-92-00640/P Preventive Maintenance, Westinghouse Hanford Company, Richland, Washington.

WHC 1995, *Vapor and Gas Sampling of Single-Shell Tank 241-SX-106 Using the Vapor Sampling System*, WHC-SD-WM-RPT-145 Rev. 0, Westinghouse Hanford Company, Richland, Washington.