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7. Abstract

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

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

X.0 INTRODUCTION

Tank C-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). Tank C-102 was vapor sampled in accordance with *Data Quality Objectives for Generic In-Tank Health and Safety Issue Resolution* (Osborne et al. 1994). Results presented here represent the best available data on the headspace constituents of tank C-102.

X.1 VENTILATION SYSTEM CONSIDERATIONS

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

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

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

Anderson (1990) notes, however, that the cascade line between tanks C-101 and C-102 was partially plugged in 1954. A comparison of vapor data indicates that the cascade line between tanks C-101 and C-102 does not effectively transport organic vapors, and may be blocked (Huckaby 1995a). To determine the origin of gases and vapors in tank C-102, it is important to understand

the extent to which tanks C-101 and C-103 breathe through tank C-102, because constituents detected in the headspace of tank C-102 may actually have originated from the waste in tanks C-101 or C-103¹. Sections X.3.4 and X.4.4 discuss what the available headspace data from tanks C-101, C-102, and C-103 indicate about whether tanks C-101 and C-103 breathe freely via their cascade lines with tank C-102.

X.2 SAMPLING EVENT

Headspace gas and vapor samples were collected from tank C-102 using the vapor sampling system (VSS) on August 23, 1994 by WHC Sampling and Mobile Laboratories (WHC 1995). Sample collection and analysis were performed as directed by the sample and analysis plan (WHC 1995, Appendix A). The tank headspace temperature was determined to be 25.8 °C. Air from the C-102 headspace was withdrawn via a 6.1-m long heated sampling probe mounted in riser 3, and transferred via heated tubing to the VSS sampling manifold. Heated zones of the VSS were maintained at approximately 50 °C. All samples were collected between 12:46 p.m. and 4:20 p.m., with no anomalies noted.

Sampling media were prepared and analyzed by WHC, Oak Ridge National Laboratories (ORNL), Pacific Northwest Laboratories (PNL), and Oregon Graduate Institute of Science and Technology (OGIST) through a contract with Sandia National Laboratories. The 39 tank air samples and 2 ambient air control samples collected are listed in Table X-1 by analytical laboratory. Table X-1 also lists the 14 trip blanks and 2 field blanks provided by the laboratories.

A general description of vapor sampling and sample analysis methods is given by Huckaby (1995b). 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.3 INORGANIC GASES AND VAPORS

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

¹ Tank C-103 is known to have a layer of semivolatile organic liquid floating on the aqueous waste (Pool and Bean 1994), and the highest total concentration of organic vapors of any waste tank known (Huckaby and Story 1994).

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

X.3.1 Ammonia, Hydrogen, and Nitrous Oxide

The reported ammonia concentration, 189 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 waste tanks sampled to date, at concentrations ranging from about 3 ppmv in tank C-108 (Lucke et al. 1995a), to 1040 ppmv in BY-108 (McVeety et al. 1995).

The concentration of hydrogen in tank C-102 was determined to be 133 ppmv. Hydrogen in the waste tanks is of concern as a fuel. Given that the lower flammability limit (LFL) for hydrogen in air is about 4 % by volume, the 133 ppmv hydrogen concentration in tank C-102 corresponds to about 0.3 % of its LFL. At this level hydrogen is not a flammability concern in tank C-102.

The nitrous oxide concentration in tank C-102, 154 ppmv, is over 6 times the NIOSH 8-hr REL of 25 ppmv for nitrous oxide (NIOSH 1995). Nitrous oxide has been detected in other waste tanks at concentrations as low as about 12 ppmv in tank TX-105 (Klinger et al. 1995b), and as high as about 800 ppmv in tank C-103 (Huckaby and Story 1994).

X.3.2 Carbon Monoxide and Carbon Dioxide

Carbon monoxide in the tank C-102 headspace, measured to be 4.0 ppmv in SUMMATM samples (Rasmussen 1994a), is much higher than in ambient air, where 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. Elevated waste tank headspace carbon monoxide concentrations are common, and are thought to be due to the decomposition of organic waste in the tanks. The 4.0 ppmv of carbon monoxide in tank C-102 is the third highest measured in any waste tank to date; tanks C-103 and C-101 were determined to have 26.7 ppmv and 15.5 ppmv, respectively, of carbon monoxide (Huckaby and Story 1994, Huckaby 1995a). The 4.0 ppmv of carbon monoxide in tank C-102 is less than the NIOSH 8-hr REL of 35 ppmv.

The average carbon dioxide concentration in the tank C-102 headspace, 8.2 ppmv, is among the lowest measured in any waste tank to date. Normally present in the ambient air at a concentration of 350 to 400 ppmv, carbon dioxide is typically at a lower concentration in the waste tank headspaces than in ambient air. 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.

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

Nitric oxide and nitrogen dioxide concentrations in the tank C-102 headspace were determined to be 0.24 ppmv and ≤ 0.05 ppmv, respectively. These are both acid gases that would have very low equilibrium concentrations above the high pH sludge in tank C-102. The measurable presence of nitric oxide may be due

to its formation from oxygen and nitrogen in the radiation field of the headspace. The NIOSH 8-hr REL is 25 ppmv for nitric oxide, and the 15-minute short term exposure limit (STEL) for nitrogen dioxide is 1 ppmv.

The water vapor concentration of tank C-102 was determined to be about 20.4 mg/L, at the tank headspace temperature of 25.8 °C and pressure of 990 mbar (742.7 torr), (WHC 1995). This corresponds to a water vapor partial pressure of 28.1 mbar (21.1 torr), to a dew point of 23.0 °C, and to a relative humidity of 85 %.

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.3.4 Discussion of Inorganic Gases and Vapors

Aside from water vapor, the most abundant waste constituents in the tank C-102 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 good. Relative standard deviations range from 1 % for nitrous oxide, to 17 % for nitric oxide results. The precision reported depends both on sampling parameters (e.g., sample flow rate and flow time for sorbent traps) and analytical parameters (e.g., sample preparation, dilutions, etc.), and the small relative standard deviations suggest good control was maintained both in the field and in the laboratories.

Table X-3 lists, for comparison, selected sampling data and inorganic gas and vapor concentrations measured in tanks C-101, C-102, and C-103. The inorganic gases and vapors in these tanks are at concentrations that support the premise that tanks C-101 and C-103 breathe primarily via their cascade lines with tank C-102. To understand this, suppose that tank C-101 did breathe only via its cascade line to tank C-102 (as per the ventilation configuration). Then all the air inhaled by tank C-101 would have the composition of air in tank C-102, so that at steady state (neglecting any losses of constituents in transit), every headspace constituent in tank C-102 would be present in tank C-101 at a concentration at least as high as it is in tank C-102. Furthermore, any gases or vapors generated or released by the waste in tank C-101 would raise the concentration of these constituents in tank C-101 above the level in tank C-102. As indicated in Table X-3, the concentrations of hydrogen, carbon dioxide, carbon monoxide, nitric oxide, and nitrous oxide are all significantly higher in tank C-101 than they are in tank C-102. Likewise, the

concentrations of these same constituents, as well as ammonia, are higher in tank C-103 than in tank C-102.

Amongst the inorganic analytes listed in Table X-3, only ammonia is at a higher concentration in tank C-102 than it is in tank C-101. This exceptional relationship of ammonia, if indeed tank C-101 breathed primarily via the cascade line with tank C-102, may be reasonable given its solubility in water. Aqueous condensate forming in the cascade line (the dewpoint of tank C-101 is about 30 °C, Huckaby 1995a) might absorb enough of the ammonia vapor in transit to tank C-101 to cause this constituent to be lower in tank C-101 than in tank C-102.

Though the data from tanks C-101, C-102, and C-103 (with special allowance for ammonia in tank C-101) are consistent with the premise that tanks C-101 and C-103 breathe primarily via their cascade lines with tank C-102, the data do not prove that this is happening. The selected gas and vapor concentrations may be higher in tanks C-101 and C-103 than in tank C-102 simply because their generation rates are higher in those tanks.

X.4 ORGANIC VAPORS

Organic vapors in the tank C-102 headspace were sampled using SUMMA™ canisters, which were analyzed by OGIST and PNL, and triple sorbent traps (TSTs), which were analyzed by ORNL. ORNL and PNL used gas chromatographs (GCs) equipped with mass spectrometer (MS) detectors to separate, identify, and quantitate the analytes. A quantitative measurement of the total organic vapor concentration by the U.S. Environmental Protection Agency (EPA) task order 12 (TO-12) method was also performed by OGIST (EPA 1988, Rasmussen 1994a). Descriptions of sample device cleaning, sample preparations, and analyses are given by Jenkins et al. (1994a), Rasmussen (1994a), and Klinger et al. (1995a).

SUMMA™ sample results should be considered to be the primary organic vapor data for tank C-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.4.1 Positively Identified Organic Analytes

Positive identification of organic analytes using the methods employed by PNL and ORNL involves matching the GC retention times and MS data from a sample with that obtained from the analysis of standards. The concentration of an analyte in the sample is said to be quantitatively measured if the response of the GC/MS has been established at several known concentrations of that analyte (i.e., the GC/MS has been calibrated for that analyte), and the MS response to

the analyte in the sample is between the lowest and highest responses to the known concentrations (i.e., the analyte is within the calibration range).

ORNL and PNL were assigned different lists of organic compounds, or target analytes, to positively identify and measure quantitatively. The ORNL target analyte list was derived from a review of the tank C-103 headspace constituents by a panel of toxicology experts (Mahlum et al. 1994). The PNL target analyte list included 39 compounds of the 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-4 lists the organic compounds positively identified and quantitated in SUMMATM samples. Analysis for methane was performed by OGIST (Rasmussen 1994a), other SUMMATM analyses were performed according to the EPA TO-14 methodology by PNL (EPA 1988, Klinger et al. 1995a). Only 2 of the 39 TO-14 target analytes (i.e., toluene and trichlorofluoromethane), but all 14 of the additional target analytes were above the 0.005 ppmv quantitation limit of the analyses. Averages reported are from analyses of 3 SUMMATM canister samples.

Jenkins et al. (1994a) report the positive identification of 26 of 27 target analytes in TST samples. 1,1-Dichloroethene was the only TST target analyte not detected in the TST samples. The average concentrations of the target analytes, from the analysis of 3 TSTs, are given in Table X-5.

The concentrations of tributyl phosphate and dibutyl butylphosphonate reported in Table X-5 probably underestimate the actual concentrations in the tank headspace. These compounds have very low volatility, and are thought to be adsorbed by glass fiber filters used during sampling to protect samples from radiolytic particulates.

Both PNL and ORNL report target analyte concentrations in ppmv of analyte in dry air. To correct for the measured water vapor content of tank C-102 and obtain concentration in ppmv of analyte in moist tank air, multiply the dry-air ppmv concentrations by 0.972.

Eleven target analytes were common to both TST and SUMMATM analyses. Table X-6 lists these, and their reported average concentrations in TST and SUMMATM samples. Results from these 2 sampling and analytical methods are in good agreement for the nitriles (acetonitrile, propanenitrile, and butanenitrile). The methods also agree reasonably well on the concentrations of acetone, n-heptane, and n-decane. However, as indicated in Table X-6, the reported concentrations of dichloromethane, benzene, toluene, and n-hexane by the 2 methods are not in agreement. The differences in reported values are not significant except for benzene. Benzene, which is reported to be at 0.32 ppmv in TST samples and < 0.005 ppmv in SUMMATM samples, has an 8-hr NIOSH REL of 0.1 ppmv. Despite the relatively poor precision of the TST benzene measurements, it is advisable to assume (to be conservative) the higher benzene concentration of 0.32 ppmv is correct.

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

X.4.2 Tentatively Identified Organic Analytes

In addition to the target analytes, the ORNL and PNL analytical procedures allow the tentative identification of other organic compounds. Tentative identification of analytes was performed by comparing the MS molecular fragmentation patterns with a library of known MS fragmentation patterns. This method allows an organic analyte to be identified (with reasonable certainty) as an alkane, a ketone, an aldehyde, etc., and may also determine its molecular weight. The method usually does not, however, allow the unambiguous identification of structural isomers, and this ambiguity increases with analyte molecular weight. Many analytes can be tentatively identified with reasonable confidence without having to inject standards of each into the GC/MS to determine their GC retention times or specific MS patterns.

By the nature of the sampling devices, virtually all organic vapors present in the tank headspace are collected by both TST and SUMMATM samples. Analyses of the samples are designed to recover, separate, identify, and quantify the organic vapors in the samples. TSTs are not good for collecting highly volatile compounds (i.e., molecules more volatile than propane), but are quite good for most others. In contrast, the recovery of very low volatility compounds (i.e., molecules with more than about 15 carbon atoms) and some polar compounds with moderate volatility (i.e., butanal) from SUMMATM samples has been problematic.

The list of tentatively identified compounds recovered from SUMMATM samples, with estimated concentrations, is given in Table X-7. Compounds are listed in Table X-7 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-8. Compounds are also listed in Table X-8 according to the order by which they eluted chromatographically. The averages reported by ORNL in Table X-8 are all 3-sample averages, and if an analyte was not detected in a sample, its concentration in that sample was considered to be zero for averaging purposes. Estimated concentrations are in mg/m³, based on dry air at 0 °C and 1.01 bar.

The ORNL and PNL methods used to tentatively identify and estimate concentrations are described by Jenkins et al. (1994a) and Klinger et al. (1995a), respectively, and should be reviewed before this data is used for decision making. Concentrations given in Tables X-7 and X-8 should be considered rough estimates. Results in Tables X-7 and X-8 are presented in terms of observed chromatographic peaks, and are not adjusted for the occurrence of split peaks (e.g., Cmpd # 123 and 124 in Table X-8) or the assignment of the same identity to different peaks (e.g., Cmpd # 105 and 113 in Table X-8). In these instances, the estimated concentration of a compound

appearing in more than 1 peak is simply the sum of the individual peak estimates.

X.4.3 Total Nonmethane Organic Compounds

OGIST measured the total nonmethane organic compound (TNMOC) concentration in 3 SUMMATM canister samples using the EPA TO-12 method (Rasmussen 1994a). The sample mean was 313 mg/m³, with a standard deviation of about 5 mg/m³. Though data on other tanks is limited, this value is much higher than typical for the waste tanks sampled to date.

A comparable analysis of 1 TST sample by gas chromatography with flame ionization detection indicated the organic vapor concentration to be 296 mg/m³ (Jenkins et al. 1994a). This is in excellent agreement with the EPA TO-12 result. EPA TO-12 method TNMOC measurements of other waste tanks have ranged from as high as 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 1994b), while the TNMOC concentration of clean ambient air ranges from about 0.03 to 0.1 mg/m³.

X.4.4 Discussion of Organic Analytes

It is useful to consider the organic vapors in the waste tanks in terms of their sources. Some organic compounds, particularly semivolatile compounds, were constituents of the waste sent to the tank farms, and are present in the tank headspaces because they are still evaporating from the wastes. Other organic compounds present in the tanks have been produced via chemical and radiolytic reactions of the original organic wastes. The most abundant of these degradation products in tank headspaces are volatile, and most contain functional groups.

Tank C-102 is known to have contained bulk quantities of a semivolatile organic liquid (Carothers 1988), and its presence is still evident in auger samples (Campbell et al. 1995). The high vapor concentrations of the semivolatile normal paraffinic hydrocarbons (NPHs), are understandable given their presence in the waste. In fact, the NPH vapor concentrations are perhaps lower than would be expected if tank C-103 were ventilated (as intended) via the cascade line to tank C-102. For example, ORNL measured the n-dodecane and n-tridecane vapor concentrations to be about 40 and 52 ppmv, respectively, in tank C-103, and only about 0.91 and 0.81 ppmv, respectively, in tank C-102.

The organic vapor distributions in tanks C-102 and C-103 are graphically illustrated in Figures X-1 and X-2. A total ion chromatogram for a SUMMATM sample from tank C-102 is displayed in the upper half of both figures (the same chromatogram appears in both figures). In the lower halves of the figures, a similar total ion chromatogram for a SUMMATM sample from tank C-103 is displayed. In Figure X-1, the ordinate scale of the tank C-103 (lower) chromatogram has been adjusted to reveal detail comparable to that given in the tank C-102 (upper) chromatogram. Note, however, that in Figure X-1 the tallest peaks of the tank C-103 (lower) chromatogram (i.e., at 44 and 48

minutes) are off-scale, and are truncated. In Figure X-2, the ordinate scale of the tank C-103 (lower) chromatogram has been adjusted so that these tallest peaks are not off-scale.

In Figures X-1 and X-2, the abscissa of the chromatograms is elution time, and the ordinate is instrumental response. The mixture of organic compounds in each sample has been separated chromatographically so that, inasmuch as the separation is complete, individual analytes elute at different times and appear as individual peaks. Each peak height is roughly proportional to the concentration of the associated analyte present in the sample. Rough comparisons of the concentrations of compounds in tanks C-102 and C-103 can be made by considering that the acetone peak, appearing as a relatively tall peak at about 9 min in both chromatograms of Figure X-1, is about 3.8 ppmv in the tank C-102 sample, and about 19.3 ppmv in the tank C-103 sample (Huckaby and Story 1994).

The tallest peak in the tank C-102 (upper) chromatogram of Figure 1, at about 18 min, is due to 1-butanol. The 5 next tallest peaks in the tank C-102 chromatogram are n-decane (at 36 min), n-undecane (at 40 min), n-dodecane (at 44 min), n-tridecane (at 48 min), and n-tetradecane (at 52 min). These are the semivolatile NPHs. Generally, the more volatile a compound is, the faster it elutes through the GC, so the volatile compounds are to the left in the chromatograms, and the semivolatile compounds are to the right.

Examination of Figures X-1 and X-2 indicates many similarities between the organic vapor distributions of tanks C-102 and C-103. Of particular interest are the peaks scattered amongst the NPH peaks between about 40 and 52 min in both chromatograms in Figure X-2. These peaks are from semivolatile organic compounds, and are thought to be impurities of the NPH PUREX process diluent. The locations and relative heights of these peaks in the 2 chromatograms are so similar that either the semivolatile paraffinic liquids in tanks C-102 and C-103 came from the same batch of PUREX process diluent, and/or these headspace constituents are being transported via the cascade line from tank C-103 to tank C-102. Waste transfer history does suggest that the organic liquid currently present in tank C-103 may have come from tank C-102 (Carothers 1988).

The relationship between the organic vapors in tanks C-102 and C-101 has been examined by Huckaby (1995a). A visual comparison of the organic vapor distributions in tanks C-102 and C-101 is provided in Figure X-3 (Klinger et al. 1995a, Lucke et al. 1995b). The ordinate scales in these 2 chromatograms are different, as are the amounts of sample analyzed, but the peak height-to-concentration relationships are similar. Specifically, the tallest peak in the tank C-101 (lower) chromatogram, at about 44 min, has an estimated concentration of 15.2 mg/m³, while the corresponding peak in the tank C-102 (upper) chromatogram (also at about 44 min), has an estimated concentration of 13.5 mg/m³.

Comparison of the chromatograms in Figure X-3 suggests that tank C-101 has its own supply of semivolatile organic waste, and that the cascade line between

them does not allow significant transfer of semivolatile organic vapors from tank C-101 to tank C-102. Specifically, the non-NPH semivolatile paraffinic compounds present in tank C-102 are at relatively low concentrations and appear well-separated in the tank C-102 (upper) chromatogram in Figure X-3. By contrast, the concentrations of compounds eluting between n-undecane (at 40 min) and n-tetradecane (at 52 min) in the tank C-101 chromatogram are so much higher that they are no longer separated by the GC. The major analytes in this region were tentatively identified as branched alkanes, cyclic alkanes, and alkenes (Huckaby 1995a). Careful examination of the locations and relative heights of these non-NPH compound peaks suggests that there are strong similarities between the organic wastes, and that tank C-101 may have stored the same organic liquid waste as tanks C-102 and C-103.

TST sample chromatograms from tanks C-101, C-102, and C-103 are similar in character to the SUMMATM sample chromatograms (Jenkins et al. 1994b, 1994a, 1994c). Like the chromatograms shown in Figures X-1 and X-3, the TST chromatograms indicate that tank C-101 has a much higher concentration of non-NPH semivolatile organic vapors than does tank C-102.

Given the apparent semivolatile organic waste similarities, it is not clear whether tank C-103 was breathing, as intended, via the cascade line with tank C-102 when their headspaces were sampled. Likewise, the data does not clearly indicate whether or not tank C-101 is breathing via its cascade line with tank C-102. However, the data do indicate that the cascade lines between tanks C-102 and C-103, and between tanks C-102 and C-101 do not transport significant amounts of the semivolatile organic vapors.

The volatile constituents identified in the SUMMATM and TST samples from tank C-102 are generally thought to be chemical and radiolytic reaction products of the semivolatile organic compounds. Supporting this is the fact that several compounds of each homologous series are commonly found in this as well as other waste tanks. Specifically, the following homologous series of straight-chain compounds were identified in tank C-102 samples:

- 2-ketones, from 2-propanone (acetone) through 2-nonanone;
- aldehydes, including acetaldehyde (ethanal), from butanal through octanal;
- nitriles, from acetonitrile (ethanenitrile) through octanenitrile;
- alkanes, including methane, from propane through nonane; and
- 1-alkenes, from propene through 1-octene.

Similarities between the volatile organic compounds in tanks C-101, C-102, and C-103 are evident in Figures X-1 and X-3. Many peaks are common to the chromatograms of all 3 tanks, and many have similar relative peak heights. However, transport of these vapors from either tanks C-101 or C-103 would not completely account for the volatile compounds in tank C-102. The

concentration of 1-butanol, for example, is much more prominent amongst the volatile constituents in tank C-102 than it is in either tanks C-101 or C-103. Furthermore, because the volatile organic vapors are thought to be produced by the degradation of the semivolatile organics (which appear to be very similar in tanks C-102 and C-103), the types and relative concentrations of volatile organic compounds in these tanks would be expected to be very similar, even if the cascade lines between them allowed no transport of vapors.

Table X-1
Tank C-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	0.1 and 0.5	Organic vapors	8 tank air samples, + 2 trip blanks + 2 field blanks
Oregon Graduate Institute of Science and Technology	SUMMA TM canister	6.0	Hydrogen, Nitrous Oxide, Carbon Dioxide, Carbon Monoxide, Methane, TNMOC ¹	3 tank air samples
Pacific Northwest Laboratories	Acidified Carbon Sorbent Trap	3.0	Ammonia	6 tank air samples + 3 trip blank
	Triethanolamine Sorbent Trap	3.0	Nitrogen Dioxide	6 tank air samples + 3 trip blank
	Oxidation Bed + Triethanolamine Sorbent Trap	3.0	Nitric Oxide	6 tank air samples + 3 trip blank
	Silica Gel Sorbent Trap	3.0	Water vapor	6 tank air samples + 3 trip blanks
	SUMMA TM canister	6.0	Organic vapors	3 tank air samples + 2 ambient air samples
WHC 222-S Laboratory	Silica Gel Sorbent Trap	1.0	Tritium-Substituted Water Vapor	1 tank air sample

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

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

Compound	CAS ² number	Sample Type	Number of samples	Average (ppmv)	Standard Deviation (ppmv)	RSD ³ (%)
Ammonia, NH ₃	7664-41-7	Sorbent Trap	6	189	3	1.6
Carbon Dioxide, CO ₂	124-38-9	SUMMA TM	3	8.2	0.36	4
Carbon Monoxide, CO	630-08-0	SUMMA TM	3	4.0	0.64	16
Hydrogen, H ₂	1333-74-0	SUMMA TM	3	133	2.64	2
Nitric Oxide, NO	10102-43-9	Sorbent Trap	6	0.24	0.04	17
Nitrogen Dioxide, NO ₂	10102-44-0	Sorbent Trap	6	≤ 0.05	--	--
Nitrous Oxide, N ₂ O	10024-97-2	SUMMA TM	3	154	1.53	1
Water Vapor, H ₂ O	7732-18-5	Sorbent Trap	6	28,400 (20.4 mg/L)	1,500 (1.1 mg/L)	5

2. CAS = Chemical Abstracts Service.

3. RSD = relative standard deviation.

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

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

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

2. Data are from Huckaby 1995a.

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

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

Table X-4
Tank C-102 Positively Identified Compounds in SUMMA™ Samples

Cmpd #	Compound	CAS ¹ Number	Average (ppmv)	Standard Deviation (ppmv)	RSD ² (%)
1	Methane ³	74-82-8	4.9	0.06	1.2
2	Ethanenitrile (acetonitrile)	75-05-8	0.33	0.04	12
3	Propanone (acetone)	67-64-1	3.18	0.54	17
4	Trichlorofluoromethane	75-69-4	0.051	0.008	16
5	Propanenitrile	107-12-0	0.058	0.0004	0.7
6	Propanol	71-23-8	0.21	0.003	1.2
7	2-Butanone	78-93-3	0.72	0.013	1.8
8	n-Hexane	110-54-3	1.62	0.029	1.8
9	Tetrahydrofuran	109-99-9	0.28	0.005	1.7
10	Butanenitrile	109-74-0	0.083	0.002	2.5
11	Cyclohexane	110-82-7	0.031	0.002	6
12	n-Heptane	142-82-5	0.20	0.005	2.4
13	4-Methyl-2-Pentanone	108-10-1	0.046	0.003	6
14	Pyridine	110-86-1	0.019	0.001	5
15	Toluene	108-88-3	0.006	0.0004	7
16	Cyclohexanone	108-94-1	0.015	0.0008	5
17	n-Decane	124-18-5	0.64	0.042	6
Sum of positively identified compounds:			mg/m ³		

1. CAS = Chemical Abstract Service.

2. RSD = relative standard deviation.

3. Methane results are from Rasmussen 1994a, all others are from Klinger et al. 1995a.

Table X-5
Tank C-102 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	0.34	0.04	11
2	Propanone ³ (acetone)	67-64-1	2.2	0.5	22
3	Dichloromethane ³ (methylene chloride)	75-09-2	0.043	0.045	104
4	Propanenitrile ³	107-12-0	0.043	0.001	3
5	Butanal ³	123-72-8	2.6	1.7	64
6	n-Hexane ³	110-54-3	0.097	0.008	8
7	Benzene	71-43-2	0.32	0.31	98
8	1-Butanol ³	71-36-3	7.6	1.7	22
9	Butanenitrile	109-74-0	0.061	0.005	9
10	2-Pentanone	107-87-9	0.15	0.02	16
11	n-Heptane	142-82-5	0.085	0.012	15
12	Toluene ³	108-88-3	0.082	0.072	88
13	Pentanenitrile ³	110-59-8	0.030	0.001	5
14	2-Hexanone	591-78-6	0.072	0.009	12
15	n-Octane	111-65-9	0.071	0.008	11
16	Hexanenitrile	628-73-9	0.030	0.001	4
17	2-Heptanone	110-43-0	0.079	0.024	31
18	n-Nonane	111-84-2	0.069	0.005	8
19	Heptanenitrile	629-08-3	0.032	0.005	15
20	2-Octanone ³	111-13-7	0.043	0.019	44
21	n-Decane	124-18-5	0.27	0.05	18
22	n-Undecane ³	1120-21-4	0.70	0.13	19
23	n-Dodecane ³	112-40-3	0.91	0.10	11
24	n-Tridecane ³	629-50-5	0.81	0.15	19
25	Dibutyl butylphosphonate ₃	78-46-6	0.0050	0.0012	24
26	Tributyl phosphate ³	126-73-8	0.075	0.007	10

Sum of positively identified compounds:	65.5 mg/m ³
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1. CAS = Chemical Abstract Service.
2. RSD = relative standard deviation.
3. Two or more samples were outside calibration range.

Table X-6
Tank C-102 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	< 0.00092	< 0.005
Dichloromethane (methylene chloride)	75-09-2	0.043	< 0.005
Propanone (acetone)	67-64-1	2.2	3.18
Ethanenitrile (acetonitrile)	75-05-8	0.34	0.33
Propanenitrile	107-12-0	0.043	0.058
Butanenitrile	109-74-0	0.061	0.083
Benzene	71-43-2	0.32	< 0.005
Toluene	108-88-3	0.082	0.006
n-Hexane	110-54-3	0.097	1.62
n-Heptane	142-82-5	0.085	0.20
n-Decane	124-18-5	0.27	0.64

1. CAS = Chemical Abstract Service.

Table X-7
Tank C-102 Tentatively Identified Compounds in SUMMA™ Samples

Cmpd #	Compound	CAS ¹ Number	Average (mg/m ³)	Standard ² Deviation (mg/m ³)
1	Propene	115-07-1	1.36	0.05
2	Propane	74-98-6	0.64	0.02
3	1-Propyne	74-99-7	0.60	0.02
4	Cyclopropane	75-19-4	0.25	0.01
5	Ethanal (acetaldehyde)	75-07-0	0.68	0.13
6	Methanol (methyl alcohol)	67-56-1	< 0.01	--
7	1-Butene	106-98-9	0.61	0.09
8	n-Butane	106-97-8	1.09	0.37
9	1-Propene, 2-methyl-	115-11-7	0.12	0.02
10	Ethanol	64-17-5	0.16	0.02
11	1-Pentene	109-67-1	0.30	0.05
12	n-Pentane	109-66-0	0.62	0.10
13	2-Pentanone	107-87-9	< 0.04	--
14	2-Pentene	109-68-2	< 0.03	--
15	Pentane, 2-methyl-	107-83-5	0.22	0.004
16	Butanal	123-72-8	0.77	0.03
17	1-Hexene	592-41-6	0.35	0.01
18	Nitric acid, ethyl ester	625-58-1	0.18	0.01
19	Nitrous acid, butyl ester ³	544-16-1	0.09	--
20	3-Buten-1-ol ³	627-27-0	0.08	--
21	Butanal, 3-methyl- ³	590-86-3	0.08	--
22	2-Butanone, 3-methyl-	563-80-4	0.13	0.003
23	1-Butanol	71-36-3	27.82	3.56
24	Nitric acid, 1-methylethyl ester	1712-64-7	0.15	0.01
25	2-Pentanone	107-87-9	1.61	0.03
26	Pentanal	110-62-3	0.90	0.01
27	1-Heptene	592-76-7	0.34	0.002

WHC-SD-WM-ER-459 REV. 0

Cmpd #	Compound	CAS ¹ Number	Average (mg/m ³)	Standard ² Deviation (mg/m ³)
28	2-Pentanone, 3-methyl-	565-61-7	0.083	0.002
29	Pentanenitrile	110-59-8	0.16	0.001
30	1-Heptanol	53535-33-4	0.30	0.01
31	Unknown Alkyl Nitrate		0.083	0.004
32	Heptane, 2-methyl-	592-27-8	0.24	0.01
33	2-Hexanone	591-78-6	0.73	0.01
34	Hexanal	66-25-1	0.50	0.02
35	1-Octene	111-66-0	0.23	0.01
36	n-Octane	111-65-9	1.22	0.03
37	2-Hexanone, 5-methyl-	110-12-3	0.19	0.01
38	Hexanenitrile	628-73-9	0.14	0.003
39	2-Furanmethanol, tetrahydro- ⁴	97-99-4	0.074	0.01
40	2-Heptanone	110-43-0	0.86	0.06
41	Heptanal	111-71-7	0.39	0.01
42	n-Nonane	111-84-2	0.87	0.02
43	Nitric acid, pentyl ester	1002-16-0	0.16	0.01
44	2-Heptanone, 4-methyl-	6137-06-0	0.082	0.002
45	2-Heptanone, 6-methyl-	928-68-7	1.25	0.02
46	Cyclohexane, propyl-	1678-92-8	0.11	0.004
47	Heptanenitrile	629-08-3	0.41	0.02
48	4-Octanone	589-63-9	0.11	0.004
49	Unknown C10 Alkane		0.17	0.01
50	Unknown C10 Alkane		0.16	0.01
51	Unknown Alkane ³		0.15	--
52	2-Octanone	111-13-7	0.66	0.01
53	Cyclohexane, 1,1,2,3-tetramethyl-	6783-92-2	0.20	0.003
54	Octanal	124-13-0	0.25	0.03
55	Unknown C9 Alkene/Cycloalkane		0.21	0.003

WHC-SD-WM-ER-459 REV. 0

Cmpd #	Compound	CAS ¹ Number	Average (mg/m ³)	Standard ² Deviation (mg/m ³)
56	Unknown C10 Alkene/Cycloalkane ⁴		0.10	0.01
57	Nitric acid, hexyl ester	20633-11-8	0.079	0.002
58	Unknown C10 Alkene/Cycloalkane ⁴		0.067	< 0.01
59	Unknown C10 Alkene/Cycloalkane		0.074	0.007
60	Unknown C11 Alkane		0.79	0.02
61	Unknown C11 Alkane		0.21	0.01
62	Unknown C10 Alkene/Cycloalkane		0.56	0.01
63	Unknown C11 Alkene/Cycloalkane		0.12	0.001
64	Octanenitrile ⁴	124-12-9	0.10	0.01
65	Unknown C11 Alkane		0.26	0.02
66	Unknown C11 Alkane		0.15	0.01
67	Unknown C11 Alkane		0.32	0.03
68	Unknown C11 Alkene/Cycloalkane		0.27	0.01
69	Unknown C11 Diene/Cycloalkene ³		0.07	--
70	Naphthalene, decahydro-, trans-	493-02-7	0.38	0.001
71	1-Undecene	821-95-4	0.23	0.01
72	Unknown C11 Alkene/Cycloalkane		0.29	0.03
73	n-Undecane	1120-21-4	11.29	1.06
74	Octane, 4-methyl- ³	2216-34-4	0.07	--
75	Unknown C11 Alkene/Cycloalkane		0.44	0.05
76	Unknown C12 Alkane		0.21	0.02
77	Unknown C12 Alkane		0.42	0.04
78	Unknown C11 Diene/Cycloalkene		0.22	0.06
79	Naphthalene, methyl-decahydro		0.68	0.10
80	Cyclohexane, pentyl-	4292-92-6	0.52	0.06
81	Unknown C12 Alkane		0.40	0.04
82	Naphthalene, methyl-decahydro		0.89	0.08
83	Unknown C12 Alkane		0.43	0.04

Cmpd #	Compound	CAS ¹ Number	Average (mg/m ³)	Standard ² Deviation (mg/m ³)
84	Unknown C12 Alkane		0.26	0.03
85	Unknown Ketone		0.19	0.02
86	Unknown C12 Alkene/Cycloalkane		0.30	0.03
87	n-Dodecane	112-40-3	12.29	1.05
88	Undecane, 2,6-dimethyl-	17301-23-4	2.56	0.26
89	Unknown C13 Alkene/Cycloalkane		0.10	0.01
90	Unknown C13 Alkene/Cycloalkane		1.03	0.11
91	Unknown C12 Alkane		0.56	0.05
92	Unknown C13 Alkene/Cycloalkane ⁴		0.39	0.04
93	Unknown C13 Alkane ³		0.46	--
94	Unknown C13 Alkane ³		0.17	--
95	Unknown Alkane ⁴		0.17	0.02
96	Octane, 2,3,7-trimethyl-	62016-34-6	2.51	0.24
97	Unknown C13 Alkene/Cycloalkane ⁴		0.10	< 0.01
98	n-Tridecane	629-50-5	12.05	0.64
99	Unknown C14 Alkene/Cycloalkane		0.39	0.05
100	Unknown Alkane		0.37	0.04
101	Unknown C13 Diene/Cycloalkene ⁴		0.096	0.005
102	Unknown C13 Alkene/Cycloalkane		0.56	0.06
103	Unknown C15 Alkene/Cycloalkane ³		0.10	--
104	Unknown Alkane ⁴		0.10	0.01
105	Unknown C15 Alkane		1.29	0.08
106	n-Tetradecane	629-59-4	4.44	0.16
107	Unknown Alkane ⁴		0.13	< 0.01
108	Unknown C15 Alkene/Cycloalkane ³		0.11	--
109	Unknown C15 Alkene/Cycloalkane ³		0.13	--
110	Unknown Alkane		0.32	0.01
111	n-Pentadecane	629-62-9	0.16	0.02

Cmpd #	Compound	CAS ¹ Number	Average (mg/m ³)	Standard ² Deviation (mg/m ³)
Sum of tentatively identified compounds:			108.7	

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 one sample.
4. Detected in only two samples.

Table X-8
Tank C-102 Tentatively Identified Organic Compounds in TST Samples

Cmpd #	Compound	CAS ¹ Number	Average (mg/m ³)	Standard Deviation (mg/m ³)
1	Methane, trichlorofluoro	75-69-4	0.51	0.88
2	2-Butanone	78-93-3	0.55	0.95
3	Furan, tetrahydro	109-99-9	0.89	0.79
4	2(3H)-furanone, dihydro-3,5-dimethyl	5145-01-7	0.24	0.22
5	Cyclobutane, 1,2-diethyl-, trans- & cis-		0.15	0.27
6	Cyclopropane, propyl	2415-72-7	0.11	0.19
7	Benzene, ethyl	100-41-4	0.090	0.155
8	Heptanal	111-71-7	0.10	0.17
9	Xylene	1330-20-7	0.40	0.39
10	Styrene	100-42-5	0.11	0.19
11	Xylene	1330-20-7	0.12	0.21
12	C8-Alkanone		0.82	0.34
13	1,1,2,3-tetramethyl-cyclohexane A		0.22	0.20
14	Nonane, 4-methyl	17301-94-9	0.12	0.20
15	3-Buten-2-ol	598-32-3	1.1	0.48
16	Benzene, (1-methylethyl)-	98-82-8	0.079	0.136
17	Cyclohexane, 1-methyl-3-propyl	4291-80-9	0.20	0.17
18	2-Decene, (E)-	20063-97-2	0.14	0.13
19	Cyclohexane, (3-methyl-pentyl)-	61142-38-9	0.11	0.19
20	Cyclohexane, 1,5-diethyl-2,3-dimethyl	74663-66-4	0.095	0.165
21	Nonane, 2,6-dimethyl	17302-28-2	1.1	0.2
22	Benzene, 1-propenyl	637-50-3	0.21	0.18
23	4,5-Nonadiene	821-74-9	0.10	0.17
24	Cyclohexane, (1-methylpropyl)-	7058-01-7	0.24	0.06
25	1,1-dimethyl-2-propylcyclohexane		0.30	0.03

Cmpd #	Compound	CAS ¹ Number	Average (mg/m ³)	Standard Deviation (mg/m ³)
26	Decane, 5-methyl	13151-35-4	0.44	0.04
27	Decane, 4-methyl	2847-72-5	0.34	0.08
28	Decane, 2-methyl	6975-98-0	1.0	0.2
29	Naphthalene, decahydro-, trans	493-02-7	0.53	0.10
30	Decane, 3-methyl	13151-34-3	0.53	0.03
31	Benzene, 1-methyl-2-propyl	1074-17-5	0.14	0.25
32	4-Nonanone	4485-09-0	0.13	0.23
33	C4-benzene & others		0.14	0.24
34	5-Undecene	4941-53-1	0.44	0.01
35	2-Nonanone	821-55-6	1.0	0.1
36	2-Decene, 4-methyl, (Z)	74630-30-1	0.11	0.19
37	5-Undecene, (E)-	764-97-6	0.18	0.32
38	1-Undecene, 4-methyl	74630-39-0	0.41	0.36
39	Cyclopropane, octyl	1472-09-9	0.62	0.12
40	Undecane, 5-methyl	1632-70-8	0.82	0.19
41	Naphthalene, decahydro-2-methyl	2958-76-1	0.39	0.54
42	Undecane, 2,8-dimethyl	17301-25-6	0.097	0.168
43	Undecane, 4,8-dimethyl	17301-33-6	0.083	0.143
44	Undecane, 3,8-dimethyl	17301-30-3	2.0	0.7
45	Mixture		0.11	0.20
46	Benzene, (2-methyl-2-propenyl)-	3290-53-7	0.099	0.171
47	1-Dodecene	112-41-4	0.14	0.13
48	5-Undecene, 7-methyl (E)-	74630-66-3	0.12	0.21
49	3-Undecene, 2-methyl, (Z)-	74630-48-1	1.1	1.7
50	Methyldecahydronaphthalene		3.1	0.5
51	6-Methylundecane	17302-33-9	1.8	1.3
52	Undecane, 4-methyl	2980-69-0	1.1	0.4
53	Undecane, 2-methyl	7045-71-8	2.3	1.1

Cmpd #	Compound	CAS ¹ Number	Average (mg/m ³)	Standard Deviation (mg/m ³)
54	Benzene, pentyl	538-68-1	0.46	0.48
55	Undecane, 3-methyl	1002-43-3	1.2	0.6
56	4-Undecene, 4-methyl	61142-40-3	0.99	0.64
57	Undecane, 3-methyl	1002-43-3	0.16	0.28
58	C13-Alkane		0.25	0.43
59	Cyclododecane	294-62-2	1.3	0.2
60	Naphthalene, decahydro-1,2-dimethyl	3604-14-6	0.71	0.18
61	4-Dodecene, (E)-	7206-15-7	0.30	0.12
62	Undecane, 2,4-dimethyl	17312-80-0	0.046	0.079
63	Undecane, 2,6-dimethyl	17301-23-4	3.4	0.2
64	Undecane, 4,7-dimethyl	17301-32-5	0.43	0.05
65	Dimethyl-decahydro naphthalene + others		0.31	0.27
66	4-Undecene, 5-methyl- (Z)-	74630-69-6	0.045	0.077
67	Undecane, 2,10-dimethyl & others		0.14	0.24
68	Cyclopentane, 1-pentyl-2-propyl	62199-51-3	0.078	0.135
69	Cyclohexane, 2-butyl-1, 1,3-trimethyl	54676-39-0	1.7	0.2
70	Undecane, 5-ethyl	17453-94-0	0.19	0.05
71	3-Hexadecyne	61886-62-2	0.25	0.01
72	Cyclohexane, (4-methylpentyl)-	61142-201-9	0.84	0.06
73	Dodecane, 4-methyl	6117-97-1	0.78	0.06
74	Dodecane, 2-methyl	1560-97-0	1.5	0.1
75	2-Hexanone, 3-cyclo-hexyliden-4-ethyl		0.18	0.16
76	Dodecane, 4,6-dimethyl	61141-72-8	3.8	0.4
77	2-Butenoic acid, 2-propenyl ester & others		0.27	0.48

Cmpd #	Compound	CAS ¹ Number	Average (mg/m ³)	Standard Deviation (mg/m ³)
78	Benzene, (1-methylpentyl)-	6031-02-3	0.15	0.26
79	Trimethyldecahydronaphthalene		0.48	0.09
80	3-Undecanone	2216-87-7	0.13	0.23
81	6-Tridecane, 7-methyl	24949-42-6	1.1	0.1
82	Undecane, 3,8-dimethyl	17301-30-3	0.055	0.096
83	Alkane		0.16	0.16
84	Heptane, 3-ethyl-5-methyl	52896-90-9	0.19	0.33
85	Alkane		0.10	0.17
86	Decane, 6-ethyl-2-methyl	62108-21-8	0.37	0.63
87	Undecane, 5-ethyl	17453-94-0	0.48	0.45
88	Cyclooctane, 1-methylpropyl- and others		0.14	0.12
89	Cyclooctane, butyl	16538-93-5	0.055	0.096
90	C4-Cyclohexane		0.095	0.165
91	C12-alkene and C7-benzene		0.19	0.16
92	C8-cyclohexane		0.41	0.29
93	C14-alkene		0.32	0.14
94	C7-Cyclohexane		0.93	0.06
95	Tridecane, 4-methyl	26730-12-1	0.51	0.11
96	Dodecane, 3-methyl	17312-57-1	0.29	0.51
97	Tridecane, 2-methyl	1560-96-9	0.70	0.22
98	C8-Cyclohexene		0.30	0.26
99	5-Undecanone, 2-methyl	50639-02-6	0.13	0.22
100	Dodecane, 2,7,10-trimethyl	74645-98-0	2.6	0.2
101	Heptane, 2-phenyl	2132-84-5	0.24	0.27
102	C8-Cyclohexane		0.043	0.074
103	3-Dodecanone	1534-27-6	0.35	0.12
104	Tetradecane	629-59-4	4.5	1.8
105	Tridecane, 4,8-dimethyl	55030-62-1	0.29	0.51

Cmpd #	Compound	CAS ¹ Number	Average (mg/m ³)	Standard Deviation (mg/m ³)
106	1,1'-biphenyl	92-52-4	0.92	0.86
107	2-Hexenoic acid, 2-hexenyl ester, (E,E)-	54845-28-2	0.052	0.090
108	1,1-Biphenyl,2-methyl	643-58-3	0.48	0.57
109	Benzene, 1,1'-methylenebis- and others		0.24	0.22
110	Tridecane, 4-methyl	26730-12-1	0.087	0.151
111	C8-cyclohexane		0.068	0.117
112	Dodecane, 2,6,11-trimethyl	31295-56-4	0.055	0.096
113	Tridecane, 4,8-dimethyl		0.047	0.081
114	Hexadecane	544-76-3	0.56	0.07
115	2-Undecanone, 6,10-dimethyl	105-42-0	0.059	0.103
116	Dimethyl-naphthalene		0.17	0.29
117	Benzene, (1-methylheptyl)-	777-22-0	0.031	0.053
118	Dodecane, 2-methyl-8-propyl	55045-07-3	0.45	0.78
119	Pentadecane, 2-methyl	1560-93-6	0.056	0.096
120	5-Undecanone, 2-methyl	50639-02-6	0.15	0.26
121	3-Tridecanone	1534-26-5	0.21	0.14
122	Pentadecane	629-62-9	0.77	0.63
123	1,1'-Biphenyl, 2-methyl	643-58-3	0.067	0.116
124	1,1'-Biphenyl, 2-methyl	643-58-3	0.039	0.067
125	9H-Fluorene	86-73-7	0.077	0.134
126	Benzenesulfonamide, N-butyl	3622-84-2	0.23	0.04
Sum of tentatively identified compounds:			67.03	

1. CAS = Chemical Abstract Service.

Figure X-1
Total Ion Chromatograms for SUMMA™ Samples from Tanks C-102 and C-103 (Expanded Ordinate Scale)

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

SUMMA sample total ion chromatogram for tank C-103 -- enlarged ordinate scale.

Figure X-2
Total Ion Chromatograms for SUMMA™ Samples from Tanks C-102 and C-103 (Full Ordinate Scale)

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

SUMMA sample total ion chromatogram for tank C-103 -- full ordinate scale.

WHC-SD-WM-ER-459 REV. 0

Figure X-3
Total Ion Chromatograms for SUMMATM Samples from Tanks C-102 and C-101

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

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

X.4 REFERENCES

- Anderson, J. D., 1990, *A History of the 200 Area Tank Farms*, WHC-MR-0132, Westinghouse Hanford Company, Richland, Washington.
- Campbell, J. A., R. M. Bean, K. L. Wahl, G. M. Wong, K. E. Bell, K. B. Wehner, A. D. Rice, R. J. Ray, D. B. Bechtold, B. R. Wels, R. W. Schroeder, J. W. Ball, B. D. Valenzuela, J. M. Frye, S. L. Fitzgerald, P. P. Bachelor, B. Griffin, R. K. Fuller, A. B. Benally, and S. M. Parong, 1995, *Analysis of Samples from Hanford Waste Tanks 241-C-102, 241-BY-108, and 241-C-103*, PNL-10531, UC-601, Pacific Northwest Laboratory, Richland, Washington.
- Carothers, K. G., 1988, *Tank 103-C Transaction History - Post January 1976*, (internal memorandum 13331-88-600 to D. A. Dodd, G. L. Dunford, G. N. Hanson, A. W. Lilly, and R. E. Van der Cook, September 22), Westinghouse Hanford Company, Richland, Washington.
- Conrad, R. B., 1994, *Engineering Evaluation of alternatives for Treatment of Tank 241-C-103 Vapor Space*, WHC-SD-WM-ES-281, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- EPA 1988, *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, PB90-127374, U.S. Environmental Protection Agency, Washington, D.C.
- Hendrickson, R. W., 1995, *Tank Vapor Characterization Oak Ridge National Laboratories Quality Assurance Assessment*, TWRSQA-95-0012, Westinghouse Hanford Company, Richland, Washington.
- Huckaby, J. L., 1994, *Tank 241-C-103 Headspace Flammability*, WHC-EP-0734 Rev. 1, Westinghouse Hanford Company, Richland, Washington.
- Huckaby, J. L., 1995a, *Tank 241-C-101 Vapor Sampling and Analysis TCR Chapter*, WHC-SD-WM-ER-458, Westinghouse Hanford Company, Richland, Washington.
- Huckaby, J. L., 1995b, *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. E. Higgins, C. Y. Ma, M. A. Palausky, J. T. Skeen, and C. K. Bayne, 1994a, *Analysis of Tank 241-C-102 Headspace Components*, ORNL-CASD-FR-241C102.95, Rev. 0, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

- Jenkins, R. A., A. B. Dindal, C. E. Higgins, C. Y. Ma, M. A. Palausky, and J. T. Skeen, 1994b, *Analysis of Tank 241-C-101 Headspace Components*, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- Jenkins, R. A., A. B. Dindal, C. E. Higgins, C. Y. Ma, J. T. Skeen, and R. R. Smith, 1994c, *Analysis of Tank 241-C-103 Headspace Components from Sampling Job 7B*, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- Klinger, G. S., T. W. Clauss, M. W. Ligothe, K. H. Pool, R. B. Lucke, B. D. McVeety, K. B. Olsen, O. P. Brett, J. S. Fruchter, and S. C. Goheen, 1995a, *Vapor Space Characterization of Waste Tank 241-C-102: Results from Samples Collected on 8/23/94*, PNL-xxxxx UC-606, Pacific Northwest Laboratory, Richland, Washington.
- Klinger, G. S., T. W. Clauss, M. W. Ligothe, K. H. Pool, R. B. Lucke, B. D. McVeety, O. P. Brett, 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. Ligothe, K. H. Pool, T. W. Clauss, A. K. Sharma, B. D. McVeety, M. McCulloch, J. S. Fruchter, and S. C. Goheen, 1995a, *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.
- Lucke, R. B., T. W. Clauss, M. W. Ligothe, K. H. Pool, B. D. McVeety, J. S. Young, M. McCulloch, J. S. Fruchter, and S. C. Goheen, 1995b, *Vapor Space Characterization of Waste Tank 241-C-101: Results from Samples Collected Through the Vapor Sampling System on 9/1/94*, PNL-xxxxx UC-606, Pacific Northwest Laboratory, Richland, Washington.
- 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. Ligothe, 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.
- Pool, K. H, and R. M. Bean, 1994, *Analysis of Liquid Samples from Hanford Waste Tank 241-C-103*, PNL-9403 UC-601, Pacific Northwest Laboratory, Richland, Washington.
- Rasmussen, R. A., 1994a, *Air Samples Collected at Waste Tank 241-C-102 on August 23, 1994 by Westinghouse Hanford in 6-L SS SUMMA® Canisters*, Oregon Graduate Institute of Science and Technology, Beaverton, Oregon.
- Rasmussen, R. A., 1994b, *Air Samples Collected at Waste Tank 241-C-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-C-102 Using the Vapor Sampling System*, WHC-SD-WM-RPT-127, Westinghouse Hanford Company, Richland, Washington.