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TANK 241C104 HEADSPACE GAS & VAPOR
CHARACTERIZATION RESULTS FOR SAMPLES COLLECTED IN
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ENGINEERING CHANGE NOTICE

Page 1 of 2

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ENGINEERING CHANGE NOTICE

Page 2 of 2

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Functional Design Criteria	☐	Stress/Design Report	☐	Health Physics Procedure	☐
Operating Specification	☐	Interface Control Drawing	☐	Spares Multiple Unit Listing	☐
Criticality Specification	☐	Calibration Procedure	☐	Test Procedures/Specification	☐
Conceptual Design Report	☐	Installation Procedure	☐	Component Index	☐
Equipment Spec.	☐	Maintenance Procedure	☐	ASME Coded Item	☐
Const. Spec.	☐	Engineering Procedure	☐	Human Factor Consideration	☐
Procurement Spec.	☐	Operating Instruction	☐	Computer Software	☐
Vendor Information	☐	Operating Procedure	☐	Electric Circuit Schedule	☐
OM Manual	☐	Operational Safety Requirement	☐	ICRS Procedure	☐
FSAR/SAR	☐	IEFD Drawing	☐	Process Control Manual/Plan	☐
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Radiation Work Permit	☐	Essential Material Specification	☐	Purchase Requisition	☐
Environmental Impact Statement	☐	Fac. Proc. Samp. Schedule	☐	Tickler File	☐
Environmental Report	☐	Inspection Plan	☐		☐
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Cog. Mgr. T. J. Kelley <i>TJK</i>	<i>9/25/95</i>	QA	_____
QA	_____	Safety	_____
Safety	_____	Design	_____
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March 1994

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7. Abstract

Significant changes have been made to all of the original vapor characterization reports. This report documents specific headspace gas and vapor characterization results for all vapor sampling events to date. In addition, changes have been made to the original vapor reports to qualify the data based on quality assurance issues associated with the performing laboratories.

8.

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Tank 241-C-104 Headspace Gas and Vapor Characterization Results for Samples Collected in March 1994

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Acronyms and Abbreviations

CES	consensus exposure standard
EPA	Environmental Protection Agency
GC	gas chromatograph
GC/MS	gas chromatograph/mass spectrometer
LFL	lower flammability limit
MS	mass spectrometer
NFPA	National Fire Protection Association
NPH	normal paraffinic hydrocarbon
OGIST	Oregon Graduate Institute of Science and Technology
ORNL	Oak Ridge National Laboratory
OSHA	Occupational Safety and Health Administration
OVS	OSHA versatile sampler
PNL	Pacific Northwest Laboratory
ppmv	parts per million by volume, 1 ppmv = 10 ⁻⁴ vol%
TNMOC	total nonmethane organic carbon
TST	triple sorbent trap
vol%	percent by volume, 1 vol% = 10,000 ppmv
VSS	vapor sampling system
WHC	Westinghouse Hanford Company

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Tank 241-C-104 Headspace Gas and Vapor Characterization Results
for Samples Collected in March 1994

1.0 INTRODUCTION

1.1 Characterization Objectives

Tank C-104 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-104 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-104.

1.2 Characterization Data Criteria

Data Quality Objectives for Generic In-Tank Health and Safety Issue Resolution describes parameters for data collection to ensure appropriate conclusions can be drawn from the data. Tank headspace characterization data were collected to help in the evaluation of 1) headspace flammability, and 2) identification and quantification of compounds of toxicological concern.

Single Shell Tank Interim Operational Safety Requirements (Dougherty 1995) specifies that combustible constituents in tank headspaces be maintained below 25 % of the lower flammability limit (LFL). This essentially agrees with National Fire Protection Association requirements that combustible concentrations be maintained at or below 25 % of the LFL (NFPA 1992). However, current governing operating specifications for single shell waste tanks, such as tank C-104, specify that combustible constituents be maintained at or below 20 % of the LFL (Boyles 1994).

Headspace characterization data are used by Westinghouse Hanford Company (WHC) Tank Waste Remediation Systems Industrial Hygiene as source term data in the industrial hygiene strategy to protect workers from tank fugitive emissions. Because selection of worker protective equipment must be based on industrial hygiene monitoring of the work place and not on source term data (29 CFR 1910.120), tank headspace characterization data can not be used for this purpose. Furthermore, because there are mechanisms by which headspace constituents can be either diluted or concentrated as they are released to the atmosphere, the headspace characterization data should not be considered to be representative of emissions at the point of emission.

These statements notwithstanding, the data quality objectives document specifies that the industrial hygiene group be advised if constituents with toxicological properties exceed 50 % of the appropriate consensus exposure standard (CES) for non-carcinogens, or 10 % of the appropriate CES for carcinogens. A CES is defined as the most stringent of known regulatory or recommended toxicological values for the workplace (Osborne et al. 1994).

1.3 Sampling Overview

Tank C-104 headspace characterization data presented here are from a single sampling event. Samples collected are thought to have been reasonably representative of the tank headspace when the tank was sampled (Meacham et al. 1995), and sample analyses were designed to provide a reasonably accurate and complete characterization of the significant headspace constituents. No assessment has been made of how the tank C-104 headspace composition changes with time.

1.4 Tank Headspace Dynamics

Gas and vapor concentrations in tank C-104 are thought to be strongly affected by active ventilation of the headspace. Though no exhaustor is used directly on tank C-104, it is connected via an underground cascade line to tank C-105, which is actively ventilated. Monthly waste tank summary reports list tank C-104 as an actively vented tank (Hanlon 1995). Though it has not been proven, it is assumed that the cascade line connection to tank C-105 is open and tank C-104 is actively ventilated.

The active ventilation of tank C-104 has 2 potential effects on the gas and vapor data presented below. First, most passively ventilated waste tanks exchange gases and vapors with the atmosphere so slowly that the headspace vapors are virtually in equilibrium with waste liquids. Active ventilation of tank C-104, however, may preclude vapor-liquid equilibrium and complicate the interpretation of vapor data. And second, diffusion and convection are thought to make the headspaces of passively ventilated tanks homogeneous, and representative samples can be drawn from any central region of the headspace. Though mixing is generally more vigorous in an actively ventilated tank headspace (other factors being equal), the discrete sources of fresh air and the single outlet would produce concentration gradients within the headspace. This would make gas and vapor concentrations a function of location, and limit the value of samples collected from a single arbitrary location, as are those discussed below.

The degree to which active ventilation affects the gas and vapor data depends most directly on 1) the ventilation rate relative to the headspace volume, and 2) the locations of air in-leakage points relative to the cascade line. Unfortunately, neither the ventilation rate nor all of its in-leakage points are known.

2.0 SAMPLING EVENT

Headspace gas and vapor samples were collected from tank C-104 using the vapor sampling system (VSS) on March 3, 1994 by WHC Sampling and Mobile Laboratories (WHC 1995b). Sample collection and analysis were performed as directed by the sample and analysis plan¹ (WHC 1995b, Appendix A). The tank headspace temperature was determined to be 28 °C. Air from the C-104 headspace was withdrawn via a heated sampling probe mounted in riser 2, and transferred via heated tubing to the VSS sampling manifold. All heated zones of the VSS were maintained at approximately 50 °C.

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 46 tank air samples and 6 ambient air control samples collected are listed in Table 2-1 by analytical laboratory. Table 2-1 also lists the 8 trip blanks and 3 spiked blanks provided by the laboratories. A general description of vapor sampling and sample analysis methods is given by Huckaby et al. (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 1995b.

Tank C-104 was the fourth tank to be sampled using the VSS, and was sampled only about 5 weeks after the first use of the VSS on a tank. Because the methods and equipment were relatively new, problems with sample handling (e.g., chain-of-custody and shipping) were encountered (WHC 1995b, Lucke et al. 1995a). The precision of the sampling results, however, is generally good. Sorbent trap collection problems noted in a subsequent sampling event² do not appear to have occurred when tank C-104 was sampled.

¹ The current requirement that sampling and analysis parameters be specified by a tank characterization plan was not in effect for gas and vapor sampling until October 1, 1994.

² Because of a valve-sequencing error, sample air volumes through specific sampling ports were not properly measured during sample job 7A of tank C-103. The error resulted in obvious and significant differences in sorbent trap results, but had no effect on SUMMA™ samples.

3.0 INORGANIC GASES AND VAPORS

Analytical results of sorbent trap and SUMMA^{TM3} canister tank air samples for selected inorganic gases and vapors are given in Table 3-1 in parts per million by volume (ppmv) in dry air. The concentration of water vapor given in Table 3-1 has been adjusted to tank conditions as given in Section 3.3. Inorganic analyte sorbent traps were prepared and analyzed by PNL. SUMMATM canisters were prepared and analyzed for inorganic analytes by OGIIST. Reports by PNL (Lucke et al. 1995a) and OGIIST (Rasmussen 1994a) describe sample preparation and analyses.

PNL sample preparation and analysis were performed at PNL quality assurance impact level 3. Analyses of sorbent traps for inorganic compounds were completed 22 days after sample collection (Ligothke 1995), and were within the allowed 60-day holding time of the WHC quality assurance project plan (Keller 1994).

OGIIST was not operating under a WHC-approved quality assurance plan when samples were analyzed, so OGIIST data have been placed in square brackets both in Table 3-1 and elsewhere in the text of this report to indicate that they represent secondary results. OGIIST started analyses of SUMMATM canisters 7 days after the sample collection. It should be noted that the inorganic compounds from SUMMATM canister analyses (i.e., the permanent gases) would be expected to be very stable in the SUMMATM canisters, and the results would not have been affected even if the 60-day holding time requirement had been exceeded.

3.1 Ammonia, Hydrogen, and Nitrous Oxide

Ammonia, hydrogen, and nitrous oxide are commonly detected in the waste tanks. Thought to be products of radiolysis and oxidation-reduction reactions of the waste, they appear ubiquitously with the high-level waste. These headspace constituents have been the most abundant waste artifacts in virtually every tank headspace sampled to date.

The reported ammonia concentration in headspace of tank C-104 was 44 ppmv. Ammonia has been observed at concentrations ranging from about 3 ppmv in tank C-108 (Lucke et al. 1995b), to 1040 ppmv in BY-108 (McVeety et al. 1995). Typically the ammonia concentration of a waste tank can be correlated to its organic vapor concentration. As is discussed below, the organic vapor concentration in tank C-104 is moderately high, and the ammonia concentration might be expected to be higher than measured. Active exhausting of the tank C-104 headspace probably accounts for the relatively low ammonia concentration in tank C-104. Given the LFL of ammonia in air is about 15 % by volume (vol%), the measured 44 ppmv corresponds to about 0.03 % of the LFL, and does not contribute appreciably to the flammability of the headspace.

The concentration of hydrogen in tank C-104 was determined to be [68 ppmv]. Hydrogen in the waste tanks is of concern as a fuel. Given that the LFL for hydrogen in air is about 4 vol%, the 68 ppmv hydrogen concentration in tank C-104 corresponds to about 0.2 % of its LFL, and at this level hydrogen is not a flammability concern in tank C-104.

The nitrous oxide concentration in tank C-104 was measured at [64 ppmv]. Nitrous oxide has been detected in other waste tanks at concentrations as low as about 12 ppmv in tank TX-105 (Klinger et al. 1995), and as high as about 868 ppmv in tank U-103 (Ligothke et al. 1995). Under the proper conditions,

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

nitrous oxide can serve as an oxidizer to support combustion. However, Cashdollar et al. (1992) found that nitrous oxide had no significant effect on the flammability of hydrogen and air mixtures for hydrogen concentrations less than 20 vol%, and that "small amounts of nitrous oxide (relative to air) do not appear to have much effect on the flammability". Their results suggest the measured nitrous oxide concentration is much too low to have a significant effect on the flammability of the tank C-104 headspace.

3.2 Carbon Monoxide

Carbon monoxide in the tank C-104 headspace, measured to be [2 ppmv] in SUMMA™ samples, is above its concentration in ambient air, where it typically ranges from 0.05 to 0.15 ppmv. Ambient air samples collected at the beginning of the tank C-104 vapor sampling event were measured to have [< 1 ppmv]. Elevated waste tank headspace carbon monoxide concentrations are common (e.g., carbon monoxide concentration in tank C-103 was [26.7 ppmv], Huckaby and Story 1994), and are thought to be due to the decomposition of organic waste in the tanks.

3.3 Nitric Oxide, Nitrogen Dioxide, Water and Tritium

Nitric oxide and nitrogen dioxide concentrations in the tank C-104 headspace were determined to be 0.37 ppmv and ≤ 0.02 ppmv, respectively. These are both acid gases that would have very low equilibrium concentrations above the high pH sludge in tank C-104. The measurable presence of nitric oxide may be due to its formation from oxygen and nitrogen in the radiation field of the headspace. These constituents could potentially serve as oxidizers to support combustion, but at the measured concentrations would have a negligible effect on the flammability of the tank C-104 headspace.

The water vapor concentration of tank C-104 was determined to be about 12.9 mg/L, at the tank headspace temperature of 28 °C and pressure of 1001 mbar (750.5 torr), (WHC 1995). This corresponds to a water vapor partial pressure of 17.8 mbar (13.4 torr), to a dew point of 15.7 °C, and to a relative humidity of 47 %. The water vapor content of the tank C-104 headspace is significantly lower than that measured in other sludge-containing 241-C farm tanks, which more typically have relative humidities of about 85 %. This may be an indication that the tank is indeed actively exhausted via its cascade line to tank C-105.

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. Analysis of the silica gel, which would have trapped approximately 44 mg of water vapor⁴, indicated the total activity of the sample to be below the method detection limit of 50 pCi (WHC 1995b).

3.4 Sulfur Oxides

Sulfur oxides were reported by PNL to be present at 0.4 ppmv. Approximately the same amount of analyte was found on both sorbent trap front and back (breakthrough) sections, indicating a sampling or analytical problem. This problem was not resolved.

⁴ The water vapor trapped by tritium traps was not directly measured.

3.5 Discussion of Inorganic Gases and Vapors

Aside from water vapor, the most abundant waste constituents in the tank C-104 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.

Neither hydrogen nor nitrous oxide is highly soluble in the aqueous wastes of the tanks, so except for situations where bubbles are trapped within the waste and released episodically, the gases are released as they are generated. The concentration of these gases in the tank headspaces is consequently determined by a simple balance between their overall generation rate and the rate at which they are vented to the atmosphere. If the tank C-104 headspace is actively exhausted by its connection to tank C-105 (as is thought), the measured concentrations of hydrogen and nitrous oxide may actually equate to relatively high gas generation rates, despite the fact that the gas concentrations are lower than in many passively ventilated waste tanks.

The relative standard deviations of the inorganic gas and vapor results given in the last column in Table 3-1 are good, except for the measurement of sulfur oxides. Relative standard deviations range from 4 % for nitrous oxide, and water vapor, to 50 % for oxides of sulfur. 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 3-2 summarizes selected gas and vapor results for tanks C-104, C-105, and C-106. Compared to these other tanks, which have relatively high ventilation rates, tank C-104 has much higher concentrations of the inorganic waste gases and vapors.

4.0 ORGANIC VAPORS

Organic vapors in the tank C-104 headspace were sampled using SUMMA™ canisters, which were analyzed by OGIST and PNL, Occupational Safety and Health Administration (OSHA) versatile samplers (OVSSs), which were analyzed by PNL, and triple sorbent traps (TSTs), which were analyzed by ORNL. PNL, OGIST, and ORNL used gas chromatographs (GCs) equipped with mass spectrometer (MS) detectors to separate, identify, and quantitate organic vapors. A quantitative measurement of the total nonmethane organic carbon (TNMOC) concentration by the U.S. Environmental Protection Agency (EPA) task order 12 (TO-12) method was also performed by OGIST (EPA 1988). Descriptions of sample device cleaning, sample preparations, and analyses are given by Jenkins et al. (1994), Rasmussen (1994a), and Lucke et al. (1995a).

PNL SUMMA™ sample results should be considered to be the primary organic vapor data for tank C-104. PNL results were produced at PNL quality assurance impact level 3. However, because of laboratory instrumentation problems and a low WHC priority assignment, PNL SUMMA™ canister analyses were not completed until 279 days after sample collection. This greatly exceeded the administratively chosen 60-day holding time of the WHC quality assurance project plan (Keller 1994). Though many of the organic analytes would be expected to be very stable, no holding time study has been performed to address organic compound stability in SUMMA™ canisters in the typical chemical matrix of the tank headspace samples.

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. In an attempt to provide ORNL with additional samples for scoping purposes, 7 of the TSTs were collected simultaneously, in parallel, with a single flow controller. Because flow through these 7 TSTs was very non-uniform, analytical results from these samples are not discussed here.

All TSTs prepared by ORNL had 3 surrogate compounds added to evaluate sample matrix effects, potential handling, storage, and shipment problems, and analytical instrumentation performance (Jenkins et al. 1994). ORNL evaluated the surrogate recoveries using a statistical approach similar to that prescribed by *SW 846 Method 8260A Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) Capillary Column Technique* (EPA 1992). Using this approach, ORNL reported that surrogate recoveries had standard deviation values outside the 95 % confidence interval for variance, suggesting that a bias may have been introduced in the measurement of analyte quantities (Jenkins 1995a).

The TST samples from tank C-104 were inadvertently stored at room temperature for several days. Mistakenly sent to PNL, the sealed TSTs were allowed remain in an ice-cooled shipping container over a weekend, during which time the ice melted and the samples reached room temperature. Though there was no apparent loss of analytes or contamination, ORNL had specified that the samples be stored and shipped at 4 °C.

Because OGIST did not have a WHC-approved quality assurance project plan in place at the time the tank C-104 samples were analyzed, the OGIST results should be considered secondary data (Burnum 1995). Rasmussen (1994a) reports that SUMMA™ canister sample analyses were begun 7 days after sample collection.

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 40 compounds of the EPA task order 14 (TO-14) method, which are primarily halocarbons and common industrial solvents (EPA 1988).

Table 4-1 lists the organic compounds positively identified and quantitated in SUMMA™ and OVS samples by PNL. SUMMA™ analyses were performed according to the EPA TO-14 methodology (EPA 1988, Lucke et al. 1995a). Only 3 of the 40 TO-14 target analytes were observed to be above the 0.002 ppmv quantitation limit of the analyses. Averages reported are from analyses of 3 SUMMA™ canister samples.

OVSs were used to sample the tank air for semivolatile normal paraffinic hydrocarbons (NPHs), specifically, n-undecane, n-dodecane, n-tridecane, n-tetradecane, and n-pentadecane. Unlike TST samples or SUMMA™ canisters, the analytical preparation of OVSs involves liquid extraction, and larger sample volumes are required for comparable detection limits. The OVS results given in Table 4-1 are from a single sample because the NPHs were below detection limits in the other 2 OVSs. It is not clear why the NPH analytes were not detected in the other 2 OVSs, whether errors were made in sample collection or analysis is not clear. Two of the NPH target analytes, n-undecane and n-pentadecane, were below detection limits in all 3 OVSs.

Table 4-2 lists the organic compounds positively identified and quantitated in SUMMA™ samples by OGIST. SUMMA™ analyses were performed according to the EPA TO-14 methodology (EPA 1988, Rasmussen 1994a). Averages reported are from analyses of 3 SUMMA™ samples. The OGIST and PNL results are in fair agreement, the most significant difference being that OGIST reported an average of [0.036 ppmv] of trichlorofluoromethane, while PNL reported an average of 0.0089 for this analyte.

Jenkins et al. (1994) report the positive identification of 24 of 26 target analytes in TST samples. Despite calibration of the instrument over about a 20-fold concentration range, 23 of the positively identified compounds were measured to be outside of the calibration range in at least 1 of the 3 TST samples, and their reported averages are not considered quantitative. The only analyte which was quantitated in all 3 TST samples was benzene, which is given in Table 4-3 with its reported average concentration.

The average concentrations for 21 positively identified (but not quantitated) analytes are given in Tables 4-4 and 4-5. The 2 identified analytes which had exceeded their ORNL practical holding times are given in Table 4-5. The ORNL practical holding time is defined as the holding time for which there is a 15 % risk that the concentration of an analyte in the sample will be below its initial concentration. As indicated in Table 4-5, 1-butanol and 2-pentanone exceeded their practical holding times, and may have been affected by the 47 day period between sample collection and analysis (Jenkins 1995b). Jenkins et al. (1995) describe the ORNL practical holding time study, and report the practical holding times of 1-butanol, and 2-

pentanone are 17 and 34 days, respectively. It should be noted that the contractual holding time for the TST samples was 60 days. Tables 4-3, 4-4, and 4-5 are mutually exclusive, so no analyte appears in more than 1 of these tables. Results in Tables 4-4 and 4-5 may not be accurate to within the $\pm 30\%$ specified by Burnum (1995).

Two other target analytes, tributyl phosphate and dibutyl butylphosphonate, were positively identified, but because the analytical instrumentation had not been calibrated for these analytes, their concentrations have only been estimated. Tributyl phosphate was estimated to be present at 0.025 ppmv (0.3 mg/m³) and dibutyl butylphosphonate was estimated to be present at 0.006 ppmv (0.07 mg/m³).

Dichloromethane, benzene, and toluene were common to both the TST and SUMMATM analyses. Dichloromethane was not detected in either TST or PNL SUMMATM samples, but [0.0025 ppmv] was reported in OGIST SUMMATM samples. The reported average concentrations of benzene, 0.0099 ppmv, and toluene, 0.082 ppmv, in TST samples are higher than in either the PNL or OGIST SUMMATM samples.

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

4.2 Tentatively Identified Organic Analytes

In addition to the target analytes, the ORNL, OGIST, 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. Using this method, 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, 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 (e.g., molecules with more than about 15 carbon atoms) and some polar compounds with moderate volatility (e.g., butanal) from SUMMATM samples has been problematic.

The tentatively identified compounds recovered from SUMMATM samples, in the order by which the eluted chromatographically, are given in Table 4-6 with estimated concentrations. 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 4-7. Compounds are listed in Table 4-7 according to the order by which the eluted chromatographically. The averages reported by ORNL in Table 4-7 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. Because the list of tentatively identified organic compounds in TST samples is particularly long and locating any given compound may be difficult, the list has been sorted alphanumerically by compound name in Table 4-8. Table 4-9 gives the same list, sorted in order of decreasing estimated concentration. Numbers in the first columns of Tables 4-8 and 4-9

(Cmpd #) identify the location of the compound in Table 4-7. Estimated concentrations are in mg/m^3 , based on dry air at 0 °C and 1.01 bar.

OGIST provided total-ion chromatograms for each of the tank C-104 SUMMA™ samples and assigned tentative identities to the significant peaks, but did not estimate their concentrations. Table 4-10 lists the analytes tentatively identified by OGIST, and designates which analytes were detected in each of the 3 SUMMA™ samples. As a rough guide, the analytes listed in Table 4-10 were probably detected at greater than 0.001 ppmv. It should also be noted that some peaks in the total-ion chromatograms were not labeled, despite being relatively high, because confidence in assigning a chemical identity was very low.

The ORNL and PNL methods used to tentatively identify and estimate concentrations are described by Jenkins et al. (1994) and Lucke et al. (1995a), respectively, and should be reviewed before this data is used for decision making. Results in Tables 4-7 through 4-9 are presented in terms of observed peaks, and are not adjusted for the occurrence of split chromatographic peaks (e.g., Cmpd # 1, 2, and 3 in Table 4-7) or the assignment of the same identity to different peaks (e.g., Cmpd # 68 and 87 in Table 4-7). In these instances, the estimated concentration of a compound appearing as a doublet or triplet is simply the sum of the individual peak estimates.

Concentrations given in Tables 4-4 and 4-5 should be considered estimates. The proper quantitation of all observed analytes is outside the scope and budget of these analyses, and the estimation of concentrations involves several important assumptions. The validity of each assumption depends on the analyte, and such factors as the specific configuration of the analytical instrumentation.

4.3 Total Nonmethane Organic Carbon

OGIST measured the TNMOC concentration in 3 SUMMA™ canister samples using the EPA TO-12 method. The sample mean was $[28.1 \text{ mg}/\text{m}^3]$, with a standard deviation of $[0.7 \text{ mg}/\text{m}^3]$. This value is moderately high compared to similar measurements for other passively ventilated waste tanks that have been sampled. It is particularly high if indeed the headspace of tank C-104 is actively ventilated.

A summation of concentrations of target and tentatively identified compounds in TST samples by GC/MS indicated the total organic vapor concentration to be about $25 \text{ mg}/\text{m}^3$, in excellent agreement with the EPA TO-12 method results. TO-12 method TNMOC measurements of other waste tanks have ranged from as high as $[3,000 \text{ to } 5,000 \text{ mg}/\text{m}^3]$ in tank C-103 (Rasmussen and Einfeld 1994), to as low as $[0.18 \text{ mg}/\text{m}^3]$ in tank C-111 (Rasmussen 1994b), while the TNMOC concentration of clean ambient air ranges from about 0.03 to $0.1 \text{ mg}/\text{m}^3$.

4.4 Discussion of Organic Analytes

The organic vapors of tank C-104 are similar in many ways to those of other 241-C farm tanks, particularly tank C-103. A convenient way to consider the organic compounds listed in Tables 4-1 through 4-10 is to classify them according to their origin. Some organic compounds were apparently added to tank C-104 as waste and are present in the headspace because they are still evaporating, and other compounds have apparently been generated by chemical and radiolytic reactions of the original waste.

Among the compounds thought to have been placed into the tank as waste are tributyl phosphate, dibutyl butylphosphonate, and the semivolatile branched alkanes and NPHs. Tributyl phosphate was an extractant used in several Hanford site chemical processes, and dibutyl butylphosphonate is a common

contaminant from the manufacture of tributyl phosphate. Semivolatile NPHs and branched alkanes were used as diluents of tributyl phosphate.

Tank C-104 is believed to have contained about a 7.5 cm (3 in.) floating layer of tributyl phosphate and NPH diluent in the early 1970s. Hall (1972) reported the tank contained about 30,000 L (8,000 gal) of a tributyl phosphate/NPH solution, and provides results from a radiochemical analysis of organic liquid samples apparently collected in January 1972. Anderson (1990) reports that various types and amounts of wastes were pumped into and out of the tank between 1972 and 1976, when tank C-104 became inactive. The pumpable supernatant liquids remaining in tank C-104 were removed in 1989, when the tank was interim stabilized (Boyles 1992).

While the amount of organic liquid that could have been removed during the various waste transfers from tank C-104 is uncertain, it is unlikely that it was all removed. The organic vapor signature of tank C-104 supports this premise. Though the semivolatile NPH concentrations reported in Tables 4-1 through 4-9 are lower than would be expected if the vapor phase were in equilibrium with a chemical process solution of NPH and tributyl phosphate, there are at least 2 reasons for this. First, preferential evaporation of the NPHs from an NPH-tributyl phosphate solution would, during 20-odd years of storage, reduce the partial pressure of the NPHs. And second, as discussed above, if the headspace of tank C-104 is indeed actively ventilated, it is unlikely that vapor-liquid equilibrium would be maintained.

One type of semivolatile compound commonly detected in the NPH-rich waste tanks, but not in tank C-104, is a group of semivolatile bicyclic alkanes. Decahydronaphthalene and several methyl-substituted decahydronaphthalenes have been detected in several of the 241-BY and 241-C farm tanks, notably tank C-103. Table 4-7 does identify several such compounds (e.g., Cmpd # 59 and 78), but their concentrations relative to other semivolatiles are much lower than in other NPH-rich tanks. This may be an indication that the organic waste in tank C-104 originated during a period when a relatively pure NPH diluent was used.

The majority of compounds listed in Tables 4-1 through 4-9 are thought to be chemical or radiolytic reaction products of the semivolatile organic waste. Specifically, the alcohols, aldehydes, ketones, nitriles, alkenes, alkyl nitrates, and volatile alkanes have all been associated with the degradation of the NPHs. By far the most abundant of these in the headspace are the short-chain volatile compounds, however, some long-chain low volatility compounds detected may also be waste reaction products.

Samples from tank C-104 were found to have several alkyl nitrates. Though it is reasonable to expect alkyl nitrates to be produced via chemical and radiolytic processes of the NPH with other waste, the solubility of alkyl nitrates in the aqueous waste supernates would also be expected to significantly reduce their vapor-phase concentrations. Indeed, their presence in other NPH-rich tanks has been minimal. That several alkyl nitrates are at detectable levels in tank C-104 may indicate dry conditions where they are formed.

The tank C-104 samples were tentatively determined to contain the following homologous series of straight-chain compounds:

- 1) nitriles from ethanenitrile (acetonitrile) through n-nonanenitrile;
- 2) alkyl nitrates from methyl to hexyl nitrate;

- 3) alkanes from propane through n-nonane⁵;
- 4) 2-ketones from propanone (acetone) through 2-decanone;
- 5) aldehydes from ethanal (acetaldehyde) through decanal;
- 6) 1-alkanols from ethanol through 1-hexanol;
- 7) 1-alkenes from propene through 1-nonene;

as well as several partially complete series of other functionally related organic compounds. As has been noted in other NPH-rich waste tanks, many of the volatile species (presumed to be degradation products of the NPHs) have functional groups on the molecule's first or second carbon atom.

1-Butanol is prominent amongst the alcohols detected. It is known to be a hydrolysis degradation product of TBP, and has been found in virtually all of the waste tanks sampled to date.

There is evidence that concentrations of compounds in the tank C-104 headspace are strongly affected by the use of an exhaustor on tank C-105. The constituents of the tank C-104 are typical of most NPH-rich tank headspaces, except that the alkyl nitrate signature is stronger than typical.

⁵ n-Decane through n-pentadecane were also detected, however, these are principally constituents of the original waste and not waste reaction products.

5.0 SUMMARY

The tank C-104 headspace was sampled in March 1994 for gases and vapors to address flammability and industrial hygiene concerns. Collection and analysis of samples has been reported. It was determined that no headspace constituents exceeded the flammability or industrial hygiene notification limits specified in the current *Vapor Sampling and Analysis Plan* (Homi 1995).

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6.0 REFERENCES

- 29 CFR 1910.120, 1993, "Hazardous Waste Operations and Emergency Response", *Code of Federal Regulations*.
- Anderson, J. D., 1990, *A History of the 200 Area Tank Farms*, WHC-MR-0132, Westinghouse Hanford Company, Richland, Washington.
- Boyles, V. C., 1992, *Single-Shell Tank Leak Stabilization Record*, WHC-RE-TI-178 Rev. 3, Westinghouse Hanford Company, Richland, Washington.
- Boyles, V. C., 1994, *Operating Specifications for Single Shell Waste Storage Tanks*, OSD-T-151-00013 Rev. D-4, Westinghouse Hanford Company, Richland, Washington.
- Burnum, S. T., 1995, *Qualification of Reported WHC Vapor Program Data*, (letter 95-CHD-065 to president, Westinghouse Hanford Company, August 18), Department of Energy, Richland Operations Office, Richland, Washington.
- Cashdollar, K. L., M. Hertzberg, I. A. Zlochower, C. E. Lucci, G. M. Green, and R. A. Thomas, 1992, *Laboratory Flammability Studies of Mixtures of Hydrogen, Nitrous Oxide, and Air*, WHC-SD-WM-ES-219 Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Dougherty, L. F., 1995, *Single Shell Tank Interim Operational Safety Requirements*, WHC-SD-WM-OSR-005 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.
- EPA 1992, *Test Methods for Evaluating Solid Waste*, SW-846 Rev. 1, U.S. Environmental Protection Agency, Washington, D.C.
- Goheen, S. C., 1994, *Untitled*, (Letter to Jerry Osborne, Westinghouse Hanford Company, September 1), Pacific Northwest Laboratories, Richland, Washington.
- Hall, J. C., 1972, *Liquid Organic Waste Collection and Disposal*, ARH-2424, Atlantic Richfield Hanford Company, Richland, Washington.
- Hanlon, B. M., 1995, *Waste Tank Summary for Month Ending December 31, 1994*, WHC-EP-0182-81, Westinghouse Hanford Company, Richland, Washington.
- Hendrickson, R. W., 1995, *Tank Vapor Characterization Oak Ridge National Laboratories Quality Assurance Assessment*, TWRSQA-95-0012, Westinghouse Hanford Company, Richland, Washington.
- Homi, C. S., 1995, *Vapor Sampling and Analysis Plan*, WHC-SD-WM-TP-335 Rev. 0G, Westinghouse Hanford Company, Richland, Washington.
- Huckaby, J. L., H. Babad, and D. R. Bratzel, 1995, *Headspace Gas and Vapor Characterization Summary for the 43 Vapor Program Suspect Tanks*, WHC-SD-WM-ER-514 Rev. 0, Westinghouse Hanford Company, Richland, Washington.

- Huckaby, J. L., and Bratzel, 1995a, *Tank 241-C-105*, WHC-SD-WM-ER-443 Rev. 1, Westinghouse Hanford Company, Richland, Washington.
- Huckaby, J. L., and Bratzel, 1995b, *Tank 241-C-106*, WHC-SD-WM-ER-444 Rev. 1, 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., 1995a, *Untitled*, (Letter 090195A to D. Bratzel, September 1), Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- Jenkins, R. A., 1995b, *Untitled*, (Letter 091495A to D. Bratzel, September 14), 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, 1994, *Analysis of Tank 241-C-104 Headspace Components*, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- Jenkins, R. A., A. B. Dindal, C. Y. Ma, M. A. Palausky, J. T. Skeen, and C. K. Bayne, 1995, *Analysis of Tank 241-TY-104 Headspace Components*, ORNL-CASD-FR-241TY104.95 Rev. 1, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- Keller, K. K., 1994, *Quality Assurance Project Plan for Tank Vapor Characterization*, WHC-SD-WM-QAPP-013 Rev. 2, Westinghouse Hanford Company, Richland, Washington.
- 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-10594 UC-606, Pacific Northwest Laboratory, Richland, Washington.
- Ligothke, M.W., K.H. Pool, T.W. Clauss, B.D. McVeety, G.S. Klinger, K.B. Olsen, O.P. Bredt, J.S. Fruchter, and S.C. Goheen, 1995b, *Vapor Space Characterization of Waste Tank 241-U-103: Results from Samples Collected on 2/15/95*, PNL-10813 UC-606, Pacific Northwest Laboratory, Richland, Washington.
- Ligothke, M. W. 1995, *PNL Vapor Project Analytical Holding Times*, (Letter to D. R. Bratzel, September 23), Pacific Northwest Laboratory, Richland, Washington.
- Lucke, R. B., B. D. McVeety, T. W. Clauss, K. H. Pool, J. S. Young, M. McCulloch, M. W. Ligothke, J. S. Fruchter, and S. C. Goheen, 1995a, *Vapor Space Characterization of Waste Tank 241-C-104: Results from Samples Collected Through the Vapor Sampling System on 3/3/94*, PNL-10499 UC-606, Pacific Northwest Laboratory, Richland, Washington.
- Lucke, R. B., M. W. Ligothke, K. H. Pool, T. W. Clauss, A. K. Sharma, B. D. McVeety, M. McCulloch, J. S. Fruchter, and S. C. Goheen, 1995b, *Vapor Space Characterization of Waste Tank 241-C-108: Results from Samples Collected Through the Vapor Sampling System on 8/5/94*, PNL-10351 UC-606, 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-10495 UC-606, Pacific Northwest Laboratory, Richland, Washington.
- Meacham, J.E., H. Babad, R.J. Cash, G.T. Dukelow, S.J. Eberlein, D.W. Hamilton, G.D. Johnson, J.W. Osborne, M.A. Payne, D.J. Sherwood, D.A. Turner, and J.L. Huckaby, 1995, *Approach for Tank Safety Characterization of Hanford Site Waste*, WHC-EP-0843 Rev.0, UC-2070, Westinghouse Hanford Company, Richland, Washington.
- NFPA 1992, *Standard on Explosion Prevention Systems*, NFPA 69, National Fire Protection Association, Quincy, Massachusetts.
- 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., 1994a, *Air Samples Collected at Waste Tanks 241-C-104, -105, and -106 on March 3 and February 15 and 16, 1994*, 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-104 Using the Vapor Sampling System*, WHC-SD-WM-RPT-127, Westinghouse Hanford Company, Richland, Washington.

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Table 2-1
Tank C-104 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	0.5	Organic vapors	7 tank air samples
		10	Organic vapors	3 tank air samples + 1 trip blank
Oregon Graduate Institute of Science and Technology	SUMMA™ canister	6.0	Hydrogen, Nitrous Oxide, Carbon Monoxide, Organic vapors	3 tank air samples, 6 ambient air samples
Pacific Northwest Laboratories	Acidified Carbon Sorbent Trap	3.0	Ammonia	6 tank air samples + 1 trip blank
	Triethanolamine Sorbent Trap	3.0	Nitrogen Dioxide	6 tank air samples + 1 trip blank
	Oxidation Bed + Triethanolamine Sorbent Trap	3.0	Nitric Oxide	6 tank air samples + 1 trip blank
	Treated Carbon Bead Sorbent Trap	3.0	Oxides of Sulfur	3 tank air samples
	Silica Gel Sorbent Trap	3.0	Water vapor	5 tank air samples + 1 trip blanks
	OSHA Versatile Sampler	3.0	Semivolatile organic vapors	3 tank air samples + 3 trip blanks + 3 spiked blanks
	SUMMA™ canister	6.0	Organic vapors	3 tank air samples
WHC 222-S Laboratory	Silica Gel Sorbent Trap	3.0	Tritium-Substituted Water Vapor	1 tank air sample

Table 3-1
Tank C-104 Inorganic Gas and Vapor Concentrations –
Analyses by Oregon Graduate Institute of Science and Technology and by Pacific Northwest Laboratory

Compound	CAS ¹ Number	Sample Type	Number of Samples	Average ² (ppmv)	Standard Deviation ² (ppmv)	RSD ^{2,3} (%)
Ammonia, NH ₃	7664-41-7	Sorbent Trap	6	44	< 1	--
Carbon Monoxide, CO	630-08-0	SUMMA™	3	[2]	[< 1]	[-]
Hydrogen, H ₂	1333-74-0	SUMMA™	3	[68]	[8.0]	[12]
Nitric Oxide, NO	10102-43-9	Sorbent Trap	6	0.37	0.05	14
Nitrogen Dioxide, NO ₂	10102-44-0	Sorbent Trap	6	≤ 0.02	--	--
Nitrous Oxide, N ₂ O	10024-97-2	SUMMA™	3	[64]	[2.6]	[4]
Sulfur Oxides, SO _x		Sorbent Trap	3	0.4	0.2	50
Water Vapor, H ₂ O	7732-18-5	Sorbent Trap	5	17,800 (12.9 mg/L)	750 (0.5 mg/L)	4

1 CAS = Chemical Abstracts Service.

2 Bracketed values are from OGIST and should be considered secondary results, non-bracketed values are from PNL and should be considered primary results.

3 RSD = relative standard deviation. Burnum (1995) specifies the RSD should be less than 25 %.

Table 3-2
Comparison of Tank C-104, C-105, and C-106 Headspace Constituents --
Inorganic Compound Analyses by Pacific Northwest Laboratory and
Oregon Graduate Institute of Science and Technology,
and Organic Compound Analyses by Oak Ridge National Laboratory¹

Tank:	C-104	C-105 ²	C-106 ³
Date sampled, (mo/day/yr)	3/3/94	2/16/94	2/15/94
Headspace temperature, (°C)	28	17	19
Ammonia, (ppmv)	44	2.4	≤ 9
Hydrogen, (ppmv)	[68]	[22]	[9.7]
Carbon monoxide, (ppmv)	[2]	[0.29]	[0.25]
Nitric oxide, (ppmv)	0.37	≤ 0.1	≤ 0.1
Nitrogen dioxide, (ppmv)	≤ 0.02	≤ 0.1	≤ 0.1
Nitrous oxide, (ppmv)	[64]	[5.3]	[3.7]
Water vapor, (mg/m ³)	12.9	6.8	17.8
Water vapor, (% relative humidity)	47	47	109
Ethanenitrile (acetonitrile), (ppmv)	(0.13)	(0.026)	(0.0023)
Propanone (acetone), (ppmv)	(0.15)	(0.014)	(0.00018)
1-Butanol, (ppmv)	(2.90)	(0.17)	(0.011)
n-Dodecane, (ppmv)	(0.072)	(0.016)	(0.0036)
n-Tridecane, (ppmv)	(0.079)	(0.019)	(0.0087)
Total nonmethane organic carbon, (mg/m ³)	[28.1]	[1.5]	[0.41]

¹ OGIST results are given in brackets to indicate the data should be considered secondary results. Organic vapor results are from ORNL, with non-quantitative values in parentheses and quantitative values not in parentheses.

² Data are from Huckaby and Bratzel 1995a.

³ Data are from Huckaby and Bratzel 1995b.

Table 4-1
Tank C-104 Quantitatively Measured Compounds in PNL SUMMA™ and OVS Samples --
Analyses by Pacific Northwest Laboratory

Cmpd #	Compound	CAS ¹ Number	Average (ppmv)	Standard Deviation (ppmv)	RSD ² (%)
1	Dichlorodifluoromethane ³	75-71-8	0.0016	0.00004	2
2	Chloromethane ³ (methyl chloride)	74-87-3	0.0024	0.0002	8
3	Trichlorofluoromethane ³	75-69-4	0.0089	0.0022	25
4	Methylbenzene (toluene) ⁴	108-88-3	0.0064	--	--
5	n-Undecane ⁵	1120-21-4	< 0.14	--	--
6	n-Dodecane ⁶	112-40-3	0.39	--	--
7	n-Tridecane ⁶	629-50-5	0.52	--	--
8	n-Tetradecane ⁶	629-59-4	0.11	--	--
9	n-Pentadecane ⁵	629-62-9	< 0.11	--	--

1 CAS = Chemical Abstract Service.

2 RSD = relative standard deviation. Burnum (1995) specifies the RSD should be less than 25 %.

3 Results from 3 SUMMA™ samples.

4 Detected in only 1 SUMMA™ sample.

5 Result of 3 OSHA versatile sampler (OVS) samples.

6 Result of 1 OSHA versatile sampler (OVS) sample.

Table 4-2
Tank C-104 Quantitatively Measured Organic Compounds in OGIST SUMMA™ Samples¹

Cmpd #	Compound	CAS ² Number	Average (ppmv)	Standard Deviation (ppmv)	RSD ³ (%)
1	Dichlorodifluoromethane	75-71-8	[0.0008]	[0.0003]	[43]
2	Chloromethane	74-87-3	[0.0028]	[0.0011]	[39]
3	1,3-Butadiene	106-99-0	[0.008]	[0.001]	[17]
4	Trichlorofluoromethane	75-69-4	[0.036]	[0.009]	[25]
5	1,1-Dichloroethene (vinylidene chloride)	75-35-4	[0.0011]	[0.00038]	[35]
6	Dichloromethane (methylene chloride)	75-09-2	[0.0025]	[0.0022]	[94]
7	1,1,2-Trichloro-1,2,2-trifluoroethane ⁴	76-13-1	[0.0003]	--	--
8	Trichloromethane (chloroform) ⁵	67-66-3	[0.00045]	--	--
9	Benzene	71-43-2	[0.0048]	[0.0016]	[33]
10	Toluene	108-88-3	[0.0024]	[0.0009]	[36]
11	Ethyl benzene	100-41-4	[0.00033]	[0.00015]	[46]
12 & 13	1,3-Dimethylbenzene (m-xylene) + 1,4-Dimethylbenzene (p-xylene) ⁶	108-38-3 106-42-3	[0.0008]	[0.0003]	[38]
14	o-Xylene	95-47-6	[0.00033]	[0.00088]	[35]

¹ Because OGIST did not have a WHC-approved quality assurance project plan in place when analyses were conducted, these results should be considered secondary (Burnum 1995).

² CAS = Chemical Abstracts Service.

³ RSD = relative standard deviation. Burnum (1995) specifies the RSD should be less than 25 %.

⁴ Detected in only 1 sample.

⁵ Detected in only 2 samples.

⁶ m-xylene and p-xylene coelute and the reported value represents the sum of their concentrations.

Table 4-3
Tank C-104 Quantitatively Measured Organic Compounds in TST Samples --
Analyses by Oak Ridge National Laboratory¹

Cmpd #	Compound	CAS ² Number	Average ³ (ppmv)	Standard Deviation (ppmv)	RSD ⁴ (%)
1	Benzene	71-43-2	0.0099	0.0034	34

1 Results in this table are quantitative (as defined in Section 4.1).

2. CAS = Chemical Abstract Service.

3 Average of 3, 10-L TST samples.

4. RSD = relative standard deviation. Burnum (1995) specifies the RSD should be less than 25 %.

Table 4-4
Tank C-104 Positively Identified Organic Compounds in TST Samples
Analyses by Oak Ridge National Laboratory¹

Cmpd #	Compound	CAS ² Number	Average ³ (ppmv)	Standard Deviation (ppmv)	RSD ⁴ (%)
1	Ethanenitrile (acetonitrile)	75-05-8	0.13	0.08	61
2	Propanone (acetone)	67-64-1	0.15	0.07	44
3	Propanenitrile	107-12-0	0.041	0.039	94
4	n-Hexane	110-54-3	0.038	0.001	3
5	n-Butanenitrile	109-74-0	0.044	0.002	5
6	n-Heptane	142-82-5	0.015	0.001	9
7	Toluene	108-88-3	0.082	0.001	14
8	n-Pentanenitrile	110-59-8	0.032	0.006	17
9	2-Hexanone	591-78-6	0.015	0.005	31
10	n-Octane	111-65-9	0.013	0.003	22
11	n-Hexanenitrile	628-73-9	0.028	0.006	20
12	2-Heptanone	110-43-0	0.014	0.002	15
13	n-Nonane	111-84-2	0.017	0.003	17
14	n-Heptanenitrile	629-08-3	0.021	0.004	19
15	2-Octanone	111-13-7	0.0075	0.0014	19
16	n-Octanenitrile	124-12-9	0.012	0.003	22
17	n-Nonanenitrile	2243-27-8	0.0072	0.0013	18
18	n-Dodecane	112-70-3	0.072	0.003	4
19	n-Tridecane	629-50-5	0.079	0.009	11

1 Results in this table are not quantitative (as defined in Section 4.1) because measured values in at least 1 of the samples are outside instrument calibration limits.

2 CAS = Chemical Abstract Service.

3 Average of 3, 10-L TST samples.

4 RSD = relative standard deviation. Burnum (1995) specifies the RSD should be less than 25 %.

Table 4-5
Tank C-104 Positively Identified Organic Compounds in TST Samples
for which Practical Holding Times were Exceeded --
Analyses by Oak Ridge National Laboratory¹

Cmpd #	Compound	CAS ² Number	Average ³ (ppmv)	Standard Deviation (ppmv)	RSD ⁴ (%)
1	1-Butanol ⁵	71-36-3	2.90	0.32	11
2	2-Pentanone ⁵	107-87-9	0.012	0.001	8

1 Practical holding times are defined and discussed in Section 4.1.

2 CAS = Chemical Abstract Service.

3 Average of 3, 10-L TST samples.

4 RSD = relative standard deviation. Burnum (1995) specifies the RSD should be less than 25 %.

5 The concentration of this analyte was not quantitatively measured (as defined in Section 4.1), because the measured concentration was outside of the instrumental calibration limits.

Table 4-6
Tank C-104 Tentatively Identified Compounds in PNL SUMMA™ Samples
Analyses by Pacific Northwest Laboratory

Cmpd #	Compound	CAS ¹ Number	Average ² (mg/m ³)	Standard ³ Deviation (mg/m ³)
1	Propene	115-07-1	0.46	0.03
2	Propane	74-98-6	0.33	0.03
3	Cyclopropane ⁴	75-19-4	0.12	—
4	Ethanal (acetaldehyde)	75-07-0	0.26	0.11
5	2-Methyl-1-propene	115-11-7	0.29	0.03
6	n-Butane	106-97-8	0.59	0.06
7	Ethanenitrile (acetonitrile)	75-05-8	0.12	0.01
8	Propanone (acetone)	67-64-1	0.32	0.02
9	n-Pentane	109-66-0	0.26	0.02
10	Butanal	123-72-8	0.47	0.03
11	2-Butanone	78-93-3	0.32	0.01
12	1-Hexene	592-41-6	0.13	0.01
13	Tetrahydrofuran	109-99-9	0.15	0.01
14	1-Butanol	71-36-3	2.45	0.29
15	Pentanal	110-62-3	0.14	0.02
16	n-Heptane	142-82-5	0.31	0.04
17	n-Octane	111-65-9	0.21	0.01
18	3-Heptanone	106-35-4	0.41	0.05
19	n-Nonane ⁵	111-84-2	0.10	—
20	n-Decane	124-18-5	0.95	0.06
21	n-Undecane	1120-21-4	4.88	0.23
22	n-Dodecane	112-40-3	6.47	0.14
23	Unknown C11 Ketone ³		0.10	—
24	Unknown Alkane		0.11	0.01
25	n-Tridecane	629-50-5	6.22	0.13
26	n-Tetradecane	629-59-4	0.96	0.08

Sum of tentatively identified compounds:

27.13

1 CAS = Chemical Abstract Service.

2 Average of 3 samples, presented values are estimates.

3 When the analyte was detected in only 2 samples, the entry is the relative difference (i.e., their difference divided by 2).

4 Detected in only 2 samples.

5 Detected in only 1 sample.

Table 4-7
Tank C-104 Tentatively Identified Organic Compounds in TST Samples
in Order of Chromatographic Elution --
Analyses by Oak Ridge National Laboratory

Cmpd #	Compound	CAS ¹ Number	Average ³ (mg/m ³)	Standard Deviation (mg/m ³)
1	Carbon Dioxide	124-38-9	0.170	0.0554
2	Carbon Dioxide	124-38-9	1.703	0.8112
3	Carbon Dioxide ²	124-38-9	0.580	---
4	Propene	115-07-1	0.764	0.1356
5	Propene	115-07-1	0.100	0.0460
6	Cyclopropane ²	115-07-1	0.024	---
7	1-Propene, 2-methyl-	115-11-7	0.876	0.0604
8	n-Butane	106-97-8	1.061	0.0705
9	2-Butene (trans) ²	624-64-6	0.042	---
10	Methylcyclopropane	594-11-6	0.115	0.0138
11	2-Butene (cis) ²	590-18-1	0.038	---
12	1-Pentene	109-67-1	0.412	0.0592
13	n-Butane ²	106-97-8	0.046	---
14	n-Pentane	109-66-0	1.098	0.1476
15	Unknown ²		0.056	---
16	Fluoroethylene ²	75-02-5	0.052	---
17	1-Hexene	592-41-6	0.273	0.0497
18	3-Buten-2-one ²	78-94-4	0.037	---
19	Butanal ²	123-72-8	0.140	---
20	2-Butanone	78-93-3	0.282	0.0198
21	C6-Alkene ²		0.030	---
22	Acetic acid, ethyl ester ²	141-78-6	0.158	---
23	Acetic Acid ²	64-19-7	0.074	---
24	Nitric acid, ethyl ester ²	625-58-1	0.052	---
25	n-Pentane and others ²		0.338	---
26	Tetrahydrofuran ²	109-99-9	0.210	---

Cmpd #	Compound	CAS ¹ Number	Average ³ (mg/m ³)	Standard Deviation (mg/m ³)
27	1-Butanol ²	71-36-3	0.029	---
28	Acetic Acid	64-19-7	0.624	0.2237
29	1-Octene	111-66-0	0.043	0.0121
30	Hexanal ²	66-25-1	0.049	---
31	Acetic acid, butyl ester	123-86-4	0.106	0.0334
32	Nitric acid, butyl ester	928-45-0	0.069	0.0578
33	Pyridine, 2-methyl ²	109-06-8	0.020	---
34	1-Hexanol	111-27-3	0.009	0.0020
35	3-Heptanone	106-35-4	0.182	0.0590
36	Pyridine, 3-methyl and 4-methyl ²		0.013	---
37	Pyridine, 2,6-dimethyl ²	108-48-5	0.004	---
38	1-Octene, 7-methyl	13151-06-9	0.014	0.0032
39	2 (3H)-Furanone, dihydro-	96-48-0	0.090	0.0298
40	C8-Alkanone		0.033	0.0090
41	Pyridine, 2,5-dimethyl-	589-93-5	0.089	0.0452
42	Alkyl amide		0.054	0.0250
43	C9-Alkane		0.019	0.0052
44	Cyclotetrasiloxane, octamethyl	556-67-2	0.018	0.0203
45	n-Decane	124-18-5	0.183	0.0531
46	Hexanenitrile and others ²		0.015	---
47	C3-Pyridine and others ²		0.002	---
48	1-Hexanol, 2-ethyl-	104-76-7	0.022	0.0084
49	Pyridine, 5-ethyl-2-methyl ²	104-90-5	0.005	---
50	Alkyl amide		0.024	0.0106
51	n-Undecane	1120-21-4	0.902	1.1760
52	Alkane ²		0.009	---
53	C13-Alkane		0.051	0.0048
54	Alkane ²		0.004	---

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Cmpd #	Compound	CAS ¹ Number	Average ³ (mg/m ³)	Standard Deviation (mg/m ³)
55	3-Undecanone ²	2216-87-7	0.005	---
56	Alkane ²		0.002	---
57	Undecane, 5-ethyl- ²	17453-94-0	0.008	---
58	Tridecane, 6-methyl-	13287-21-3	0.010	0.0072
59	Alkane and Alkyl-decahydronaphthalene ²		0.002	---
60	C14-Alkene ²		0.004	---
61	Cyclohexane, hexyl- ²	4292-75-5	0.006	---
62	Mixture ²		0.004	---
63	Cyclohexane, undecyl- and others ²		0.006	---
64	C14-Alkanone		0.238	0.0251
65	C15-Alkane		0.007	0.0012
66	Alkane		0.015	0.0017
67	Alkane + Others		0.020	0.0017
68	n-Hexadecane	544-76-3	0.090	0.0062
69	Alkane		0.011	0.0014
70	C14-Alkane		0.216	0.0287
71	2(3H)-Furanone, dihydro-5-propyl- ²	105-21-5	0.002	---
72	2(3H)-Furanone, 5-hexyldihydro- ²	706-14-9	0.002	---
73	C14-Alkanone		0.131	0.0150
74	C14-Alkane		0.035	0.0010
75	Thiophene, 2-methoxy-5-methyl-	31053-55-1	0.023	0.0002
76	Alkane + Others		0.029	0.0016
77	Phenol, 2,6-bis(1,1-dimethylethyl)-4-methyl-	128-37-0	0.010	0.0106
78	C4-Dihydronaphthalene ²		0.003	---
79	Alkane ²		0.002	---
80	Undecane, 5-methyl- ²	1632-70-8	0.002	---
81	C16-Alkane		0.006	0.0009
82	Pyrazine, 2,5-dimethyl 3-(3-methylbutyl)- ²	18433-98-2	0.003	---

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Cmpd #	Compound	CAS ¹ Number	Average ³ (mg/m ³)	Standard Deviation (mg/m ³)
83	Alkanol		0.004	0.0001
84	Alkane		0.011	0.0014
85	C15-Alkane		0.106	0.0029
86	Mixture ²		0.004	---
87	n-Hexadecane	544-76-3	0.061	0.0048
88	3-Dodecanone ²	1534-27-6	0.031	---
89	C-14-Alkanone		0.055	0.0114
90	C-14-Alkanone		0.043	0.0108
91	Alkanol ²		0.001	---
92	Dibutyl butyl phosphate	78-46-6	0.066	0.0236
93	C14-Alkanone ²		0.008	---
94	2-Pentene, 5-(pentyloxy)-, (E)- ²	56052-85-8	0.008	---
95	Dodecane, 4,9-dipropyl- ²	3054-63-5	0.002	---
96	Benzene, (1-butylheptyl)- ²	4537-15-9	0.002	---
97	Tributyl phosphate (TBP)	126-73-8	0.272	0.0573
98	Mixture ²		0.002	---
99	(+)-(1R,4R,5R)-2-(10)-Pinen-4-ol ²		0.002	---
100	Alkanol ²		0.008	---
101	Undecane, 3-methyl- ²	1002-43-3	0.004	---
102	2-Decanone, 5,9-dimethyl- ²	33933-82-3	0.008	---
103	5-Tetradecene, (E)- ²	41446-66-6	0.012	---
104	Mixture ²		0.005	---
105	Methylamine, N-(1-methylhexylidene) ²	22058-71-5	0.004	---
106	Butyl myristate (Butyl tetradecylate) ²	110-36-1	0.007	---
107	1-Dodecanol ²	112-53-8	0.003	---
108	n-Heptadecane	629-78-7	0.019	0.0022
109	Alkyl dihydrofuranone ²		0.006	---
110	Oxirane, 2-methyl-2-pentyl- ²	53907-75-8	0.005	---

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Cmpd #	Compound	CAS ¹ Number	Average ³ (mg/m ³)	Standard Deviation (mg/m ³)
111	Tributyl phosphate ²	126-73-8	0.008	---
112	Mixture ²		0.004	---
113	Benzene, (1-methyldecyl)-	4536-88-3	0.004	0.0011
114	Undecane, 3-methyl- ²	1002-43-3	0.002	---
115	Benzene, (1-pentylheptyl)- ²	2719-62-2	0.002	---
116	Nonane, 5-butyl- ²	17312-63-9	0.001	---
117	Benzene, (1-propylnonyl)- ²	2719-64-4	0.002	---
118	Nonane, 5-propyl- ²	998-35-6	0.001	---
119	Alkane		0.005	0.0007
120	Butyl myristate (butyl tetradecylate)	110-36-1	0.009	0.0073
121	n-Octadecane	593-45-3	0.005	0.0039
122	2(3H)-Furanone, dihydro-5-propyl- ²	105-21-5	0.001	---
123	Isopropyl myristate ²	110-27-0	0.002	---
124	Benzene, (1-methylundecyl)- ²	2719-61-1	0.002	---
125	Butyl myristate (butyl tetradecylate) ²	110-36-1	0.004	---
126	Alkane ²		0.002	---
127	1,2-Benzenedicarboxylic acid, dibutyl ester ²	84-74-2	0.002	---
128	1,2-Benzenedicarboxylic acid, butyl-ethylhexyl ester ²	85-69-8	0.003	---
129	Alkane ²		0.002	---
Sum of tentatively identified compounds:			13.13	

1. CAS = Chemical Abstract Service

2. Detected in only 1 sample.

3. Average of 3, 10-L TST samples; presented values are estimates.

Table 4-8
Tank C-104 Tentatively Identified Organic Compounds in TST Samples
Sorted Alphanumerically --
Analyses by Oak Ridge National Laboratory

Cmpd #	Compound	CAS ¹ Number	Average ³ (mg/m ³)	Standard Deviation (mg/m ³)
99	(+)-(1R,4R,5R)-2-(10)-Pinen-4-ol ²		0.002	---
38	1-Octene, 7-methyl-	13151-06-9	0.014	0.0032
12	1-Pentene	109-67-1	0.412	0.0592
29	1-Octene	111-66-0	0.043	0.0121
107	1-Dodecanol ²	112-53-8	0.003	---
34	1-Hexanol	111-27-3	0.009	0.0020
7	1-Propene, 2-methyl-	115-11-7	0.876	0.0604
27	1-Butanol ²	71-36-3	0.029	---
48	1-Hexanol, 2-ethyl-	104-76-7	0.022	0.0084
17	1-Hexene	592-41-6	0.273	0.0497
127	1,2-Benzenedicarboxylic acid, dibutyl ester ²	84-74-2	0.002	---
128	1,2-Benzenedicarboxylic acid, butyl-ethylhexyl ester ²	85-69-8	0.003	---
20	2-Butanone	78-93-3	0.282	0.0198
11	2-Butene (cis) ²	590-18-1	0.038	---
39	2 (3H)-Furanone, dihydro-	96-48-0	0.090	0.0298
102	2-Decanone, 5,9-dimethyl- ²	33933-82-3	0.008	---
9	2-Butene (trans) ²	624-64-6	0.042	---
94	2-Pentene, 5-(pentyloxy)-, (E)- ²	56052-85-8	0.008	---
122	2(3H)-Furanone, dihydro-5-propyl- ²	105-21-5	0.001	---
72	2(3H)-Furanone, 5-hexyldihydro- ²	706-14-9	0.002	---
71	2(3H)-Furanone, dihydro-5-propyl ²	105-21-5	0.002	---
55	3-Undecanone ²	2216-87-7	0.005	---
18	3-Buten-2-one ²	78-94-4	0.037	---
88	3-Dodecanone ²	1534-27-6	0.031	---

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Cmpd #	Compound	CAS ¹ Number	Average ³ (mg/m ³)	Standard Deviation (mg/m ³)
35	3-Heptanone	106-35-4	0.182	0.0590
103	5-Tetradecene, (E)- ²	41446-66-6	0.012	---
22	Acetic acid, ethyl ester ²	141-78-6	0.158	---
23	Acetic Acid ²	64-19-7	0.074	---
28	Acetic Acid	64-19-7	0.624	0.2237
31	Acetic acid, butyl ester	123-86-4	0.106	0.0334
59	Alkane and Alkyl-decahydronaphthalene ²		0.002	---
66	Alkane		0.015	0.0017
67	Alkane + Others		0.020	0.0017
69	Alkane		0.011	0.0014
76	Alkane + Others		0.029	0.0016
84	Alkane		0.011	0.0014
119	Alkane		0.005	0.0007
126	Alkane ²		0.002	---
79	Alkane ²		0.002	---
129	Alkane ²		0.002	---
52	Alkane ²		0.009	---
54	Alkane ²		0.004	---
56	Alkane ²		0.002	---
83	Alkanol		0.004	0.0001
100	Alkanol ²		0.008	---
91	Alkanol ²		0.001	---
42	Alkyl amide		0.054	0.0250
50	Alkyl amide		0.024	0.0106
109	Alkyl dihydrofuranone ²		0.006	---
96	Benzene, (1-butylheptyl)- ²	4537-15-9	0.002	---
113	Benzene, (1-methyldecyl)-	4536-88-3	0.004	0.0011
115	Benzene, (1-pentylheptyl)- ²	2719-62-2	0.002	---

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Cmpd #	Compound	CAS ¹ Number	Average ³ (mg/m ³)	Standard Deviation (mg/m ³)
117	Benzene, (1-propylnonyl)- ²	2719-64-4	0.002	---
124	Benzene, (1-methylundecyl)- ²	2719-61-1	0.002	---
19	Butanal ²	123-72-8	0.140	---
106	Butyl myristate (Butyl tetradecylate) ²	110-36-1	0.007	---
120	Butyl myristate (butyl tetradecylate)	110-36-1	0.009	0.0073
125	Butyl myristate (butyl tetradecylate) ²	110-36-1	0.004	---
89	C-14-Alkanone		0.055	0.0114
90	C-14-Alkanone		0.043	0.0108
53	C13-Alkane		0.051	0.0048
60	C14-Alkene ²		0.004	---
70	C14-Alkane		0.216	0.0287
64	C14-Alkanone		0.238	0.0251
93	C14-Alkanone ²		0.008	---
73	C14-Alkanone		0.131	0.0150
74	C14-Alkane		0.035	0.0010
85	C15-Alkane		0.106	0.0029
65	C15-Alkane		0.007	0.0012
81	C16-Alkane		0.006	0.0009
47	C3-Pyridine and others ²		0.002	---
78	C4-Dihydronaphthalene ²		0.003	---
21	C6-Alkene ²		0.030	---
40	C8-Alkanone		0.033	0.0090
43	C9-Alkane		0.019	0.0052
1	Carbon Dioxide	124-38-9	0.170	0.0554
2	Carbon Dioxide	124-38-9	1.703	0.8112
3	Carbon Dioxide ²	124-38-9	0.580	---
61	Cyclohexane, hexyl- ²	4292-75-5	0.006	---
63	Cyclohexane, undecyl- and others ²		0.006	---

Cmpd #	Compound	CAS ¹ Number	Average ³ (mg/m ³)	Standard Deviation (mg/m ³)
6	Cyclopropane ²	115-07-1	0.024	---
44	Cyclotetrasiloxane, octamethyl	556-67-2	0.018	0.0203
92	Dibutyl butyl phosphate	78-46-6	0.066	0.0236
95	Dodecane, 4,9-dipropyl- ²	3054-63-5	0.002	---
16	Fluoroethylene ²	75-02-5	0.052	---
30	Hexanal ²	66-25-1	0.049	---
46	Hexanenitrile and others ²		0.015	---
123	Isopropyl myristate ²	110-27-0	0.002	---
105	Methylamine, N-(1-methylhexylidene) ²	22058-71-5	0.004	---
10	Methylcyclopropane	594-11-6	0.115	0.0138
86	Mixture ²		0.004	---
62	Mixture ²		0.004	---
112	Mixture ²		0.004	---
98	Mixture ²		0.002	---
104	Mixture ²		0.005	---
8	n-Butane	106-97-8	1.061	0.0705
13	n-Butane ²	106-97-8	0.046	---
45	n-Decane	124-18-5	0.183	0.0531
108	n-Heptadecane	629-78-7	0.019	0.0022
68	n-Hexadecane	544-76-3	0.090	0.0062
87	n-Hexadecane	544-76-3	0.061	0.0048
121	n-Octadecane	593-45-3	0.005	0.0039
14	n-Pentane	109-66-0	1.098	0.1476
25	n-Pentane and others ²		0.338	---
51	n-Undecane	1120-21-4	0.902	1.1760
24	Nitric acid, ethyl ester ²	625-58-1	0.052	---
32	Nitric acid, butyl ester	928-45-0	0.069	0.0578
116	Nonane, 5-butyl- ²	17312-63-9	0.001	---

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Cmpd #	Compound	CAS ¹ Number	Average ³ (mg/m ³)	Standard Deviation (mg/m ³)
118	Nonane, 5-propyl- ²	998-35-6	0.001	---
110	Oxirane, 2-methyl-2-pentyl- ²	53907-75-8	0.005	---
77	Phenol, 2,6-bis(1,1-dimethylethyl)-4-methyl-	128-37-0	0.010	0.0106
4	Propene	115-07-1	0.764	0.1356
5	Propene	115-07-1	0.100	0.0460
82	Pyrazine, 2,5-dimethyl 3-(3-methylbutyl)- ²	18433-98-2	0.003	---
33	Pyridine, 2-methyl- ²	109-06-8	0.020	---
36	Pyridine, 3-methyl- and 4-methyl ²		0.013	---
37	Pyridine, 2,6-dimethyl- ²	108-48-5	0.004	---
41	Pyridine, 2,5-dimethyl-	589-93-5	0.089	0.0452
49	Pyridine, 5-ethyl-2-methyl- ²	104-90-5	0.005	---
26	Tetrahydrofuran ²	109-99-9	0.210	---
75	Thiophene, 2-methoxy-5-methyl-	31053-55-1	0.023	0.0002
97	Tributyl phosphate (TBP)	126-73-8	0.272	0.0573
111	Tributyl phosphate ²	126-73-8	0.008	---
58	Tridecane, 6-methyl-	13287-21-3	0.010	0.0072
57	Undecane, 5-ethyl- ²	17453-94-0	0.008	---
80	Undecane, 5-methyl- ²	1632-70-8	0.002	---
101	Undecane, 3-methyl- ²	1002-43-3	0.004	---
114	Undecane, 3-methyl- ²	1002-43-3	0.002	---
15	Unknown ²		0.056	---
Sum of tentatively identified compounds:			13.13	

1. CAS = Chemical Abstract Service

2. Detected in only 1 sample.

3. Average of 3, 10-L TST samples; values presented are estimates.

Table 4-9
Tank C-104 Tentatively Identified Organic Compounds in TST Samples
Sorted by Estimated Concentration --
Analyses by Oak Ridge National Laboratory

Cmpd #	Compound	CAS ¹ Number	Average ³ (mg/m ³)	Standard Deviation (mg/m ³)
2	Carbon Dioxide	124-38-9	1.703	0.8112
14	n-Pentane	109-66-0	1.098	0.1476
8	n-Butane	106-97-8	1.061	0.0705
51	n-Undecane	1120-21-4	0.902	1.1760
7	1-Propene, 2-methyl-	115-11-7	0.876	0.0604
4	Propene	115-07-1	0.764	0.1356
28	Acetic Acid	64-19-7	0.624	0.2237
3	Carbon Dioxide ²	124-38-9	0.580	---
12	1-Pentene	109-67-1	0.412	0.0592
25	n-Pentane and others ²		0.338	---
20	2-Butanone	78-93-3	0.282	0.0198
17	1-Hexene	592-41-6	0.273	0.0497
97	Tributyl phosphate (TBP)	126-73-8	0.272	0.0573
64	C14-Alkanone		0.238	0.0251
70	C14-Alkane		0.216	0.0287
26	Tetrahydrofuran ²	109-99-9	0.210	---
45	n-Decane	124-18-5	0.183	0.0531
35	3-Heptanone	106-35-4	0.182	0.0590
1	Carbon Dioxide	124-38-9	0.170	0.0554
22	Acetic acid, ethyl ester ²	141-78-6	0.158	---
19	Butanal ²	123-72-8	0.140	---
73	C14-Alkanone		0.131	0.0150
10	Methylcyclopropane	594-11-6	0.115	0.0138
31	Acetic acid, butyl ester	123-86-4	0.106	0.0334
85	C15-Alkane		0.106	0.0029
5	Propene	115-07-1	0.100	0.0460

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Cmpd #	Compound	CAS ¹ Number	Average ³ (mg/m ³)	Standard Deviation (mg/m ³)
39	2 (3H)-Furanone, dihydro-	96-48-0	0.090	0.0298
68	n-Hexadecane	544-76-3	0.090	0.0062
41	Pyridine, 2,5-dimethyl-	589-93-5	0.089	0.0452
23	Acetic Acid ²	64-19-7	0.074	---
32	Nitric acid, butyl ester	928-45-0	0.069	0.0578
92	Dibutyl butyl phosphate	78-46-6	0.066	0.0236
87	n-Hexadecane	544-76-3	0.061	0.0048
15	Unknown ²		0.056	---
89	C-14-Alkanone		0.055	0.0114
42	Alkyl amide		0.054	0.0250
16	Fluoroethylene ²	75-02-5	0.052	---
24	Nitric acid, ethyl ester ²	625-58-1	0.052	---
53	C13-Alkane		0.051	0.0048
30	Hexanal ²	66-25-1	0.049	---
13	n-Butane ²	106-97-8	0.046	---
90	C-14-Alkanone		0.043	0.0108
29	1-Octene	111-66-0	0.043	0.0121
9	2-Butene (trans) ²	624-64-6	0.042	---
11	2-Butene (cis) ²	590-18-1	0.038	---
18	3-Buten-2-one ²	78-94-4	0.037	---
74	C14-Alkane		0.035	0.0010
40	C8-Alkanone		0.033	0.0090
88	3-Dodecanone ²	1534-27-6	0.031	---
21	C6-Alkene ²		0.030	---
76	Alkane + Others		0.029	0.0016
27	1-Butanol ²	71-36-3	0.029	---
50	Alkyl amide		0.024	0.0106
6	Cyclopropane ²	115-07-1	0.024	---

Cmpd #	Compound	CAS ¹ Number	Average ³ (mg/m ³)	Standard Deviation (mg/m ³)
75	Thiophene, 2-methoxy-5-methyl-	31053-55-1	0.023	0.0002
48	1-Hexanol, 2-ethyl-	104-76-7	0.022	0.0084
33	Pyridine, 2-methyl ²	109-06-8	0.020	---
67	Alkane + Others		0.020	0.0017
108	n-Heptadecane	629-78-7	0.019	0.0022
43	C9-Alkane		0.019	0.0052
44	Cyclotetrasiloxane, octamethyl-	556-67-2	0.018	0.0203
46	Hexanenitrile and others ²		0.015	---
66	Alkane		0.015	0.0017
38	1-Octene, 7-methyl-	13151-06-9	0.014	0.0032
36	Pyridine, 3-methyl- and 4-methyl ²		0.013	---
103	5-Tetradecene, (E)- ²	41446-66-6	0.012	---
84	Alkane		0.011	0.0014
69	Alkane		0.011	0.0014
77	Phenol, 2,6-bis(1,1-dimethylethyl)-4-methyl-	128-37-0	0.010	0.0106
58	Tridecane, 6-methyl-	13287-21-3	0.010	0.0072
52	Alkane ²		0.009	---
34	1-Hexanol	111-27-3	0.009	0.0020
111	Tributyl phosphate ²	126-73-8	0.008	---
57	Undecane, 5-ethyl- ²	17453-94-0	0.008	---
102	2-Decanone, 5,9-dimethyl- ²	33933-82-3	0.008	---
100	Alkanol ²		0.008	---
93	C14-Alkanone ²		0.008	---
94	2-Pentene, 5-(pentyloxy)-, (E)- ²	56052-85-8	0.008	---
120	Butyl myristate (butyl tetradecylate)	110-36-1	0.009	0.0073
106	Butyl myristate (Butyl tetradecylate) ²	110-36-1	0.007	---
65	C15-Alkane		0.007	0.0012

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Cmpd #	Compound	CAS ¹ Number	Average ³ (mg/m ³)	Standard Deviation (mg/m ³)
63	Cyclohexane, undecyl- and others ²		0.006	---
81	C16-Alkane		0.006	0.0009
61	Cyclohexane, hexyl- ²	4292-75-5	0.006	---
109	Alkyl dihydrofuranone ²		0.006	---
104	Mixture ²		0.005	---
49	Pyridine, 5-ethyl-2-methyl- ²	104-90-5	0.005	---
119	Alkane		0.005	0.0007
110	Oxirane, 2-methyl-2-pentyl- ²	53907-75-8	0.005	---
55	3-Undecanone ²	2216-87-7	0.005	---
121	n-Octadecane	593-45-3	0.005	0.0039
37	Pyridine, 2,6-dimethyl- ²	108-48-5	0.004	---
86	Mixture ²		0.004	---
60	C14-Alkene ²		0.004	---
83	Alkanol		0.004	0.0001
62	Mixture ²		0.004	---
54	Alkane ²		0.004	---
113	Benzene, (1-methyldecyl)-	4536-88-3	0.004	0.0011
112	Mixture ²		0.004	---
105	Methylamine, N-(1-methylhexylidene) ²	22058-71-5	0.004	---
101	Undecane, 3-methyl- ²	1002-43-3	0.004	---
78	C4-Dihydronaphthalene ²		0.003	---
128	1,2-Benzenedicarboxylic acid, butyl-ethylhexyl ester ²	85-69-8	0.003	---
82	Pyrazine, 2,5-dimethyl 3-(3-methylbutyl)- ²	18433-98-2	0.003	---
107	1-Dodecanol ²	112-53-8	0.003	---
80	Undecane, 5-methyl- ²	1632-70-8	0.002	---
95	Dodecane, 4,9-dipropyl- ²	3054-63-5	0.002	---
79	Alkane ²		0.002	---
96	Benzene, (1-butylheptyl)- ²	4537-15-9	0.002	---

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Cmpd #	Compound	CAS ¹ Number	Average ³ (mg/m ³)	Standard Deviation (mg/m ³)
72	2(3H)-Furanone, 5-hexyldihydro- ²	706-14-9	0.002	---
71	2(3H)-Furanone, dihydro-5-propyl- ²	105-21-5	0.002	---
99	(+)-(1R,4R,5R)-2-(10)-Pinen-4-ol ²		0.002	---
98	Mixture ²		0.002	---
114	Undecane, 3-methyl- ²	1002-43-3	0.002	---
115	Benzene, (1-pentylheptyl)- ²	2719-62-2	0.002	---
126	Alkane ²		0.002	---
117	Benzene, (1-propylnonyl)- ²	2719-64-4	0.002	---
124	Benzene, (1-methylundecyl)- ²	2719-61-1	0.002	---
47	C3-Pyridine and others ²		0.002	---
129	Alkane ²		0.002	---
56	Alkane ²		0.002	---
123	Isopropyl myristate ²	110-27-0	0.002	---
122	2(3H)-Furanone, dihydro-5-propyl- ²	105-21-5	0.001	---
118	Nonane, 5-propyl- ²	998-35-6	0.001	---
116	Nonane, 5-butyl- ²	17312-63-9	0.001	---
91	Alkanol ²		0.001	---
59	Alkane and Alkyl-decahydronaphthalene ²		0.002	---
125	Butyl myristate (butyl tetradecylate) ²	110-36-1	0.004	---
127	1,2-Benzenedicarboxylic acid, dibutyl ester ²	84-74-2	0.002	---
Sum of tentatively identified compounds:			13.13	

1. CAS = Chemical Abstract Service

2. Detected in only 1 sample.

3. Average of 3, 10-L TST samples; values presented are estimates.

Table 4-10
Tank C-104 Tentatively Identified Compounds in OGIST SUMMA™ Samples

Cmpd #	Compound	CAS ³ Number	Sample Number ¹		
			1	2	3
1	Propene	115-07-1	x	x	x
2	Propane	74-98-6	x	x	x
3	Propadiene	463-49-0	x	x	
4	Propyne	74-99-7		x	x
5	Cyclopropane	75-19-4	x	x	x
6	2-Methylpropane	75-28-5	x	x	x
7	Ethanal (acetaldehyde)	75-07-0	x	x	x
8	1-Butene	106-98-9	x	x	x
9	n-Butane	106-97-8	x	x	x
10	trans-2-Butene	624-64-6		x	
11	Cyclobutane	287-23-0	x	x	x
12	cis-2-Butene	590-18-1		x	
13	3-Methyl-1-butene	563-45-1	x	x	
14	Ethanol	64-17-5	x	x	x
15	Ethanenitrile (acetonitrile)	75-05-8	x	x	x
16	Propanone (acetone)	67-64-1	x	x	x
17	Propanal (propionaldehyde)	123-38-6	x	x	x
18	1-Pentene	109-67-1	x	x	x
19	2-Propanol	67-63-0	x	x	x
20	n-Pentane	109-66-0	x	x	x
21	Methyl nitrate	598-58-3	x	x	x
22	Carbon disulfide	75-15-0	x	x	x
23	Propanenitrile	107-12-0	x	x	x
24	1-Propanol	71-23-8	x	x	x
25	3-Buten-2-one (methylvinyl ketone)	78-94-4	x	x	x
26	2-Methylpentane	107-83-5	x	x	x
27	Butanal	123-72-8	x	x	x

Cmpd #	Compound	CAS ³ Number	Sample Number ¹		
			1	2	3
28	2-Butanone	78-93-3	x	x	x
29	1-Hexene	592-41-6	x	x	x
30	2-Butanol	78-92-2	x	x	x
31	n-Hexane	110-54-3	x	x	x
32	Ethyl nitrate	625-58-1	x	x	x
33	Tetrahydrofuran	109-99-9	x	x	x
34	2-Butenal (crotonaldehyde)	4170-30-3		x	
35	Butanenitrile	109-74-0	x	x	x
36	1-Butanol	71-36-3	x	x	x
37	2-Pentanone	107-87-9	x	x	x
38	Pentanal	110-62-3	x	x	x
39	1-Heptene	592-76-7	x	x	x
40	Propyl nitrate	627-13-4	x		x
41	n-Heptane	142-82-5	x	x	x
42	Pentanenitrile	110-59-8	x	x	x
43	1-Pentanol	71-41-0			x
44	3-Hexanone	589-38-8		x	x
45	2-Hexanone	591-78-6	x	x	x
46	Hexanal	66-25-1	x	x	x
47	1-Octene	111-66-0	x	x	x
48	n-Octane	111-65-9	x	x	x
49	Butyl nitrate	928-45-0	x	x	x
50	Hexanenitrile	628-73-9	x	x	x
51	1-Hexanol	111-27-3	x	x	x
52	4-Heptanone	123-19-3	x	x	x
53	3-Heptanone	106-35-4	x	x	x
54	2-Heptanone	110-43-0	x	x	x
55	Heptanal	111-71-7	x	x	x

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Cmpd #	Compound	CAS ³ Number	Sample Number ¹		
			1	2	3
56	1-Nonene	124-11-8	x	x	x
57	n-Nonane	111-84-2	x	x	x
58	Pentyl nitrate	1002-16-0	x	x	x
59	Heptanenitrile	629-08-3	x	x	x
60	2-Octanone	111-13-7	x	x	x
61	Octanal	124-13-0	x	x	x
62	n-Decane	124-18-5	x	x	x
63	Hexyl nitrate	20633-11-8	x	x	x
64	2-Ethyl-1-hexanol	104-76-7		x	
65	Octanenitrile	124-12-9	x	x	x
66	2-Nonanone	821-55-6	x	x	x
67	Nonanal	124-19-6	x	x	x
68	1-Undecene	821-95-4	x	x	x
69	n-Undecane	1120-21-4	x	x	x
70	2-Decanone	693-54-9	x	x	x
71	Decanal	112-31-2		x	
72	1-Dodecene	112-41-4	x		x
73	n-Dodecane	112-40-3	x	x	x
74	2,6-Dimethylundecane	17301-23-4	x	x	x
75	n-Tridecane	629-50-5	x	x	x
76	n-Tetradecane	629-59-4	x	x	x

³ CAS = Chemical Abstract Service.

¹ An x is placed in the column if the analyte was tentatively identified in the sample. Here 1 = sample S4004-01.C03; 2 = sample S4004-02.C03; and 3 = sample S4004-03.C03 (Rasmussen 1994a, WHC 1995).