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TANK 241BY111 HEADSPACE GAS & VAPOR
CHARACTERIZATION RESULTS FOR SAMPLES COLLECTED IN
5/1994 & 11/1994

ENGINEERING CHANGE NOTICE

Page 1 of 2

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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.

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Tank 241-BY-111 Headspace Gas and Vapor Characterization Results for Samples Collected in May 1994 and November 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
ISS	<i>in situ</i> sampling
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
PNL	Pacific Northwest Laboratory
ppmv	parts per million by volume, 1 ppmv = 10 ⁻⁴ vol%
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-BY-111 Headspace Gas and Vapor Characterization Results
for Samples Collected in May 1994 and November 1994

1.0 INTRODUCTION

1.1 Characterization Objectives

Tank BY-111 headspace gas and vapor samples were collected and analyzed to help determine the potential risks of fugitive emissions to tank farm workers. The drivers and objectives of waste tank headspace sampling and analysis are discussed in *Program Plan for the Resolution of Tank Vapor Issues* (Osborne and Huckaby 1994). This report primarily discusses results from the November 1994 sampling event, but also includes selected results of the May 1994 sampling event. The tank BY-111 headspace was sampled in May 1994 in accordance with *Safety Assessment for Gas Sampling All Ferrocyanide Tanks* (Farley 1991), and in November 1994 in accordance with *Data Quality Objectives for Generic In-Tank Health and Safety Issue Resolution* (Osborne et al. 1994).

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). Current governing operating specifications for Watchlist tanks, such as tank BY-111, specify that combustible constituents be maintained at or below 20 % of the LFL (WHC 1995a).

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 BY-111 was vapor sampled in May 1994 using the *in situ* sampling (ISS) method, and again in November 1994 using the more robust vapor sampling system (VSS) method. Unfortunately, the ISS event sorbent trap samples were radiologically contaminated, and were never analyzed (Huckaby et al. 1995). Furthermore, there are discrepancies between results from the ISS and VSS methods that are not understood (Huckaby 1994a), and until the ISS method has been validated and the discrepancies resolved, results from early ISS events should be considered suspect.

Nevertheless, a brief description of the ISS event and the total nonmethane organic carbon (TNMOC) measurement from the May 1994 ISS event are presented below, because this analysis was not performed on samples from the VSS event. All other results presented here are from the November 1994 VSS sampling event.

Samples collected are thought to have been 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 BY-111 headspace composition changes with time, though studies of tank C-103 suggest that composition changes probably occur very slowly in passively ventilated tanks, such as tank BY-111 (Huckaby and Story 1994).

1.4 Tank Headspace Dynamics

Tank BY-111 is the second tank in a 3-tank cascade with tanks BY-110 and BY-112. It is connected to tanks BY-110 and BY-112 via a 7.4-cm (2.9-in.) inside diameter, 7.6-m (25-ft) long underground cascade lines. Since these cascade lines connect the headspaces of these tanks, gases and vapors originating from the wastes in tank BY-110 or BY-112 may be transferred to tank BY-111 (unless the cascade lines are obstructed).

The cascade of tanks BY-110, BY-111, and BY-112 is passively ventilated, which means that the tanks are allowed to exhale air, waste gases, and vapors as the barometric pressure falls, and inhale ambient air as the barometric pressure rises. Each of these tanks has its own filtered breather riser. Barometric pressure typically rises and falls on a diurnal cycle, producing an average daily exchange of air equal to about 0.46 % of each tank headspace (Huckaby 1994b). Changes in the concentrations of tank headspace constituents due to barometric pressure changes are consequently very slow.

2.0 SAMPLING EVENTS

2.1 May 1994 *In Situ* Sampling Event

Tank BY-111 was sampled using ISS methods on May 11, 1994 by WHC Sampling and Mobile Laboratories. This sampling was conducted to satisfy requirements of *Safety Assessment for Gas Sampling All Ferrocyanide Tanks* (Farley 1991). Sorbent trap and SUMMA™ canister samples were collected from a point approximately 6.7 m below the top of the flange on riser 12A, between 10:44 a.m. and 12:10 p.m. Though the sorbent traps were physically lowered down into the headspace to minimize loss of analytes through condensation, adsorption, or absorption by condensate, the SUMMA™ canister samples were collected using unheated transfer tubing.

Huckaby et al. (1995) give a general description of the ISS method and equipment. Pingel (1994) provides field sampling information for the tank BY-111 May 1994 ISS event. In addition to the TNMOC measurement results presented below, McVeety et al. (1995a) and Rasmussen (1994) provide other sample analysis results.

2.2 November 1994 Vapor Sampling System Sampling Event

Headspace gas and vapor samples were collected from tank BY-111 using the VSS on November 16, 1994 by WHC Sampling and Mobile Laboratories (WHC 1995). Sample collection and analysis were performed as directed by *Tank 241-BY-111 Tank Characterization Plan* (TCP), (Horn 1994). The tank headspace temperature was determined to be 27 °C. Air from the tank BY-111 headspace was withdrawn via a 7.3 m-long heated sampling probe mounted in riser 12A, 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), and Pacific Northwest Laboratories (PNL). The 32 tank air samples and 2 ambient air control samples collected are listed in Table 2-1 by analytical laboratory. Table 2-1 also lists the 13 trip blanks and 1 field blank that accompanied the samples.

A general description of vapor sampling and sample analysis methods is given by Huckaby and Babad (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).

3.0 INORGANIC GASES AND VAPORS

Analytical results of sorbent trap and SUMMA^{TM,1} canister tank air samples for selected inorganic gases and vapors are given in Table 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 and SUMMATM canisters were prepared and analyzed by PNL at PNL quality assurance impact level 2 (Lucke et al. 1995a).

Analyses of the inorganic vapor sorbent traps were performed within 33 days of sample collection, analyses of SUMMATM canisters for inorganic compounds were performed 76 days after sample collection. Thus the 60-day holding time requirement of the WHC quality assurance project plan (Keller 1994) was satisfied for sorbent traps, but not for the SUMMATM analyses. It should be noted that these inorganic compounds (i.e., the permanent gases) would be expected to be very stable in the SUMMATM canisters, and the results may not have been affected even though the 60-day holding time requirements were exceeded.

3.1 Ammonia, Hydrogen, and Nitrous Oxide

Ammonia concentration in the headspace of tank BY-111 was measured at 59 ppmv. Ammonia has been observed in virtually all of the passively ventilated tanks sampled to date, at concentrations ranging from about 3 ppmv in tank C-108 (Lucke et al. 1995b), to 1040 ppmv in tank BY-108 (McVeety et al. 1995b). Given the LFL of ammonia in air is about 15 % by volume (vol%), the measured 59 ppmv corresponds to less than 0.04 % of the LFL, and does not contribute appreciably to the flammability of the headspace.

Hydrogen was not detected in the SUMMATM canister samples, and determined to be present at < 160 ppmv. In general, hydrogen is of concern as a fuel. The upper bound 160 ppmv of hydrogen in tank BY-111, however, represents only about 0.4 % of the LFL for hydrogen in air, and hydrogen would not be a flammability concern at this level.

Nitrous oxide was not detected in SUMMATM canister samples either. Analyses indicated that nitrous oxide was present at < 67 ppmv. Under proper conditions, 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 BY-111 headspace.

3.2 Carbon Dioxide and Carbon Monoxide

The average measured headspace carbon dioxide concentration, 219 ppmv, is significantly lower than the normal ambient air concentration of about 350 to 400 ppmv. 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. It is reasonable to expect the level of carbon dioxide in a tank headspace will therefore depend on the tank's breathing rate, and the pH and surface area of aqueous waste (i.e., supernate, interstitial liquid, and condensate) in the tank. The 219 ppmv carbon dioxide concentration measured in tank BY-111 is typical of other tanks sampled to date.

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

Carbon monoxide in the tank BY-111 headspace was measured to be < 67 ppmv. Elevated carbon monoxide concentrations have been observed in other waste tanks, and are thought to be due to the decomposition of organic waste in the tanks. The highest measured waste tank carbon monoxide concentration was [26.7 ppmv] in tank C-103² (Huckaby and Story 1994).

3.3 Nitric Oxide, Nitrogen Dioxide, Water and Tritium

Nitric oxide and nitrogen dioxide concentrations in the tank BY-111 headspace were determined to be ≤ 0.15 ppmv and ≤ 0.05 ppmv, respectively. These are both acid gases that would have very low equilibrium concentrations above the high pH waste in tank BY-111. Nitric oxide has been found at trace concentrations in other waste tanks, presumably 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 BY-111 headspace.

The water vapor concentration of tank BY-111 was measured to be 6.9 mg/L, at the tank headspace temperature of 27 °C and pressure of 976 mbar (732 torr), (WHC 1995b). This corresponds to a water vapor partial pressure of 9.6 mbar (7.2 torr), to a dew point of 6.4 °C, and to a relative humidity of 27 %. This is a very low water vapor concentration compared to other waste tanks. Hanlon (1995) reports tank BY-111 has essentially no aqueous supernate; the low water vapor concentration may be indicative of the lack of free water near the waste surface in tank BY-111.

A test of the efficiency of the silica gel traps used to collect water vapor was performed during the tank BY-111 sampling event (Lucke et al. 1995a). The test indicated that the normal sampling system trapped 96 % of the total water vapor. The water vapor concentrations in Table 3-1 and discussed above have been corrected for the additional 4 %.

Tritium was tested for using silica gel sorbent traps. It is assumed that tritium ions produced by the waste combine 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 indicated the total activity of the sample to be below the method detection limit of 50 pCi/L (WHC 1995b).

3.4 Discussion of Inorganic Gases and Vapors

Aside from water vapor and carbon dioxide, the most abundant waste constituent in the tank BY-111 headspace is ammonia. The ammonia concentration is low compared to many other passively ventilated tanks that have been sampled, as are the hydrogen and nitrous oxide concentrations. These 3 constituents are usually the dominant species.

The relative standard deviations of the results, given in the last column in Table 3-1, are acceptable for the analytical methods used. Relative standard deviations range from 3 % for ammonia, to 28 % for carbon dioxide results. Poor precision is not a significant problem for the carbon dioxide measurements, because it is neither a flammability or industrial hygiene concern. 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

² The carbon monoxide measurement in tank C-103 was made by Oregon Graduate Institute of Science and Technology, and placed in brackets to emphasize it should be considered secondary data.

preparation, dilutions, etc.), and the relative standard deviations suggest there were no significant problems in the field or in the laboratories.

As discussed briefly in Section 1.4, it is possible that gases and vapors generated by the waste in tanks BY-110 and BY-112 could be transferred to tank BY-111 via the cascade lines. If significant exchange of selected inorganic gases and vapors were taking place between adjacent tanks, either their headspace compositions would be very similar, or all waste products detected in one tank would be at or equal or higher concentrations in the other tank. Table 3-2 lists selected inorganic compound concentrations for tanks BY-110, BY-111, and BY-112 for comparison. In this cascade of tanks there are no clear indications that gases and vapors are or are not being exchanged between the tanks.

4.0 ORGANIC VAPORS

Organic vapors in the tank BY-111 headspace were sampled using SUMMA™ canisters, which were analyzed at PNL, and triple sorbent traps (TSTs), which were analyzed by ORNL. Both laboratories used gas chromatographs (GCs) equipped with mass spectrometer (MS) detectors to separate, identify, and quantitate the analytes. Descriptions of sample device cleaning, sample preparations, and analyses are given by Jenkins et al. (1995a) and Lucke et al. (1995a). A quantitative measurement of the total organic vapor concentration by the U.S. Environmental Protection Agency (EPA) task order 12 (TO-12) method (EPA 1988) was also performed by Oregon Graduate Institute of Science and Technology (OGIST) on samples collected in May 1994 by the ISS method (Pingel 1994, Rasmussen 1994).

PNL SUMMA™ sample results should be considered to be the primary organic vapor data for tank BY-111. These results were produced at PNL quality assurance impact level 2. However, analyses of SUMMA™ canisters for organic vapors were not completed until 80 days after sample collection, and this exceeded the administratively chosen 60-day holding time (Keller 1994). No holding time study has been performed to determine the stability of analytes in SUMMA™ canisters in the chemical matrix of the tank 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.

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. 1995a). 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 all surrogates had standard deviation values within the 95 % confidence interval for variance, indicating that no bias was introduced in the measurement of analyte quantities (Jenkins 1995a).

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 by analysis of standards. The concentration of an analyte in the sample is said to be quantitatively measured if the response of the GC/MS has been established at several known concentrations of that analyte (i.e., the GC/MS has been calibrated for that analyte), and the MS response to the analyte in the sample is between the lowest and highest responses to the known concentrations (i.e., the analyte is within the calibration range).

ORNL and PNL were assigned different lists of organic compounds, or target analytes, to positively identify and measure quantitatively. The ORNL target analyte list was derived from a review of the tank C-103 headspace constituents by a panel of toxicology experts (Mahlum et al. 1994). The PNL target analyte list included 39 compounds in the Environmental Protection Agency (EPA) task order 14 (TO-14) method, which are primarily halocarbons and common industrial solvents (EPA 1988), plus 14 analytes selected mainly from the toxicology panel's review of vapor data on tank C-103.

Listed in Table 4-1 are 5 organic compounds positively identified and quantitated in SUMMA™ canister samples, and the methane analyses result. PNL performed analyses according to the EPA task order 14 (TO-14) methodology, but expanded the number of target analytes from 40 to 54 to include waste tank analytes of particular interest (EPA 1988, Lucke et al. 1995a). Methane was analyzed with the inorganic gases, because it is not analyzable by the TO-14 method. Of the original 40 TO-14 analytes, only

trichlorofluoromethane was detected above the 0.002 ppmv quantitation limit, and only 4 of the 15 additional target analytes were above the 0.005 ppmv method quantitation limit. Averages reported are from analyses of 3 SUMMA™ canister samples.

ORNL positively identified 15 of 27 target analytes selected by WHC. Despite calibration of the instrument over about a 20-fold concentration range, only 3 of the positively identified compounds were within the instrument calibration range, and were quantitated. These are given with the 3-TST sample average concentration in Table 4-2. Table 4-3 lists 9 positively identified compounds for which the measurement in at least 1 of the TSTs was outside of the instrument calibration range, and consequently not quantitated. Table 4-4 lists the 3 remaining positively identified analytes, for which their analyte-specific ORNL practical holding time had been exceeded. Tables 4-2, 4-3, and 4-4 are mutually exclusive, so that no analyte appears in more than 1 of these tables. Data in Tables 4-3 and 4-4 should not be considered quantitative and may not be accurate to within $\pm 30\%$ as specified by Burnum (1995).

Based on a practical holding time study performed by ORNL the reported concentrations of propanone, butanal, and n-pentanenitrile may have been affected by the 61 day period between sample collection and analysis (Jenkins 1995b). The concentration of these 3 analytes are reported in Table 4-4. The 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. Jenkins et al (1995b) describe the ORNL practical holding time study, and report practical holding times for these compounds.

Nine target analytes were common to both the ORNL and PNL analyses. These are listed in Table 4-5 with the average concentrations reported by ORNL and PNL. Comparison of the results from the 2 laboratories indicates the following:

- 1) 2 of the analytes, vinylidene chloride and dichloromethane, were not detected in either sample type;
- 2) TST samples had 0.050 ppmv of ethanenitrile, but SUMMA™ canister samples were found to have < 0.005 ppmv;
- 3) propanenitrile and n-butanenitrile were found to be < 0.005 ppmv in both TST and SUMMA™ samples; and
- 4) the 2 methods disagree on the concentrations propanone, n-hexane, benzene, n-heptane, and toluene.

Though the discrepancies between the TST and SUMMA™ sample analyses are currently not understood, the reported concentrations are not above action limits. Furthermore, at the reported concentrations, the Table 4-1 analytes do not individually or cumulatively represent a flammability hazard.

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. Using this method, many analytes can be tentatively identified with reasonable confidence without having to inject each into the GC/MS to determine their GC retention times or specific MS patterns.

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

The organic compounds tentatively identified in SUMMA™ canister samples by PNL are listed, with their estimated concentrations, in Table 4-6. Compounds are listed in Table 4-6 in the order by which they eluted chromatographically, and only non-zero results are included in the reported averages. The list of tentatively identified compounds detected in TST samples, and their estimated concentrations, is given in Table 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. Estimated concentrations are in mg/m^3 , 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. (1995a) and Lucke et al. (1995a), respectively, and should be reviewed before this data are used for decision making. Concentrations given in Tables 4-6 and 4-7 should be considered rough 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 collected on May 11, 1994 using the EPA TO-12 method (Rasmussen 1994). Because OGIST did not perform analyses with a WHC-approved quality assurance project plan in place, the OGIST results should be considered secondary data, and have been placed in brackets to emphasize this. The sample mean was $[9.6 \text{ mg}/\text{m}^3]$, with a standard deviation of $[0.2 \text{ mg}/\text{m}^3]$. MS analyses indicated only $2.2 \text{ mg}/\text{m}^3$ of organic vapors in TST samples (Jenkins et al. 1995a).

4.4 Discussion of Organic Analytes

Some of the compounds listed in Tables 4-1 through 4-7 were introduced to the tank with process waste streams, and are detected in the headspace because the original inventory has not been completely evaporated or degraded. Examples of these are the semivolatile normal paraffinic hydrocarbons (NPHs), (i.e., n-dodecane, n-tridecane, n-tetradecane, n-pentadecane) and methyl-substituted decahydronaphthalenes that were used as diluents for tributyl phosphate.

Though there is no toxicological or flammability hazard associated with the 0.13 ppmv of trichlorofluoromethane measured in tank BY-111, its presence has been noted in many of the tanks sampled to date. The origin of trichlorofluoromethane in the waste tanks has not been established, however, it may be present from its use in urethane foam that were applied to concrete tank pits as a sealant.

Most of the compounds in Tables 4-1 through 4-7 are believed to be chemical reaction and radiolytic reaction products of the semivolatile or nonvolatile organic waste stored in the tank. For example, 1-

butanol is known to be formed by the hydrolysis of tributyl phosphate, and it has been suggested that the alcohols, aldehydes, ketones, nitriles, alkenes, and short chain alkanes are all degradation products of NPHs.

Neither TST nor SUMMA™ methods detected tributyl phosphate as a headspace constituent. The relatively high concentration of 1-butanol, however, is a strong indication that tributyl phosphate does exist in tank BY-111. That tributyl phosphate was not observed in the TST samples may be due to the facts that tributyl phosphate has a very low vapor pressure, and it has a tendency to adsorb on to the high efficiency particulate air filters used during sampling to protect the samples from radiological particulate contamination.

In general, the character of organic vapors in tank BY-111 appears to be very similar to other NPH-rich waste tanks in 241-C and 241-BY farms. As indicated in Table 3-2, tank BY-111 has the lowest levels of organic vapors in the tank BY-110, BY-111, and BY-112 cascade.

5.0 SUMMARY

The tank BY-111 headspace was sampled in May 1994 and November 1994 for gases and vapors to address flammability and industrial hygiene concerns. Results unique to the May 1994 event and essentially all results from the November 1994 event have 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* (Horn 1995).

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Table 2-1
Tank BY-111 Gas and Vapor Sample Type and Number

Laboratory	Sampling Device	Nominal Sample Volume (L)	Target Analytes	Number of Samples
Oak Ridge National Laboratories	Triple Sorbent Trap	2.0	Organic vapors	4 tank air samples + 1 trip blank + 1 field blank
	Acidified Carbon Sorbent Trap	3.0	Ammonia	6 tank air samples + 3 trip blanks
Pacific Northwest Laboratories	Triethanolamine Sorbent Trap	3.0	Nitrogen Dioxide	6 tank air samples + 3 trip blanks
	Oxidation bed + Triethanolamine Sorbent Trap	3.0	Nitric Oxide	6 tank air samples + 3 trip blanks
	Silica Gel Sorbent Trap	3.0	Water vapor	6 tank air samples + 3 trip blanks
	SUMMA™ canister	6.0	Organic vapors	3 tank air samples + 2 ambient air samples
	Silica Gel Sorbent Trap	1.0	Tritium-Substituted Water Vapor	1 tank air sample

Table 3-1
 Tank BY-111 Inorganic Gas and Vapor Concentrations
 Analyses by Pacific Northwest Laboratory, and Oregon Graduate Institute of Science and Technology.

Compound	CAS ¹ Number	Sample Type	Number of samples	Average (ppmv)	Standard Deviation (ppmv)	RSD ² (%)
Ammonia, NH ₃	7664-41-7	Sorbent Trap	6	59	2	3
Carbon Dioxide, CO ₂	124-38-9	SUMMA™	3	219	61	28
Carbon Monoxide, CO	630-08-0	SUMMA™	3	< 67	--	--
Hydrogen, H ₂	1333-74-0	SUMMA™	3	< 160	--	--
Nitric Oxide, NO	10102-43-9	Sorbent Trap	6	≤ 0.15	--	--
Nitrogen Dioxide, NO ₂	10102-44-0	Sorbent Trap	6	≤ 0.05	--	--
Nitrous Oxide, N ₂ O	10024-97-2	SUMMA™	3	< 67	--	--
Water Vapor, H ₂ O	7732-18-5	Sorbent Trap	6	9,830 (6.9 mg/L)	950 (0.7 mg/L)	9.7

¹ CAS = Chemical Abstracts Service.

² RSD = relative standard deviation.

Table 3-2
Comparison of Tank BY-110, BY-111, and BY-112 Headspace Constituents¹

Tank:	BY-110 ²	BY-111	BY-112 ³
Date sampled, (mo/day/yr)	11/11/94	5/11/94 11/16/94	11/18/94
Headspace temperature, (°C)	27	27	23.2
Ammonia, (ppmv)	401	59	63
Hydrogen, (ppmv)	< 160	< 160	< 94
Carbon dioxide, (ppmv)	229	219	121
Carbon monoxide, (ppmv)	< 76	< 76	< 12
Nitric oxide, (ppmv)	≤ 0.09	≤ 0.15	0.18
Nitrogen dioxide, (ppmv)	≤ 0.05	≤ 0.05	≤ 0.02
Nitrous oxide, (ppmv)	103	< 67	40
Water vapor, (mg/m ³)	8.0	6.9	11.2
Water vapor, (% relative humidity)	31	27	53
Ethanenitrile (acetonitrile), (ppmv)	0.81	0.050	0.10
Propanone (acetone), (ppmv)	(3.8)	(0.48)	(1.0)
1-Butanol, (ppmv)	0.30	< 0.0011	0.059
n-Dodecane, (ppmv)	0.079	< 0.00046	0.0097
n-Tridecane, (ppmv)	0.13	(0.0015)	0.020
Total organic compounds ⁴ , (mg/m ³)	29	2.2	5.8

1 Inorganic gas or vapor results are from PNL; organic vapor results are from ORNL, with semiquantitative 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.

4 Total organic compound concentration was estimated from TST sample results.

Table 4-1
Tank BY-111 Quantitatively Measured Organic Compounds in SUMMA™ Samples --
Analyses by Pacific Northwest Laboratory

Cmpd #	Compound	CAS ¹ Number	Average ² (ppmv)	Standard Deviation (ppmv)	RSD ³ (%)
1	Trichlorofluoromethane	75-69-4	0.129	0.007	6
2	Propanone (acetone)	67-64-1	1.55	0.10	6
3	2-Butanone	78-93-3	0.106	0.003	3
4	n-Heptane	142-82-5	0.040	0.001	15
5	Toluene	108-88-3	0.044	0.003	6
6	Methane	74-82-8	< 61	—	—

1 CAS = Chemical Abstract Service.

2 Average of 3 samples.

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

Table 4-2
Tank BY-111 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	Ethanenitrile (acetonitrile)	75-05-8	0.050	0.003	5
2	n-Hexane	110-54-3	0.011	0.002	20
3	Benzene	71-43-2	0.011	0.003	31

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

2 CAS = Chemical Abstract Service.

3 Average of 3, 2-L TST samples.

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

Table 4-3
 Tank BY-111 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	Propanenitrile	107-12-0	0.0021	0.0002	8
2	Butanenitrile	109-74-0	0.0024	0.0004	18
3	n-Heptane	142-82-5	0.0017	0.0004	26
4	Toluene	108-88-3	0.0031	0.0011	35
5	n-Octane	111-65-9	< 0.0002	--	--
6	n-Nonane	111-84-2	0.00017	0.00001	7
7	n-Undecane	1120-21-4	< 0.00032	--	--
8	n-Dodecane	112-40-3	< 0.00046	--	--
9	n-Tridecane	629-50-5	0.0015	0.0015	18

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, 2-L TST samples.

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

Table 4-4
Tank BY-111 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	Propanone (acetone) ⁵	67-64-1	0.48	0.02	3
2	Butanal ⁵	123-72-8	0.0026	0.0005	20
3	Pentanenitrile ⁵	110-59-8	< 0.00042	0.00014	33

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

2 CAS = Chemical Abstract Service.

3 Average of 3, 2-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 4-5
Tank BY-111 Comparison of Organic Compounds in TST and SUMMA™ Samples--
Analyses by Pacific Northwest Laboratory
and Oak Ridge National Laboratory

Compound	CAS ¹ Number	TST Average ² (ppmv)	SUMMA™ Average ³ (ppmv)	PRD ⁴ (%)
Ethanenitrile (acetonitrile)	75-05-8	0.050	< 0.005	> 164
Propanone (acetone)	67-64-1	0.48	1.55	105
Propanenitrile	107-12-0	0.0021	< 0.005	—
n-Hexane	110-54-3	0.011	< 0.005	> 75
Benzene	71-43-2	0.011	< 0.005	> 75
Butanenitrile	109-74-0	0.0024	< 0.005	—
n-Heptane	142-82-5	0.0017	0.040	184
Toluene	108-88-3	0.0031	0.044	174
Pentanenitrile	110-59-8	< 0.00042	< 0.005	—

1 CAS = Chemical Abstract Service.

2 Average of 3, 2-L TST samples.

3 Average of 3 samples from PNL.

4 PRD = percent relative difference. Keller (1994) requires the PRD to be less than 20 %.

Table 4-6
Tank BY-111 Tentatively Identified Organic Compounds in SUMMA™ Samples --
Analyses by Pacific Northwest Laboratory

Cmpd #	Compound	CAS ¹ Number	Average ⁵ (mg/m ³)	Standard ² Deviation (mg/m ³)
1	Propene	115-07-1	0.23	0.04
2	Propane	74-98-6	0.19	0.05
3	Cyclopropane	75-19-4	0.12	0.01
4	Isobutane	75-28-5	0.18	0.01
5	1-Butene	106-98-9	0.07	0.00
6	Butane	106-97-8	0.18	0.02
7	2-Methyl-1-propene ³	115-11-7	0.06	—
8	Ethanol	64-17-5	0.07	0.00
9	Pentane	109-66-0	0.28	0.03
10	2-Methyl-2-propanol	75-65-0	0.15	0.01
11	2-Methyl-pentane	107-83-5	0.11	0.01
12	Butanal ⁴	123-72-8	0.06	0.01
13	1-Butanol	71-36-3	0.17	0.00
14	2-Pentanone ⁴	107-87-9	0.16	< 0.01
15	Cyclopentanol	96-41-3	0.06	< 0.01
16	Cyclopentanol	96-41-3	0.06	< 0.01
17	2-Hexanone	591-78-6	0.08	< 0.01
18	Octane	111-65-9	0.06	< 0.01
19	3-Heptanone	106-35-4	0.18	0.01
21	2-Heptanone ⁴	110-43-0	0.07	< 0.01
22	Unknown Ketone ³		0.07	—
24	Undecane	1120-21-4	0.07	0.00
25	Dodecane	112-40-3	0.09	0.00
26	Tridecane	629-50-5	0.07	0.01
Sum of tentatively identified compounds:			2.84	

† 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 1 sample.

4 Detected in only 2 samples.

5 Average of 3 samples, values listed are estimates.

Table 4-7
 Tank BY-111 Tentatively Identified Organic Compounds in TST Samples --
 Analyses by Oak Ridge National Laboratory

Cmpd #	Compound	CAS ¹ Number	Average ² (mg/m ³)	Standard Deviation (mg/m ³)
1	Cyclopropane	75-19-4	0.0120	0.00163
2	Isobutane	75-28-5	0.0158	0.00337
3	1-Propene, 2-methyl-	115-11-7	0.0804	0.00591
4	Butane	106-97-8	0.1851	0.03169
5	1-Butene	106-98-9	0.0229	0.00217
6	Cyclobutane	287-23-0	0.0165	0.00202
7	Butane, 2-methyl- & Ethanol		0.0555	0.00860
8	Trichloromonofluoromethane	75-69-4	0.1117	0.00342
9	1-Pentene	109-67-1	0.0125	0.00195
10	1,3-Butadiene, 2-methyl-	78-79-5	0.0089	0.00225
11	Isopropyl alcohol	67-63-0	0.0087	0.00798
12	2-Butene, 2-methyl-	513-35-9	0.0019	0.00326
13	1-Pentene	109-67-1	0.0056	0.00485
14	Butane, 2,2-dimethyl-	75-83-2	0.0077	0.00095
15	Pentane, 2-methyl-	107-83-5	0.0308	0.00484
16	2-Propenal, 2-methyl-	78-85-3	0.0024	0.00409
17	1-Propanol	71-23-8	0.0024	0.00409
18	Pentane, 3-methyl-	96-14-0	0.0082	0.00082
19	1-Hexene	592-41-6	0.0054	0.00472
20	3-Buten-2-one	78-94-4	0.0061	0.00568
21	Propanal, 2-methyl-	78-84-2	0.0019	0.00322
22	Furan, tetrahydro-	109-99-9	0.0075	0.00111
23	Hexane, 3-methyl-	589-34-4	0.0054	0.00475
24	2-Butanone, 3,3-dimethyl-	75-97-8	0.0189	0.00102
25	2-Pentanone, 4,4-dimethyl-	590-50-1	0.0076	0.00161
26	Cyclohexane, 1,1,3-trimethyl-	3073-66-3	0.0014	0.00237
27	Cyclotetrasiloxane, octamethyl-	556-67-2	0.0031	0.00281

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Cmpd #	Compound	CAS ¹ Number	Average ² (mg/m ³)	Standard Deviation (mg/m ³)
28	Naphthalene, decahydro-2-methyl-	2958-76-1	0.0014	0.00244
29	Cyclohexane, 2-butyl-1,1,3-trimethyl-	54676-39-0	0.0108	0.00221
30	Methenamine	100-97-0	0.0316	0.01372
31	Cyclohexane, 1,3,5-trimethyl-2-octadecyl-	55282-34-3	0.0026	0.00231
32	2(3H)-Benzofuranone, 3a,4,5,6-tetra-	16778-26-0	0.0034	0.00291
33	Cyclohexane, 1-(cyclohexylmethyl)2-ethyl-	54934-93-9	0.0056	0.00171
34	Benzenesulfonamide, N-butyl-	3622-84-2	0.0161	0.00967
35	Eicosane	112-95-8	0.0226	0.02784
36	Isopropyl Palmitate	142-91-6	0.0017	0.00303
37	Hexadecanal	629-80-1	0.0016	0.00271
Sum of tentatively identified compounds:			0.74	

1 CAS = Chemical Abstract Service.

2 Average of 3, 2-L TST samples, values listed are estimates.