

Waste Tank Vapor Project:

**Vapor Space Characterization of
Waste Tank 241-BY-104: Results
from Samples Collected on 6/24/94**

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Summary

This report describes inorganic and organic results from tank-headspace samples collected from the Hanford single-shell waste-storage Tank 241-BY-104 (referred to as Tank BY-104). The results described here were obtained to support safety and toxicological evaluations. Quantitative results were obtained for NH₃, NO, NO₂, and H₂O. A summary of the results for inorganic analytes is listed in Summary Table 1.

Summary Table 1. Summary Results of Samples Collected from the Tank Headspace of Tank BY-104 on 6/24/94

<u>Analyte</u>	<u>Concentration</u>
NH ₃	248 ± 5 ppmv ^(a)
NO ₂	≤ 0.07 ppmv ^(a)
NO	0.4 ± 0.1 ppmv
H ₂ O	16 ± 1 mg/L ^(a)
various organics	45.0 ± 13.0 mg/m ³ ^(b)

(a) See Section 2.4.

(b) Determined as the sum of estimated quantities of individual components.

Organic analytes that are listed in the U.S. Environmental Protection Agency (EPA) TO-14 were quantitatively determined. Approximately 60 tentatively identified organic analytes were observed above the detection limit of (ca.) 10 ppbv, but standards for most of these were not available at the time of analysis, and their quantitative determination is beyond the scope of this study. The SUMMA™ canister samples were also analyzed for the 41 organic components listed in EPA compendium Method TO-14. Of these only a few were observed above the 2-ppbv detection limits. These are summarized in Table 3.1. Estimated quantitations also determined were of tentatively identified compounds (TIC). A summary of these results is shown in Table 3.2. Table 3.2 shows quantities of all TICs above the concentration of ca. 10 ppbv. This consists of more than 60 organic analytes. The 10 organic analytes with the highest estimated concentrations are shown in Summary Table 2 below. These 10 analytes account for approximately 45% of the total organic components in Tank BY-104. Detailed descriptions of the results appear in the text.

Summary Table 2. Summary Results of Selected Organic Analytes

<u>Selected Organic Analytes (TIC)</u>	<u>Average Concentrations^(a) (mg/m³)</u>
Propene	1
Propane	1
n-Butane	1
Acetone	2
Trichlorofluoromethane	1
n-Pentane	1
2-Methylpentane	1
n-Dodecane	2
n-Tridecane	2
n-Tetradecane	1

(a) Concentrations were based on sampling and sample volumes performed by WHC.

Acknowledgments

The authors gratefully acknowledge the support of other project staff at Pacific Northwest Laboratory (PNL) who contributed to the successful completion of this sampling and analysis activity. Jeff Edwards served as the PNL single-point-of-contact and coordinated sample handling and communications with Westinghouse Hanford Company. Jeff also supported work in the organic analytical laboratory. Amit Sharma assisted in the organic analytical laboratory and assisted in preparing this report. Bruce Lerner performed method development and validation work that supported the inorganic vapor sampling. Sally Slate and May-Lin Thomas analyzed inorganic samples, and Annalisa Krupsha and Gary Dennis prepared the solid-sorbent sample trains.

Abbreviations

A%RSD	average percent relative standard deviation
ACL	Analytical Chemistry Laboratory
COC	chain of custody
DIW	deionized water
emf	electromotive force
EPA	U.S. Environmental Protection Agency
GC/MS	gas chromatography/mass spectrometry
IC	ion chromatography
IS	internal standard
MDL	minimum detection limit
NIST	National Institute for Standards and Technology
OSHA	Occupational Safety and Health Administration
PFA	perfluoralkoxy
PNL	Pacific Northwest Laboratory
ppbv	parts-per-billion by volume
ppmv	parts-per-million by volume
REL	recommended exposure limit
SCIC	suppressed conductivity ion chromatography
SIE	selective-ion electrode
SRM	standard reference material
STP	standard temperature and pressure
TEA	triethanolamine
TIC	tentatively identified compounds
VSS	vapor sampling system
WHC	Westinghouse Hanford Company

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1.0 Introduction

This report describes results of the analyses of tank-headspace samples taken from Hanford waste Tank 241-BY-104 (referred to as Tank BY-104) on June 24, 1994. The Pacific Northwest Laboratory (PNL)^(a) contracted with Westinghouse Hanford Company (WHC) to provide sampling devices and analyze inorganic and organic samples collected from the tank headspace. The sample job was designated S4019 and was performed by WHC on June 24, 1994 using the vapor sampling system (VSS). The results of the analyses are expected to be used in the determination of safety and toxicological issues related to the tank-headspace gas as described in the WHC report entitled *Data Quality Objectives for Generic In-Tank Health and Safety Vapor Issue Resolution*, WHC-SD-WM-DQO-002, Rev. 0.

Sampling devices, including 16 sorbent trains (for inorganic analyses), and 5 SUMMATM canisters (for organic analyses), were supplied to the WHC sampling staff on June 20, 1994. Samples were taken (by WHC) on June 24. The samples were returned from the field on June 27. The inorganic samples delivered to PNL on chain-of-custody (COC) 006893 (Figure 1a) included 16 sorbent trains as described in Tables 2.2, 2.3, and 2.4. Additional inorganic blank spikes were obtained from related sample jobs. SUMMATM samples delivered to PNL on COC 006896 (Figure 1b) included one ambient air sample, one ambient-air sample through the sampling system, and three tank-headspace SUMMATM canister samples.

The samples were inspected upon delivery to the 326/23B laboratory and logged into PNL laboratory record book 55408. Custody of the sorbent trains was transferred to PNL personnel performing the inorganic analysis and stored at refrigerated ($\leq 10^{\circ}\text{C}$) temperature until the time of analysis. Access to the 326/23B laboratory is limited to PNL personnel working on the waste-tank safety program. Analyses described in this report were performed at PNL in the 300 area of the Hanford Reservation. Methods used for organic and inorganic analyses are described in the text of this report. In summary, sorbent trains for inorganic analyses containing sample materials were either weighed (for water analysis) or desorbed with water (for ammonia or NO_x analyses). The water extracts were analyzed either by selective electrode or by ion chromatography (IC). Organic analyses were performed using gas chromatography/mass spectrometry (GC/MS).

(a) Pacific Northwest Laboratory is operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

Westinghouse Hanford Company	CHAIN OF CUSTODY	WHC 006893
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Custody Form Initiator	J. A. Edwards	Telephone (509)373 -0141
		Pager 85-3009
Company Contact	R. Westberg	Telephone (509) 373-5734
Project Designation/Sampling Locations	200 East Tank Farm	Collection Date 06-24-94
BY 104 Tank Vapor Sample SAF S4019		Preparation Date 06-15-94
Ice Chest No. (VSS Truck)		Field Logbook No. WHC-N-677L
Bill of Lading/Airbill No.	N/A	Offsite Property No. N/A
Method of Shipment	Government Truck	Sample Job # _____
Shipped to	PNL	
Possible Sample Hazards/Remarks	Unknown at time of sampling	

Sample Identification

- | | |
|---------------------|--|
| ✓ S4019 - A16 . W32 | NH ₃ /NO _x /H ₂ O (Sample #1) |
| ✓ S4019 - A17 . W33 | NH ₃ /NO _x /H ₂ O (Sample #2) |
| ✓ S4019 - A18 . W34 | NH ₃ /NO _x /H ₂ O (Sample #3) |
| ✓ S4019 - A19 . W35 | NH ₃ /NO _x /H ₂ O (Sample #4) |
| ✓ S4019 - A20 . W36 | NH ₃ /NO _x /H ₂ O (Sample #5) |
| | |
| ✓ S4019 - A21 . W37 | NH ₃ (Blank) |
| ✓ S4019 - A22 . W38 | NH ₃ (Spiked Blank) |
| | |
| ✓ S4019 - A23 . W39 | NO _x /H ₂ O (Sample #1) |
| ✓ S4019 - A24 . W40 | NO _x /H ₂ O (Sample #2) |
| ✓ S4019 - A25 . W41 | NO _x /H ₂ O (Sample #3) |
| ✓ S4019 - A26 . W42 | NO _x /H ₂ O (Sample #4) |
| ✓ S4019 - A27 . W43 | NO _x /H ₂ O (Sample #5) |
| | |
| ✓ S4019 - A28 . W44 | NO _x (Blank) |
| ✓ S4019 - A29 . W45 | NO _x (Spiked Blank) |
| | |
| ✓ S4019 - A30 . W46 | H ₂ O (Blank) |
| ✓ S4019 - A31 . W47 | H ₂ O (Spiked Blank) |

[X] Field Transfer of Custody		[] Chain of Possession		(Sign and Print Names)		
Relinquished By	Date	Time	Received By	Date	Time	
J. A. Edwards	06-20-94	1015	SM Brown	6-20-94	1015	
SM Brown	06-24-94	0430	RA Westberg	6-24-94	0430	
RA Westberg	6-24-94	1400	SM Brown	6-24-94	1400	
SM Brown	6-27-94	1400	J.A. Edwards	6-27-94	1400	

(Revised 02/28/94)

Final Sample Disposition

Disposal Method:

A-6000-407 (12/92) WEF061

June 20, 1994 @ 9:01

Figure 2a. Chain-of-Custody Form for Inorganics Samples for Tank BY-104

**Westinghouse
Hanford Company**

CHAIN OF CUSTODY

WHC 006896

Custody Form Initiator J. A. Edwards Telephone (509)373 -0141
 Pager 85-3009

Company Contact R. A. Westberg Telephone (509) 373-5734

Project Designation/Sampling Locations 200 East Tank Farm
 241-BY-104 Tank Vapor Sample SAF S4019
 Ice Chest No. (VSS Truck) Collection Date 06-24-94
 Preparation Date 06-15-94
 Field Logbook No. WHC-N-41-

Bill of Lading/Airbill No. N/A Offsite Property No. N/A

Method of Shipment Government Truck Sample Job # _____

Shipped to PNL

Possible Sample Hazards/Remarks Unknown at time of sampling

Sample Identification

S4019 - A01 . S142 Ambient Air SUMMA (PNL)

S4019 - A02 . S143 Ambient SUMMA #1 (PNL)

S4019 - A05 . S144 Sample SUMMA #3 (PNL)

S4019 - A07 . S145 Sample SUMMA #5 (PNL)

S4019 - A09 . S146 Sample SUMMA #7 (PNL)

[X] Field Transfer of Custody		[] Chain of Possession		(Sign and Print Names)			
Relinquished By	Date	Time	Received By	Date	Time		
J. A. Edwards	06-20-94	1010	S.M. Brown	6-20-94	1010		
S.M. Brown	06-20-94	0430	R.A. Westberg	6-24-94	0430		
R.A. Westberg	6-24-94	1400	S.M. Brown	6-24-94	0400		
S.M. Brown	6/27/94	1400	J.A. Edwards	6/27/94	0400		

(Revised 02/28/94)

Final Sample Disposition

Disposal Method:

Disposed by:

Date/Time:

A-6000-407 (12/92) WEP061

June 18, 1994 @ 15:20

Figure 2b. Chain-of-Custody Form for Organics Samples for Tank BY-104

2.0 Inorganic Task

Solid sorbent traps, prepared in sampling trains, were supplied to WHC for sampling from the tank headspace using the VSS. Blanks, spiked blanks (when requested), and exposed samples were returned to PNL for analysis. Analyses were performed to provide information on the tank-headspace concentration of some or all of the following analytes: ammonia, nitrogen dioxide, nitric oxide, hydrogen cyanide, sulfur oxides, and water. Procedures were similar to those developed previously during sample jobs performed with the VSS connected to the tank headspace of Tank C-103 (Ligotke et al. 1994a). Analytical accuracy was estimated based on procedures used. Sampling preparation and analysis were performed at Quality Assurance Impact Level III.

2.1 Standard Sampling Methodology

Standard glass tubes containing sorbent materials to trap vapors of the NH_3 , NO_2 , NO , and H_2O (SKC Inc., Eighty Four, Pennsylvania) were obtained, prepared, and submitted for use by WHC. The sorbent traps were selected based on their use by the Occupational Safety and Health Administration (OSHA) to perform workplace monitoring, and because of available procedures and verification results associated with that particular application. The typical sorbent traps used consisted of a glass tube containing a sorbent material specific to the compound of interest. In general, the tubes contained two sorbent layers, or sections; the first layer was the primary trap, and the second layer provided an indication of breakthrough. Within the glass tubes of the sorbent traps, sorbent layers are generally held in packed layers separated by glass wool. The tubes were received from the vendor with glass-sealed ends.

The type and nominal quantity of sorbent material varied by application. Sorbent traps selected for the tank sample job included the following products. The NH_3 sorbent traps contained carbon beads impregnated with sulfuric acids; nominally, 500 mg were contained in the primary and 250 mg in the breakthrough sections. The NH_3 was chemisorbed as ammonium sulfate. The NO_2 traps contained a zeolite impregnated with triethanolamine (TEA), with 400 mg in the primary and 200 mg in the breakthrough sections. The NO_2 was adsorbed and oxidized to equi-molar quantities of nitrite ions (NO_2^-) and nitrate ions (NO_3^-). Glass tubes containing 800 mg of an oxidant were used to convert NO to NO_2 . The converted NO was then collected as nitrite and nitrate in a NO_2 trap. The water traps contained 300 mg of silica gel in the primary and 150 mg in the breakthrough sorbent sections.

The sorbent traps were prepared in multi-trap sorbent trains configured so sample flow passed in order through the traps, targeting specific analytes, and then through a desiccant trap. The specific order of traps within the various sorbent trains is described in Section 2.4. The ends of the glass-tube traps were broken, and the traps were weighed and then connected to each other using uniform lengths of 3/8-in. perfluoralkoxy (PFA)-grade Teflon[®] tubing. The tubing was heated in hot air and forced over the open ends of the traps to form a tight seal. The inlets of the sorbent trains each consisted of a short section of tubing having a 3/8-in. stainless steel Swagelok[®] nut, sealed using a Swagelok[®] cap. The trailing ends of the sorbent trains (the downstream end of the silica-gel tubes) were each sealed with red-plastic end caps provided by the manufacturer.

The leading and trailing ends of the sorbent trap trains remained sealed other than during the actual sampling periods. C-Flex[®] tubing was provided by WHC to connect the downstream ends of the sorbent trains to the sampling exhaust-manifold connections.

Samples provided by PNL to trap inorganic compounds included samples, spiked samples, spares, single-tube blanks, and spiked blanks (see Section 2.4). The samples of each type were prepared from same-lot batches. The oxidizer sections of the NO_x sorbent trains (NO₂ trap + oxidizer tube + NO₂ trap) were stored previously in a freezer. After sample preparation, all samples, spiked samples, blanks, and spiked blanks were stored in a freezer, primarily because of handling recommendations for the oxidizer tubes attached to some samples. After WHC delivered exposed and radiologically cleared samples to PNL, and PNL disassembled the sorbent trains, controls and samples were provided to the analytical laboratory at ambient temperature. Selected oxidizer sections were returned to a freezer for possible subsequent use in laboratory method-validation studies.

2.1.1 Concentration Calculations. The concentrations of target compounds in the tank headspace were determined from sample results, assuming effective sample transport to the sorbent traps. Concentration, in parts-per-million by volume (ppmv), was determined by dividing the mass of the compound, in μmol, by the volume of dry tank air samples, in mol. The micromolar sample mass was determined by dividing the compound mass, in μg, by the molecular weight of the compound, in g/mol. The volume of the sample was determined, excluding water vapor, by dividing the standard sample volume (at 0°C and 760 torr), in L, by 22.41 L/mol. For example, the concentration of a 3.00-L sample containing 75.0 μg of ammonia equals

$$C_v = \frac{75.0 \mu\text{g}}{17 \text{ g/mol}} \left(\frac{3.00\text{L}}{22.4 \text{ L/mol}} \right)^{-1} = 33.0 \text{ ppmv} \quad (2.1)$$

This calculation method produces concentration results that are slightly conservative (greater than actual) because the volume of water vapor in the sample stream is neglected. The volume of water vapor is not included in the measured sampled volume because of its removal in desiccant traps upstream of the mass flowmeters. However, the bias is generally expected to be small. For a tank-headspace temperature of 35°C, the magnitude of the bias would be about 1 to 6%, assuming tank-headspace relative humidities of 20 to 100%, respectively. The concentration of mass (determined gravimetrically) was also per dry-gas volume at standard conditions.

2.2 Analytical Procedures

The compounds of interest were trapped using solid sorbents and chemisorption (adsorption for water vapor). Analytical results were based on extraction and analysis of selected ions. Analytical procedures used are specified in the text and compiled in PNL-MA-599^(a).

2.2.1 Ammonia Analysis. The sorbent material from the ammonia-selective sorbent traps was placed into labeled 20-mL glass scintillation vials. Vials containing front, or primary, section sorbent material were treated with 10.0 mL of deionized water (DIW), and vials containing back-up section sorbent material were treated with 5.0 mL of DIW. After extraction, the NH₃ sorbent traps were analyzed using the selective-ion electrode (SIE) procedure PNL-ALO-226 {Ammonia (Nitrogen) in Aqueous Samples}. Briefly, this method includes 1) preparing a 1000-ppm NH₃ stock standard solution from dried reagent-grade NH₄Cl and DIW on the day analyses are performed; 2) preparing 0.1-, 0.5-, 1.0-, 10-, and 100-ppm NH₃ working calibration standards by serial dilution of the freshly made stock standard; 3) generating an initial calibration curve from the measured emf (electromotive force) signal versus NH₃ concentration

(a) Analytical Laboratory Operations Procedure Compendium, PNL-MA-599. Procedures PNL-ALO-212, -226, and -271. Pacific Northwest Laboratory, Richland, Washington.

data obtained for the set of working standards; 4) performing a calibration-verification check, using one of the midrange standards, after the analysis of every 4 or 5 samples; 5) continuing this sequence until all samples of the batch have been measured, including duplicates and spiked samples; and 6) remeasuring the complete set of calibration standards at the end of the session. The emf signal measurements obtained for samples are compared to those for standards, either graphically or algebraically (using linear regression) to determine ammonia concentration in the samples.

2.2.2 Nitrite Analysis. The sorbent traps for NO_2 and NO were desorbed in an aqueous TEA and n-butanol solution and analyzed by suppressed-conductivity ion chromatography (SCIC) for nitrite according to PNL-ALO-212, Rev. 1 (*Determination of Inorganic Anions by Ion Chromatography*) modified to obviate interferences by concentrations of non-target analytes. Specifically, the modifications used were as follows: 1) the eluent was 1.44 mM Na_2CO_3 + 1.8 mM NaHCO_3 at 2.0 mL/min, 2) one guard column (AG4A) and two separator columns (AS4A) were in series instead of just one separator column, 3) all standards, samples, and blanks were injected into the IC sample loop through 0.45- μm syringe filters.

For the analysis, the sorbent materials were placed into labeled 20-mL glass scintillation vials. To each vial, 3.0 mL of desorbing solution (15 g TEA + 1 mL N-butanol in 1.0 L DIW) was added. Primary sorbent-tube sample materials and back-up (breakthrough) sorbent-tube materials were analyzed separately using identical procedures. Each analytical session was conducted as follows. Working nitrite standards (0, 0.1, 0.25, and 0.5 ppm) were prepared by diluting a stock nitrite standard with desorbing solution. An initial calibration curve was prepared from the instrument response (chromatographic peak height) versus nitrite standard-concentration data for the set of working standards. A calibration verification check using one of the midrange standards was performed after the analysis of every six samples. If the instrument response indicated that sample nitrite concentration was outside the calibration range (> 0.5 ppm nitrite), the sample was diluted with desorbing solution and reanalyzed. After all samples of a batch were analyzed, the complete set of calibration standards was remeasured to verify consistent instrument response, and the analytical session was terminated.

Instrument responses (peak heights) observed for samples were compared to those for standards to determine the nitrite concentration of the samples. Because NO_2 and NO converted to NO_2 were collected on the sorbent as equal quantities of nitrite and nitrate, and the analysis was specific for nitrite, the molar masses of NO_2 and NO was determined by doubling the analytically determined molar mass of nitrite.

2.2.3 Mass (Water) Analysis. Sorbent traps used to make each sample train were weighed using a semi-micro mass balance after labeling and breaking the glass tube ends, without plastic end caps. After receipt of exposed samples, the sorbent traps were again weighed to determine the change in mass. Records of the measurements were documented on sample-preparation data sheets. The mass concentration, generally roughly equal to the concentration of water, was determined by dividing the combined change in mass from all traps in a sorbent train by the actual volume of gas sampled. Blanks and spiked blanks were included to provide information on uncertainty.

2.3 Quality Assurance/Quality Control

Analytical work was performed according to quality levels identified in the project quality-assurance plan and several PNL documents. The PNL Quality Impact Level was IL III. The PNL documents include PNL-MA-70 (Part 2)^(a), PNL-MA-599, PNL-ALO-212, PNL-ALO-226, PNL-ALO-271, and MCS-033^(b). A summary of the analysis procedures and limits for the target inorganic compounds is provided in Table 2.1. From the table, it can be seen that the minimum detection limit (MDL) required to resolve the analyte at one-tenth of the National Institute of Occupational Safety and Health (NIOSH) recommended exposure limit (REL) for each of the target analytes is achieved using current procedures, a vapor-sample volume of 3 L, and a desorption-solution volume of 3 mL (10 mL for ammonia).

Table 2.1. Analysis Procedures and Detection Limits of Target Inorganic Analytes

Analyte	Formula	Procedure	REL ^(a) (ppmv)	0.1 x REL ^(a) (ppmv)	MDL ^(b) (ppmv)
Ammonia	NH ₃	PNL-ALO-226	25	2.5	0.5
Nitrogen dioxide	NO ₂	PNL-ALO-212	1	0.1	0.02
Nitric oxide	NO	PNL-ALO-212	25	2.5	0.02
Mass (water) ^(c)	n/a	n/a	n/a	n/a	n/a

- (a) Target analytical limits are equal to one-tenth of the REL.
- (b) MDL is defined as the vapor concentration that can be detected with an uncertainty equal to about the magnitude of the measurement. The uncertainty is expected to reduce to about one-quarter of the magnitude of the measurement at a concentration of four times the MDL. The MDLs were based on the assumption that 3 L of vapor are sampled; if greater volumes of vapor are sampled, correspondingly smaller MDLs can be obtained. The MDLs were also based on desorbing solution volumes of 10 mL for ammonia and 3 mL for the other analytes.
- (c) The vapor mass concentration, thought to be largely water vapor, is determined for estimates of humidity.

The accuracy of concentration measurements depends on errors associated with both sampling and analysis. Sampling information was provided by WHC. The accuracy of analytical results depends on the method used. For ammonia analyses, the accuracy of laboratory measurements by SIE was estimated to be $\pm 5\%$ relative, independent of concentration at 1 $\mu\text{g}/\text{mL}$ or greater levels. The uncertainty includes preparation of standards, purity of the ammonium salt used to prepare standards, potential operator bias, ambient temperature variations, etc. Unfortunately, no known National Institute for Standards and Technology (NIST)-traceable standard reference material (SRM) is available against which to compare our working standards. As for ammonia, no known NIST SRM is available for nitrite analyses (NO₂ and NO). Based on our experience in comparing nitrite working standards prepared from several different sources and factors mentioned for ammonia above, the estimated maximum bias for samples derived from sampling for NO₂ is $\pm 10\%$, and for samples derived from sampling for NO it is $\pm 5\%$ relative. The accuracy of measurements of sample mass is ± 0.05 mg, or much less than 1% of the mass changes of samples, and roughly 5% or less of the mass change of blanks.

- (a) Quality Assurance Manual, Part 2: Good Practices Standard, PNL-MA-70. Pacific Northwest Laboratory, Richland, Washington
- (b) Quality Assurance Plan for Activities Conducted by the Analytical Chemistry Laboratory (ACL), MCS-033. Pacific Northwest Laboratory, Richland, Washington.

2.4 Inorganic Sample Results

Samples were obtained from the tank headspace of Tank BY-104 on 6/24/94 using the VSS. The sample-job designation number was S4019. Samples were prepared, submitted to WHC, and then analyzed to provide information on the concentrations of ammonia, nitrogen dioxide, nitric oxide, and water. Sampling and analysis for hydrogen cyanide and sulfur oxides was not requested. Blank and spiked-blank samples were pooled with those provided for similar sampling jobs associated with Tank BY-105 (S4020) and Tank BY-106 (S4021). The inorganic samples from Tank BY-104 were received from WHC on and before 6/27/94; the sample volume information was received on 6/27/94.

A list of samples, sampling information, sample volumes, and gravimetric results is shown in Table 2.2. Percentage recovery results from spiked blanks are shown in Table 2.3. Analytical mass and concentration results are shown in Table 2.4. Sample volumes (Table 2.2) were provided by WHC; sample-volume uncertainty was not provided. Tank-headspace concentration results (Table 2.4) are based on this information, and uncertainties are listed as plus-or-minus one standard deviation (absolute) of the average of the individual results from each set of samples. Sample results were not corrected for the percentage recoveries of spiked blanks.

2.4.1 Ammonia Results. The concentration of NH_3 was 248 ± 5 ppmv, based on all five samples (Table 2.4). The quantity of NH_3 ranged from 32 to 34 μmol in the front sorbent sections and was ≤ 0.03 μmol in the two back sections that were analyzed. The MDL was 0.03 or 0.06 μmol , depending on the volume of desorbing solution used, and was equivalent to vapor concentrations of ≤ 1 ppmv. The quantity of NH_3 on the front and back sections of three blanks was ≤ 0.06 μmol , and no blank correction was applied to the results. The percentage recovery of three blanks spiked with 12.2 μmol NH_3 was $101 \pm 4\%$. Past blanks spiked with 22.3 and 46.4 μmol yielded percentage recoveries of 109 ± 2 and $104 \pm 1\%$, respectively (Ligotke et al. 1994a). Two sample leachates were spiked after initial analysis with quantities of NH_3 equal to half or all of the mass of NH_3 in the sample and yielded repeatabilities of 4 and 7%. The analysis of one sample was duplicated and yielded a repeatability of 2%. A 5-point calibration was performed over an NH_3 range of 0.1 to 1000 $\mu\text{g}/\text{mL}$. The NH_3 concentration was not affected by the sample port number.

2.4.2 Nitric Oxides Results. Measurements of NO_2 and NO were made using NO_x sorbent-trap trains (NO_2 trap, oxidizer, NO_2 trap) with and without an NH_3 sorbent trap attached upstream. Five samples of each sample-train type were obtained. The presence of the upstream NH_3 trap resulted in NO concentrations that were about 1.3-fold less than those from unprotected NO_2 traps. The NO_2 concentrations were also potentially less following an NH_3 trap; however, greater relative uncertainties made the comparison unclear.

The concentration of NO_2 was ≤ 0.05 ppmv from sorbent traps downstream of NH_3 traps, and ≤ 0.07 ppmv from sorbent tubes leading the sample trains. The concentration of NO was 0.30 ± 0.10 ppmv from sorbent traps downstream of NH_3 traps, and 0.39 ± 0.05 ppmv from sorbent traps leading the sample trains. Uncorrected NO_2^- quantities in the tubes ranged from 0.013 to 0.047 μmol in the front sorbent sections and 0.007 to 0.009 μmol in the back sections. The MDL of NO_2^- was about 0.02 μmol . The NO_2^- content of three front and back blank sorbent sections were 0.016 ± 0.002 and 0.0087 ± 0.0007 μmol , respectively, and these values were used to correct the quantity of NO_2^- measured in the samples. The percentage recovery of three blanks spiked with 0.047 μmol NO_2^- was $103 \pm 4\%$. Past blanks spiked with 0.0064, 0.11, and 0.74 μmol NO_2^- yielded percentage recoveries of 153 ± 14 , 106 ± 8 , and $111 \pm 7\%$, respectively (Ligotke et al. 1994a). No sample leachates were spiked after initial analysis with

quantities of NO_2^- to test analytical repeatability. No samples were duplicated to check repeatability. A 4-point calibration was performed over a concentration range of 0 to $0.5 \mu\text{g NO}_2^-$ per mL in the desorbing matrix.

Table 2.2 List of PNL Inorganic Samples and Gravimetric Results Obtained From a Heated Tube Inserted in the Tank Headspace of Tank BY-104 on 6/24/94. Blanks and spiked blanks were included from three similar sample jobs. Estimated sample information was provided by WHC.

Sample	Type	Sample Port	Planned Flow Rate (mL/min)	Actual Duration (min)	Sample Volume ^(a) (L)	Mass Gain (g)
S4019-A16-W32	$\text{NH}_3/\text{NO}_x/\text{H}_2\text{O}$ Sample	8	200	15.0	3.00	0.0496
S4019-A17-W33	$\text{NH}_3/\text{NO}_x/\text{H}_2\text{O}$ Sample	10	200	15.0	3.00	0.0424
S4019-A18-W34	$\text{NH}_3/\text{NO}_x/\text{H}_2\text{O}$ Sample	9	200	15.05	3.01	0.0436
S4019-A19-W35	$\text{NH}_3/\text{NO}_x/\text{H}_2\text{O}$ Sample	10	200	15.05	3.01	0.0488
S4019-A20-W36	$\text{NH}_3/\text{NO}_x/\text{H}_2\text{O}$ Sample	8	200	15.0	3.00	0.0501
S4019-A23-W39	$\text{NO}_x/\text{H}_2\text{O}$ Sample	10	200	15.0	3.00	0.0498
S4019-A24-W40	$\text{NO}_x/\text{H}_2\text{O}$ Sample	9	200	15.0	3.00	0.0485
S4019-A25-W41	$\text{NO}_x/\text{H}_2\text{O}$ Sample	10	200	15.0	3.00	0.0494
S4019-A26-W42	$\text{NO}_x/\text{H}_2\text{O}$ Sample	8	200	15.0	3.00	0.0482
S4019-A27-W43	$\text{NO}_x/\text{H}_2\text{O}$ Sample	10	200	15.0	3.00	0.0493
S4019-A21-W37	NH_3 Blank	n/a	n/a	n/a	n/a	0.0004
S4020-A21-W53	NH_3 Blank	n/a	n/a	n/a	n/a	0.0022
S4021-A21-W69	NH_3 Blank	n/a	n/a	n/a	n/a	0.0013
S4019-A28-W44	NO_2^- Blank	n/a	n/a	n/a	n/a	-0.0008
S4020-A28-W60	NO_2^- Blank	n/a	n/a	n/a	n/a	0.0025
S4021-A28-W76	NO_2^- Blank	n/a	n/a	n/a	n/a	0.0008
S4019-A30-W46	H_2O Blank	n/a	n/a	n/a	n/a	0.0005
S4020-A30-W62	H_2O Blank	n/a	n/a	n/a	n/a	0.0016
S4021-A30-W78	H_2O Blank	n/a	n/a	n/a	n/a	-0.0001
S4019-A22-W38	NH_3 Spiked Blank	n/a	n/a	n/a	n/a	0.0008
S4020-A22-W54	NH_3 Spiked Blank	n/a	n/a	n/a	n/a	0.0025
S4021-A22-W70	NH_3 Spiked Blank	n/a	n/a	n/a	n/a	0.0015
S4019-A29-W45	NO_2^- Spiked Blank	n/a	n/a	n/a	n/a	0.0006
S4020-A29-W61	NO_2^- Spiked Blank	n/a	n/a	n/a	n/a	0.0023
S4021-A29-W77	NO_2^- Spiked Blank	n/a	n/a	n/a	n/a	0.0010
S4019-A31-W47	H_2O Spiked Blank	n/a	n/a	n/a	n/a	0.0005
S4020-A31-W63	H_2O Spiked Blank	n/a	n/a	n/a	n/a	0.0020
S4021-A31-W79	H_2O Spiked Blank	n/a	n/a	n/a	n/a	0.0013

(a) Sample volumes were provided by WHC and were for dry gas at 0°C and 760 torr. Uncertainty values were not provided with sample volume results.

Table 2.3 Percentage Recovery Results of Inorganic Spiked Blanks Sent to the Field but not Opened During Sampling of Tanks BY-104, -105, and -106 in June and July, 1994. Spikes were applied to the center of front sorbent sections. Analysis of selected back sections yielded levels comparable to those found in the blanks.

Sample Identifier	Tank	Compound	Spike Added ^(a) (μmol)	Analytical Result ^(b) (μmol)	Percentage Recovery	
					Sample (%)	Average ^(c) (%)
S4019-A22-W38	BY-104	NH ₃	12.4	13.2	106	101 \pm 4
S4020-A22-W54	BY-105	NH ₃	12.1	12.0	99	
S4021-A22-W70	BY-106	NH ₃	12.2	12.0	98	
S4019-A29-W45	BY-104	NO ₂ ⁻	0.0472	0.0465	99	103 \pm 4
S4020-A29-W61	BY-105	NO ₂ ⁻	0.0463	0.0484	105	
S4021-A29-W77	BY-106	NO ₂ ⁻	0.0480	0.0508	106	
S4019-A31-W47	BY-104	H ₂ O	2811 ^(d)	2839	101	103 \pm 2
S4020-A31-W63	BY-105	H ₂ O	2856	2967	104	
S4021-A31-W79	BY-106	H ₂ O	2878	2950	103	

- (a) The NH₃ spike solutions were 20 μL of 10,000 ppm by weight (3.142 g NH₄Cl per 100 mL). The NO₂ spike solutions were 20 μL of 100-ppm nitrite. The H₂O spike was 50 μL of distilled water. The μmol of spiked material added were determined gravimetrically (e.g., 0.021 g x 10,000 μg NH₃/mL + 17 g/mol = 12.4 μmol).
- (b) No correction was necessary for the NH₃ analytical results because blank levels were \leq 0.06 μmol . Analytical results for NO₂⁻ were corrected for blank levels, with each result corrected by the single blank associated with the same tank.
- (c) Summary results are listed as average recovery \pm 1 standard deviation (absolute).
- (d) Water measured in μg and converted to μmol by dividing by the molecular weight of water (18).

2.4.3 Gravimetric Results. The mass concentration of material collected in the sorbent-trap trains, believed to be primarily water vapor, was 16 ± 1 mg/L. The result was based on all 10 sets of NH₃/NO_x and NO_x sample trains. The percentage recovery of mass from three blank silica-gel traps spiked with 51 μg water was $103 \pm 2\%$. The six blank and spiked-blank traps generally gained mass, and ranged between -0.001 and 0.001 g gained per trap. Based on four traps per sample train, a blank correction would result in an additional uncertainty of ± 1 mg/L; no correction was made.

Table 2.4 Inorganic Vapor Sample Results Obtained From a Heated Tube Inserted in the Tank Headspace of Tank BY-104 on 6/24/94

Sample	Tank if Other Than BY-104	Port	Mass Collected		Vapor ^(a) Concentration (ppmv)
			Front (μmol)	Back (μmol)	
<u>NH₃ Samples</u>					<u>248 ± 5^(b)</u>
S4019-A16-W32		8	32.4	NA ^(c)	
S4019-A17-W33		10	32.9	< 0.03	
S4019-A18-W34		9	33.5	NA	
S4019-A19-W35		10	34.1	NA	
S4019-A20-W36		8	32.9	< 0.03	
S4019-A21-W37		blank	< 0.03	< 0.03	n/a
S4020-A21-W53	BY-105	blank	< 0.06	0.03	n/a
S4021-A21-W69	BY-106	blank	< 0.06	< 0.06	n/a
<u>NO₂ Blanks</u>					
S4019-A28-W44		blank	0.0182	0.0095	n/a
S4020-A28-W60	BY-105	blank	0.0148	0.0082	n/a
S4021-A28-W76	BY-106	blank	0.0148	0.0085	n/a
<u>NO₂ Samples (Protected by NH₃ sorbent trap):</u>					<u>≤ 0.05</u>
S4019-A16-W32		8	0.0131	0.0066	
S4019-A17-W33		10	NA	0.0070	
S4019-A18-W34		9	0.0169	0.0072	
S4019-A19-W35		10	0.0163	0.0068	
S4019-A20-W36		8	0.0166	0.0075	
<u>NO₂ Samples (Not Protected by NH₃ sorbent trap):</u>					<u>≤ 0.07</u>
S4019-A23-W39		10	0.0184	0.0072	
S4019-A24-W40		9	0.0174	0.0071	
S4019-A25-W41		10	0.0186	0.0069	
S4019-A26-W42		8	0.0186	0.0071	
S4019-A27-W43		10	0.0178	0.0077	
<u>NO Samples (Protected by NH₃ sorbent trap):</u>					<u>0.30 ± 0.10</u>
S4019-A16-W32		8	0.0346	0.0066	
S4019-A17-W33		10	0.0337	0.0063	
S4019-A18-W34		9	0.0467	0.0076	
S4019-A19-W35		10	0.0343	0.0075	
S4019-A20-W36		8	0.0315	0.0083	
<u>NO Samples (Not Protected by NH₃ sorbent trap):</u>					<u>0.39 ± 0.05</u>
S4019-A23-W39		10	0.0414	0.0085	
S4019-A24-W40		9	0.0416	0.0068	
S4019-A25-W41		10	0.0416	0.0094	
S4019-A26-W42		8	0.0438	0.0076	
S4019-A27-W43		10	0.0422	0.0074	
<u>Gravimetric Samples:</u>					<u>16 ± 1 mg/L</u>

- (a) Blank-corrected concentrations were calculated using WHC-reported sample volumes at STP (0°C and 760 torr), neglecting the 1 to 2% volume contribution of water vapor (condensed and collected before flow-rate measurement). Nitrite values (listed) were doubled to account for unanalyzed nitrate. Mass concentration was determined per L of dry air at STP, based on 10 of 10 samples; no blank correction was necessary.
- (b) Underlined values represent the average ± 1 standard deviation for each set of samples.
- (c) NA = not analyzed. Only selected back-sorbent sections were analyzed.

3.0 Organic Task

3.1 SUMMA™ Canister Preparation

Before sending SUMMA™ canisters out to the field for sampling, the canisters are cleaned and verified contaminant free according to PNL Technical Procedure PNL-TVP-02^(a). The cleaning procedure uses an EnTech 3000 cleaning system that controls 1) filling the canisters with purified humid air and 2) evacuating, for several cycles with applied heat, before allowing the canister to evacuate overnight. The canister is filled a final time with purified humid air for analysis by PNL Technical Procedure PNL-TVP-01^(b), which is a modification of U.S. Environmental Protection Agency (EPA) compendium Method TO-14. If the canister is verified as clean, free of TO-14 contaminants to a level of 5 ppbv, the canister is evacuated to 30 in. Hg, tagged, and stored for use in the field. Before sending the canisters out to the field for sampling, the canisters are prehumidified with 100 µL of distilled water and labeled with a field sampling identification. Canisters not used after 30 days of storage are recleaned and validated before use.

3.2 Sample Analysis Method

The SUMMA™ canister samples were analyzed according to PNL Technical Procedure PNL-TVP-03, *Determination of TO-14 Volatile Organic Compounds in Hanford Waste Tank Headspace Samples Using SUMMA™ Passivated Canister Sampling and Gas Chromatographic -Mass Spectrometry Analysis*. This method is a modified version of EPA compendium Method TO-14. The method uses an EnTech cryoconcentration system, which is interfaced with a Hewlett Packard 5971 GC/MS. The EnTech concentrator is used to pull a metered volume of sample air from the SUMMA™ canister, cryogenically concentrate organic vapors in the air volume, and then transfer the volume to the GC/MS for analysis. A 100-mL volume of air is measured and analyzed from each ambient, blank, and headspace sample. The organic components in the sampled air are separated on an analytical column, J&W Scientific DB-1 phase, 60-m by 0.32-mm inside diameter with 3-µm film thickness. The GC column is programmed for a temperature gradient beginning at 40 °C, holding for 5 min, ramping at 4°C per min to a final temperature of 260 °C, with a 5-min hold.

3.3 Quality Assurance/Quality Control

Before the tank sample was analyzed, a diagnostic check was performed on the GC/MS instrument by running an instrument "quick tune," as described in PNL-TVP-03. Upon satisfactory completion of the instrument diagnostic check, a blank volume of purified nitrogen was analyzed to check the cleanliness of the system. The instrument was then calibrated over 6 data points ranging from 2 ppbv to 100 ppbv, using a standard gas mixture containing 40 volatile organic compounds listed in EPA compendium Method TO-14. A gas mixture containing bromochloromethane, 1,4-difluorobenzene, and chlorobenzene-d₅ was used as an internal standard for all blank, calibration standard, and sample analyses. The calibration curve was generated by calculating the relative response ratios of the internal standard to calibration standard responses and plotting the ratios against the ratio of the calibration

(a) Pacific Northwest Laboratory. 8/94. *Cleaning SUMMA™ Canisters and the Validation of the Cleaning Process*, PNL-TVP-02 (Rev. 0), PNL Technical Procedure, Richland, Washington.

(b) Pacific Northwest Laboratory. 8/94. *Determination of TO-14 Volatile Organic Compounds in Ambient Air Using SUMMA™ Passivated Canister Sampling and Gas Chromatographic-Mass Spectrometric Analysis*, PNL-TVP-01 (Rev. 0). PNL Technical Procedure, Richland, Washington.

standard concentration (in ppbv) to the internal standard (IS) concentration. A least-squares linear-regression routine was applied to the data set to generate the best fit line for each compound. The equation for that line was then used to determine the concentration of the specific compounds in the tank samples.

3.3.1 Quantitation of TO-14 Results. The quantitative-analysis results for the TO-14 volatile organic compounds were calculated directly from the calibration curve generated using the IS method described above and in PNL-TVP-03. The conversion from ppmv to mg/m³ assumes dry air at standard temperature and pressure (STP) conditions of 273°K and 760 torr and was calculated directly from the following equation:

$$\text{mg/m}^3 = \frac{\text{ppmv} \times \text{molecular weight of compound}}{22.4} \quad (3.1)$$

3.3.2 Identification and Quantitation of Tentatively Identified Compounds. The tentatively identified compounds (TIC) are determined by mass-spectral interpretation and comparison of the spectra with the EPA/NISI/WILEY Library, which is a part of the HP 5971 instrument operating system. Only chromatographic peaks with an area count greater than or equal to, one half of the total area count of the chlorobenzene-d₅ IS peak at the 20-ppbv calibration level were searched. This standard was chosen to determine the integration cutoff as it is in the middle of the chromatographic range, and not in a region affected by coelution of other compounds. The quality of the mass-spectral searches were then reviewed by the principal investigators before the identification was assigned to each chromatographic peak.

The concentrations of each TIC were estimated using relative response factors calculated using corrected total-peak area for the ISs, chlorobenzene-d₅. Specifically, the total integrated areas for the internal chlorobenzene-d₅ peak had to be corrected for possible coeluting compounds before calculating the response factor. The corrected total-peak area for the IS was calculated by multiplying the IS quantitation ion by a correction factor based on the ratio of the total integrated-peak area to the quantitation ion as measured in blank runs. The corrected peak area was then used to calculate a response factor using the concentration of the IS in mg/m³:

$$\text{Response Factor} = \frac{\text{IS conc. (mg/m}^3\text{)}}{\text{IS peak area}} \quad (3.2)$$

The calculated response factor was then multiplied by the TIC-peak area to give an estimated concentration for that compound. For acetone, the total-peak area in sample S4019-A05-144 was multiplied by the response factor for chlorobenzene-d₅ to give an estimated concentration of 3.16 mg/m³. Internal standards bromochloromethane and difluorobenzene were not used to quantitate the TIC because coeluting compounds appeared to have greatly altered the signal of the quantitation ions for those two ISs.

The IS level added to all blank, standard, and sample injections was 18.3 ppbv for bromochloromethane, 20.3 ppb for 1,4-difluorobenzene, and 18.2 ppb for chlorobenzene-d₅. The IS concentrations were converted from ppbv to mg/m³ at STP using a molecular weight of 129.39 (g/mol) for bromochloromethane, 114.09 for 1,4-difluorobenzene, and 117.6 for chlorobenzene-d₅.

3.4 Analysis Results

The results from the GC/MS analysis of the tank-headspace samples are presented in Tables 3.1 and 3.2. A representative total ion chromatograph showing the identity of major constituents is given in Figure 3.1.

Table 3.1 lists the quantitative results for compounds listed in Method TO-14. The levels of TO-14 analytes observed in the samples collected from Tank BY-104 were low, near the quantitation limit of 2 ppbv.

Table 3.2 lists the semi-quantitative results for the TIC. The predominant species observed in these samples were acetone, hexane, pentane, propene, trichlorofluoromethane, 2-methylpentane, and normal paraffin hydrocarbons (NPH) defined as n-alkanes from C₁₁ to C₁₅. However, it should be noted that because the SUMMA™ canisters were not heated at the time of analysis, the NPH concentrations listed after the retention time of decane may not be a true accounting of all the NPH in the sample. Similarly, polar compounds that may adhere to the inside surface of the canister may also be under represented in this analysis. Tentatively identified compounds were not seen in the ambient samples taken without the VSS and through the VSS above the 10-ppb cut off.

The average total concentration of the TIC was 29 mg/m³. The average percent relative standard deviation (A%RSD) for TIC measured in the three samples was 35%. An apparent difference was noted in the TIC concentrations measured in PNL 144, as compared with PNL 145 and PNL 146. The A%RSD for PNL 145 and PNL 146 is <1%. The concentration of TIC in PNL 144 was about two times greater than the average of the TIC concentration measured in PNL 145 and 146. Currently, no explanation for this anomaly has been determined.

4.0 Conclusions

The concentrations of selected inorganic compounds were determined from samples of the tank headspace of Hanford waste Tank BY-104. The ammonia concentration was found to be 10-fold greater than the REL of 25 ppmv. The concentration of NO₂ was less than one-tenth of the REL of 2 ppmv. The concentration of NO was less than one-tenth of the REL of 25 ppmv. The mass concentration of material collected in the solid sorbent trains, assumed to be largely water, was 16 ± 1 mg/L. Organic analytes were approximately 10% of the concentration of organics in Tank C-103 (Ligotke, et al. 1994b).

5.0 References

Ligotke, M. W., K. H. Pool, and B. D. Lerner. 1994a. *Vapor Space Characterization of Waste Tank C-103: Inorganic Results from Sample Job 7B (5/12/94 - 5/25/94)*, PNL-10172, Pacific Northwest Laboratory, Richland, Washington.

Ligotke, M. W., T. R. Clauss, J. S. Fruchter, R. B. Lucke, D. W. Dennis, G. M. Mong, R. E. Hohimer, M. McCulloch, M. T. Dana, and S. C. Goheen. 1994b. *Aerosol and Vapor Characterization of Tank 241-C-103: Data Report for In Situ OVS Samples Obtained 12/02/93*, PNL-9368, Pacific Northwest Laboratory, Richland, Washington.

Table 3.1 TO-14 Analysis Results for Samples Collected from Tank BY-104 in SUMMA™ Canisters on 6/24/94

TO-14 ANALYTE	CAS #	S4019- A05.144 ^(a)		S4019-A07.145		S4019-A09.146		S4019-A01.142		S4019-A02.143	
		PNL 144 ^(b)		PNL 145		PNL 146		PNL 142		PNL 143	
		(ppbv)	(mg/m ³) ^(c)	(ppbv)	(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)	(mg/m ³)
Dichlorodifluoromethane (FREON-12)	75-71-8	9.84	0.05	7.07	0.04	7.25	0.04	<2	<.01	<2	<.01
Methylchloride (Chloromethane)	74-87-3	1.68	<.004	<2	<.004	<2	<.004	<2	<.004	<2	<.004
1,2-Dichloro-1,1,2,2,-Tetrafluoroethane (FREON 114)	76-14-2	<2	<.02	<2	<.02	<2	<.02	<2	<.02	<2	<.02
Chloroethene (Vinyl Chloride)	75-01-4	<2	<.006	<2	<.006	<2	<.006	<2	<.006	<2	<.006
Methylbromide (Bromomethane)	74-83-9	<2	<.009	<2	<.009	<2	<.009	<2	<.009	<2	<.009
Ethylchloride	75-00-3	<2	<.006	<2	<.006	<2	<.006	<2	<.006	<2	<.006
Trichlorofluoromethane (FREON-11)	75-69-4	413.1	2.53	330.8	2.03	337	2.07	<2	<.01	<2	<.01
1,1-Dichloroethene (1,1-Dichloroethylene)	75-35-4	<2	<.009	<2	<.009	<2	<.009	<2	<.009	<2	<.009
Dichloromethane (Methylene Chloride)	75-09-2	1.83	0.01	<2	<.01	<2	<.01	<2	<.01	<2	<.01
1,1,2-Trichloro-1,2,2-Trifluoroethane (FREON 113)	76-13-1	<2	<.02	<2	<.02	<2	<.02	<2	<.02	<2	<.02
1,1-Dichloroethane	75-34-3	<2	<.009	<2	<.009	<2	<.009	<2	<.009	<2	<.009
cis-1,2-Dichloroethene (cis-1,2-Dichloroethylene)	156-60-5	<2	<.009	<2	<.009	<2	<.009	<2	<.009	<2	<.009
Trichloromethane (Chloroform)	67-66-3	<2	<.01	<2	<.01	<2	<.01	<2	<.01	<2	<.01
cis-1,2-Dichloroethane	107-06-2	<2	<.009	<2	<.009	<2	<.009	<2	<.009	<2	<.009
1,1,1-Trichloroethane	71-55-6	<2	<.01	<2	<.01	<2	<.01	<2	<.01	<2	<.01
Benzene	71-43-2	3.88	<.01	2.96	<.01	2.55	<.01	<2	<.01	<2	<.01
Carbontetrachloride	56-23-5	<2	<.01	<2	<.01	<2	<.01	<2	<.01	<2	<.01
1,2-Dichloropropane	78-87-5	<2	<.01	<2	<.01	<2	<.01	<2	<.01	<2	<.01
Trichloroethylene	79-01-6	<2	<.01	<2	<.01	<2	<.01	<2	<.01	<2	<.01
cis-1,3-Dichloropropene	10061-02-6	<2	<.01	<2	<.01	<2	<.01	<2	<.01	<2	<.01
trans-1,3-Dichloropropene	10061-01-5	<2	<.01	<2	<.01	<2	<.01	<2	<.01	<2	<.01
1,1,2-Trichloroethane	79-00-5	<2	<.01	<2	<.01	<2	<.01	<2	<.01	<2	<.01
Methylbenzene (Toluene)	108-88-3	12.80	0.05	10.13	0.04	7.79	0.03	<2	<.01	<2	<.01
1,2-Dibromoethane	106-93-4	<2	<.02	<2	<.02	<2	<.02	<2	<.02	<2	<.02
Tetrachloroethene (Tetrachloroethylene)	127-18-4	1.57	0.01	<2	<.01	<2	<.01	<2	<.01	<2	<.01
Chlorobenzene	108-90-7	<2	<.01	<2	<.01	<2	<.01	<2	<.01	<2	<.01
Ethylbenzene	100-41-4	1.84	0.01	1.76	0.01	1.68	<.01	<2	<.01	<2	<.01
m-Xylene (1,3-Dimethylbenzene)	108-38-3	5.07	0.02	4.80	0.02	4.66	0.02	1.97	<.01	1.91	<.01
p-Xylene (1,4-Dimethylbenzene) (coeluent)	106-42-3	(d)	(d)	(d)	(d)	(d)	(d)	(d)	(d)	(d)	(d)
Styrene	100-42-5	<2	<.009	<2	<.009	<2	<.009	<2	<.009	<2	<.009
1,1,2,2-Tetrachloroethane	79-34-5	<2	<.02	<2	<.02	<2	<.02	<2	<.02	<2	<.02

Table 3.1 Contd

TO-14 ANALYTE	CAS #	S4019-A05.144 ^(a) PNL 144 ^(b)		S4019-A07.145 PNL 145		S4019-A09.146 PNL 146		S4019-A01.142 PNL 142		S4019-A02.143 PNL 143	
		(ppbv)	(mg/m ³) ^(c)	(ppbv)	(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)	(mg/m ³)
o-Xylene (1,2-Dimethylbenzene)	95-47-6	1.87	0.01	1.67	0.01	1.62	<.01	<2	<.01	<2	<.01
1,3,5-Trimethylbenzene	108-67-8	<2	<.01	<2	<.01	<2	<.01	<2	<.01	<2	<.01
1,2,4-Trimethylbenzene	95-63-6	<2	<.01	<2	<.01	<2	<.01	<2	<.01	<2	<.01
Chloromethylbenzene, alpha (Benzyl Chloride)	100-44-7	<2	<.01	<2	<.01	<2	<.01	<2	<.01	<2	<.01
m-Dichlorobenzene (1,3-Dichlorobenzene)	541-73-1	<2	<.01	<2	<.01	<2	<.01	<2	<.01	<2	<.01
p-Dichlorobenzene (1,4-Dichlorobenzene)	106-46-7	<2	<.01	<2	<.01	<2	<.01	<2	<.01	<2	<.01
o-Dichlorobenzene (1,2-Dichlorobenzene)	95-50-1	<2	<.01	<2	<.01	<2	<.01	<2	<.01	<2	<.01
1,2,4-Trichlorobenzene	120-82-1	<2	<.02	<2	<.02	<2	<.02	<2	<.02	<2	<.02
Hexachloro-1,3-Butadiene	87-68-3	<2	<.02	<2	<.02	<2	<.02	<2	<.02	<2	<.02

(a) WHC ID number

(b) PNL SUMMA™ canister number

(c) Calculated from ppbv using molecular weight, 760 nm torr, and 0°C

(d) Contributions from individual isomers cannot be determined.

Table 3.2 Table of Tentatively Identified Compounds and Estimated Concentrations in Tank BY-104
SUMMA™ Canisters Collected on 6/24/94

Tentative ^(e) Identification	Molecular Weight	Average Retention Time	S4019-A05.144 ^(a) PNL 144 ^(b)		S4019-A07.145 PNL 145		S4019-A09.146 PNL 146		Average Conc. (mg/m ³)	Std. Dev. Conc. (mg/m ³)
			(mg/m ³) ^(c)	(ppmv)	(mg/m ³)	(ppmv)	(mg/m ³)	(ppmv)		
Carbon Dioxide	44	3.42	(e)	(e)	(e)	(e)	(i)	(i)	(f)	(f)
Carbon Dioxide	44	3.49	(e)	(e)	(e)	(e)	(e)	(e)	(f)	(f)
Propene	42	4.29	2.11	1.12	0.93	0.50	1.01	0.54	1.35	0.66
Propane	44	4.38	0.92	0.47	0.42	0.22	0.46	0.23	0.60	0.28
Cyclopropane	42	5.17	0.26	0.14	0.12	0.06	0.12	0.06	0.17	0.08
2-Methylpropane	58	5.50	0.55	0.21	0.24	0.09	0.25	0.10	0.35	0.17
2-Butene	56	6.09	1.04	0.41	0.45	0.18	0.47	0.19	0.65	0.33
n-Butane	58	6.35	1.18	0.46	0.52	0.20	0.57	0.22	0.76	0.37
2-Methylpropene	58	7.00	0.24	0.09	0.10	0.04	0.11	0.04	0.15	0.08
2-Methyl-2-Butene	56	8.20	0.16	0.06	(h)	(h)	(h)	(h)	(i)	(i)
Acetone	58	8.81	3.16	1.22	1.45	0.56	1.36	0.53	1.99	1.01
Trichlorofluoromethane	137.4	9.23	1.20	0.20	1.15	0.19	1.31	0.21	1.22	0.08
1-Pentene	70	9.49	0.52	0.17	0.19	0.06	0.20	0.06	0.30	0.19
n-Pentane	72	10.00	1.46	0.45	0.44	0.14	0.48	0.15	0.79	0.57
Unknown	(f)	10.67	0.10	(f)	(h)	(h)	(h)	(h)	(i)	(i)
4-Methyl-1-Pentane	84	12.75	0.15	0.04	(h)	(h)	(h)	(h)	(i)	(i)
2-Methylpentane	86	13.43	1.28	0.33	0.91	0.24	0.90	0.23	1.03	0.22
Butanal	72	13.64	0.19	0.06	0.16	0.05	0.14	0.04	0.16	0.03
2-Butanone	72	13.83	0.63	0.19	0.49	0.15	0.41	0.13	0.51	0.11
3-Methylpentane	86	14.24	0.25	0.07	0.22	0.06	0.21	0.05	0.23	0.02
1-Hexene	84	14.50	0.26	0.07	0.21	0.06	0.21	0.06	0.23	0.03
Bromochloromethane (IS)	129.4	15.12								
n-Hexane (coeluent)	86		1.01	0.26	0.70	0.18	0.67	0.17	0.79	0.19
Tetrahydrofuran	72	16.12	0.25	0.08	0.19	0.06	0.16	0.05	0.20	0.04
Methyl Cyclopentane	84	16.86	0.12	0.03	0.11	0.03	0.10	0.03	0.11	0.01
1-Butanol	74	17.82	0.86	0.26	0.60	0.18	0.58	0.17	0.68	0.15
1,4-Difluorobenzene (IS)	114	18.82	0.00		0.14	0.03	0.16			

Table 3.2 Contd

Tentative ^(e) Identification	Molecular Weight	Average Retention Time	S4019-A05.144 ^(a) PNL 144 ^(b)		S4019-A07.145 PNL 145		S4019-A09.146 PNL 146		Average Conc. (mg/m ³)	Std. Dev. Conc. (mg/m ³)
			(mg/m ³) ^(c)	(ppmv)	(mg/m ³)	(ppmv)	(mg/m ³)	(ppmv)		
2-Pentanone	86	18.92	0.67	0.17	0.37	0.10	0.31	0.08	0.45	0.19
3-Methyl hexane	100	19.47	0.41	0.09	0.33	0.07	0.30	0.07	0.35	0.06
Heptene ^(d)	98	20.14	0.13	0.03	0.12	0.03	0.08	0.02	0.11	0.03
n-Heptane	100	20.78	0.63	0.14	0.50	0.11	0.44	0.10	0.53	0.10
C ₆ Ketone ^(d)	100	22.03	0.08	0.02	(h)	(h)	(h)	(h)	(g)	(g)
Methylcyclohexane	98	22.40	0.11	0.03	0.10	0.02	0.09	0.02	0.10	0.01
2-Methylheptane	114	24.46	0.24	0.05	0.19	0.04	0.18	0.03	0.20	0.03
2-Hexanone	100	24.59	0.22	0.05	0.17	0.04	0.16	0.04	0.18	0.03
n-Octane	114	26.26	0.25	0.05	0.21	0.04	0.20	0.04	0.22	0.03
C ₉ Alkane ^(d)	128	27.87	0.10	0.02	0.08	0.01	0.08	0.01	0.09	0.01
Chlorobenzene-d₅ (IS)	117.6	28.34								
1-Heptanol	114	28.84	0.13	0.02	0.10	0.02	0.09	0.02	0.10	0.02
Trimethylcyclohexane (coeluent)	126		(g)	(g)	(h)	(h)	(h)	(h)	(g)	(g)
3-Heptanone	114	29.76	0.19	0.04	0.16	0.03	0.15	0.03	0.17	0.02
2-Heptanone	114	29.89	0.19	0.04	0.14	0.03	0.14	0.03	0.16	0.03
Unknown	(f)	30.46	0.08	(f)	(h)	(h)	(h)	(h)	(i)	(i)
2-Butoxyethanol	116	30.89	0.12	0.02	0.08	0.02	0.09	0.02	0.10	0.02
n-Nonane	128	31.35	0.16	0.03	0.14	0.02	0.13	0.02	0.14	0.02
6-Methylheptanone	114	33.14	0.36	0.07	0.28	0.06	0.28	0.06	0.31	0.05
2-Octanone	128	34.79	0.09	0.02	0.00	(h)	0.07	0.01	0.05	0.05
n-Decane	142	36.05	0.17	0.03	0.13	0.02	0.13	0.02	0.14	0.03
C ₁₁ Alkane ^(d)	156	37.19	0.09	0.01	(h)	(h)	(h)	(h)	(i)	(i)
Unknown	(f)	38.10	0.12	(f)	0.09	(f)	0.09	(f)	0.10	0.01
n-Undecane	156	40.39	0.46	0.07	0.33	0.05	0.32	0.05	0.37	0.08
Methyldecahydronaphthalene ^(d)	152	42.10	0.11	0.02	0.08	0.07	0.01	0.01	0.09	0.02
C Cyclohexane ^(d)	154	42.46	0.16	0.02	0.12	0.11	0.02	0.02	0.13	0.02
C ₁₀ ⁵ Alkane ^(d)	142	42.67	0.17	0.03	0.13	0.12	0.02	0.02	0.14	0.03

Table 3.2 Contd

Tentative ^(e) Identification	Molecular Weight	Average Retention Time	S4019-A05.144 ^(a) PNL 144 ^(b)		S4019-A07.145 PNL 145		S4019-A09.146 PNL 146		Average Conc. (mg/m ³)	Std. Dev. Conc. (mg/m ³)
			(mg/m ³) ^(c)	(ppmv)	(mg/m ³)	(ppmv)	(mg/m ³)	(ppmv)		
Methyldecahydronaphthalene ^(d)	152	42.86	0.20	0.03	0.16	0.02	0.16	0.02	0.17	0.02
C ₁₂ Alkane ^(d)	170	43.04	0.14	0.03	0.11	0.02	0.11	0.02	0.13	0.02
n-Dodecane	170	44.42	2.01	0.26	1.38	0.18	1.36	0.18	1.58	0.37
C ₁₂ Alkane ^(d)	170	45.06	1.49	0.20	1.01	0.13	1.03	1.18	0.14	0.27
Alkane	(f)	46.49	0.78	(f)	0.57	(f)	0.57	0.64	(f)	0.12
C ₁₃ Alkane ^(d)	184	47.32	1.78	0.22	1.26	0.15	1.26	1.43	0.15	0.30
n-Tridecane	184	48.18	2.73	0.33	1.81	0.22	1.84	2.13	0.22	0.52
C ₁₄ Alkane ^(d)	198	51.05	1.36	0.15	0.99	0.11	1.04	1.13	0.12	0.20
n-Tetradecane	198	51.68	1.52	0.17	1.11	1.15	0.13	1.26	0.13	0.22
C ₁₅ Alkane ^(d)	212	53.88	0.46	0.05	0.36	0.38	0.04	0.40	0.04	0.05
n-Pentadecane	212	54.96	0.2	0.02	0.17	0.18	0.02	0.18	0.02	0.02

- (a) WHC ID number
 (b) PNL SUMMA™ canister number.
 (c) Estimated concentration calculated using the chlorobenzene-d₅ IS.
 (d) Other structural isomers should be considered.
 (e) Carbon dioxide cannot be determined by this analytical method.
 (f) Molecular weight information not available for this TIC.
 (g) Individual percent contribution cannot be determined for coeluting TIC.
 (h) This TIC peak is not seen in this sample.
 (i) Mean and standard deviation not meaningful for this TIC.

6.0 Further Reading

Pacific Northwest Laboratory (PNL). 1994a. Quality Assurance Manual, Part 2: Good Practices Standards. PNL-MA-70. Richland, Washington.

Pacific Northwest Laboratory (PNL). 1994b. *Determination of TO-14 Volatile Organic Compounds in Ambient Air Using SUMMA™ Passivated Canister Sampling and Gas Chromatographic-Mass Spectrometry Analysis*, Technical Procedure PNL-TVP-01 (Rev. 0) 8/93, Richland, Washington.

Pacific Northwest Laboratory (PNL). 1994c. *Cleaning SUMMA™ Canisters and the Validation of the Cleaning Process*, Technical Procedure PNL-TVP-02 (Rev. 0) 8/94, Richland, Washington.

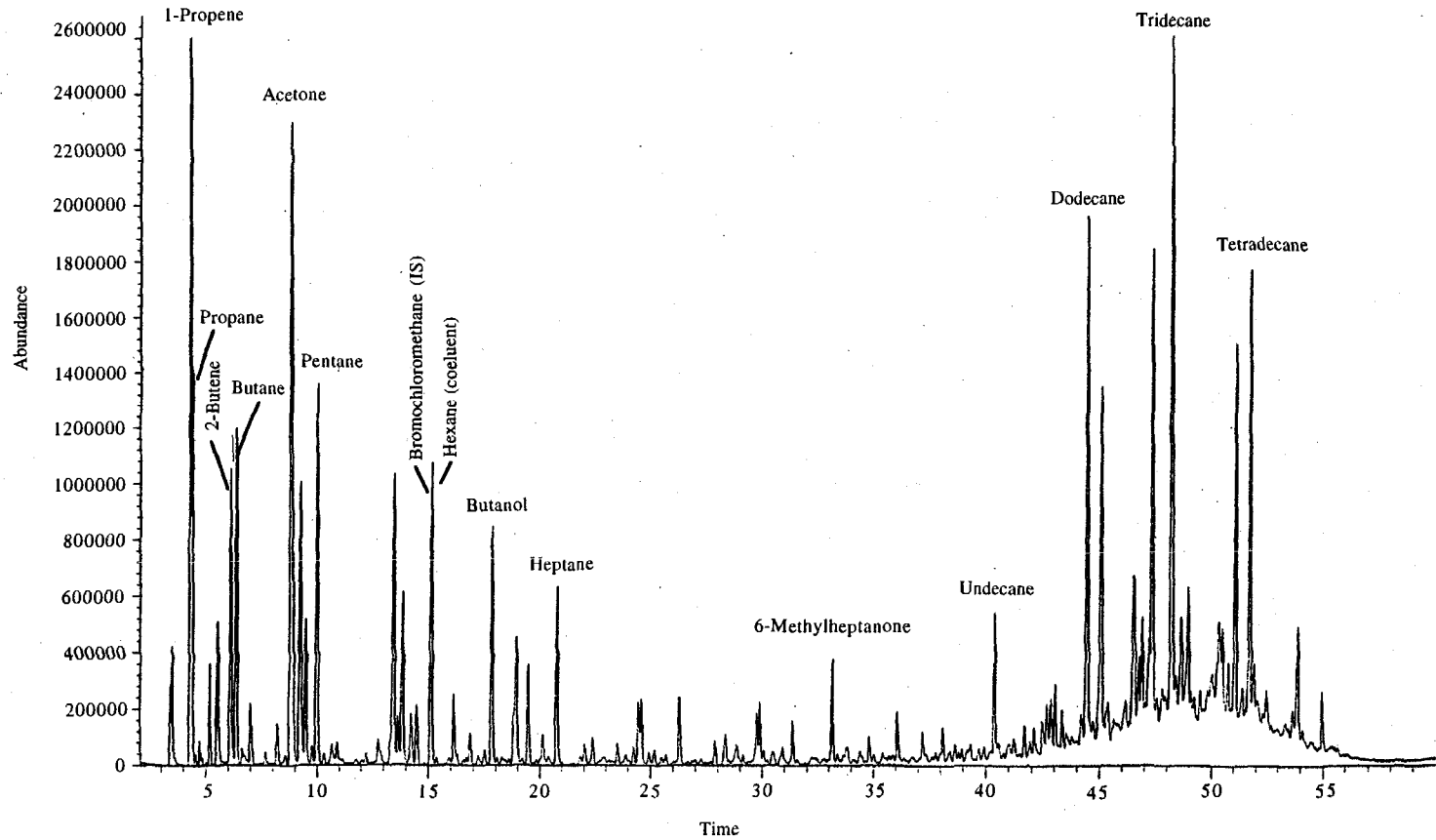


Figure 3.1. GC/MS Chromatogram of Hanford Waste Tank BY-104 SUMMA™ Canister Tank Headspace Sample S4019-A05-144 Collected through the WHC Vapor Sampling System on 6/24/94

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