PNL-10491
UC-606

Vapor Space Characterization of Waste Tank 241-C-101: Results from Samples Collected on 9/1/94

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November 1995

Prepared for Westinghouse Hanford Company
under a Related Services Agreement
with the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest National Laboratory
Operated for the U.S. Department of Energy
by Battelle Memorial Institute

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PNL-10491

PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC06-76RLO 1830

Printed in the United States of America

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831;
prices available from (615) 576-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161

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Pacific Northwest Laboratory
Richland, Washington 99352

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Summary

This report describes inorganic and organic analyses results from samples obtained from the headspace of the Hanford waste storage Tank 241-C-101 (referred to as Tank C-101) and the ambient air collected near the tank. The results described here were obtained to support safety and toxicological evaluations. A summary of the results for inorganic and organic analytes is listed in Table 1. Detailed descriptions of the results appear in the text.

Quantitative results were obtained for the inorganic compounds ammonia (NH_3), nitrogen dioxide (NO_2), nitric oxide (NO), and water (H_20). Sampling for hydrogen cyanide (HCN) and sulfur oxides (SO_x) was not requested. Organic compounds were also quantitatively determined. One hundred twelve organic tentatively identified compounds (TICs) 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 the reported concentrations are semiquantitative estimates. In addition, we looked for the 40 standard TO-14 analytes. Of these, only three were observed above the 2-ppbv detection limit. The 10 organic analytes with the highest estimated concentrations are listed in Table 1 and account for approximately 58% of the total organic components in Tank C-101.

Table 1. Summary Results of Inorganic and Organic Samples Collected from the Headspace of Tank C-101 on 9/1/94

Category	Analyte	Vapor[(a)] Concentration	Units
Inorganic	NH_3	98 ± 1	ppmv
	NO_2	≤ 0.04	ppmv
	NO	1.5 ± 0.1	ppmv
	H_2O	36 ± 1	mg/L
Organic	Dodecane	13.61	mg/m^3
	Tridecane	7.04	mg/m^3
	Undecane	6.45	mg/m^3
	Unknown C13 Alkane	5.70	mg/m^3
	Tridecane, 7-methyl-	5.28	mg/m^3
	Unknown Alkene/Cycloalkane	4.05	mg/m^3
	Heptane	2.01	mg/m^3
	Unknown Alkene/Cycloalkane	1.87	mg/m^3
	Unknown Alkyl decahydronaphthalene	1.46	mg/m^3
	Decane	1.46	mg/m^3

(a) Vapor concentrations were determined using sample-volume data provided by Westinghouse Hanford Company and are based on averaged data.

Acknowledgments

The authors gratefully acknowledge the support of other project staff at Pacific Northwest Laboratory 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. K. B. Olsen assisted with the organic portion of this report. Bruce Lerner performed method development and validation work that supported the inorganic vapor sampling. Sally Slate, May-Lin Thomas, and Karen Schielke analyzed inorganic samples, and Annalisa Krupsha and Gary Dennis prepared the solid-sorbent sample trains. Brenda Thornton provided word processing support.

Abbreviations

CAS	Chemical Abstracts Service
COC	chain of custody
C_v	concentration by volume
DIW	deionized water
emf	electromotive force
EPA	U.S. Environmental Protection Agency
GC/MS	gas chromatography/mass spectrometry
HP	Hewlett Packard
IC	ion chromatography
IL	impact level
IS	internal standard
MDL	minimum detection limit
NIST	National Institute for Standards and Technology
NPH	normal paraffin hydrocarbon
OSHA	Occupational Safety and Health Administration
PFA	perfluoroalkoxy
PNL	Pacific Northwest Laboratory
ppbv	part per billion by volume
ppmv	part per million by volume
QA	quality assurance
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 compound
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 the Hanford waste Tank 241-C-101 (referred to as Tank C-101) and the ambient air collected ~30 ft upwind near the tank and through the VSS near the tank. Pacific Northwest Laboratory (PNL)[(a)] contracted with Westinghouse Hanford Company (WHC) to provide sampling devices and to analyze inorganic and organic analytes collected from the tank headspace and ambient air near the tank. The sample job was designated S4056, and samples were collected by WHC on September 1, 1994, using the vapor sampling system (VSS).

Sampling devices, including six sorbent trains (for inorganic analyses), and five SUMMA™ canisters (for organic analyses) were supplied to the WHC sampling staff on August 15, 1994. Samples were taken (by WHC) from the tank headspace on September 1 and were returned to PNL from the field on September 8. Inorganic (sorbent trap) samples were delivered to PNL on chain of custody (COC) 007502 (see Figure 1.1a). The SUMMA™ canisters were delivered on COC 007501 (see Figure 1.1b).

The samples were inspected upon delivery to the 326/23B laboratory and logged into PNL record book 55408 before implementation of PNL Technical Procedure PNL-TVP-07[(b)]. Custody of the sorbent traps was transferred to PNL personnel performing the inorganic analysis and stored at refrigerated (≤ 10°C) temperature until the time of analysis. The canisters were stored in the 326/23B laboratory at ambient (25°C) temperature until the time of the 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. Analytical methods that were used are described in the text. In summary, sorbent traps for inorganic analyses containing sample materials were either weighed (for water analysis) or desorbed with the appropriate aqueous solutions (for NH_3, NO_2, and NO analyses). The aqueous extracts were analyzed either by selective electrode or by ion chromatography (IC). Organic analyses were performed using cryogenic preconcentration followed by 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.

(b) PNL-TVP-07, Rev. 0, October 1994, *Sample Shipping and Receiving Procedure for PNL Waste Tank Samples*, PNL-Technical Procedure, Tank Vapor Project, Richland, Washington.

Westinghouse Hanford Company | CHAIN OF CUSTODY | WHC 007502

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-C-101 Tank Vapor Sample SAF S4056
Ice Chest No. (VSS Truck)

Collection Date ~~08- _ _ -94~~ Smb/9-1-94 9-1-94
Preparation Date 08- 1 5 -94
Field Logbook No. WHC-N-147-4

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

S4056 - A22 . 80W	$NH_3/NO_x/H_2O$ (Trap # 1) Line # 8
S4056 - A23 . 81W	$NH_3/NO_x/H_2O$ (Trap # 2) Line #10
S4056 - A24 . 82W	$NH_3/NO_x/H_2O$ (Trap # 3) Line # 9
S4056 - A25 . 83W	$NH_3/NO_x/H_2O$ (Trap # 4) Line #10
S4056 - A26 . 84W	$NH_3/NO_x/H_2O$ (Trap # 5) Line # 8
S4056 - A27 . 85W	$NH_3/NO_x/H_2O$ (Trap # 6) Line #10
S4056 - A28 . 86W	$NH_3/NO_2/H_2O$ a-b-c (Trip Blank# 1)
S4056 - A29 . 87W	$NH_3/NO_2/H_2O$ a-b-c (Trip Blank# 2)
S4056 - A30 . 88W	$NH_3/NO_2/H_2O$ a-b-c (Trip Blank# 3)

[ ] Field Transfer of Custody [X] Chain of Possession (Sign and Print Names)

Relinquished By	Date	Time	Received By	Date	Time
J. A. Edwards / J. A. Edwards	08-15-94	1015	Andy Johnson / A. Johnson	08-15-94	10:15
	9/1/94	1340	S.M. BROWN / S.M. Brown	9/1/94	~~1340~~ 1340 Smb 9-1-94
SM BROWN / S M Brown			AMIT SHARMA / Amit Sharma	9/8/94	1330

(Revised 02/28/94)

Final Sample Disposition

Disposal Method:

Disposed by:

Date/Time:

Figure 1.1a Chain of Custody for Inorganic Samples for Tank C-101

A-6000-407 (12/92) WEF061

Westinghouse Hanford Company	**CHAIN OF CUSTODY**	**WHC 007501**

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-C-101 Tank Vapor Sample SAF S4056
Ice Chest No. (VSS Truck)

Collection Date ~~08- _ _ -94~~ 9-1-94 SMB 9-1-94
Preparation Date 08- 1 5 -94
Field Logbook No. WHC-N-647-4

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

S4056 - A01 - 026	SAP Ref ___	Ambient air SUMMA #1, Upwind VSS (PNL)
S4056 - A02 - 031	SAP Ref ___	Ambient air SUMMA #2, Through VSS (PNL)
S4056 - A05 - 033	SAP Ref ___	SUMMA #4 (PNL)
S4056 - A07 - 058	SAP Ref ___	SUMMA #6 (PNL)
S4056 - A09 - 062	SAP Ref ___	SUMMA #8 (PNL)

[X] Field Transfer of Custody [ ] Chain of Possession (Sign and Print Names)

Relinquished By	Date	Time	Received By	Date	Time
J. A. Edwards - JA Edwards	08-15-94	1015	Andy Johnson / E. A. Johnson	08-15-94	10:15
E. A. Johnson	9/1/94	1340	S. M BROWN / SM Brown	9-1-94	1340
S.M. BROWN / SM Brown)	9/8/94	1340	AMIT SHARMA / Amit Sharma	9-8-94	1330

(Revised 02/28/94)

Final Sample Disposition

Disposal Method:

Disposed by:

Date/Time:

A-6000-407 (12/92) WEF061

Figure 1.1b Chain of Custody for Inorganic Samples for Tank C-101

2.0 Inorganic

Solid sorbent traps, prepared in multi-trap sampling trains, were supplied to WHC for sampling the headspace of Tank C-101 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 the following analytes: ammonia (NH_3), nitrogen dioxide (NO_2), nitric oxide (NO), and water (H_20). Procedures were similar to those developed previously during sample jobs performed with the VSS connected to the headspace of Tank C-103 (Ligotke et al. 1994). During those sample jobs, control samples provided validation that samples were effectively trapping NH_3 and mass. Analytical accuracy was estimated based on procedures used. Sample preparation and analyses were performed following PNL quality assurance (QA) impact level (IL) III requirements.

2.1 Standard Sampling Methodology

Standard glass tubes containing sorbent materials to trap vapors of selected analytes of 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. In the tubes, sorbent layers are generally held in packed layers separated by glass wool. The sorbent traps, having glass-sealed ends, were received from the vendor.

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 acid; nominally, 500 mg were contained in the primary and 250 mg in the breakthrough sections. The NH_3 was chemisorbed as ammonium sulfate $\{(NH_4)_2SO_4\}$. 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 absorbed and disproportionated to equi-molar quantities of nitrite ions (NO_2^-) and nitrate ions (NO_3^-). Glass tubes containing 800 mg of an oxidant such as chromate were used to convert NO to NO_2. The converted NO was then collected as nitrite and nitrate in an NO_2 trap. The water traps contained 300 mg of silica gel in the primary and 150 mg in the breakthrough sorbent sections.

Samples provided by PNL to trap inorganic compounds include all or some of the following: samples, spiked samples, spares, single-trap blanks, and spiked blanks. The samples of each type were prepared from same-lot batches, with the oxidizer sections of the NO_x sorbent trains having been 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 receipt of exposed and radiologically cleared samples from WHC and disassembly of the sorbent trains, samples were provided to the analytical laboratory at ambient temperature, and selected oxidizer sections were returned to a freezer until completion of analysis.

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. perfluoroalkoxy (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 traps containing silica gel) were each sealed with red-plastic end caps provided by the manufacturer. 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.

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 the dried tank air sampled 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 molar sample volume was determined, excluding water vapor, by dividing the standard sample volume (at 0°C and 760 torr), in L, by 22.4 L/mol. For example, the concentration (C_v) of a 3.00-L sample containing 75.0 μg of NH_3 equals

$$C_v = \frac{75.0\ \mu g}{17\ g/mol}\left(\frac{3.00\ L}{22.4\ L/mol}\right)^{-1} = 32.9\ ppmv \tag{2.1}$$

This calculational 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 of water vapor). Analytical results were based on extraction and analysis of selected ions. Analytical procedures used are specified herein and compiled in PNL-MA-599.

2.2.1 Ammonia Analysis. The sorbent material from the NH_3-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 NH_3 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-μg/mL (ppm) NH_3 stock standard solution from dried reagent-grade NH_4Cl and DIW on the day analyses are performed; 2) preparing 0.1-, 0.5-, 1.0-, 10-, and 100-ppm NH_3 working calibration standards by serial dilution of the freshly made stock standard; 3) generating an initial calibration curve from the measured electromotive force (emf) signal versus NH_2 concentration data obtained for the set of working standards; 4) performing a calibration-verification check, using one of the midrange standards, after analyzing every four or five 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). Emf signal measurements obtained for samples are compared to those for standards, either graphically or algebraically (using linear regression), to determine NH_3 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 1) eluent 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) in series instead of just one separator column, and 3) all standards, samples, and blanks 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-trap 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 height) 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 were 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 QA plan and several PNL documents. The samples were analyzed following PNL QA IL III. The PNL documents include PNL-MA-70 (Part 2), PNL-MA-599, PNL-ALO-212, PNL-ALO-226, PNL-ALO-271, and MCS-033. 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 recommended exposure limit (REL) for each of the target analytes is achieved using current procedures and with a vapor-sample volume of 3 L and a desorption-solution volume of 3 mL (10 mL for NH_3).

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 achieved. The MDLs were also based on desorbing-solution volumes of 10 mL for NH_3 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 (see Section 2.4). Sampling information, including sample volumes, was provided by WHC; sample volume uncertainty was not provided. The accuracy of analytical results depends on the method used. For NH_3 analyses, the accuracy of laboratory measurements by SIE was estimated to be ± 5% relative, independent of concentration at 1 μg/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 working standards. Similarly, no known NIST SRM is available for nitrite analysis (for NO_2 and NO). Based on experience in comparing nitrite working standards prepared from several different sources and factors mentioned for NH_3 above, the estimated maximum bias for samples derived from sampling for NO_2 is ± 10%, and for samples derived from sampling for NO, it is ± 5% relative. The accuracy of measurements of sample mass is ± 0.05 mg, or much less than 1% of the mass changes of most samples, and roughly 5% or less of the mass change of most blanks.

2.4 Inorganic Sample Results

Samples were obtained by WHC from the headspace of Tank C-101 on 9/1/94 using the VSS. The sample job designation number was S4056. Samples were prepared, submitted to WHC, and then returned and analyzed to provide information on the concentrations of NH_3, NO_2, NO, and H_2O. Sampling and analysis for SO_x and HCN were not requested. The inorganic samples were received from WHC on 9/8/94; the sample-volume information was received on 9/12/94.

A list of samples, sampling information, sample volumes, and gravimetric results is shown in Table 2.2. The types of sample trains used and the order of sorbent traps within each train are also shown in the table. For example, the sorbent train $NH_3/NO_x/H_2O$ contained an NH_3 trap at the inlet end, an NO_x series in the middle (Section 2.4.2), and a desiccant trap at the outlet end. Analytical mass and concentration results are shown in Table 2.3. Sample volumes were provided by WHC; sample-volume uncertainty was not provided. Tank-headspace concentration results (Table 2.3) are based on this information, and the listed uncertainties equal plus-or-minus one standard deviation of the individual results from each set of samples. Where analytical results from each set of samples were nearly indistinguishable from those of blanks, indicating very low vapor concentrations of the analyte, the concentration results (Table 2.3) are listed as "less than or equal to" a probable maximum value determined by subtracting the average of the blanks less one standard deviation from the average of the samples plus one standard deviation. Results of control samples, such as spiked blanks, are discussed in this section. Spiked blanks, when used, were transported to the field but not opened. Spiked samples, when used, were opened in the field and used to collect tank vapors. Sample results were not corrected for the percentage recoveries of spiked blanks.

2.4.1 Ammonia Results. The concentration of NH_3 was 98 ± 1 ppmv, based on all six samples. The NH_3 quantities found in the sorbent traps ranged from 12.9 to 13.3 μmol in the front sorbent sections with no indication of breakthrough. Blank corrections, ≤ 0.06 μmol in front and ≤ 0.03 μmol in back sorbent sections, were less than 1% of collected quantities and were neglected. Although spiked blanks were not tested, the percentage recoveries of three sets of blanks spiked with 12.2, 22.3, and 46.4 μmol NH_3 were 101 ± 4%, 109 ± 2%, and 104 ± 1%, respectively, during related sample jobs (Clauss et al. 1994; Ligotke et al. 1994). The analysis of one sample was duplicated and yielded repeatabilities of ± 4%. One sample leachate was spiked after initial analysis with roughly the quantity of NH_3 in the sample and yielded a percentage recovery of 97%. A 5-point calibration was performed over an NH_3 range of 0.1 to 1000 μg/mL.

2.4.2 Nitrogen Oxides Results. Measurements of NO_2 and NO were made using six 5-segment $NH_3/NO_x/H_2O$ sorbent-trap trains (the NO_x trains consisted of NO_2 trap, oxidizer, and NO_2 trap). Related sample jobs, performed using the VSS in Tanks BY-104, -105, and -106 both with and without NO_x trains protected by a leading NH_3 trap (e.g., Clauss et al. 1994), indicated that the presence of the upstream NH_3 traps resulted in NO concentrations that were about 1.3- to 1.6-fold less than those from unprotected NO_2 traps. The NO_2 concentrations were also potentially less following an NH_3 trap.

The concentrations of NO_2 and NO were ≤ 0.04 and 1.5 ± 0.1 ppmv, respectively. Blank-corrected NO_2^- quantities in the sorbent traps averaged ≤ 0.0027 μmol (NO_2 samples) and 0.099 μmol (NO samples). Nitrite blank levels used to correct data were 0.0142 ± 0.0016 μmol in front and 0.0071 ± 0.0004 μmol in back sorbent sections and were based on blanks from this sample job and those from the related sample job for Tank C-102. The blanks from the two sample jobs were pooled because analyses were only performed on selected blanks. Although spiked blanks were not tested,

Table 2.2 Inorganic Samples, Controls, and Gravimetric Results Obtained From a Heated Tube Inserted into the Headspace of Tank C-101 on 9/1/94

		Sample Port and Volume Information(a)				
Sample Number	Sorbent Train Type	Sample Port	Flow Rate (mL/min)	Duration (min)	Volume (L)	Mass Gain (g)
Samples:						
S4056-A22-80W	$NH_3/NO_x/H_2O$ Train	8	200	15.0	3.00	0.1138
S4056-A23-81W	$NH_3/NO_x/H_2O$ Train	10	200	15.0	3.00	0.1164
S4056-A24-82W	$NH_3/NO_x/H_2O$ Train	9	200	15.0	3.00	0.1140
S4056-A25-83W	$NH_3/NO_x/H_2O$ Train	10	200	15.0	3.00	0.1122
S4056-A26-84W	$NH_3/NO_x/H_2O$ Train	8	200	15.0	3.00	0.1161
S4056-A27-85W	$NH_3/NO_x/H_2O$ Train	10	200	15.0	3.00	0.1130
Controls:						
S4056-A28-86W	$NH_3/NO_2/H_2O$ Blanks	n/a(b)	n/a	n/a	n/a	0.0029
S4056-A29-87W	$NH_3/NO_2/H_2O$ Blanks	n/a	n/a	n/a	n/a	0.0021
S4056-A30-88W	$NH_3/NO_2/H_2O$ Blanks	n/a	n/a	n/a	n/a	NA(b)

(a) Sampling information and dry-gas sample volumes, corrected to 0°C and 760 torr, were provided by WHC. Uncertainty values were not provided with sample-volume results.

(b) n/a = not applicable. NA = not analyzed.

blanks spiked with 0.0064, 0.047, 0.11, and 0.74 μmol NO_2^- during related sample jobs yielded percentage recoveries of 153 ± 14%, 103 ± 4%, 106 ± 8%, and 111 ± 7%, respectively (Clauss et al. 1994; Ligotke et al.). No samples were reanalyzed to check repeatability. No sample leachates were spiked after initial analysis with quantities of NO_2^- to test analytical percentage recoveries. A 4-point calibration was performed over a concentration range of 0 to 0.5 μg NO_2^- per mL in the desorbing matrix.

2.4.3 Gravimetric Results. The mass concentration of material collected in the sorbent-trap trains, believed to be primarily water vapor, was 36 ± 1 mg/L. The result was based on an average mass gain of 109 mg from all six $NH_3/NO_2/H_2O$ sample trains. The blank correction applied to the results was 5 ± 2 mg per sample train, based on an average per-trap mass loss of 1.0 ± 0.4 mg from eight of nine blank traps. Three traps each of NH_3, NO_2, and H_2O were prepared and analyzed as trip blanks. Although no spiked blanks were tested, the percentage recovery of mass from three blank H_2O traps spiked with 51 mg water was 103 ± 2% during a related sample job (Clauss et al. 1994).

Table 2.3 Inorganic Vapor Sample Results Obtained From a Heated Tube Inserted into the Headspace of Tank C-101 on 9/1/94

	Analytical Results (μmol)				
Sample	Front Section	Back Section	Total[b] Blank-Corrected	Sample Volume (L)	Vapor[a] Concentration (ppmv)
NH_3 Samples:			13.2[c]	3.00[c]	98 ± 1[c]
S4056-A22-80W	13.3	≤0.03	13.3	3.00	99
S4056-A23-81W	12.9	NA[d]	12.9	3.00	96
S4056-A24-82W	13.2	NA	13.2	3.00	99
S4056-A25-83W	13.2	NA	13.2	3.00	99
S4056-A26-84W	13.3	NA	13.3	3.00	99
S4056-A27-85W	13.2	NA	13.2	3.00	99
NO_2 Samples:			≤0.0029	3.00	≤ 0.04
S4056-A22-80W	0.0142	0.0078	n/a[d]	3.00	n/a
S4056-A23-81W	0.0128	NA	n/a	3.00	n/a
S4056-A24-82W	0.0128	NA	n/a	3.00	n/a
S4056-A25-83W	0.0130	0.0066	n/a	3.00	n/a
S4056-A26-84W	0.0141	NA	n/a	3.00	n/a
S4056-A27-85W	0.0133	NA	n/a	3.00	n/a
NO Samples:			0.099	3.00	1.5 ± 0.1
S4056-A22-80W	0.111	0.0081	0.097	3.00	1.4
S4056-A23-81W	0.108	NA	0.094	3.00	1.4
S4056-A24-82W	0.104	NA	0.090	3.00	1.3
S4056-A25-83W	0.121	0.0080	0.107	3.00	1.6
S4056-A26-84W	0.121	NA	0.107	3.00	1.6
S4056-A27-85W	0.114	NA	0.100	3.00	1.5
Gravimetric Samples (mg,mg/L):			109 mg	3.00	36 ± 1 mg/L
S4056-A22-80W	n/a	n/a	109	3.00	36
S4056-A23-81W	n/a	n/a	111	3.00	37
S4056-A24-82W	n/a	n/a	109	3.00	36
S4056-A25-83W	n/a	n/a	107	3.00	36
S4056-A26-84W	n/a	n/a	111	3.00	37
S4056-A27-85W	n/a	n/a	108	3.00	36

(a) Blank-corrected vapor concentrations were calculated using WHC-reported dry-air sample volumes (corrected to 0°C and 760 torr). In the calculation for concentration, the nitrite values (listed) were doubled to account for unanalyzed nitrate. Sample results were not corrected for percentage recovery of spiked samples or spiked blanks.

(b) Total blank-corrected analyte masses (nitrite for NO_2 and NO) were determined, when significant, by subtracting the quantity of analyte found in blanks from that found in samples. The levels of analytes found in blanks are described in the subsections of Section 2.4.

(c) Underlined values represent the average of the set of samples. Concentrations uncertainty equals ± 1 standard deviation (absolute) for each set of samples. The use of "≤" is defined in Section 2.4.

(d) NA = not analyzed; n/a = not applicable. Only selected back sorbent sections were analyzed.

3.0 Organic

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 clean, free of TO-14 contaminants to a level of five parts per billion by volume (ppbv), the canister is evacuated in 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 stored more than 30 but less than 60 days are re-evacuated and rehumidified before use. If stored more than 60 days, the canisters 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*, which is a modified version of EPA compendium Method TO-14. The method uses an EnTech cryoconcentration system interfaced with a Hewlett Packard (HP) 5971 GC/MS. The EnTech concentrator is used to pull a metered volume of sample air from the SUMMA™ canister, cryogenically concentrate the air volume, then transfer the volume to the GC/MS for analysis. A 100-mL volume of sample is measured and analyzed from the tank headspace. 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 internal diameter with 3-μm film thickness. The GC oven is programmed to run a temperature gradient beginning at 40°C, holding for 5 min, and 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 SUMMA™ tank samples were 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 six 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

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(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.

bromochloromethane, 1,4-difluorobenzene, and chlorobenzene-d_5 was used as an internal standard (IS) for all blank, calibration standard, and sample analyses. Analyte responses from sample components, ISs, and standards were obtained from the extracted ion plot from their selected mass ion. The calibration curve was generated by calculating the relative response ratios of the IS to calibration-standard responses and plotting the ratios against the ratio of the calibration-standard concentration (in ppbv) to the 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 quantify the TO-14 compounds found 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 ppbv to mg/m^3 assumes standard temperature and pressure (STP) conditions of 760 torr and 273K and was calculated directly from the following equation:

$$\text{mg/m}^3 = \frac{(\text{ppbv}/1000) \times \text{g mol wt of compound}}{22.4 \text{ L/mol}} \tag{3.1}$$

3.3.2 Identification and Quantitation of Tentatively Identified Compounds. The tentatively identified compounds (TICs) are determined by mass-spectral interpretation and comparison of the spectra with the EPA/NIST/WILEY Library, which is a part of the HP 5971 instrument operating system. Chromatographic peaks with an area count greater than, or equal to, one half of the total area count of the chlorobenzene-d_5 IS peak at the 20-ppbv calibration level are tentatively identified and quantitatively estimated. This standard was chosen to determine the integration cutoff as it is in the middle of the chromatographic range and not in a region typically affected by coelution of other compounds. The quality of the mass-spectral searches was then reviewed by the principal investigators before the identification was assigned to each chromatographic peak.

The concentration of each TIC was estimated using a relative response factor calculated using a corrected total peak area for the IS chlorobenzene-d_5. Specifically, the total integrated area for the chlorobenzene-d_5 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 IS concentration in mg/m^3:

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

The calculated response factor was then multiplied by the TIC peak area to give an estimated concentration for that compound. For butane, the total peak area was multiplied by the response factor for chlorobenzene-d_5 to give an estimated concentration of 0.67 mg/m^3. The ISs bromochloromethane and difluorobenzene were not used to quantitate the TICs because coeluting compounds appeared to have greatly altered the signal of the quantitation ions for those two ISs.

The ppbv concentrations are calculated from mg/m^3 and the molecular weight of the analyte.

$$\text{TIC in ppbv} = \frac{\text{TIC (mg/m}^3\text{) x 22.4 L/mol x 1000}}{\text{TIC g mol wt}} \qquad (3.3)$$

The IS level added to all blank, standard, and sample injections was 18.3 ppbv for bromochloromethane, 20.3 ppbv for 1,4-difluorobenzene, and 18.2 ppbv for chlorobenzene-d_5. The IS concentrations were converted from ppbv to mg/m^3 at STP using a molecular weight of 129.39 (g/mol) for bromochloromethane, 114.09 for 1,4-difluorobenzene, and 117.6 for chlorobenzene-d_5.

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. Results of the analysis of ambient air samples are presented in Table 3.3. A representative total ion chromatogram 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. Three target analytes were detected with trichlorofluoromethane (FREON 11) at the highest concentration of 0.73 mg/m^3.

Table 3.2 lists the semiquantitative results for the TICs observed in the samples. The predominant species observed in this sample were normal paraffin hydrocarbons (NPH), defined as n-alkanes from C_{11} to C_{15}. Dodecane had the highest concentration (13.61 mg/m^3). 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, which may adhere to the inside surface of the canister, may also be under represented in this analysis. The total concentration of the TIC compounds was found to be 83.87 mg/m^3.

Table 3.3 lists the TIC and estimated concentrations for ambient air samples, one collected ~10 m upwind and the other collected through the VSS positioned near Tank C-101. Six compounds were detected upwind of Tank C-101 with butanal at the highest concentration (0.45 mg/m^3). Three compounds were detected in the samples collected near the tank through the VSS with acetaldehyde at the highest concentration (0.21 mg/m^3). No TO-14 target analytes were observed in the ambient air.

4.0 Conclusions

The concentrations of selected inorganic and organic compounds were determined from samples of the headspace of Tank C-101 on 9/1/94. Sampling and analysis methods followed those described by Ligotke et al. (1994) for samples obtained from C-103, a tank containing a relatively complex headspace composition. Method-validation measurements during that study did appear to validate the trapping and analysis of NH_3, but did not eliminate the possibility of interferences that could affect NO_x results. It is recommended that additional control samples be obtained if a tank is discovered in the future to contain significant quantities of NO_x. In the current sample job, NO_x samples were obtained after first passing the sample flow through an NH_3 trap. The NH_3 concentration was found to be 98 ± 1 ppmv. The concentration of NO_2 was ≤ 0.04 ppmv. The concentration of NO was 1.5 ± 0.1 ppmv. The mass concentration was 36 ± 1 mg/L, and was expected to consist largely of water vapor.

Organic analysis of the headspace samples from Tank C-101 identified three TO-14 target analyte compounds above the 2-ppbv detection limit and 120 TIC compounds above the 10-ppbv detection limit. The concentration of the total TO-14 target analytes accounted for less than 1% of the total compounds identified by organic analysis. For the TIC compounds, dodecane accounted for 16% of the total TIC concentration. The results of the TIC identified NPH-type compounds as the predominant species present. The TIC results of the ambient air samples, collected ~10 m upwind of Tank C-101, identified six compounds, with butanal at the highest concentration. Three compounds were detected in the sample collected near the tank through the VSS, with acetaldehyde at the highest concentration. No TO-14 target analytes were observed in the ambient air sample.

5.0 References

Clauss, T. W., M. W. Ligotke, B. D. McVeety, K. H. Pool, R. B. Lucke, J. S. Fruchter, and S. C. Goheen. 1994. *Vapor Space Characterization of Waste Tank 241-by-104: Results from Samples Collected on 6/24/94.* PNL-10208. Pacific; Northwest Laboratory, Richland, Washington.

Ligotke, M. W., K. H. Pool, and B. D. Lerner. 1994. *Vapor Space Characterization of Waste Tank 241-C-103: Inorganic Results from Sample Job 7B (5/12/94).* PNL-10172, Pacific Northwest Laboratory, Richland, Washington.

6.0 Further Reading

Pacific Northwest Laboratory. Analytical Laboratory Procedure Compendium. Procedures PNL-ALO-212, -226, -271. PNL-MA-599, Richland, Washington.

Pacific Northwest Laboratory. Quality Assurance Manual, Part 2: Good Practices Standard. PNL-MA-70, Part 2, Richland, Washington.

Pacific Northwest Laboratory. Quality Assurance Plan for Activities Conducted by the Analytical Chemistry Laboratory (ACL). MCS-033, Analytical Chemistry Laboratory, Richland, Washington.

Pacific Northwest Laboratory. 1994. *Determination of TO-14 Volatile Organic Compounds in Hanford Waste Tank Headspace Samples Using SUMMA" Passivated Canister Sampling and GAs Chromatographic-Mass Spectrometry Analysis,* PNL-TVP-03 (Rev. 0), PNL Technical Procedure, Richland, Washington.

Pacific Northwest Laboratory. 1994. *Sample Shipping and Receiving Procedure - DRAFT for PNL Waste Tank Samples.* PNL-TVP-07 (Rev. 0), PNL Technical Procedure, Richland, Washington.

Table 3.1 TO-14 Analysis for Samples from the Headspace of Tank C-101 in SUMMA™ Canister Samples Collected on 9/1/94

			S4056-A05-033[(a)] PNL 033[(b)] Concentration		S4056-A07-058[(a)] PNL 058[(b)] Concentration		S4056-A07-062[(a)] PNL 062[(b)] Concentration		Means and Standard Deviations	
TO-14 Analyte	CAS No.	Mol Wt	(mg/m³)	(ppbv)	(mg/m³)	(ppbv)	(mg/m³)	(ppbv)	(mg/m³)	St Dev
Dichlorodifluoromethane (FREON-12)	75-71-8	120	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
Methyl Chloride (Chloromethane)	74-87-3	50	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
1,2-Dichloro-1,1,2,2,-Tetrafluoroethane (FREON-114)	76-14-2	170	< 0.02	< 2	< 0.02	< 2	< 0.02	< 2	(c)	(c)
Chloroethene (Vinyl Chloride)	75-01-4	64	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
Methyl Bromide (Bromomethane)	74-83-9	94	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
Ethyl Chloride	75-00-3	62	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
Trichlorofluoromethane (FREON-11)	75-69-4	136	0.98	161	0.63	104	0.58	95.7	0.73	92.6
1,1-Dichloroethene (1,1-Dichloroethylene)	75-35-4	96	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
Dichloromethane (Methylene Chloride)	75-09-2	84	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
1,1,2-Trichloro-1,2,2-Trifluoroethane (FREON-113)	76-13-1	186	< 0.02	< 2	< 0.02	< 2	< 0.02	< 2	(c)	(c)
1,1-Dichloroethane	75-34-3	98	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
cis-1,2-Dichloroethene (cis-1,2-Dichloroethylene)	156-59-2	96	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
Trichloromethane (Chloroform)	67-66-3	118	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
cis 1,2-Dichloroethane	107-06-2	98	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
1,1,1-Trichloroethane	71-55-6	132	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
Benzene	71-43-2	78	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
Carbon Tetrachloride	56-23-5	152	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
1,2-Dichloropropane	78-87-5	112	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
Trichloroethylene	79-01-6	130	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
cis 1,3-Dichloropropene	61-01-5	110	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
trans 1,3-Dichloropropene	61-02-6	110	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
1,1,2-Trichloroethane	79-00-5	132	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
Methyl Benzene (Toluene)	108-88-3	92	0.05	11.5	0.05	11.5	0.04	10.6	0.05	6.61
1,2-Dibromoethane	106-93-4	186	< 0.02	< 2	< 0.02	< 2	< 0.02	< 2	(c)	(c)
Tetrachloroethene (Perchloroethylene)	127-18-4	164	0.02	2.79	0.03	4.66	0.03	4.23	0.03	1.59
Chlorobenzene	108-90-7	112	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
Ethylbenzene	100-41-4	106	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
m-Xylene (1,3-Dimethylbenzene)[(d)]	108-38-3	106	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
p-Xylene (1,4-Dimethylbenzene)[(d)]	106-42-3	106								
Styrene	100-42-5	104	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)

Table 3.1 (Contd)

			S4056-A05-033[a] PNL 033[b] Concentration		S4056-A07-058[a] PNL 058[b] Concentration		S4056-A07-062[a] PNL 062[b] Concentration		Means and Standard Deviations	
TO-14 Analyte	CAS No.	Mol Wt	(mg/m^3)	(ppbv)	(mg/m^3)	(ppbv)	(mg/m^3)	(ppbv)	(mg/m^3)	St Dev
1,1,2,2-Tetrachloroethane	79-34-5	166	< 0.02	< 2	< 0.02	< 2	< 0.02	< 2	(c)	(c)
o-Xylene (1,2-Dimethylbenzene)	95-47-6	106	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
1,3,5-Trimethylbenzene	108-67-8	120	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
1,2,4-Trimethylbenzene	95-63-6	120	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
Chloromethylbenzene, alpha (Benzyl Chloride)	100-44-7	126	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
m-Dichlorobenzene (1,3-Dichlorobenzene)	541-73-1	146	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
p-Dichlorobenzene (1,4-Dichlorobenzene)	106-46-7	146	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
o-Dichlorobenzene (1,2-Dichlorobenzene)	95-50-1	146	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
1,2,4-Trichlorobenzene	120-82-1	180	< 0.02	< 2	< 0.02	< 2	< 0.02	< 2	(c)	(c)
Hexachloro-1,3-Butadiene	87-68-3	258	< 0.02	< 2	< 0.02	< 2	< 0.02	< 2	(c)	(c)

(a) WHC sample identification number.

(b) PNL canister number.

(c) Average and standard deviation data are not meaningful for this analyte.

(d) m-Xylene and p-Xylene coelute; the reported concentration is the sum of these two compounds.

Table 3.2 Tentatively Identified Compounds and Estimated Concentrations(a) from the Headspace of Tank C-101 in SUMMA™ Canister Samples Collected on 9/1/94

Tentatively Identified Compound(d)	CAS No.(d)	Mol. Wt	Ret Tim	S4056-A05-033(b) PNL 033(c) Concentration (mg/m^3)	(ppbv)	S4056-A07-058(b PNL 058(c) Concentration (mg/m^3)	(ppbv)	S4056-A09-062(b) PNL 062(c) Concentration (mg/m^3)	(ppbv)	Means and Standard Deviations (mg/m^3)	St Dev	(ppbv)	St Dev
Propene	115-07-1	42	3.88	0.27	145	0.28	150	0.27	146	0.28	0.01	147	2.8
Propane	74-98-6	44	3.98	0.50	255	0.49	248	0.50	252	0.49	0.01	252	3.3
Propyne	74-99-7	40	4.34	0.55	309	0.57	318	0.56	311	0.56	0.01	313	4.3
Cyclopropane	75-19-4	42	4.76	0.26	138	0.27	141	0.26	140	0.26	0.00	140	1.9
Acetaldehyde	75-07-0	44	5.09	< 0.02	< 10.0	< 0.02	< 10.0	0.07	33.6	(e)		(e)	
Isobutane	75-28-5	58	5.10	0.06	23.9	0.06	23.2	0.07	25.9	0.06	0.00	24.3	1.4
1-Butene	106-98-9	56	5.77	0.17	68.8	0.17	66.4	0.17	69.2	0.17	0.00	68.1	1.5
Butane	106-97-8	58	5.97	0.69	265	0.64	248	0.67	260	0.67	0.02	257	8.9
2-Methyl-1-propene	115-11-7	56	6.62	0.15	58.8	0.14	54.4	0.15	60.0	0.14	0.01	57.7	2.9
Acetonitrile	75-05-8	41	7.92	0.24	129	0.24	130	0.25	134	0.24	0.00	131	2.7
Acetone	67-64-1	58	8.46	0.90	349	0.92	356	0.90	348	0.91	0.01	351	4.3
1-Pentene	109-67-1	70	9.16	0.07	21.8	< 0.03	< 10.0	0.07	21.8	0.07	0.00	21.8	0.0
Pentane	109-66-0	72	9.65	0.37	114	0.36	112	0.36	112	0.36	0.00	112	1.0
Methyl nitrate	598-58-3	77	10.47	0.08	22.7	0.07	21.5	0.07	21.5	0.08	0.00	21.9	0.7
Propanenitrile	107-12-0	55	11.91	< 0.02	< 10.0	0.08	31.4	< 0.02	< 10.0	(e)		(e)	
2-Pentene	109-68-2	70	13.01	< 0.03	< 10.0	< 0.03	< 10.0	0.07	21.4	(e)		(e)	
2-Pentanone	107-87-9	86	13.02	< 0.04	< 10.0	< 0.04	< 10.0	< 0.04	< 10.0	(e)		(e)	
2-Methylpentane	107-83-5	86	13.14	0.24	61.5	0.24	62.5	0.24	62.8	0.24	0.00	62.3	0.7
Butanal	123-72-8	72	13.41	0.22	68.8	0.23	70.6	0.22	67.8	0.22	0.00	69.1	1.4
2-Butanone	78-93-3	72	13.55	0.36	111	0.35	108	0.34	107	0.35	0.01	109	2.1
1-Hexene	592-41-6	84	14.21	0.08	20.8	0.08	22.1	0.08	22	0.08	0.00	21.5	0.7
Tetrahydrofuran	109-99-9	72	15.83	0.25	76.2	0.43	132	0.42	132	0.36	0.10	113	32.2
2-Methyl-2-propanenitrile	126-98-7	67	17.05	< 0.03	< 10.0	< 0.03	< 10.0	0.11	36.4	(e)		(e)	
Butanenitrile	109-74-0	69	17.05	0.13	43.2	0.12	38.0	< 0.03	< 10.0	0.13	0.01	40.6	3.7
3-Methyl-2-butanone	563-80-4	86	17.21	0.13	34.6	0.12	30.5	< 0.03	< 10.0	0.13	0.01	32.6	2.9
2-Pentanone	107-87-9	86	17.23	< 0.04	< 10.0	< 0.04	< 10.0	0.11	29.7	(e)		(e)	
3-Methyl-2-butanone	563-80-4	86	17.24	0.13	34.6	0.12	30.5	< 0.04	< 10.0	0.13	0.01	32.6	2.9
1-Butanol	71-36-3	74	17.57	0.76	229	0.87	264	0.61	183	0.75	0.13	226	40.5
1-Methylethylnitrate	1712-64-7	105	18.34	0.16	33.7	0.14	30.3	0.14	29.0	0.15	0.01	31.0	2.4
2-Pentanone	107-87-9	86	18.66	0.67	174	0.58	151	0.56	145	0.60	0.06	157	15.3
Pentanal	110-62-3	86	19.19	1.01	263	0.90	234	0.84	219	0.92	0.09	239	22.6

C101 Table 3.2 (Contd)

				S4056-A05-033(b)		S4056-A07-058(b		S4056-A09-062(b)					
				PNL 033(c)		PNL 058(c)		PNL 062(c)		Means and			
Tentatively				Concentration		Concentration		Concentration		Standard Deviations			
Identified Compound(d)	CAS No.(d)	Mol. Wt	Ret Tim	(mg/m^3)	(ppbv)	(mg/m^3)	(ppbv)	(mg/m^3)	(ppbv)	(mg/m^3)	St Dev	(ppbv)	St Dev
Heptane	142-82-5	100	20.52	2.21	494	1.95	437	1.88	421	2.01	0.17	451	38.6
Unknown C7 Alkane		100	21.74	0.27	60.5	0.26	58.5	0.23	51.5	0.25	0.02	56.8	4.7
Methylcyclohexane	108-87-2	98	22.11	0.14	31.8	0.13	29.7	0.13	29.3	0.13	0.01	30.2	1.3
2-Methyl-1-butanol	137-32-6	88	23.24	< 0.04	< 10.0	0.16	41.2	< 0.04	< 10.0	(e)		(e)	
Unknown C7 Alkene/Cycloalkane		98	23.25	0.20	45.0	< 0.04	< 10.0	0.15	33.4	0.17	0.04	39.2	8.2
Unknown C3 Nitrate		105	23.76	0.09	19.8	0.09	18.6	0.09	18.1	0.09	0.00	18.8	0.9
Unknown C8 Alkane		114	24.21	0.30	59.3	0.30	59.1	0.30	58.2	0.30	0.00	58.9	0.6
2-Hexanone	591-78-6	100	24.34	0.29	64.7	0.27	60.3	0.27	59.6	0.27	0.01	61.5	2.8
Hexanal	66-25-1	100	24.91	0.40	89.2	0.37	82.7	0.34	76.4	0.37	0.03	82.7	6.4
Octane	111-65-9	114	26.02	1.28	252	1.20	236	1.19	233	1.22	0.05	240	10.0
Hexamethylcyclotrisiloxane	541-05-9	222	26.78	< 0.10	< 10.0	0.99	100	< 0.10	< 10.0	(e)		(e)	
3-Methylcyclopentanone	1757-42-2	98	27.39	0.10	22.4	0.10	22.4	0.09	21.0	0.10	0.00	21.9	0.8
Unknown C9 Alkane		128	27.61	0.16	28.7	0.16	28.0	0.16	27.1	0.16	0.00	27.9	0.8
Methylpyridine	108-99-6	93	28.42	< 0.04	< 10.0	0.13	30.8	0.17	41.4	0.15	0.03	36.1	7.5
Unknown C9 Alkane		128	29.45	0.09	15.2	< 0.06	< 10.0	< 0.06	< 10.0	(e)		(e)	
2-Heptanone	110-43-0	114	29.65	0.31	59.9	0.29	56.6	0.28	54.2	0.29	0.01	56.9	2.9
Cyclohexanone	108-94-1	98	29.93	0.13	29.3	0.20	45.7	0.19	43.0	0.17	0.04	39.3	8.8
Heptanal	111-71-7	114	30.24	0.32	62.3	0.32	61.9	0.29	57.8	0.31	0.01	60.7	2.5
Nonane	111-84-2	128	31.13	0.61	107	0.60	104	0.57	98.9	0.59	0.02	104	4.3
Penstet Nitrate	1002-16-0	133	31.32	0.12	19.9	0.12	19.7	0.11	18.9	0.12	0.00	19.5	0.5
6-Methyl-2-heptanone	928-68-7	128	32.90	0.63	110	0.60	105	0.57	100	0.60	0.03	105	5.2
Unknown C9 Alkane		142	34.15	< 0.06	< 10.0	< 0.06	< 10.0	0.09	14.2	(e)		(e)	
Unknown C9 Ketone		140	34.15	0.09	14.9	0.10	15.4	< 0.06	< 10.0	0.09	0.00	15.1	0.3
2-Octanone	111-13-7	128	34.56	0.16	28.4	0.16	28.0	0.16	27.5	0.16	0.00	27.9	0.4
Unknown C10 Alkene/Cycloalkane		140	34.74	0.10	15.7	0.09	14.4	< 0.06	< 10.0	0.09	0.01	15.0	0.9
Octanal	124-13-0	128	35.16	0.20	35.2	< 0.06	< 10.0	0.23	40.4	0.22	0.02	37.8	3.7
Octamethylcyclotetrasiloxane	556-67-2	296	35.17	< 0.13	< 10.0	0.39	29.1	< 0.13	< 10.0	(e)		(e)	
Unknown Alkene/Cycloalkane			35.60			0.10	(f)	0.10	(f)	0.10	0.00		
Decane	124-18-5	142	35.84	1.52	240	1.43	225	1.43	225	1.46	0.05	230	8.7
Hexane Nitrate	20633-11-8	147	36.13	0.09	13.0	0.09	13.3	0.09	13.1	0.09	0.00	13.1	0.2
4-Methyldecane	2847-72-5	156	36.97	0.50	71.8	0.50	72.2	0.52	74.5	0.51	0.01	72.8	1.5

C101 Table 3.2 (Contd)

Tentatively Identified Compound(d)	CAS No.(d)	Mol. Wt	Ret Tim	S4056-A05-033(b) PNL 033(c) Concentration (mg/m^3)	(ppbv)	S4056-A07-058(b PNL 058(c) Concentration (mg/m^3)	(ppbv)	S4056-A09-062(b) PNL 062(c) Concentration (mg/m^3)	(ppbv)	Means and Standard Deviations (mg/m^3)	St Dev	(ppbv)	St Dev
Unknown C10 Alkene/Cycloalkane		140	37.36	0.10	16.5	0.11	16.8	0.10	16.3	0.10	0.00	16.5	0.2
Unknown C10 Alkene/Cycloalkane		140	37.85	0.19	29.9	0.19	29.9	0.18	29.3	0.19	0.00	29.7	0.4
Unknown C11 Alkene/Cycloalkane		154	38.14	0.09	13.5	0.11	16.3	0.10	14.3	0.10	0.01	14.7	1.4
Unknown C11 Alkane		156	38.42	0.09	13.4	0.08	11.9	0.09	12.5	0.09	0.01	12.6	0.7
Unknown C12 Alkane		170	38.73	0.11	15.0	0.11	14.4	0.11	14.6	0.11	0.00	14.7	0.3
Unknown C11 Alkene/Cycloalkane		154	38.91	0.11	16.1	0.11	16.0	0.11	16.4	0.11	0.00	16.2	0.2
Unknown C11 Alkane		156	39.05	0.16	22.5	0.15	21.5	0.15	21.0	0.15	0.01	21.7	0.8
trans-Decahydronaphthalene	493-02-7	138	39.42	0.14	23.2	0.14	22.6	0.12	20.0	0.14	0.01	21.9	1.7
Unknown C12 Alkene/Cycloalkane		154	39.69	0.13	18.9	0.17	24.1	0.17	25.2	0.16	0.02	22.7	3.4
Unknown C11 Alkene/Cycloalkane		168	40.00	0.17	22.5	0.15	19.9	0.18	24.5	0.17	0.02	22.3	2.3
Undecane	1120-21-4	156	40.22	7.06	1013	6.26	898	6.05	869	6.45	0.53	927	76.1
Unknown Alkene/Cycloalkane		168	40.75	0.32	43.1	0.31	41.3	0.30	39.7	0.31	0.01	41.4	1.7
Unknown C12 Alkane		170	41.02	0.38	49.8	0.36	46.9	0.34	45.1	0.36	0.02	47.3	2.4
Unknown C12 Alkane		170	41.47	0.50	66.1	0.47	61.9	0.45	59.2	0.47	0.03	62.4	3.5
2-Methyldecahydronaphthalene	2958-76-1	152	41.85	0.27	39.6	0.35	50.8	0.37	53.8	0.33	0.05	48.1	7.5
Pentylcyclohexane	4292-92-6	154	42.26	0.66	96.3	0.62	89.9	0.44	64.0	0.57	0.12	83.4	17.1
Unknown C12 Alkane		170	42.49	1.52	200	1.42	188	0.84	110	1.26	0.37	166	48.7
Unknown C12 Alkane		170	42.70	0.70	92.1	0.61	80.1	0.42	54.9	0.57	0.14	75.7	19.0
Unknown C13 Alkane		184	42.87	1.43	174	1.32	160	1.16	141	1.30	0.14	158	16.6
Unknown C12 Alkane		170	43.17	0.91	120	0.84	110	0.76	100	0.84	0.08	110	9.9
Unknown C12 Alkene/Cycloalkane		168	43.33	0.21	28.5	0.21	27.3	0.20	27.2	0.21	0.01	27.7	0.7
Unknown C12 Alkene/Cycloalkane		168	43.59	0.19	25.1	0.17	22.8	0.16	20.9	0.17	0.02	22.9	2.1
Unknown C13 Alkane		184	44.01	1.49	182	1.39	169	1.27	155	1.38	0.11	169	13.4
Dodecane	112-40-3	170	44.34	15.22	2005	13.10	1726	12.51	1648	13.61	1.42	1793	187.8
Unknown C12 Alkene/Cycloalkane		168	44.52	0.62	82.7	<0.08	<10.0	0.48	64.1	0.55	0.10	73.4	13.1
2,6-Dimethyldecahydronaphthalen	1618-22-0	166	44.74	0.86	116	0.80	108	0.83	112	0.83	0.03	112	3.9
Unknown C13 Alkane		184	44.90	6.59	803	5.49	668	5.01	610	5.70	0.81	693	98.9
Unknown C13 Alkane		184	45.22	1.07	131	1.01	123	0.96	117	1.01	0.06	123	7.0
Unknown C13 Alkane		184	45.41	0.26	32.0	0.21	25.4	0.19	23.4	0.22	0.04	26.9	4.5
Unknown			45.52	0.25	(f)	0.22	(f)	0.22	(f)	0.23	0.02		
Unknown C2 Decahydronaphthalene		166	45.95	1.28	173	1.22	164	1.12	151	1.21	0.08	163	10.7

C101 Table 3.2 (Contd)

				S4056-A05-033(b) PNL 033(c) Concentration		S4056-A07-058(b PNL 058(c) Concentration		S4056-A09-062(b) PNL 062(c) Concentration		Means and Standard Deviations			
Tentatively Identified Compound(d)	CAS No.(d)	Mol. Wt	Ret Tim	(mg/m^3)	(ppbv)	(mg/m^3)	(ppbv)	(mg/m^3)	(ppbv)	(mg/m^3)	St Dev	(ppbv)	St Dev
Unknown C3 Alkene/Cycloalkane		182	46.30	4.42	544	3.95	486	3.79	467	4.05	0.33	499	40.1
Unknown C2 Alkyl Decahydronaphthalene		166	46.56	1.63	220	1.31	176	1.45	195	1.46	0.16	197	21.8
Unknown C13 Alkane		184	46.74	1.65	201	1.20	146	1.40	170	1.42	0.22	172	27.4
Unknown C2 Decahydronaphthalene		166	46.88	0.41	54.9	< 0.07	< 10.0	0.34	46.3	0.38	0.05	50.6	6.1
Unknown Alkane			47.02	1.02	(f)	0.84	(f)	0.95	(f)	0.94	0.09		
7-Methyltridecane	26730-14-3	198	47.17	5.81	658	4.99	564	5.03	569	5.28	0.47	597	52.7
Unknown Alkene/Cycloalkane			47.61	1.11	(f)	1.04	(f)	0.86	(f)	1.00	0.13		
Tridecane	629-50-5	184	48.05	7.66	933	6.48	788	6.98	849	7.04	0.60	857	72.5
Unknown Alkene/Cycloalkane			48.43	2.00	(f)	1.87	(f)	1.74	(f)	1.87	0.13		
Unknown Alkane			48.77	0.66	(f)	0.56	(f)	0.63	(f)	0.61	0.05		
Unknown Alkene/Cycloalkane			49.05	0.44	(f)					(e)			
Unknown C12 Ketone		184	50.20	0.90	109	0.84	102	1.68	204	1.14	0.47	139	57.0
3-Dodecanone	1534-27-6	184	50.73	0.12	14.4	0.13	15.2	0.14	17.3	0.13	0.01	15.6	1.5
Unknown Alkane			50.89	0.52	(f)	0.50	(f)	0.65	(f)	0.56	0.08		
Unknown			51.17	0.43	(f)	0.40	(f)	0.42	(f)	0.42	0.02		
Tetradecane	629-59-4	198	51.53	0.12	13.1	0.13	14.6	0.27	30.3	0.17	0.08	19.3	9.5
Unknown Alkene/Cycloalkane			52.27	0.17	(f)	0.14	(f)	0.18	(f)	0.16	0.02		

(a) Semi-quantitative estimate calculated using concentration of closest eluting internal standard.
(b) WHC sample identification number.
(c) PNL SUMMA^{TM} canister number.
(d) Obtained by mass spectral interpretation amd comparison with the EPA/NIST/WILEY Library.
(e) Average and standard deviation are not meaningful for this analyte.
(f) No molecular weight available for calculation.

Table 3.3 Tentavtively Identified Compounds and Estimated Concentrations[a] for Ambient Air Collected Near Tank C-101 in SUMMA™ Canisters on 9/1/94

Tentatively Identified Compound[d]	CAS No.[d]	Mol. Wt	Ret Time	Upwind S4056-A01-026[b] PNL 026[c] Concentration (mg/m3)	(ppbv)	Through VSS S4056-A02-031[b] PNL 031[c] Concentration (mg/m^3)	(ppbv)
Acetaldehyde	75-07-0	44	5.09	0.212	108	0.21	106
Acetone	67-64-1	58	8.46	0.15	57.9	0.17	64.5
3-Butenone	78-94-4	70	12.95	0.65	208	< 0.03	< 10.0
2-Pentanone	107-87-9	86	13.02	< 0.04	< 10.0	0.08	19.5
Butanal	123-72-8	72	13.41	0.449	140	< 0.03	< 10.0
2-Butanone	78-93-3	72	13.55	0.066	20.5	< 0.03	< 10.0
1-Butanol	71-36-3	74	17.57	0.058	17.6	< 0.03	< 10.0

(a) Semi-quantitative estimate calculated using concentration of closest eluting internal standard.

(b) WHC sample identification number.

(c) PNL SUMMA™ canister number.

(d) Obtained by mass spectral interpretation amd comparison with the EPA/NIST/WILEY Library.

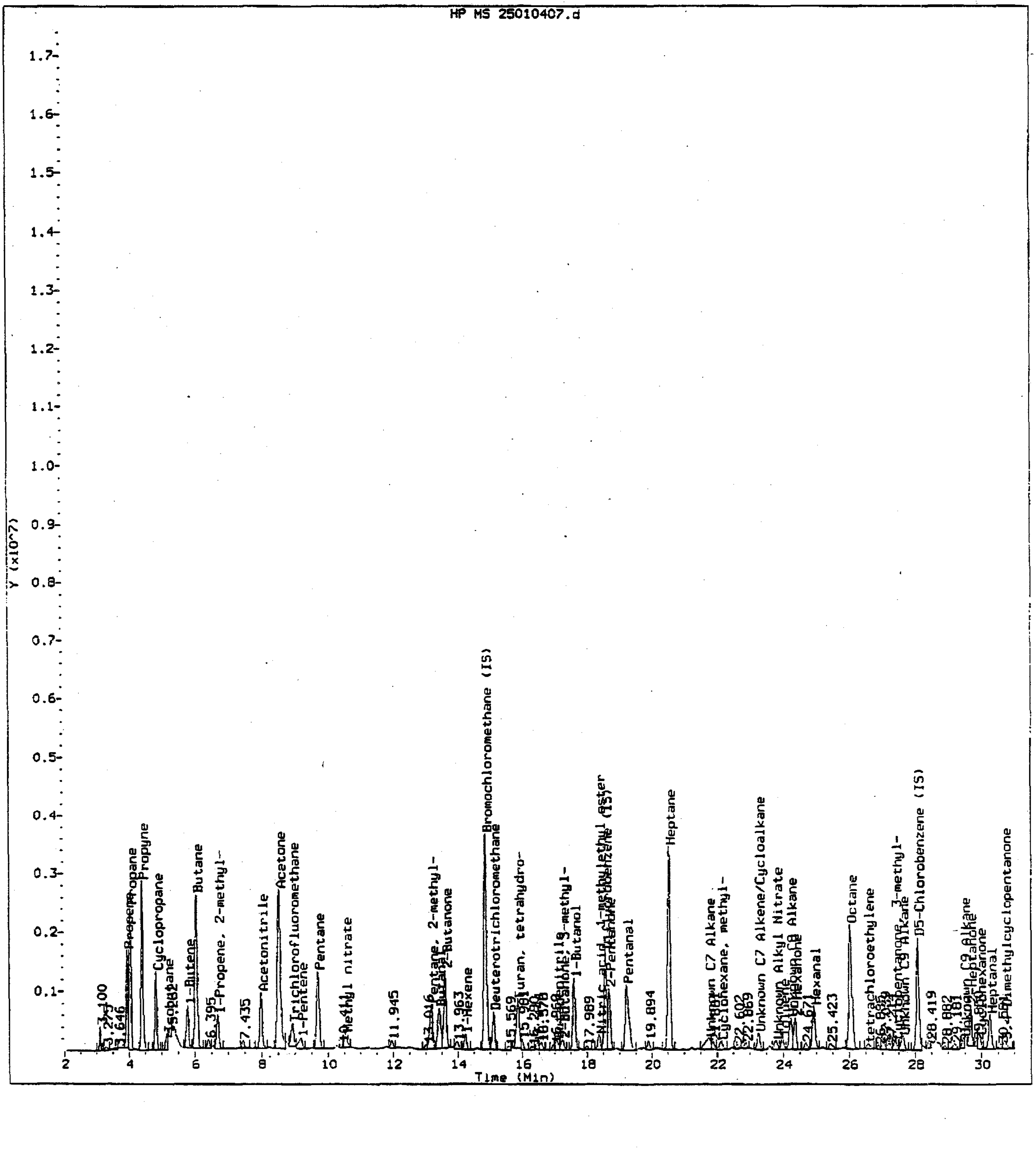

Figure 3.1a Total Ion Chromatogram (2 through 30 min) for Hanford Waste Tank C-101 SUMMA™ Canister Sample S4056-A05-033 Collected on 9/1/94

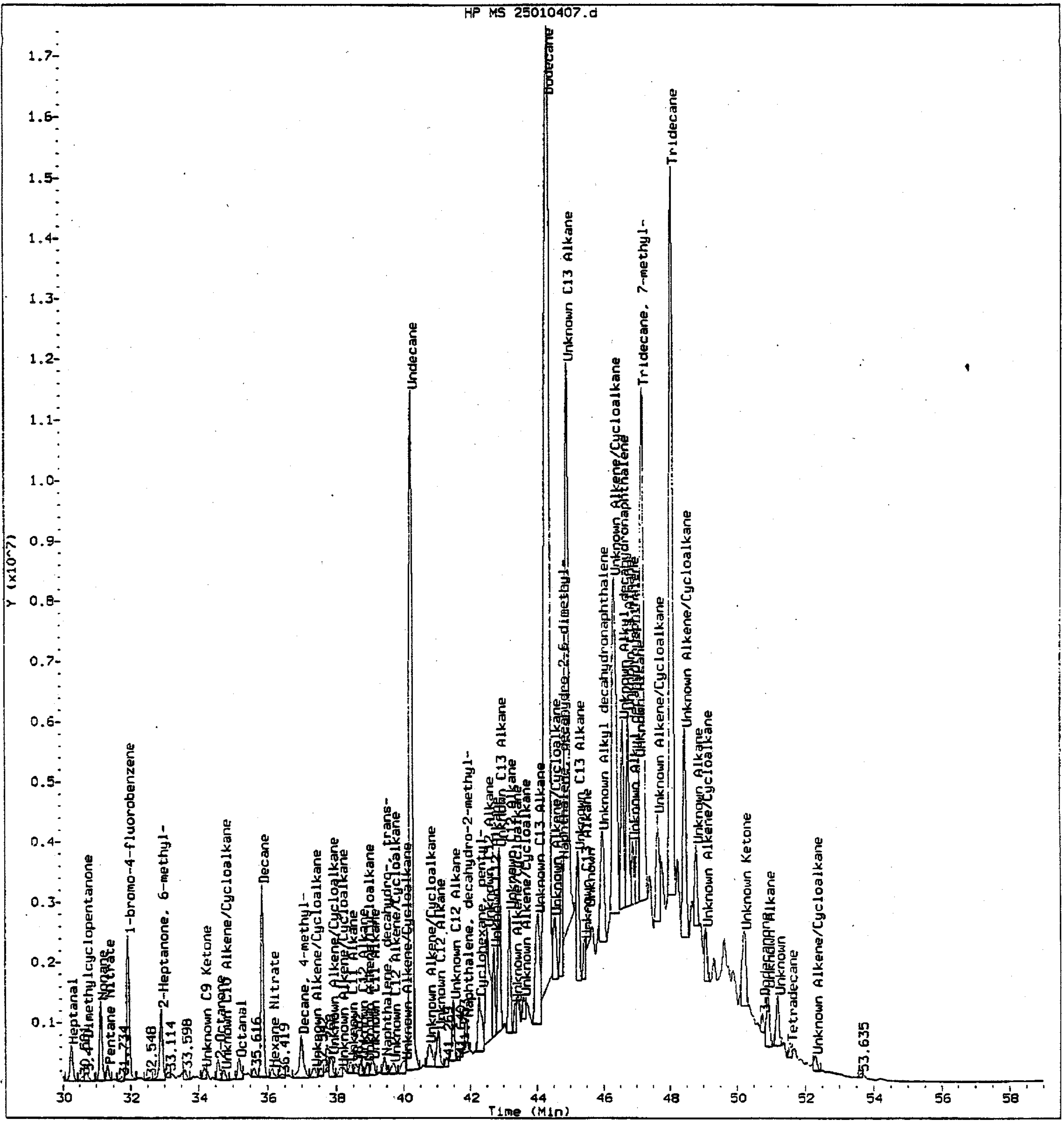

Figure 3.1b Total Ion Chromatogram (30 through 58 min) for Hanford Waste Tank C-101 SUMMA™ Canister Sample S4056-A05-033 Collected on 9/1/94