RECEIVED

NOV - 8 1995

OSTI

**Vapor Space Characterization of
Waste Tank 241-BY-108: Results
from Samples Collected on
10/27/94**

**B. D. McVeety
T. W. Clauss
M. W. Ligothke
K. H. Pool
R. B. Lucke**

**G. S. Klinger
J. S. Young
M. McCulloch
J. S. Fruchter
S. C. Goheen**

October 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 Laboratory
Operated for the U.S. Department of Energy
by Battelle Memorial Institute**

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor Battelle Memorial Institute, nor any of their employees, makes **any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights.** Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or Battelle Memorial Institute. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE MEMORIAL INSTITUTE
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**

This document was printed on recycled paper.

**Vapor Space Characterization of Waste
Tank 241-BY-108: Results from
Samples Collected on 10/27/94**

B. D. McVeety
T. W. Clauss
M. W. Ligothe
K. H. Pool
R. B. Lucke
G. S. Klinger
J. S. Young
M. McCulloch
J. S. Fruchter
S. C. Goheen

October 1995

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

Pacific Northwest Laboratory
Richland, Washington 99352

DISCLAIMER

**Portions of this document may be illegible
electronic image products. Images are
produced from the best available original
document.**

Summary

This report describes inorganic and organic analyses results from samples obtained from the headspace of the Hanford waste storage Tank 241-BY-108 (referred to as Tank BY-108). 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_2O). Trends in NH_3 and H_2O samples indicated a possible sampling problem. Sampling for hydrogen cyanide (HCN) and sulfur oxides (SO_x) was not requested. In addition, we looked for the 40 TO-14 compounds plus an additional 15 analytes. Of these, 17 were observed above the 5-ppbv reporting cutoff. Also, eighty-one organic tentatively identified compounds (TICs) were observed above the reporting cutoff (ca.) 10 ppbv, and are reported with concentrations that are semiquantitative estimates based on internal standard response factors. The nine organic analytes with the highest estimated concentrations are listed in Summary Table 1 and account for approximately 48% of the total organic components in the headspace of Tank BY-108. Three permanent gases, hydrogen (H_2), carbon dioxide (CO_2), and nitrous oxide (N_2O) were also detected.

Table 1. Summary Results of Inorganic and Organic Samples Collected from the Headspace of Tank BY-108 on 10/27/94

<u>Category</u>	<u>Analyte</u>	<u>Vapor^(a) Concentration</u>	<u>Units</u>
Inorganic	NH_3	1040 ± 80	ppmv
	NO_2	≤ 0.02	ppmv
	NO	≤ 0.03	ppmv
	H_2O	15 ± 5	mg/L
Organic	1-Butanol	12.6	mg/m^3
	Acetone	11.4	mg/m^3
	Dodecane	6.2	mg/m^3
	Hexane	5.7	mg/m^3
	Tridecane	5.3	mg/m^3
	Unknown C_{14} Alkane	4.9	mg/m^3
	2,6-Dimethylundecane	4.2	mg/m^3
	Tetrahydrofuran	4.2	mg/m^3
	Undecane	3.3	mg/m^3

(a) Vapor concentrations were determined using sample-volume data provided by Westinghouse Hanford Company and are based on averaged data. Sample volume uncertainty data was not provided.

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 in preparing the organic portion of this report. Sally Slate, May-Lin Thomas and Karen Schielke analyzed inorganic samples, 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
GC/TCD	gas chromatography/thermal conductivity detection
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
OGI	Oregon Graduate Institute
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

Contents

Summary	iii
Acknowledgments	v
Abbreviations	vii
1.0 Introduction	1
2.0 Inorganic	5
2.1 Standard Sampling Methodology	5
2.2 Analytical Procedures	6
2.3 Quality Assurance/Quality Control	8
2.4 Inorganic Sample Results	9
3.0 Organic	13
3.1 SUMMA™ Canister Preparation	13
3.2 Sample Analysis Method	13
3.3 Quality Assurance/Quality Control	14
3.4 Analysis Results	16
4.0 Conclusions	17
5.0 References	19
6.0 Further Reading	19
Distribution	Dist. 1

Tables

2.1	Analysis Procedures and Typical Detection Limits of Target Inorganic Analytes	8
2.2	List of PNL Inorganic Samples, Controls, and Gravimetric Results from a Heated Tube Inserted into the Headspace of Tank BY-108 on 10/27/94	10
2.3	Inorganic Vapor Sample Results obtained from a Heated Tube Inserted into the Headspace of Tank BY-108 on 10/27/94	11
3.1	Positively Identified and Quantitated T0-14 Compounds and Extended Analytes of Samples Collected from the Headspace of Tank BY-108 in SUMMA™ Canisters on 10/27/94	20
3.2	Tentatively Identified Compounds and Estimated Concentrations of Samples from the Headspace of Tank BY-108 in SUMMA™ Canister Samples Collected on 10/27/94	22
3.3	Positively Identified and Quantitated TO-14 Compounds and Extended Analytes for Ambient Air Collected Near Tank BY-108 in SUMMA™ Canisters on 10/27/94	26
3.4	Tentatively Identified Compounds and Estimated Concentrations for Ambient Air Collected Near Tank BY-108 in SUMMA™ Canisters on 10/27/94	27
3.5	Permanent Gas Analysis Results for Samples Collected from the Headspace of Tank BY-108 and for Ambient Air Collected Near Tank BY-108 in SUMMA™ Canisters on 10/27/94	28

Figures

1.1	Chain-of-Custody for Tank BY-108	2
3.1	Total Ion Chromatogram for Hanford Waste Tank BY-108 SUMMA™ Canister Sample S4076-A04-220 Collected on 10/27/94	29

1.0 Introduction

This report describes results of the analyses of tank-headspace samples taken from the Hanford waste Tank 241-BY-108 (referred to as Tank BY-108). 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 organic analytes for TO-14 compounds were extended to include 15 analytes identified by the Toxicological Review Panel for Tank C-103 and reported in 1994 by Mahlum et al. in *Toxicological Evaluation of Analytes from Tank 241-C-103*, PNL-10189. While these analytes (shown in Table 3.1) are only of toxicological concern for Tank C-103, program management included these analytes for future tank analyses as identified in the fiscal year work plan. WHC program management included these analytes for future tank analyses as identified in the fiscal year work plan. This plan is attached to a letter addressed to the WHC Tank Characterization Program Manager^(b). The plan also required PNL to analyze for selected permanent gases. The sample job was designated S4076 and samples were collected by WHC on October 27, 1994, using the vapor sampling system (VSS). Guidance specific to the sample job was provided in the tank characterization plan by Carpenter (1994) and was based in part on the data quality objectives by Osborne et al. (1994).

Sampling devices, including six sorbent trains (for inorganic analyses), and eight SUMMA™ canisters (for organic analyses) were supplied to the WHC sampling staff on October 24. Samples were taken (by WHC) from the tank headspace on October 27 and were returned to PNL from the field on November 8. Inorganic (sorbent trap) samples were delivered to PNL on chain of custody (COC) 008065 (see Figure 1.1a). The SUMMA™ canisters were delivered on COC 008064 (see Figure 1.1b). Three SUMMA™ canister samples were stored at PNL for future analysis by the Oregon Graduate Institute (OGI).

Project work at PNL was governed by an approved quality assurance plan^(c). The samples were inspected upon delivery to the 326/23B laboratory and logged into PNL record book 55408 as described in PNL Technical Procedure PNL-TVP-07^(d). Custody of the sorbent traps was transferred to PNL personnel performing the inorganic analysis and stored at refrigerated ($\leq 10^{\circ}\text{C}$) temperature until the time of analysis. The canister was stored in the 326/23B laboratory at ambient (25°C) temperature until 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. 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 weighed and desorbed with the appropriate aqueous solutions for ammonia, nitrogen dioxide, and nitric oxide 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) Letter from Mr. P.J. Mellinger (PNL) to Mr. T.J. Kelly (WHC), September 30, 1994, Multi-Year Work Plan for PNL Support of TWRS Characterization for Fiscal Years 1995, 1996, and 1997. TWRS Characterization Project, Pacific Northwest Laboratory, Richland, Washington.
- (c) PNL-MCS-027, Rev. 4, August 1994, TWRS Waste Tank Safety Program, PNL Quality Assurance Plan, Tank Vapor Project, Richland, Washington.
- (d) 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

WHIC 008064

Custody Form Initiator

J. A. Edwards-PNL

Telephone (509) 373-0141

Page 85-3009 / FAX 376-0418

Company Contact

R. D. Mahon-WHC

Telephone (509) 373-1101

Page 85-9656 / FAX 373-3193

Project Designation/Sampling Locations 200 East Tank Farm
241-BY-108 Tank Vapor Sample SAF S4076
(VSS Truck)

Collection date 10-27-94

Preparation date 10-24-94

Ice Chest No.

Field Logbook No. WHC-_____-_____-_____-

Bill of Lading/Airbill No.

N/A

Offsite Property No. N/A

Method of Shipment

Government Truck

Shipped to

PNL

Sample Job # _____

Possible Sample Hazards/Remarks Unknown at time of sampling

Sample Identification

S4076-A01.218

S4076-A02.219

Ambient Air #1 Upwind @ VSS (PNL)

Ambient Air #2 Through VSS (PNL)

S4076-A04.220

S4076-A05.221

S4076-A06.222

S4076-A07.228

S4076-A08.229

S4076-A09.230

Sample #3 (PNL)

Sample #4 (PNL)

Sample #5 (PNL)

Sample #6 (OGI)

Sample #7 (OGI)

Sample #8 (OGI)

Field Transfer of Custody			Chain of Possession		(Sign and Print Names)	
Relinquished By	Date	Time	Received By	Date	Time	
J. A. Edwards	10-24-94	1415	R. D. Mahon	10-24-94	1415	
R. D. Mahon	11-8-94	1330	J. A. Edwards	11-8-94	1338	

Final Sample Disposition

Comments:

PNL (only) Checklist	Pick-up / Delivery	Comments:
Media labeled and checked?	☒ Y	
Letter of instruction?	☒ Y	
Media in good condition?	☒ Y	
COC info/signatures complete?	☒ Y	
Sorbents shipped on ice?	☒ Y	
Red release stickers on samples?	☒ Y	
Activity report from 222S7	☒ Y	
COC cop	☒ Y	
COC cop	☒ Y	

Figure 1.1a Chain of Custody for Inorganic Samples for Tank BY-108

Custody Form Initiator

J. A. Edwards-PNL

Telephone (509) 373-0141
Page 85-3009 / FAX 376-0418

Company Contact

R. D. Mahon-WHC

Telephone (509) 373-1101
Page 85-9656 / FAX 373-3193Project Designation/Sampling Locations 200 East Tank Farm
241-BY-108 Tank Vapor Sample SAF S4076
(VSS Truck)Collection date 10-27-94
Preparation date 10-2 4-94

Ice Chest No.

Field Logbook No. WHC-_____-

Bill of Lading/Airbill No.

N/A

Offsite Property No. N/A

Method of Shipment

Government Truck

Shipped to

PNL

Sample Job # _____

Possible Sample Hazards/Remarks Unknown at time of sampling

Sample Identification

S4076 - A26 . 50V	NH ₃ /NO _x /H ₂ O (Trap # 1) Line # 9
S4076 - A27 . 51V	NH ₃ /NO _x /H ₂ O (Trap # 2) Line # 10
S4076 - A28 . 52V	NH ₃ /NO _x /H ₂ O (Trap # 3) Line # 8
S4076 - A29 . 53V	NH ₃ /NO _x /H ₂ O (Trap # 4) Line # 10
S4076 - A30 . 54V	NH ₃ /NO _x /H ₂ O (Trap # 5) Line # 9
S4076 - A31 . 55V	NH ₃ /NO _x /H ₂ O (Trap # 6) Line # 10
S4076 - A32 . 56V	NH ₃ /NO _x /H ₂ O a-b-c (Trap Trip Blank# 1)
S4076 - A33 . 57V	NH ₃ /NO _x /H ₂ O a-b-c (Trap Trip Blank# 2)
S4076 - A34 . 58V	NH ₃ /NO _x /H ₂ O a-b-c (Trap Trip Blank# 3)

Field Transfer of Custody			Chain of Possession			(Sign and Print Names)	
Relinquished By	Date	Time	Received By	Date	Time		
AL KRUPSKA	10-24-94	1440	J. A. Edwards	10-24-94	1440		
J. A. Edwards	10-24-94	1440	R. D. Mahon	10-24-94	1440		
R. D. Mahon	10-24-94	1345	J. A. Edwards	11-8-94	1345		

Final Sample Disposition

Comments:

PNL (only) Checklist	Pick-up / Delivery	Comments:
Media labeled and checked?	☒ N	
Letter of instruction?	☒ N	
Media in good condition?	☒ N	
COC info/signatures complete?	☒ N	
Sorbents shipped on ice?	☒ N	
Rud release stickers on samples?	☒ N	
Activity report from 222S?	☒ N	
COC e	☒ N	
COC c	☒ N	

Figure 1.1b Chain of Custody for Organic Samples for Tank BY-108

(Revised 10/17/94 PNL)

2.0 Inorganic Task

Solid sorbent traps, prepared in multi-trap sampling trains, were supplied to WHC for sampling 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 the following analytes: ammonia (NH_3), nitrogen dioxide (NO_2), nitric oxide (NO), and water (H_2O). 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. Sample preparation, handling, and disassembly were performed as described in Technical Procedure PNL-TVP-09^(a). Analytical accuracy was estimated based on procedures used. Sample preparation and analyses were performed following PNL quality assurance (QA) impact level (IL) II 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 were selected for the tank sample job and 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 $\{(\text{NH}_4)_2\text{SO}_4\}$. 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 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 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

(a) Pacific Northwest Laboratory. 10/94. *Sorbent Trap Preparation for sampling and Analysis: Waste Tank Inorganic Vapor Samples*, PNL-TVP-09 (Rev.0), PNL Technical Procedure, Richland, Washington.

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 analyses.

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 consist 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

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

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 flowmeter. However, the bias is generally expected to be small. For a tank-headspace temperature of 35°C, the magnitude of the bias would be roughly 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 in the text. All were 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- $\mu\text{g/mL}$ (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 IL II. The PNL documents include PNL-MA-70 (Part 2), PNL-MA-599, PNL-ALO-212, PNL-ALO-226, PNL-ALO-271, MCS-033, MCS-027, and MCS-046. 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 NH₃).

Table 2.1 Analysis Procedures and Typical Detection Limits of Target Inorganic Analytes. Not all analytes are included in every sample job.

<u>Analyte</u>	<u>Formula</u>	<u>Procedure</u>	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) Current target analytical limits are equal to one-tenth of the REL.

(b) MDL is 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 NH₃ and 3 mL for the other analytes.

(c) The vapor-mass concentration, thought to be largely water vapor, is determined gravimetrically.

The accuracy of concentration measurements depends on errors associated with both sampling and analysis. 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 NH₃ analyses, the accuracy of laboratory measurements by SIE was estimated to be $\pm 5\%$ relative, independent of concentration at 1 $\mu\text{g/mL}$ 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 NO₂ 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 $\pm 10\%$, 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 most samples, and roughly 10% or less of the mass change of most blanks. The analytical accuracy of measurements of the change in mass of sorbent trains is estimated to be ± 1 mg per 5-trap sorbent train; this estimate is based largely on preliminary information that unopened field-blank sorbent trains gain 0.3 ± 0.4 mg per train.

2.4 Inorganic Sample Results

Samples were obtained by WHC from the headspace of Tank BY-108 on 10/27/94 using the VSS. The sample job designation number was S4076. 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 hydrogen cyanide (HCN) and sulfur oxides (SO_x) was not requested. The inorganic samples were received from WHC on 11/8/94; the sample-volume information was received on 11/9/94.

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 $\text{NH}_3/\text{NO}_x/\text{H}_2\text{O}$ 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 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 1040 ± 80 ppmv, based on all six samples. The blank-corrected NH_3 quantities in the sorbent traps ranged from 126 to 152 μmol in the front sorbent sections; back sections were not analyzed. Blank corrections, ≤ 0.06 μmol in front sections, and back sections were less than 0.1% 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 of NH_3 were $101 \pm 4\%$, $109 \pm 2\%$, and $104 \pm 1\%$, respectively, during related sample jobs (Clauss et al. 1994; Ligothe et al. 1994). The analysis of one sample was duplicated and yielded a repeatability of less than $\pm 1\%$. One sample leachate was spiked after initial analysis with roughly the quantity of NH_3 in the sample and yielded a percentage recovery of 100%. A 5-point calibration was performed over an NH_3 range of 0.1 to 1000 $\mu\text{g/mL}$.

A steady 15% increase in NH_3 concentration was observed between the first and third pair of samples. The reason for this increase was not identified. The fact that the first NH_3 trap (Sample

Table 2.2 List of PNL Inorganic Samples, Controls, and Gravimetric Results Obtained From a Heated Tube Inserted into the Headspace of Tank BY-108 on 10/27/94

Sample Number	Sorbent Type	Sample Port and Volume Information ^(a)				
		Sample Port	Flow Rate (mL/min)	Duration (min)	Volume (L)	Mass Gain
Samples:						
S4076- A26-50V	NH ₃ /NO _x /H ₂ O Train	9	200	15.0	3.01	NA ^(b)
S4076- A27-51V	NH ₃ /NO _x /H ₂ O Train	10	200	15.0	3.00	0.0672
S4076- A28-52V	NH ₃ /NO _x /H ₂ O Train	8	200	15.0	3.00	0.0505
S4076- A29-53V	NH ₃ /NO _x /H ₂ O Train	10	200	15.0	3.00	0.0399
S4076- A30-54V	NH ₃ /NO _x /H ₂ O Train	9	200	15.0	3.00	0.0387
S4076- A31-55V	NH ₃ /NO _x /H ₂ O Train	10	200	15.0	3.00	0.0332
S4076- A32-56V	NH ₃ /NO _x /H ₂ O Blanks	n/a ^(b)	n/a	n/a	n/a	0.0006
S4076- A33-57V	NH ₃ /NO _x /H ₂ O Blanks	n/a	n/a	n/a	n/a	0.0025
S4076- A34-58V	NH ₃ /NO _x /H ₂ O Blanks	n/a	n/a	n/a	n/a	NA

(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.

S4076-A26-50V) was returned broken was not expected to be a factor in the trend of the concentration results; the other sample in the first pair (S4076-A27-51V) and both other pairs of samples also supported the trend in concentration.

2.4.2 Nitrogen Oxides Results. Measurements of NO₂ and NO were made using six 5-segment NH₃/NO_x/H₂O sorbent-trap trains (the NO_x trains consisted of NO₂ trap, oxidizer, and NO₂ trap). Related sample jobs, performed using the VSS in BY-104, -105, and -106 both with and without NO_x trains protected by a leading NH₃ trap (e.g., Clauss et al. 1994), indicated that the presence of the upstream NH₃ traps resulted in NO concentrations that were about 1.3- to 1.6-fold less than those from unprotected NO₂ traps. The NO₂ concentrations were also potentially less following an NH₃ trap.

The concentrations of NO₂ and NO were ≤ 0.02 and ≤ 0.03 ppmv, respectively. Blank-corrected NO₂⁻ quantities in the sorbent traps averaged ≤ 0.001 μmol (NO₂ samples) and ≤ 0.002 μmol (NO samples). Nitrite blank levels used to correct data were 0.0140 ± 0.0004 μmol in front (three of six blanks analyzed) and 0.0074 μmol in back (one of six blanks analyzed) sorbent sections. Although spiked blanks were not tested, blanks spiked with 0.0064, 0.047, 0.11, and 0.74 μmol of NO₂⁻ during related sample jobs yielded percentage recoveries of $153 \pm 14\%$, $103 \pm 4\%$, $106 \pm 8\%$, and $111 \pm 7\%$, respectively (Clauss et al. 1994; Ligotke et al. 1994). The analysis of one sample was duplicated and yielded a repeatability of $\pm 1\%$. Two sample leachates were spiked with 0.25 ppm NO₂⁻ and yielded percentage recoveries of 94% and 98%. A 4-point calibration was performed over a concentration range of 0 to 0.5 μg NO₂⁻ per mL in the desorbing matrix.

Table 2.3 Inorganic Vapor Sample Results Obtained From a Heated Tube Inserted into the Headspace of Tank BY-108 on 10/27/94

Sample	Analytical Results (μmol)			Sample Volume (L)	Vapor ^(a) Concentration (ppmv)
	Front Section	Back Section	Total ^(b) Blank-Corrected		
<u>NH₃ Samples:</u>			<u>139^(c)</u>	<u>3.00^(c)</u>	<u>1040 $\pm$ 80^(c)</u>
S4076- A26-50V	130	NA ^(d)	130	3.01	969
S4076- A27-51V	126	NA	126	3.00	941
S4076- A28-52V	141	NA	141	3.00	1050
S4076- A29-53V	141	NA	141	3.00	1050
S4076- A30-54V	152	NA	152	3.00	1140
S4076- A31-55V	149	NA	149	3.00	1110
<u>NO₂ Samples:</u>			<u>≤ 0.001</u>	<u>3.00</u>	<u>≤ 0.02</u>
S4076- A26-50V	0.0128	0.0080	n/a ^(d)	3.01	n/a
S4076- A27-51V	0.0124	NA	n/a	3.00	n/a
S4076- A28-52V	0.0122	NA	n/a	3.00	n/a
S4076- A29-53V	0.0124	NA	n/a	3.00	n/a
S4076- A30-54V	0.0117	NA	n/a	3.00	n/a
S4076- A31-55V	0.0126	NA	n/a	3.00	n/a
<u>NO Samples:</u>			<u>≤ 0.002</u>	<u>3.00</u>	<u>≤ 0.03</u>
S4076- A26-50V	0.0148	NA	n/a	3.01	n/a
S4076- A27-51V	0.0154	NA	n/a	3.00	n/a
S4076- A28-52V	0.0151	NA	n/a	3.00	n/a
S4076- A29-53V	0.0155	NA	n/a	3.00	n/a
S4076- A30-54V	0.0154	0.0086	n/a	3.00	n/a
S4076- A31-55V	0.0145	NA	n/a	3.00	n/a
<u>Gravimetric Samples (mg/mg/L):</u>			<u>46.2 mg</u>	<u>3.00</u>	<u>15 $\pm$ 5 mg/L</u>
	n/a	n/a	NA	3.01	NA
S4076- A26-50V	n/a	n/a	67.5	3.00	22.5
S4076- A27-51V	n/a	n/a	50.8	3.00	16.9
S4076- A28-52V	n/a	n/a	40.2	3.00	13.4
S4076- A29-53V	n/a	n/a	39.0	3.00	13.0
S4076- A30-54V	n/a	n/a	33.5	3.00	11.2
S4076- A31-55V					

- (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 NO₂ and NO) were determined, when significant, by subtracting the quantity of analyte found in blanks from that found in samples. The level of analytes found in blanks is described in the subsections of Section 2.4.
- (c) Underlined values represent the average of the set samples. Concentration uncertainty equals ± 1 standard deviation (absolute) for each set of samples. The use of " $\leq$ " is defined in Section 2.4.
- (d) NA = not analyzed; n/a = not applicable. Only selected back sorbent sections were analyzed. Past results have shown back sections of NH₃ samples to contain insignificant quantities of the analyte.

2.4.3 Gravimetric Results. The mass concentration of material collected in the 5-trap sorbent trains, believed to be primarily water vapor, was 15 ± 5 mg/L. The result was based on an average

mass gain of 45.8 mg from five of six $\text{NH}_3/\text{NO}_2/\text{H}_2\text{O}$ sample trains. Only five sample trains were analyzed because one NH_3 trap was damaged before its return to PNL (see Section 2.4.1.) An unexplained trend of decreasing mass gain with sample number was observed. The blank correction applied to the results was 0.3 mg per sample train, based on mass loss of 0.3 ± 0.4 mg per three blank 5-trap sorbent trains. The blanks, first assembled as complete 5-trap sorbent trains, accompanied samples from three related VSS sample jobs in December 1994 (TX-105, TX-118, and BX-104). Although no spiked blanks were tested, the percentage recovery of mass from three blank H_2O traps spiked with 51 mg of water was $103 \pm 2\%$ during a related sample job (Clauss et al. 1994).

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 and unknown contaminants to a level of 5 parts per billion by volume (ppbv), the canister is evacuated to 5 mtorr, tagged, and stored for use in the field. Before sending the canisters out to the field for sampling, the canisters vacuum is measured to determine if any leakage has occurred. If the vacuum has remained constant during storage, the canisters are prehumidified with 100 μ L 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 sample was 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 either a 5971 or a 5972 Hewlett Packard (HP) benchtop 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- μ m 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. Twenty-four hours before the analysis, the SUMMA™ canister samples were pressurized with purified air (Aadco Instruments, Inc., 1920 Sherwood St., Clearwater, Florida 34625). The starting pressure was first measured using a calibrated diaphragm gauge (Cole Parmer) then pressurized to a level exactly twice the original pressure. For example, if the canister had a starting pressure of 740 torr, it was pressurized to 1480 torr. This dilution was an effort to improve the precision of the analysis. The sample dilution was taken into account when calculating the analysis results.

-
- (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.

The instrument calibration mixture for the TO-14 analysis consists of the standard 40 organic analytes with an additional 15 tank related compounds. Together, these 55 compounds make up the target compound list that are directly quantified in this analysis. The calibration mixture was prepared by blending a commercially prepared 40 compound TO-14 calibration mixture with a 15 compound mixture created using a KinTech® permeation tube standard generation system. The operation of the permeation tube system follows the method detailed in *Preparation of TO-14 Volatile Organic Compounds Gas Standards* PNL Technical Procedure PNL-TVP-06. The standard calibration mix was analyzed using six aliquot sizes ranging from 5 mL to 300 mL. Depending on the concentration of each analyte in the mixture, either five or six points were used to construct the calibration curve. Butanoic acid was added to the mixture, but was not detected in the analysis. Butanal was recovered very poorly, producing a much lower than expected response. This results in a much higher measured amount reported in the sample analysis. This problem is currently under investigation. Performance-based detection limits for the TO-14 compounds and extended analytes will be developed as a pool of calibration data becomes available. Currently, the nominal detection limit of 5 ppbv are met.

The SUMMA™ canister samples were analyzed for permanent gases according to PNL Technical Procedure PNL-TVP-05, *Analysis Method for the Determination of Permanent Gases in Hanford Waste Tank Vapor Samples Collected in SUMMA™ Passivated Stainless Steel Canisters*, with the exceptions listed in the following text and in the Quality Assurance/Quality Control section of this report. This method was developed in-house for the analysis of permanent gases defined as hydrogen, (H₂), carbon dioxide (CO₂), carbon monoxide (CO), methane (CH₄), and nitrous oxide (N₂O) by gas chromatography-thermal conductivity detection (GC-TCD) and is not validated in any other laboratory. No previous work up of the sample canister is necessary before permanent gas analysis. Aliquots of sampled air are manually drawn from each canister into a 5-mL gas-tight syringe and directly injected into a GC-TCD fitted with a 1.0-mL injection loop. An aliquot of 5 mL is used so that the injection loop is flushed and filled with sample air, ensuring that no dilution of sample concentration takes place within the injection loop. One set of GC conditions is used to analyze CO, CO₂, N₂O, and CH₄ using Helium (He) as the carrier gas. A second GC analysis is performed for H₂ using nitrogen as the carrier gas to enhance the signal sensitivity and decrease the detection limit for this analyte. A total of 30 to 60 mL may be drawn from each 6 L canister, depending upon the number of repeat analyses performed.

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 5 to 6 data points ranging from 5 ppbv to 300 ppbv, using a standard gas mixture containing 40 volatile organic compounds listed in EPA compendium Method TO-14 and an additional 15 tank-related compounds. A gas mixture containing bromochloromethane, 1,4-difluorobenzene, and chlorobenzene-d₅ 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.

Standards for the permanent gas analysis were blended from commercially prepared and certified standards for each of the analytes reported in Table 3.5. The instrument was calibrated over three data points for CO, CO₂, N₂O, and CH₄ using He as a carrier gas, and then the samples were analyzed. The carrier was changed to N₂, the calibration was performed for H₂ only, and the samples were reanalyzed. A least-squares linear-regression routine was applied to the data set to generate the best fit for each compound. The quantitation for each analyte was performed by direct comparison of sample analyte peaks to the plot generated for the compound. The lowest calibration standard for each analyte is reported as the method detection limit. An MDL for the instrument has not been determined. A nitrogen reagent blank was not analyzed with this set of samples. The ambient air sample collected ~30 ft upwind of the tank and the ambient air collected through the VSS were used as method blanks and used to determine the potential for analyte interferences in the samples. Continuing calibration standards for this sample set fell within $\pm 25\%$ of the expected concentrations for the analytes reported.

3.3.1 Quantitation Results of TO-14 and 15 Additional Analytes. The quantitative-analysis results for the TO-14 extended analyte 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/m³ assumes standard temperature and pressure (STP) conditions of 760 torr and 273°K and was calculated directly from the following equation:

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

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 5971/5972 instrument operating system. Chromatographic peaks with an area count greater than, or equal to, 1/10th of the total area count of the nearest eluting internal standard are tentatively identified and quantitatively estimated. 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 total peak area for the nearest eluting IS. The IS peak area was used to calculate a response factor using the IS concentration 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.

The ppbv concentrations are calculated from mg/m³ and the molecular weight of the analyte.

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

The IS level added to all blank, standard, and sample injections was 104 ppbv for bromochloromethane, 101 ppbv for 1,4-difluorobenzene, and 98.5 ppbv 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.

All sample concentrations were multiplied by a factor of two to account for the dilution step described in Section 3.2.

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. The results of GC/MS analysis of ambient air samples collected upwind of Tank BY-108 and through the VSS near Tank BY-108 are presented in Tables 3.3 and 3.4. The GC/MS analysis results for permanent gases for both the ambient samples and from the tank headspace are presented in Table 3.5. 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 and the 15 additional analytes. Seventeen analytes were above the 5 ppbv detection limit. Acetone was the major constituent found in this group, with a concentration of about 4.5 ppbv.

Table 3.2 lists the semi-quantitative results for the TICs. The predominant species observed were 1-butanol, hexane, tridecane, and dodecane. The normal paraffin hydrocarbons (NPHs), defined as n-alkanes from C₁₁ to C₁₅, were observed at high ppbv levels. 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 89.02 mg/m³.

Tables 3.3 and 3.4 list results of TO-14 extended analyte and TIC analyses for ambient air collected ~30 ft upwind of Tank BY-108 and ambient air collected through the VSS. Pyridine, acetaldehyde, hexamethylcyclotrisiloxane, and octamethylcyclotetrasiloxane were detected in the upwind sample. Acetone, pyridine, and 1,1,2-trichloro-1,2,2-trifluoroethane were observed in the sample collected through the VSS.

Table 3.5 lists results of permanent gas analysis from samples collected from the headspace of Tank BY-108, ambient air collected ~30 ft upwind of the tank, and ambient air through the VSS. Permanent gases observed in the headspace were CO₂, N₂O, and H₂.

A replicate analysis of SUMMA™ canister PNL 220 resulted in a CO₂ concentration approximately 29% lower than the first analysis. The results of the first analysis are reported. The N₂O was not detected either in the ambient air collected ~30 ft upwind of Tank BY-108 or ambient air collected through the VSS. The concentration of H₂ observed in the samples averaged 399 ppmv with the highest concentration detected in SUMMA™ canister PNL 222 reported at 486 ppmv.

4.0 Conclusions

The concentrations of selected inorganic and organic compounds were determined from samples of the headspace of Tank BY-108 on 10/27/94. Sampling and analysis methods followed those described by Ligothke 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 average and standard deviation of the concentration results from inorganic sorbent trains were 1040 ± 80 ppmv (NH_3), ≤ 0.02 ppmv (NO_2), ≤ 0.03 ppmv (NO), and 15 ± 5 mg/L (vapor-mass concentration). The vapor-mass concentration is expected to consist largely of water vapor. The NH_3 and mass results displayed trends with the order in which the six sorbent-train samples were obtained (in three pairs) from the headspace of BY-108. The concentration of NH_3 apparently increased from 955 to 1125 ppmv from the first to the last pair of sorbent trains. The mass concentration results from the same sorbent trains indicated decreasing vapor mass concentration. The reason for the trends is not known, but was likely caused by a sampling problem. It is also not known which, if any, of the three pairs of sorbent trains represents the actual conditions in the tank headspace. It is doubtful that the changes, which occurred over an overall sampling period of less than 56 min, were an indication of changing headspace characteristics. All analytical results were within the target criteria ($\pm 25\%$ precision, 70 - 130% accuracy, Carpenter, 1994) for inorganic analytes found at concentrations exceeding the lower target analytical limits (see Table 2.1).

Organic analysis of the headspace samples from Tank BY-108 identified 17 TO-14 extended analytes above the 5-ppbv detection limit and 81 TICs above the 10-ppbv reporting cutoff. The concentration of the TO-14 compound extended analytes accounted for 26% of the total compounds identified by both organic analyses. The results of the TIC analysis identified numerous NPH type compounds as the predominant species present in the tank-headspace samples. The headspace samples also contained 1-butanol, which accounted for 10% of the total TIC concentration. The results of the ambient air collected ~30 ft upwind of Tank BY-108 identified three TO-14 compounds. Four TICs were also identified. Four TO-14 extended analytes were detected in the ambient air sample collected through the VSS. Three permanent gases, CO_2 , N_2O , and H_2 , were also detected in the tank-headspace sample. The average level of CO_2 in the headspace samples was 224 ppmv as compared to 470 ppmv observed in the ambient air samples.

5.0 References

Carpenter, B. C. 1994. *Tank 241-BY-108 Tank Characterization Plan*. WHC-SD-WM-TP-275, Westinghouse Hanford Company, Richland, Washington.

Clauss, T. W., M. W. Ligothe, 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.

Ligothe, 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 - 5/25/94)*. PNL-10172, Pacific Northwest Laboratory, Richland, Washington.

Osborne, J. W., J. L. Huckaby, E. R. Hewitt, C. M. Anderson, D. D. Mahlum, B. A. Pulsipher, and J. Y. Young. 1994. *Data Quality Objectives for Generic In-Tank Health and Safety Vapor Issue Resolution*. WHC-SD-WM-DQO-002, Rev. 0., Westinghouse Hanford Company, 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 Positively Identified and Quantitated TO-14 Compounds and Extended Analytes^(a) of Samples Collected from the Headspace of Tank BY-108 in SUMMATM Canisters on 10/27/94

Analyte	CAS No.	Mol Wt	S4076-A04.220 ^(b)		S4076-A05.221 ^(b)		S4076-A06.222 ^(b)		Means and	
			PNL 220(d)		PNL 221(d)		PNL 222(d)		Standard Deviation	
			Concentration	Concentration	Concentration	Concentration	(mg/m ³)	St Dev		
			(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)		
Dichlorodifluoromethane (FREON-12)	75-71-8	120	<0.03	<5	<0.03	<5	<0.03	<5	(d)	(d)
Methyl Chloride (Chloromethane)	74-87-3	50	<0.01	<5	<0.01	<5	<0.01	<5	(d)	(d)
1,2-Dichloro-1,1,2,2,-Tetrafluoroethane (FREON-114)	76-14-2	170	<0.04	<5	<0.04	<5	<0.04	<5	(d)	(d)
Chloroethene (Vinyl Chloride)	75-01-4	64	<0.01	<5	<0.01	<5	<0.01	<5	(d)	(d)
Methyl Bromide (Bromomethane)	74-83-9	94	<0.02	<5	<0.02	<5	<0.02	<5	(d)	(d)
Ethyl Chloride	75-00-3	62	<0.01	<5	<0.01	<5	<0.01	<5	(d)	(d)
Trichlorofluoromethane (FREON-11)	75-69-4	136	0.83	135	0.76	125	0.76	123	0.78	0.04
1,1-Dichloroethene (1,1-Dichloroethylene)	75-35-4	96	<0.02	<5	<0.02	<5	<0.02	<5	(d)	(d)
Dichloromethane (Methylene Chloride)	75-09-2	84	<0.02	<5	<0.02	<5	<0.02	<5	(d)	(d)
1,1,2-Trichloro-1,2,2-Trifluoroethane (FREON-113)	76-13-1	186	<0.04	<5	<0.04	<5	<0.04	<5	(d)	(d)
1,1-Dichloroethane	75-34-3	98	<0.02	<5	<0.02	<5	<0.02	<5	(d)	(d)
cis-1,2-Dichloroethene (cis-1,2-Dichloroethylene)	156-59-2	96	<0.02	<5	<0.02	<5	<0.02	<5	(d)	(d)
Trichloromethane (Chloroform)	67-66-3	118	<0.02	<5	<0.02	<5	<0.02	<5	(d)	(d)
1,2-Dichloroethane	107-06-2	98	<0.02	<5	<0.02	<5	<0.02	<5	(d)	(d)
1,1,1-Trichloroethane	71-55-6	132	<0.03	<5	<0.03	<5	<0.03	<5	(d)	(d)
Benzene	71-43-2	78	0.09	24.4	0.09	25.3	0.09	25.6	0.09	0.00
Carbon Tetrachloride	56-23-5	152	<0.03	<5	<0.03	<5	<0.03	<5	(d)	(d)
1,2-Dichloropropane	78-87-5	112	<0.03	<5	<0.03	<5	<0.03	<5	(d)	(d)
Trichloroethylene	79-01-6	130	<0.03	<5	<0.03	<5	<0.03	<5	(d)	(d)
cis 1,3-Dichloropropene	61-01-5	110	<0.02	<5	<0.02	<5	<0.02	<5	(d)	(d)
trans 1,3-Dichloropropene	61-02-6	110	<0.02	<5	<0.02	<5	<0.02	<5	(d)	(d)
1,1,2-Trichloroethane	79-00-5	132	<0.03	<5	<0.03	<5	<0.03	<5	(d)	(d)
Methyl Benzene (Toluene)	108-88-3	92	0.18	43.5	0.19	46.5	0.19	45.5	0.19	0.01
1,2-Dibromoethane	106-93-4	186	<0.04	<5	<0.04	<5	<0.04	<5	(d)	(d)
Tetrachloroethene (Perchloroethylene)	127-18-4	164	<0.04	<5	<0.04	<5	<0.04	<5	(d)	(d)
Chlorobenzene	108-90-7	112	<0.03	<5	<0.03	<5	<0.03	<5	(d)	(d)
Ethylbenzene	100-41-4	106	0.08	17.9	0.09	18.9	0.09	18.6	0.09	0.01
m-Xylene (1,3-Dimethylbenzene) ^(c)	108-38-3	106	0.35	73.1	0.38	79.3	0.37	77.3	0.37	0.02
p-Xylene (1,4-Dimethylbenzene) ^(c)	106-42-3	106								
Styrene	100-42-5	104	<0.02	<5	<0.02	<5	<0.02	<5	(d)	(d)
1,1,2,2-Tetrachloroethane	79-34-5	166	<0.02	<5	<0.02	<5	<0.02	<5	(d)	(d)
o-Xylene (1,2-Dimethylbenzene)	95-47-6	106	0.11	22.3	0.12	24.4	0.12	24.4	0.12	0.01

Table 3.1 (Contd)

Analyte	CAS No.	Mol Wt	S4076-A04.220 ^(b)		S4076-A05.221 ^(b)		S4076-A06.222 ^(b)		Means and	
			PNL 220(d)		PNL 221(d)		PNL 222(d)		Standard Deviation	
			Concentration	Concentration	Concentration	Concentration	(mg/m ³)	St Dev		
			(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)	(mg/m ³)	
1,3,5-Trimethylbenzene	108-67-8	120	0.01	1.45	0.01	1.49	0.01	1.42	0.01	0.00
1,2,4-Trimethylbenzene	95-63-6	120	0.02	3.5	0.02	3.91	<0.03	<5	(d)	(d)
Chloromethylbenzene, alpha (Benzyl Chloride)	100-44-7	126	<0.03	<5	<0.03	<5	<0.03	<5	(d)	(d)
m-Dichlorobenzene (1,3-Dichlorobenzene)	541-73-1	146	<0.03	<5	<0.03	<5	<0.03	<5	(d)	(d)
p-Dichlorobenzene (1,4-Dichlorobenzene)	106-46-7	146	<0.03	<5	<0.03	<5	<0.03	<5	(d)	(d)
o-Dichlorobenzene (1,2-Dichlorobenzene)	95-50-1	146	<0.03	<5	<0.03	<5	<0.03	<5	(d)	(d)
1,2,4-Trichlorobenzene	120-82-1	180	<0.04	<5	<0.04	<5	<0.04	<5	(d)	(d)
Hexachloro-1,3-Butadiene	87-68-3	258	<0.60	<5	<0.60	<5	<0.60	<5	(d)	(d)
2-Butanone	78-93-3	72	1.63	507	1.83	570	1.78	554	1.75	0.10
Acetone	67-64-1	58	12.8	4939	10.5	4061	10.9	4195	11.4	1.22
Acetonitrile	75-05-8	41	<0.01	<5	<0.01	<5	<0.01	<5	(d)	(d)
Heptane	142-82-5	100	2.37	529	2.34	524	2.28	511	2.33	0.05
Tetrahydrofuran	109-99-9	72	4.10	1275	4.23	1314	4.16	1291	4.16	0.07
Pyridine	110-86-1	79	0.44	123	0.44	125	0.42	119	0.43	0.01
Butanenitrile	109-74-0	69	<0.02	<5	<0.02	<5	<0.02	<5	(d)	(d)
Cyclohexane	110-82-7	84	0.55	146	0.53	140	0.52	137	0.53	0.02
Decane	124-18-5	142	0.59	92.7	0.57	89.9	0.56	88.1	0.57	0.02
Hexane	110-54-3	86	5.84	1519	5.59	1454	5.61	1458	5.68	0.14
4-Methyl-2-Pentanone	108-10-1	100	0.16	36.2	0.17	37.6	0.16	36.3	0.16	0.01
Propanenitrile	107-12-0	55	<0.01	<5	<0.01	<5	<0.01	<5	(d)	(d)
Cyclohexanone	108-94-1	98	0.05	11.2	0.05	10.6	0.04	8.24	0.05	0.01
Propanol	71-23-8	60	1.70	635	2.24	834	2.44	910	2.13	0.38

(a) TO-14 plus 15 additional target analytes.

(b) WHC sample identification number.

(d) PNL canister number.

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

(e) 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) of Samples from the Headspace of Tank BY-108 in SUMMATM Canisters Collected on 10/27/94

Tentatively Identified Compound ^(d)	CAS No. ^(d)	Mol Wt	Ret Time	S4076-A04.220 ^(b)		S4076-A05.221 ^(b)		S4076-A06.222 ^(b)		Means and Standard Deviations			
				PNL 220 ^(e)		PNL 221 ^(e)		PNL 222 ^(e)					
				(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)	(mg/m ³)	St Dev	(ppbv)	St Dev
Propene	115-07-1	42	3.9	1.85	989	1.78	950	1.81	966	1.82	0.04	968	19.5
Propane	74-98-6	44	4.0	0.95	485	0.89	452	0.89	451	0.91	0.04	462	19.4
Cyclopropane	75-19-4	42	4.7	0.29	155	0.29	153	0.29	153	0.29	0.00	153	1.2
Isobutane	75-28-5	58	5.1	0.60	232	0.57	220	0.57	220	0.58	0.02	224	6.8
1-Butene	106-98-9	56	5.7	2.17	868	1.92	769	1.97	790	2.02	0.13	809	52.5
Butane	106-97-8	58	5.9	1.47	567	1.34	516	1.32	511	1.38	0.08	531	30.7
2-Methyl-1-Propene	115-11-7	56	6.2	<0.03	<10.0	0.23	90	0.22	88	0.22	0.00	89	1.4
Cyclobutane	287-23-0	56	6.6	0.41	164	0.41	162	0.40	159	0.40	0.01	162	2.8
2-Methyl-1-Butene	563-46-2	70	7.8	0.21	68	<0.03	<10	<0.03	<10	(e)	(e)	(e)	(e)
Isopropyl Alcohol	67-63-0	60	9.0	0.21	77	0.22	83	0.23	86	0.22	0.01	82	4.6
1-Pentene	109-67-1	70	9.1	0.68	218	0.69	219	0.69	221	0.69	0.00	219	1.6
Pentane	109-66-0	72	9.6	1.47	458	1.31	408	1.33	414	1.37	0.09	427	27.1
4-Methyl-1-Pentene	691-37-2	84	12.4	0.49	130	0.56	149	0.55	146	0.53	0.04	142	10.2
2-Methylpentane	107-83-5	86	13.1	2.00	521	2.11	550	2.11	549	2.07	0.06	540	16.3
Butanal	123-72-8	72	13.2	0.12	39	0.14	44	0.13	41	0.13	0.01	41	2.6
3-Methylpentane	96-14-0	86	13.9	0.38	99	0.41	106	0.40	104	0.40	0.01	103	3.7
1-Hexene	592-41-6	84	14.1	0.70	187	0.77	205	0.76	202	0.74	0.04	198	9.6
Methylcyclopentane	96-37-7	84	16.5	0.29	77	0.28	75	0.28	73	0.28	0.01	75	1.6
1-Butanol	71-36-3	74	17.6	11.9	3602	12.6	3814	13.4	4056	12.6	0.75	3824	227
2-Pentanone	107-87-9	86	18.6	1.58	412	1.72	447	1.68	436	1.66	0.07	432	18.2
3-Methylhexane	589-34-4	100	19.1	1.63	366	1.73	387	1.71	383	1.69	0.05	379	11.3
1-Heptene	592-76-7	98	19.8	1.23	281	1.16	265	1.02	233	1.14	0.11	259	24.5
Unknown C8 Alkene/Cycloalkane		112	23.5	0.38	75	0.32	65	0.32	64	0.34	0.03	68	6.3
Unknown C8 Alkane		114	24.1	1.22	241	1.25	246	1.29	254	1.26	0.03	247	6.8
2-Hexanone	591-78-6	100	24.2	0.61	136	0.68	152	0.68	153	0.66	0.04	147	9.7
Unknown C8 Alkane		114	24.6	<0.05	<10	<0.05	<10	0.23	44	(e)	(e)	(e)	(e)
Unknown C8 Alkene/Cycloalkane		112	24.8	0.20	40	0.22	44	0.21	43	0.21	0.01	42	1.9
1,2-Dimethylcyclohexane	583-57-3	112	25.1	0.24	48	0.26	52	0.26	52	0.25	0.01	51	1.9

Table 3.2 (Contd)

Tentatively Identified Compound ^(d)	CAS No. ^(a)	Mol Wt	Ret Time	S4076-A04.220 ^(b)		S4076-A05.221 ^(b)		S4076-A06.222 ^(b)		Means and Standard Deviations			
				PNL 220 ^(e)		PNL 221 ^(e)		PNL 222 ^(e)		(mg/m ³)	St Dev	(ppbv)	St Dev
1-Octene	111-66-0	112	25.3	0.30	60	0.31	63	0.31	62	0.31	0.01	61	1.2
Octane	111-65-9	114	25.9	1.34	262	1.42	279	1.34	263	1.36	0.05	268	9.4
2,6-dimethylheptane	1072-05-5	128	27.5	0.41	72	0.44	78	0.43	76	0.43	0.02	75	2.9
Unknown Alkene/Cycloalkane			28.4	0.40	(f)	0.42	(f)	0.40	(f)	0.41	0.02		
2-Heptanone	110-43-0	114	29.6	0.30	59	0.34	66	0.33	64	0.32	0.02	63	3.5
3-Methyloctane	2216-33-3	128	29.7	0.42	73	<0.06	<10	<0.06	<10	(e)	(e)	(e)	(e)
Nonane	111-84-2	128	31.0	0.77	135	0.83	145	0.81	141	0.80	0.03	140	5.1
Unknown Ketone			32.8	0.71	(f)	0.78	(f)	0.76	(f)	0.75	0.04		
Unknown C9 Alkene/Cycloalkane		126	33.0	0.25	45	0.28	50	0.27	49	0.27	0.02	48	2.9
Unknown C10 Alkane		142	34.1	0.24	38	0.26	41	0.25	39	0.25	0.01	39	1.4
2-Octanone	111-13-7	128	34.5	0.29	51	0.31	54	0.30	53	0.30	0.01	53	1.8
Unknown C10 Alkene/Cycloalkane		140	34.6	0.35	56	0.39	63	0.37	60	0.37	0.02	59	3.4
Unknown C10 Alkene/Cycloalkane		140	35.4	0.19	31	0.21	33	0.21	33	0.20	0.01	32	1.5
Unknown C10 Alkene/Cycloalkane		140	35.5	0.23	36	0.25	39	0.24	38	0.24	0.01	38	1.6
Unknown C11 Alkane		156	36.9	0.99	142	1.08	154	1.04	149	1.03	0.04	148	6.1
Unknown C11 Alkane		156	37.7	0.21	30	0.24	34	0.22	32	0.22	0.01	32	1.9
Unknown C10 Alkene/Cycloalkane		140	37.8	0.45	73	0.49	78	0.48	77	0.47	0.02	76	2.7
Unknown C11 Alkane		156	38.3	0.21	30	0.22	32	0.22	31	0.22	0.01	31	0.9
Unknown C11 Alkane		156	38.6	0.26	37	0.28	40	0.27	39	0.27	0.01	39	1.5
Unknown C11 Alkene/Cycloalkane		154	38.8	<0.07	<10	0.20	29	<0.07	<10	(e)	(e)	(e)	(e)
Unknown C11 Alkane		156	39.0	0.26	37	0.28	41	0.27	39	0.27	0.01	39	1.9
Decahydronaphthalene	91-17-8	138	39.3	0.31	50	0.33	54	0.32	52	0.32	0.01	52	2.2
Unknown C11 Alkene/Cycloalkane		154	39.9	<0.07	<10	<0.07	<10	0.29	42	(e)	(e)	(e)	(e)
1-Undecene	821-95-4	154	39.9	0.30	43	0.34	50	<0.07	<10	0.32	0.03	46	4.4
Undecane	1120-21-4	156	40.1	3.20	460	3.47	499	3.34	479	3.34	0.13	479	19.2
Unknown C11 Alkene/Cycloalkane		154	40.7	0.56	81	0.63	92	0.60	87	0.60	0.04	87	5.5
Unknown C12 Alkane		170	40.9	0.47	62	0.54	71	0.51	67	0.51	0.04	67	4.7
Unknown C12 Alkane		170	41.4	0.49	65	0.56	74	0.52	69	0.53	0.04	69	4.6

Table 3.2 (Contd)

Tentatively Identified Compound ^(a)	CAS No. ^(a)	Mol Wt	Ret Time	S4076-A04.220 ^(b)		S4076-A05.221 ^(b)		S4076-A06.222 ^(b)		Means and Standard Deviations			
				PNL 220 ^(c) (mg/m ³)	(ppbv)	PNL 221 ^(c) (mg/m ³)	(ppbv)	PNL 222 ^(c) (mg/m ³)	(ppbv)	(mg/m ³)	St Dev	(ppbv)	St Dev
Naphthalene, decahydro-2-methyl-	2958-76-1	152	41.8	0.64	94	0.70	103	0.68	101	0.67	0.03	99	4.8
Unknown C11 Alkene/Cycloalkane		154	42.2	0.75	109	0.85	123	0.81	118	0.80	0.05	117	7.0
Unknown C12 Alkane		170	42.4	0.49	65	0.53	70	0.52	69	0.52	0.02	68	2.7
Decahydro-2-Methylnaphthalene	2958-76-1	152	42.5	0.29	43	0.31	46	0.31	46	0.30	0.01	45	1.8
Unknown C12 Alkane		170	42.8	0.81	107	0.90	119	0.88	115	0.86	0.05	114	6.0
Unknown C12 Alkane		170	43.1	0.48	63	0.54	71	<0.08	<10	0.51	0.05	67	6.0
Unknown C13 Alkane		170	43.1	<0.08	<10	<0.08	<10	0.53	69	(e)	(e)	(e)	(e)
Unknown Alkyl Decahydronaphthalene			43.9	0.56	(f)		(f)	0.61	(f)	0.58	0.03		
Dodecane	112-40-3	170	44.2	5.88	774	6.41	844	6.20	817	6.16	0.27	812	35.1
Unknown C12 Alkene/Cycloalkane		168	44.4	0.29	39	0.34	45	0.31	41	0.31	0.02	42	3.1
Decahydro-2,6-Dimethylnaphthalene	1618-22-0	166	44.6	0.55	75	0.61	82	0.59	80	0.58	0.03	79	3.7
2,6-Dimethylundecane	17301-23-4	184	44.8	3.95	481	4.39	534	4.22	513	4.18	0.22	509	26.9
Unknown C13 Alkane			45.1	0.40	(f)	0.51	(f)	0.47	(f)	0.46	0.06		
Unknown Alkyl Decahydronaphthalene		166	45.8	0.53	72	0.61	82	0.58	79	0.57	0.04	78	5.3
Unknown C13 Alkene/Cycloalkane		182	46.2	2.17	267	2.54	313	2.38	293	2.36	0.19	291	23.0
Unknown Alkyl Decahydronaphthalene		166	46.5	0.68	92	0.79	107	0.66	89	0.71	0.07	96	9.9
Unknown C12 Alkane		184	46.6	0.93	113	1.12	136	0.90	109	0.98	0.12	119	14.5
Unknown Alkane			46.9	0.63	(f)	0.80	(f)	0.68	(f)	0.70	0.09		
Unknown C14 Alkane		198	47.1	4.55	515	5.22	591	4.99	565	4.92	0.34	557	38.7
Unknown C13 Alkene/Cycloalkane		182	47.5	0.35	42	0.41	50	0.38	47	0.38	0.03	47	3.9
Tridecane	629-50-5	184	47.9	4.91	598	5.61	682	5.39	656	5.30	0.36	645	43.2
Unknown C13 Alkene/Cycloalkane		182	48.1	0.30	37	0.35	43	0.34	42	0.33	0.03	40	3.2
Unknown C14 Alkene/Cycloalkane		196	48.3	0.84	96	0.95	109	0.93	106	0.91	0.06	104	6.9
Unknown C14 Alkane		198	48.7	<0.09	<10	<0.09	<10	1.14	129	(e)	(e)	(e)	(e)
Unknown Alkane			48.7	1.02	(f)	1.21	(f)		(f)	1.11	0.14		
Unknown C14 Alkane		198	49.8	<0.09	<10	<0.09	<10	0.24	27	(e)	(e)	(e)	(e)
Unknown C14 Alkene/Cycloalkane		196	49.8	0.23	26	0.26	30	<0.09	<10	0.25	0.02	28	2.8
Unknown C13 Alkene/Cycloalkane		182	50.1	0.88	108	1.08	133	0.99	122	0.99	0.10	121	12.6

Table 3.2 (Contd)

Tentatively Identified Compound ^(d)	CAS No. ^(a)	Mol Wt	Ret Time	S4076-A04.220 ^(b)		S4076-A05.221 ^(b)		S4076-A06.222 ^(b)		Means and Standard Deviations			
				PNL 220 ^(e)		PNL 221 ^(e)		PNL 222 ^(e)		(mg/m ³)	St Dev	(ppbv)	St Dev
2-Methyltridecane	1560-96-9	198	50.2	0.37	41	0.46	52	0.40	45	0.41	0.05	46	5.2
Unknown Alkane			50.5	0.21	(f)	0.26	(f)	0.23	(f)	0.23	0.03		
2,6,10-Trimethyldodecane,	3891-98-3	212	50.8	2.22	234	2.69	285	2.38	252	2.43	0.24	257	25.6
Unknown C4 Alkyl Decahydronaphthalene		194	51.1	0.28	32	0.35	40	0.33	38	0.32	0.04	37	4.1
Tetradecane	629-59-4	198	51.5	1.75	198	2.23	252	1.88	213	1.95	0.25	221	27.9
Unknown C15 Alkene/Cycloalkane		210	52.2	0.31	33	0.51	55	<0.09	<10	0.41	0.14	44	15.1

- (a) Semi-quantitative estimate calculated using concentration of closest eluting IS.
 (b) WHC sample identification number.
 (c) PNL SUMMATM canister number.
 (d) Obtained by mass spectral interpretation and 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 Positively Identified and Quantitated TO-14 Compounds and Extended Analytes^(a) for Ambient Air Collected Near Tank BY-108 in SUMMATM Canisters on 10/27/94

<u>Analyte</u>	<u>CAS No.</u>	<u>Mol Wt</u>	Upwind S4076-A01.218 ^(b) PNL 218 ^(c)		Through VSS S4076-A02.219 ^(b) PNL 219 ^(c)	
			<u>Concentration</u>		<u>Concentration</u>	
			(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)
Acetone	67-64-1	58	< 0.01	< 5	0.03	10.1
Pyridine	110-86-1	79	0.06	16.6	0.07	18.5
1,1,2-Trichloro-1,2,2-Trifluoroethane	76-13-1	187	< 0.04	< 5	0.12	13.9

- (a) TO-14 plus 15 additional analytes.
 (b) WHC sample identification number.
 (c) PNL canister number.

Table 3.4 Tentatively Identified Compounds and Estimated Concentrations^(a) for Ambient Air Collected Near Tank BY-108 in SUMMATM Canisters on 10/27/94

Tentatively Identified Compound ^(d)	CAS No. ^(d)	Mol. Wt	Ret. Time	Upwind S4076-A01.218 ^(b) PNL 218 ^(c)		Through VSS S4076-A02.219 ^(b) PNL 219 ^(c)	
				(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)
Acetaldehyde	75-07-0	44	5.1	0.11	57.3	< 0.02	< 10.0
Butanal	123-72-8	72	13.2	0.02	< 10.0	0.02	< 10.0
Hexamethylcyclotrisiloxane	541-05-9	222	26.7	0.28	28.6	< 0.10	< 10.0
Octamethylcyclotetrasiloxane	556-67-2	296	35.1	0.10	7.55	< 0.13	< 10.0

- (a) Semi-quantitative estimate calculated using concentration of closest eluting IS.
 (b) WHC sample identification number.
 (c) PNL SUMMATM canister number.
 (d) Obtained by mass spectral interpretation and comparison with the EPA/NIST/WILEY Library.

Table 3.5 Permanent Gas Analysis Results for Samples Collected from the Headspace of Tank BY-108 and for Ambient Air Collected Near Tank BY-108 in SUMMA™ Canisters on 10/27/94

Permanent Gas Analyte	Ambient Air Upwind S4076-A01.218 ^(a) PNL 218 ^(b) Concentration (ppmv)	Ambient Air Through VSS S4076-A02.219 ^(a) PNL 219 ^(b) Concentration (ppmv)	S4076-A05.220 ^(a) PNL 220 ^{(b),(c)} Concentration (ppmv)	S4076-A05.221 ^(a) PNL 221 ^(b) Concentration (ppmv)	S4077-A06.222 ^(a) PNL 222 ^(b) Concentration (ppmv)
Hydrogen	< 160	< 160	377	335	486
Methane	< 61	< 61	< 61	< 61	< 61
Carbon Dioxide	449	490	311	221	140
Carbon Monoxide	< 76	< 76	< 76	< 76	< 76
Nitrous Oxide	< 67	< 67	519	672	731

(a) WHC sample identification number.

(b) PNL canister number.

(c) Replicate analysis for PNL 220 resulted in a concentration of 411 ppmv for H₂, 220 ppmv for CO₂, and 423 ppmv for N₂O.

Figure 3.1a Total Ion Chromatogram (2 - 30 min) for Hanford Waste Tank BY-108 SUMMA™ Canister Sample S4076-A04-220 Collected on 10/27/94

SUMMA™ Canister Sample S4076-A04-220 Collected on 10/27/94

Figure 3.1b Total Ion Chromatogram (30 - 58 min) for Hanford Waste Tank BY-108 SUMMA™ Canister Sample S4076-A04-220 Collected on 10/27/94

Distribution

No. of Copies

No. of Copies

Offsite

Onsite

2 DOE/Office of Scientific and Technical
Information

R. A. Jenkins
Oak Ridge National Laboratory
P.O. Box 2008
Building 4500-5, MS 6120
Oak Ridge, Tennessee 37831-6120

B. C. Kowalski
CPAC
University of Washington
MS BG-10
Seattle, Washington 98195

2 DOE Richland Operations Office

J. M. Clark, S7-54
T. Noble, S7-54

1 Core of Engineers

T. W. Gardner-Clayson, A5-19

8 Westinghouse Hanford Company

H. Babad, R2-78
D. R. Bratzel, S7-31
R. J. Cash, S7-15
T. J. Kelley, S7-30
J. E. Meacham, S7-15
J. W. Osborne, S7-15
D. A. Turner, S7-15
R. S. Viswanath, S3-90

28 Pacific Northwest Laboratory

S. C. Goheen, P8-08 (20)
J. L. Huckaby, K6-55
M. W. Ligothe, P7-59

Publishing Coordination
Technical Report Files (5)