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**Vapor Space Characterization of
Waste Tank 241-C-104: Results
from Samples Collected on
2/17/94 and 3/3/94**

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B. D. McVeety
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K. H. Pool
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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

PNL-10499

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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-104 (referred to as Tank C-104). 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 Summary Table 1. Detailed descriptions of the results appear in the text.

Quantitative results were obtained for the inorganic compounds ammonia (NH_3), nitrogen oxide (NO_2), nitric oxide (NO), sulfur oxide (SO_x), and water (H_2O). Organic compounds were also quantitatively determined. Occupational Safety and Health Administration (OSHA) versatile sampler (OVS) tubes were analyzed for tributyl phosphate. Twenty-four 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, two were observed above the 2-ppbv calibrated instrument detection limit. The 10 organic analytes with the highest estimated concentrations are listed in Summary Table 1. These 10 analytes account for approximately 88% of the total organic components in Tank C-104.

Summary Table 1. Summary Results of Inorganic and Organic Samples Collected from the Headspace of Tank C-104 on 2/7/94 and 3/3/94

<u>Category</u>	<u>Analyte</u>	<u>Vapor^(a) Concentration</u>	<u>Units</u>
Inorganic	NH_3	44 ± 0	ppmv
	NO_2	≤ 0.02	ppmv
	NO	0.37 ± 0.05	ppmv
	SO_x	0.4 ± 0.2	ppmv
	H_2O	15 ± 1	mg/L
Organic	Dodecane	6.47	mg/m ³
	Tridecane	6.22	mg/m ³
	Undecane	4.88	mg/m ³
	1-Butanol	2.45	mg/m ³
	Tetradecane	0.96	mg/m ³
	Decane	0.95	mg/m ³
	Butane	0.59	mg/m ³
	Butanal	0.47	mg/m ³
	Propane	0.46	mg/m ³
	3-Heptanone	0.41	mg/m ³

(a) Vapor concentrations were determined using sample-volume data provided by Westinghouse Hanford Company and are based on averaged data. The inorganic samples were obtained and analyzed using procedures that were subsequently improved. The SO_x values, in particular, may have been biased by unknown sampling or analytical errors.

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. Khris Olsen assisted in preparing the organic portion of this report. Bruce Lerner performed method development and validation work that supported the inorganic vapor sampling. Sally Slate and May-Lin Thomas analyzed inorganic samples, and Annalisa Krupsha and Gary Dennis prepared the solid-sorbent sample trains. Bonnie Lehrman, Rose Nipper, and Trina Burruss provided word processing support.

Abbreviations

CAS	Chemical Abstracts Service
COC	chain of custody
Cv	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
OGI	Oregon Graduate Institute
OSHA	Occupational Safety and Health Administration
OVS	OSHA versatile sampler
PFA	perfluoroalkoxy
PNL	Pacific Northwest Laboratory
ppbv	part per billion by volume
ppmv	part per million by volume
PVF	polyurethane foam
QA	quality assurance
REL	recommended exposure limit
SCIC	suppressed-conductivity ion chromatography
SIE	selective ion electrode
STP	standard temperature and pressure
TBP	tributyl phosphate
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 Hanford waste Tank 241-C-104 (referred to as Tank C-104). 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. A letter of instruction (9451099) was sent by Jerry Osborne to Steve Goheen on February 15, 1994, requesting the analysis of SUMMA™ canisters and sorbent traps by PNL quality assurance (QA) impact level (IL) III. The sample job was designated S4004, and samples were collected by WHC on February 17 and March 3, 1994, using the vapor sampling system (VSS). The results of the analyses are expected to be used to estimate the potential toxicity of tank-headspace gas as described in *Data Quality Objectives for Generic In-Tank Health and Safety Vapor Issue Resolution*, WHC-SD-WM-DQO-002, Rev. 0.

Fifty-eight sorbent tubes were prepared and sent to WHC on 2/14/94 on chain-of-custody (COC) 006109-B and C (see Figures 1.1a and 1.1b). Samples were taken (by WHC) from the tank headspace on February 17 and March 3, 1994 (see COC forms for sample identifications). Sorbent-tube samples were returned to PNL on 2/18/94 on COC 006109-B (Figure 1.1a) and 3/4/94 on COC 6109-C (Figure 1.1b). In all, there were nine Occupational Safety and Health Administration (OSHA) versatile sampler (OVS), six NH₃, six NO_x, three SO_x, and five silica tubes for each sampling event.

Seven SUMMA™ canisters were delivered to WHC on COC 006018 (Figure 1.1c), six SUMMA™ canisters were delivered on COC 006111 (Figure 1.1d), and six SUMMA™ canisters were delivered on COC 006115 (Figure 1.1e), all on 2/14/94.

Five samples were collected on 3/3/94 by WHC in SUMMA™ canisters and three canisters were delivered to PNL on COC 006108 (Figure 1.1f) on 3/4/94. These canister numbers were not the same canister numbers delivered to WHC on the original COC 006018 (Figure 1.1c). After receipt, PNL shipped two of the canisters, S4004-15-C03 and S4004-14-C03, to the Oregon Graduate Institute (OGI) on 3/18/94. The remaining two canisters from this sampling event were received by PNL on 3/29/94 from OGI. The canisters were analyzed and results were delivered to WHC in a preliminary report in April 1994. The canisters were reanalyzed in December to reflect improvements made in the analytical systems, and this report describes the organic results of the December analysis.

The samples were inspected upon delivery to building 329, room 2, and logged into PNL record book 55409 before analyses. 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 SUMMA™ canisters were 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 desorbed with the appropriate aqueous solutions (for ammonia NH₃,

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

nitrogen dioxide (NO_2), or sulfur oxide (SO_x) analyses. The aqueous extracts were analyzed either by selective electrode or by ion chromatography (IC). Organic analyses were performed using either cryogenic preconcentration (for SUMMA™), or desorption in CS_2 (for OVS) followed by gas chromatography/mass spectrometry (GC/MS).

Westinghouse Hanford Company	CHAIN OF CUSTODY	PNL	006109 -B
Custody Form Initiator C.M. Jones / J.E. Darling			
Company Contact J.L. Huckaby		Telephone (509) 373-3443	
Project Designation/Sampling Locations 200 East Tank Farm: Tank C-104 Vapor Sample. SAF S4004, 241-C-104		Collection Date	
Ice Chest No.		Field Logbook No. WHC-N-647-4	
Bill of Lading/Airbill No.		Offsite Property No.	
Method of Shipment Government Truck			
Shipped to PNL			
Possible Sample Hazards/Remarks No hazards detected at time of sampling.			

Sample Identification			
S4004-19.B17	SAP Reference 2	PNL NO ₂ #1	PNL ID#
S4004-20.B17	SAP Reference 2	PNL NO ₂ #1	PNL ID#
✓S4004-21.B17	SAP Reference 3	PNL OVS #1	PNL ID#
✓S4004-22.B17	SAP Reference 3	PNL OVS #2	PNL ID#
S4004-23.B17	SAP Reference 4	PNL SO _x #1	PNL ID#
S4004-24.B17	SAP Reference 4	PNL SO _x #1	PNL ID#
S4004-25.B17	SAP Reference 5A	Silica Gel #1	
S4004-27.B17	SAP Reference 6	PNL NH ₃ #1	PNL ID#
S4004-28.B17	SAP Reference 6	PNL NH ₃ #1	PNL ID#
S4004-29.B17	SAP Reference 7A	Silica Gel #2	
S4004-30.B17	SAP Reference 7B	Silica Gel #3	
S4004-39.B17	SAP Reference 12	PNL NO ₂ #2	PNL ID#
S4004-40.B17	SAP Reference 12	PNL NO ₂ #2	PNL ID#
S4004-41.B17	SAP Reference 13	PNL NH ₃ #2	PNL ID#
S4004-42.B17	SAP Reference 13	PNL NH ₃ #2	PNL ID#
2/14/94 2nd { S4004-43.B17	SAP Reference 14	PNL OVS #3	PNL ID#
S4004-44.B17	SAP Reference 14	PNL SO _x #2	PNL ID#
S4004-45.B17	SAP Reference 15	Silica Gel #4	
S4004-46.B17	SAP Reference 15	Silica Gel #5	
2/14/94 2nd { S4004-51.B17	SAP Reference --	PNL OVS Blank #1	PNL ID#
S4004-52.B17	SAP Reference --	PNL OVS Blank #2	PNL ID#
S4004-53.B17	SAP Reference --	PNL OVS Blank #3	PNL ID#
S4004-54.B17	SAP Reference --	PNL OVS Surrogate #1	PNL ID#
S4004-55.B17	SAP Reference --	PNL OVS Surrogate #2	PNL ID#
S4004-56.B17	SAP Reference --	PNL OVS Surrogate #3	PNL ID#
S4004-57.B17	SAP Reference --	PNL NH ₃ #3	PNL ID#
S4004-58.B17		NH ₃	
S4004-59.B17		NO ₂ #3	
S4004-60.B17		NO ₂ #3	

[x] Field Transfer of Custody		Chain of Possession		(Sign and Print Names)	
Relinquished By	Date	Time	Received By	Date	Time
C.N. Jones			J.E. Darling	2-14-94	1631
<i>John Olson</i>	2/14/94	16:31	<i>[Signature]</i>		
<i>B. Jones</i>	2-18-94	1310	<i>[Signature]</i>	2-18-94	

Final Sample Disposition		
Disposal Method:	Disposed by:	Date/Time:
Comments:		

Figure 1.1a Chain-of-Custody for Inorganic Samples and OVS Tubes

Westinghouse Hanford Company	CHAIN OF CUSTODY	PNL	006109 - C
Custody Form Initiator R.D. Mahon / J.E. Darling		Telephone (509) 373-3443	
Company Contact J.L. Huckaby		Collection Date 03-03-94	
Project Designation/Sampling Locations 200 East Tank Farm: Tank C-104 Vapor Sample. SAF S4004, 241-C-104		Field Logbook No. WHC-N-647-4	
Ice Chest No.		Offsite Property No.	
Bill of Lading/Airbill No.			
Method of Shipment Government Truck			
Shipped to PNL			
Possible Sample Hazards/Remarks No hazards detected at time of sampling.			

Sample Identification

S4004-19.C03	SAP Reference 2	PNL NO ₂ #1	PNL ID#
S4004-20.C03	SAP Reference 2	PNL NO ₂ #1	PNL ID#
S4004-21.C03	SAP Reference 3	PNL OVS #1	PNL ID#
S4004-22.C03	SAP Reference 3	PNL OVS #2	PNL ID#
S4004-23.C03	SAP Reference 4	PNL SO _x #1	PNL ID#
S4004-24.C03	SAP Reference 4	PNL SO _x #1	PNL ID#
S4004-25.C03	SAP Reference 5A	Silica Gel #1	
S4004-27.C03	SAP Reference 6	PNL NH ₃ #1	PNL ID#
S4004-28.C03	SAP Reference 6	PNL NH ₃ #1	PNL ID#
S4004-29.C03	SAP Reference 7A	Silica Gel #2	
S4004-30.C03	SAP Reference 7B	Silica Gel #3	
S4004-39.C03	SAP Reference 12	PNL NO ₂ #2	PNL ID#
S4004-40.C03	SAP Reference 12	PNL NO ₂ #2	PNL ID#
S4004-41.C03	SAP Reference 13	PNL NH ₃ #2	PNL ID#
S4004-42.C03	SAP Reference 13	PNL NH ₃ #2	PNL ID#
S4004-43.C03	SAP Reference 14	PNL OVS #3	PNL ID#
S4004-44.C03	SAP Reference 14	PNL SO _x #2	PNL ID#
S4004-45.C03	SAP Reference 15	Silica Gel #4	
S4004-46.C03	SAP Reference 15	Silica Gel #5	
S4004-51.C03	SAP Reference --	PNL OVS Blank #1	PNL ID#
S4004-52.C03	SAP Reference --	PNL OVS Blank #2	PNL ID#
S4004-53.C03	SAP Reference --	PNL OVS Blank #3	PNL ID#
S4004-54.C03	SAP Reference --	PNL OVS Surrogate #1	PNL ID#
S4004-55.C03	SAP Reference --	PNL OVS Surrogate #2	PNL ID#
S4004-56.C03	SAP Reference --	PNL OVS Surrogate #3	PNL ID#
S4004-57.C03	SAP Reference 19	PNL NH ₃ #3	PNL ID#
S4004-60.C03	SAP Reference 19	PNL NO ₂ #3	PNL ID#
S4004-61.C03	SAP Reference 19	PNL NO ₂ #3	PNL ID#
S4004-58.C03	SAP Reference 20	PNL NH ₃ #3	

[X] Field Transfer of Custody		Chain of Possession		(Sign and Print Names)	
Relinquished By	Date	Time	Received By	Date	Time
R.D. Mahon	3 MAR 94	2309	J.E. Darling	3-3-94	2309
J.E. Darling	3-4-94	1420	B. J. J. J.	3-4-94	1420

Figure 1.1b Chain-of-Custody for Inorganic Samples and OVS Tubes

Westinghouse Hanford Company	CHAIN OF CUSTODY	PNL 006108
Custody Form Initiator C. M. Jones/ J. E. Darling		
Company Contact J. L. Huckaby	Telephone (509) 373-3443	
Project Designation/Sampling Locations 200 East Tank Farm: Tank 241-C-104 vapor sample SAF S4004, 241-C-104		Collection Date 02- -94
Ice Chest No.	Field Logbook No. WHC-N-647-4	
Bill of Lading/Airbill No. N/A	Offsite Property No. N/A	
Method of Shipment		
Shipped to PNL		
Possible Sample Hazards/Remarks Unknown at time of sampling		

Sample Identification					
S4004- 04 .B17	SAP Ref	11A	PNL summa	PNL# 074	
S4004- 05 .B17	SAP Ref	11B	PNL summa	PNL# 056	
S4004- 06 .B17	SAP Ref	22	PNL summa	PNL# 060	
S4004- 07 .B17	SAP Ref	---	PNL surrogate	PNL# 072	
S4004- 08 .B17	SAP Ref	---	PNL surrogate	PNL# 070	
S4004- 09 .B17	SAP Ref	---	PNL surrogate	PNL# 067	
S4004- 49 .B17	SAP Ref	18A	PNL surrogate	PNL# 057	

[] Field Transfer of Custody			Chain of Possession		(Sign and Print Names)
Relinquished By	Date	Time	Received By	Date	Time
<i>Sharon Elam</i>	2/14/94	16:30			

Final Sample Disposition		
Disposal Method:	Disposed by:	Date/Time:

Comments: WHC purchased canisters are returned from PNL to WHC.
 PNL # above can be removed. PNL will not receive
 canister samples for this ^{2nd tank} ~~1st tank~~ sample job.
Sharon Elam
 2/14/94

Figure 1.1c Chain-of-Custody for Organic Samples

Westinghouse Hanford Company	CHAIN OF CUSTODY	PNL 006111
---------------------------------	------------------	------------

Custody Form Initiator C. M. Jones/ J. E. Darling

Company Contact J. L. Huckaby

Telephone (509) 373-3443

Project Designation/Sampling Locations 200 East Tank Farm: Tank
241-C-105 vapor sample SAF S4005, 241-C-105

Collection Date 02-16-94

Ice Chest No.

Field Logbook No. WHC-N-647-4

Bill of Lading/Airbill No. N/A

Offsite Property No. N/A

Method of Shipment

Shipped to PNL

Possible Sample Hazards/Remarks Unknown at time of sampling

Sample Identification					
S4005- 04 .B16	SAP Ref	9A	PNL summa	PNL# 073	
S4005- 05 .B16	SAP Ref	9B	PNL summa	PNL# 063	
S4005- 06 .B16	SAP Ref	19	PNL summa	PNL# 054	
S4005- 07 .B16	SAP Ref	15A	PNL surrogate	PNL# 055	
S4005- 08 .B16	SAP Ref	---	PNL surrogate	PNL# 062	
S4005- 09 .B16	SAP Ref	---	PNL surrogate	PNL# 066	

Field Transfer of Custody		Chain of Possession		(Sign and Print Names)	
Relinquished By	Date	Time	Received By	Date	Time
<i>Sherril Clark</i>	<i>2/14/94</i>	<i>14:27</i>			

Final Sample Disposition		
Disposal Method:	Disposed by:	Date/Time:

Comments:

WHC purchased canisters are returned from PNL to WHC.
PNL # above can be removed. PNL will not receive
canister samples for this tank sample job. *Sherril Clark*
2/14/94

Westinghouse Hanford Company	CHAIN OF CUSTODY	PNL 006115
Custody Form Initiator C. M. Jones/ J. E. Darling		
Company Contact J. L. Huckaby	Telephone (509) 373-3443	
Project Designation/Sampling Locations 200 East Tank Farm: Tank 241-C-106 vapor sample SAF S4006, 241-C-106	Collection Date 02-15-94	
Ice Chest No.	Field Logbook No. WHC-N-647-4	
Bill of Lading/Airbill No. N/A	Offsite Property No. N/A	
Method of Shipment		
Shipped to PNL		
Possible Sample Hazards/Remarks Unknown at time of sampling		
Sample Identification		
S4006- 04 .B15	SAP Ref 9A	PNL summa PNL# 065
S4006- 05 .B15	SAP Ref 9B	PNL summa PNL# 064
S4006- 06 .B15	SAP Ref 19	PNL summa PNL# 058
S4006- 07 .B15	SAP Ref 15A	PNL surrogate PNL# 061
S4006- 08 .B15	SAP Ref ---	PNL surrogate PNL# 071
S4006- 09 .B15	SAP Ref ---	PNL surrogate PNL# 059

[] Field Transfer of Custody		Chain of Possession		(Sign and Print Names)	
Relinquished By	Date	Time	Received By	Date	Time
<i>Theresa Clauer</i>	<i>2/14/94</i>	<i>16:29</i>			

Final Sample Disposition		
Disposal Method:	Disposed by:	Date/Time:
Comments: <i>WHC purchased canisters and returned from PNL to WHC. PNL # above can be removed. PNL will not receive canister samples for this tank sample job.</i> <div style="text-align: right;"><i>Theresa Clauer</i> <i>2/14/94</i></div>		

Figure 1.1e Chain-of-Custody for Organic Samples

Westinghouse Hanford Company	CHAIN OF CUSTODY	PNL 006108
Custody Form Initiator R.D. Mahon / J. E. Darling		
Company Contact J. L. Huckaby	Telephone (509) 373-3443	
Project Designation/Sampling Locations 200 East Tank Farm: Tank 241-C-104 vapor sample SAF S4004, 241-C-104	Collection Date 03-03-94	
Ice Chest No.	Field Logbook No. WHC-N-647-4	
Bill of Lading/Airbill No. N/A	Offsite Property No. N/A	
Method of shipment Government Truck		
Shipped to PNL		
Possible Sample Hazards/Remarks Unknown at time of sampling		
Sample Identification		
Custody tape removed from 2 boxes on 3/9/94. <i>2WC</i>		
S4004- 04 .C03	SAP Ref 11A	PNL summa PNL# PNL 071 Not Received <i>2WC 3/9/94</i>
S4004- 05 .C03	SAP Ref 11B	PNL summa PNL# PNL 065 Not Received <i>2WC 3/9/94</i>
S4004- 06 .C03	SAP Ref 22	PNL summa PNL# PNL 066 Received <i>2WC 3/9/94</i>
* 54004-15.C03 SAP Ref. 06I V53-3 PNL# 057 Received. <i>2WC 3/9/94</i>		
* 54004-14.C03 SAP Ref. 06I V153-2 PNL# 069 Received <i>2WC 3/9/94</i>		
* SHIPPED TO OGI VIA FEDEX 03/18/94 (E)		

[X] Field Transfer of Custody		Chain of Possession		(Sign and Print Names)	
Relinquished By	Date	Time	Received By	Date	Time
R.D. Mahon <i>R.D. Mahon</i>	3 MAR 94	2309	J.E. Darling <i>J.E. Darling</i>	3-3-94	2309
<i>J.E. Darling</i>	3-04-94	1430	<i>D. Jen</i>	3-7-94	1430

Final Sample Disposition		
Disposal Method:	Disposed by:	Date/Time:
Comments:		

Rec'd PNL 065 & 071 from OGI 03/29/94 (E)

2.0 Inorganic Task

Solid sorbent traps were supplied to WHC for sampling the tank headspace using the VSS. Samples were returned to PNL for analysis. Analyses were performed to provide information on the tank-headspace concentration of the following analytes: NH_3 , NO_2 , nitric oxide (NO), SO_x , and water (H_2O). It is important to note that both sampling and analytical procedures were developmental as Tank C-104 was one of the first four trial sample jobs. Differences in sample preparation, sampling, and sample handling, compared with subsequent jobs, varied from those used after April 1994 (Ligotke et al. 1994). Analytical accuracy was estimated based on procedures used. Sample preparation and analyses were performed following PNL QA 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 , SO_x , 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 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 provided an indication of breakthrough. In the tubes, sorbent layers are generally held in packed layers separated by glass wool. The sorbent types, 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 200 mg in the primary and 100 mg in the breakthrough sections. The NO_2 was adsorbed and disproportionated to equi-molar quantities of nitrite ions (NO_2^-) and nitrate ions (NO_3^-). The SO_x traps consisted of a proprietary mix of metal hydroxides coated on carbon beads, with 100 mg in the primary and 50 mg in the breakthrough sorbent sections.

Samples provided by PNL to trap inorganic compounds included samples and single-trap blanks. The samples of each type were prepared from same-lot batches, with the NO_x sorbent traps having been stored previously in a freezer. 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.

2.1.1 Concentration Calculations. The concentration of target compounds in the tank headspace was 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 ammonia equals

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

The 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 in the text. All were compiled in PNL-MA-599.

2.2.1 Ammonia Analysis. The sorbent material from the ammonia-selective sorbent traps was placed into labeled 20-mL glass scintillation vials. Vials containing front, or primary, section sorbent material were treated with 10.0 mL of deionized water (DIW), and vials containing back-up-section sorbent material were treated with 5.0 mL of DIW. After extraction, the 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- $\mu\text{g}/\text{mL}$ (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 emf signal versus NH_3 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 ammonia concentration in the samples.

2.2.2 Nitrite Analysis. The sorbent traps for NO_2 and NO were desorbed in an aqueous TEA and n-butanol solution and analyzed by suppressed-conductivity ion chromatography (SCIC) for nitrite according to PNL-ALO-212, Rev. 1 (*Determination of Inorganic Anions by Ion Chromatography*) and 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-tube materials were analyzed separately using identical procedures. Each analytical session was conducted as follows. Working nitrite standards (0, 0.1, 0.25, and 0.5 ppm) were prepared by diluting a stock nitrite standard with desorbing solution. An initial calibration curve was prepared from the instrument response (chromatographic peak height) versus nitrite standard concentration data for the set of working standards. A calibration verification check using one of the midrange standards was performed after the analysis of every six samples. If the instrument response indicated that sample nitrite concentration was outside the calibration range (≥ 0.5 ppm nitrite), the sample was diluted with desorbing solution and reanalyzed. After all samples of a batch were analyzed, the complete set of calibration standards was remeasured to verify consistent instrument response, and the analytical session was terminated.

Instrument responses (peak 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 Sulfur Oxide Analysis. The SO_x samples were desorbed in 0.015 N sodium hydroxide plus 1% hydrogen peroxide and analyzed by SCIC for sulfate ion following the modified PNL-ALO-212 procedure (see Section 2.2.2).

2.2.4 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 in 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 some or all of the following: 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 ammonia).

Table 2.1 Analysis Procedures and Detection Limits of Target Inorganic Analytes

Analyte	Formula	Procedure	REL ^(a) (ppmv)	0.1 X REL ^(a) (ppmv)	MDL ^(b) (ppmv)
Ammonia	NH ₃	PNL-ALO-226	25	2.5	0.5
Nitrogen Dioxide	NO ₂	PNL-ALO-212	1	0.1	0.02
Nitric Oxide	NO	PNL-ALO-212	25	2.5	0.02
Sulfur Oxide	SO _x	PNL-ALO-212	2	0.2	0.02
Mass (Water) ^(c)	n/a ^(d)	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 ammonia and 3 mL for the other analytes.

(c) The vapor-mass concentration, thought to be largely water vapor, is determined for estimates of humidity.

(d) n/a = not applicable

The accuracy of concentration measurements depends on errors associated with both sampling and analysis. Sampling information was provided by WHC. The accuracy of analytical results depends on the method used. For ammonia analyses, the accuracy of laboratory measurements by SIE was estimated to be $\pm 5\%$ relative. For SO_x analysis, the IC determination of sulfate derived from SO_x trapped in sorbent tubes is judged to be biased no more than 10%, even at the very low concentrations of solutions actually analyzed. Comparisons of working standards to a National Institute for Standards and Technology (NIST) standard reference material solution for sulfate exhibit no more than a 2 to 3% difference at concentrations of 2 ppm or greater. 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-104 on 3/3/94 using the VSS. The sample job designation number was S4004. Samples were prepared, submitted to WHC, and then analyzed to provide information on the concentrations of NH₃, NO₂, NO, SO_x, and H₂O. Sampling and analysis for hydrogen cyanide was not requested. The inorganic samples were received from WHC on 3/4/94; the sample-volume information was received on 3/25/94.

A list of samples, sampling information, and sample volumes is shown in Table 2.2. The types of solid sorbent traps used are also shown in the table. 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 2.2 List of PNL Inorganic Samples, Controls, and Gravimetric Results Obtained From a Heated Tube Inserted into the Headspace of Tank C-104 on 3/3/94

Sample Port and Volume Information ^(a)					
<u>Sample Number</u>	<u>Sorbent Type</u>	<u>Sample Port</u>	<u>Flow Rate (mL/min)</u>	<u>Duration (min)</u>	<u>Volume (L)</u>
<u>Samples:</u>					
S4004- 27-C03	NH ₃ Trap	1	200	15.0	3.00
S4004- 28-C03	NH ₃ Trap	10	200	15.0	3.00
S4004- 41-C03	NH ₃ Trap	3	200	15.0	3.00
S4004- 42-C03	NH ₃ Trap	10	200	15.0	3.00
S4004- 57-C03	NH ₃ Trap	3	200	15.0	3.00
S4004- 58-C03	NH ₃ Trap	10	200	15.0	3.00
S4004- 19-C03	NO _x Trap	1	200	15.0	3.00
S4004- 20-C03	NO _x Trap	10	200	15.0	3.00
S4004- 39-C03	NO _x Trap	1	200	15.0	3.00
S4004- 40-C03	NO _x Trap	10	200	15.0	3.00
S4004- 59-C03	NO _x Trap	1	200	15.0	3.00
S4004- 60-C03	NO _x Trap	10	200	15.0	3.00
S4004- 23-C03	SO _x Trap	3	200	15.0	3.00
S4004- 25-C03	SO _x Trap	10	200	15.0	3.00
S4004- 44-C03	SO _x Trap	10	200	15.0	3.00
S4004- 25-C03	H ₂ O Trap	3	200	15.0	3.00
S4004- 29-C03	H ₂ O Trap	3	200	15.0	3.00
S4004- 30-C03	H ₂ O Trap	10	200	15.0	3.00
S4004- 45-C03	H ₂ O Trap	3	200	15.0	3.00
S4004- 46-C03	H ₂ O Trap	10	200	15.0	3.00
<u>Controls:</u>					
S4004- 50-C03	NH ₃ Blank/Spare	n/a ^(b)	n/a	n/a	n/a
S4005- 52-B16	NO ₂ Blank (C-105)	n/a	n/a	n/a	n/a
S4005- 53-B16	H ₂ O Blank (C-105)	n/a	n/a	n/a	n/a

(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.

(Table 2.3) are listed as "less than or equal to," a probable maximum value determined by subtracting the blank result from the sample result. Sample results were not corrected for the percentage recoveries of spiked samples.

2.4.1 Ammonia Results. The concentration of NH₃ was 44 ± 0 ppmv, based on all six samples. The NH₃ quantity found in each exposed sorbent trap was 5.9 μ mol in the front sorbent section and ≤ 0.1 μ mol in the back section (indicating no breakthrough). Blank corrections, ≤ 0.06 μ mol in front and ≤ 0.03 μ mol 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 μ mol of NH₃ were $101 \pm 4\%$, $109 \pm 2\%$, and $104 \pm 1\%$, respectively, during related sample jobs (Clauss et al. 1994; Ligothke et al. 1994). No sample

Table 2.3 Inorganic Vapor Sample Results Obtained From a Heated Tube Inserted into the Headspace of Tank C-104 on 3/3/94

Sample	Analytical Results (μmol)			Sample Volume (L)	Vapor ^(b) Concentration (ppmv)
	Front Section	Back Section	Total ^(a) Blank-Corrected		
<u>NH₃ Samples:</u>			<u>5.9^(c)</u>	<u>3.00^(c)</u>	<u>44 ± 0^(c)</u>
S4004- 27-CO3	5.9	0.06	5.9	3.00	44
S4004- 28-CO3	5.9	0.06	5.9	3.00	44
S4004- 41-CO3	5.9	0.06	5.9	3.00	44
S4004- 42-CO3	5.9	0.06	5.9	3.00	44
S4004- 57-CO3	5.9	0.06	5.9	3.00	44
S4004- 58-CO3	5.9	0.06	5.9	3.00	44
<u>NO₂ Samples:</u>			<u>≤ 0.001</u>	<u>3.00</u>	<u>≤ 0.02</u>
S4004- 19-CO3	0.0056	NA ^(d)	n/a	3.00	n/a
S4004- 20-CO3	0.0059	NA	n/a	3.00	n/a
S4004- 39-CO3	0.0059	NA	n/a	3.00	n/a
S4004- 40-CO3	0.0056	NA	n/a	3.00	n/a
S4004- 59-CO3	0.0053	NA	n/a	3.00	n/a
S4004- 60-CO3	0.0057	NA	n/a	3.00	n/a
<u>NO Samples:</u>			<u>0.0248</u>	<u>3.00</u>	<u>0.37 ± 0.05</u>
S4004- 19-CO3	0.0109	NA	0.0004 x	3.00	0.01 x
S4004- 20-CO3	0.0152	NA	0.0048 x	3.00	0.07 x
S4004- 39-CO3	0.0323	NA	0.0218	3.00	0.33
S4004- 40-CO3	0.0349	NA	0.0245	3.00	0.37
S4004- 59-CO3	0.0399	NA	0.0295	3.00	0.44
S4004- 60-CO3	0.0339	NA	0.0235	3.00	0.35
<u>SO_x Samples:</u>			<u>0.050</u>	<u>3.00</u>	<u>0.4 ± 0.2</u>
S4004- 23-CO3	0.046	0.033	0.043	3.00	0.32
S4004- 24-CO3	0.033	0.033	0.031	3.00	0.23
S4004- 44-CO3	0.058	0.054	0.077	3.00	0.57
<u>Gravimetric Samples (mg.mg/L):</u>			<u>43.9 mg</u>	<u>3.00</u>	<u>15 ± 1 mg/L</u>
S4004- 25-CO3	n/a	n/a	42.7	3.00	14.2
S4004- 29-CO3	n/a	n/a	43.4	3.00	14.5
S4004- 30-CO3	n/a	n/a	46.4	3.00	15.5
S4004- 45-CO3	n/a	n/a	41.8	3.00	13.9
S4004- 46-CO3	n/a	n/a	45.0	3.00	15.0

- (a) 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 levels of analytes found in blanks are described in the subsections of Section 2.4.
- (b) Blank-corrected vapor concentrations as per Section 2.1.1. In the calculation for concentration, the nitrite values (listed) were doubled to account for unanalyzed nitrate.
- (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; x = not included in determination of average concentration.

analyses were duplicated to check repeatability. Two sample leachates were spiked after initial analysis yielded percentage recoveries of 96 to 98%.

2.4.2 Nitrogen Oxide Results. Measurements of NO_2 and NO were made using six NO_x sorbent-trap trains (the NO_x trains consisted of NO_2 trap, oxidizer, NO_2 trap).

The concentrations of NO_2 and NO were ≤ 0.02 and 0.37 ± 0.05 ppmv, respectively. Blank-corrected NO_2^- quantities in the sorbent traps averaged ≤ 0.001 μmol (NO_2 samples) and 0.023 μmol (NO samples). One nitre blank was analyzed and used to correct data: 0.0053 μmol for NO_2 and 0.0104 μmol for NO. Although spiked blanks were not tested, blanks spiked with 0.0064 , 0.047 , 0.11 , and 0.74 μmol NO_2 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; Ligothke et al. 1994). 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.

2.4.3 Sulfur Oxides Results. The result of three sorbent traps for SO_x indicated a concentration of 0.4 ± 0.2 ppmv. This result was based on an average blank-corrected level of 0.050 μmol SO_x in the samples. Because the quantity of SO_x present in both front and back sections was similar, it is possible that an unresolved sampling or analytical problem affected these results. Such an effect would likely bias the results high (indicating a greater concentration than actually exists in the headspace).

2.4.4 Gravimetric Results. The mass concentration of material collected in the sorbent-trap trains, believed to be primarily water vapor, was 15 ± 1 mg/L. The result was based on an average mass gain of 44 mg from all five silica-gel sorbent traps.

3.0 Organic Task

3.1 SUMMA™ Canister and OVS Tube Preparation

The SUMMA™ canisters sent out to the field for sampling were new and clean. Before sending the canisters out to the field, they were prehumidified with 100 μ L of distilled water and labeled with a field-sampling identification. The OVS tubes were purchased from SKS and prepared using a procedure described in lab book 55409.

3.2 Sample Analysis Method

Problems arose with the SUMMA™ canisters collected from this tank. These were described in a letter sent to Jerry Osborne on March 18, 1994. Briefly, some of the SUMMA™ canisters delivered to PNL and OGL were swapped during the sampling/delivery process. The appropriate canisters were later traded and 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 U. S. Environmental Protection Agency (EPA) compendium Method TO-14. The method uses an EnTech cryoconcentration system interfaced with a Hewlett Packard (HP) 5971 GC/MS. The InTech 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.

Samples obtained using OVS tubes in the headspace of Tank C-104 were removed from plastic (outer) and aluminum foil (inner) wrappings, and each OVS was divided into two portions. The front portion contained the glass-fiber filter and front XAD-2 sorbent bed. The retainer ring was removed but not extracted. The back portion contained the polyurethane foam (PUF) separator, the second XAD-2 sorbent bed, and the PUF plug. Each portion was placed in a labeled 4-mL vial fitted with a Teflon®-lined screw cap.

Front and back portions of the OVS tubes were desorbed by adding 1 mL of carbon disulfide to each vial, recapping the vials, and sonicating the vials for 30 min. Portions of the extract were transferred to an auto-sampler vial to which portions of naphthalene- d_8 internal standard (IS) were also added. The remainder is archived against future analyses. The samples were analyzed using a HP 5890/5970 GC/MS instrument under scan acquisition. Quantitation was performed by monitoring a single ion at 57 amu for the n-alkane analytes (C_{11} - C_{15}), at 99 amu for tributyl phosphate (TBP) and at 136 amu for the IS. Calculations were performed using the IS method.

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 bromochloromethane, 1,4-difluorobenzene, and chlorobenzene- d_5 was used as an IS for all blank, calibration standard, and sample analyses. Analyte response 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 273 K and was calculated directly from the following equation:

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

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 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

(a) Nominal molecular weight.

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 :

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

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 $0.59 \text{ mg}/\text{m}^3$. 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.

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

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 SUMMA™ GC/MS analysis of the tank-headspace samples are presented in Tables 3.1 and 3.2. 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. The levels of TO-14 analytes observed in the sample collected from Tank C-104 were significantly low, close to the quantitation limit (2 ppb).

Table 3.2 lists the semi-quantitative results for the TICs observed in the samples. Twenty-four compounds were observed above the instrumental detection limit, a total average concentration of $26.93 \text{ mg}/\text{m}^3$. The normal paraffin hydrocarbons (NPHs), defined as n-alkanes from C_{11} to C_{15} , present were undecane, dodecane, tridecane, and tetradecane, which accounted for 69% of the TIC compounds. A high concentration of 1-butanol was also present.

Table 3.3 lists OVS sample analyte results for all OVS samples collected. The results are expressed as micrograms of analyte per liter of tank headspace. These results have been corrected for experimentally determined adsorption of the OVS for NPH. All of the mass reported for the samples was observed in the front portions of the OVS. Analysis of the back portions of the OVS indicated that no breakthrough occurred during sampling. Results of all trip blanks, field, and laboratory surrogates are also included. A comparison of OVS field and laboratory surrogate-analysis results

(a) Nominal molecular weight.

show no appreciable variations between analytical and expected (spiked) values.

No measurable tributyl phosphate (TBP) was seen on the collected OVS samples. The detection limit for these 4 min samples is estimated to be less than 50 μg per collected sample. Tributyl phosphate was not spiked on to the field surrogates. No other compounds were evaluated from the OVS tubes.

Table 3.1 TO-14 Analysis for Samples from the Headspace of Tank C-104 from SUMMA™ Canister Samples Collected on 3/3/94.

TO-14 Analyte	CAS No.	Mol Wt	S4004-04.C03 ^(a) PNL 071 ^(b)		S4004-05C03 ^(a) PNL 065 ^(b)		S4004-06.C03 ^(a) PNL 066 ^(b)		Means and Standard Deviations	
			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	0.009	1.61	0.008	1.54	0.008	1.58	0.008	0.000
Methyl Chloride (Chloromethane)	74-87-3	50	< 0.01	2.21	0.006	2.55	0.005	2.35	0.005	0.000
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	0.08	12.65	0.08	12.68	0.05	8.91	0.070	0.017
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	0.03	6.37	< 0.01	< 2	< 0.01	< 2	(c)	(c)
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	< 0.02	< 2	< 0.02	< 2	(c)	(c)
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)
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)

Table 3.1 TO-14 Analysis for Samples from the Headspace of Tank C-104 from SUMMA™ Canister Samples Collected on 3/3/94 (continued).

TO-14 Analyte	CAS No.	Mol Wt	S4004-04.C03 ^(a)		S4004-05C03 ^(a)		S4004-06.C03 ^(a)		Means and Standard Deviations	
			PNL 071 ^(b)		PNL 065 ^(b)		PNL 066 ^(b)		(mg/m ³)	St Dev
			Concentration		Concentration		Concentration			
			(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)		
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 is 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) in Headspace of Tank C-104 from SUMMATM Canister Samples Collected on 3/3/94.

Tentatively Identified Compound ^(d)	CAS No. ^(d)	Mol. Wt.	Ret Time	S4004-04.C03 ^(b) PNL 071 ^(c)		S4004-05.C03 ^(b) PNL 065 ^(c)		S4004-06.C03 ^(b) PNL 066 ^(c)		Means and Standard Deviations			
				(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	3.896	0.48	254.59	0.47	252.92	0.42	222.98	0.46	0.03	243.5	17.79
Propane	74-98-6	44	3.989	0.34	174.48	0.35	175.8	0.3	151.41	0.33	0.03	167.23	13.72
Cyclopropane	75-19-4	42	4.763	0.11	60.99	0.12	62.19	< 0.02	< 0.01	0.12		61.59	
Acetaldehyde	75-07-0	44	5.227	0.31	160.3	0.33	167.79	0.13	68.16	0.26	0.11	132.08	55.49
2-Methyl -1-Propene	115-11-7	56	5.701	0.30	121.42	0.32	128.32	0.26	104.38	0.29	0.03	118.04	12.32
Butane	106-97-8	58	5.97	0.61	235.76	0.64	246.03	0.53	205.87	0.59	0.06	229.22	20.86
Acetonitrile	75-05-8	41	7.847	0.13	68.96	0.12	67.14	0.11	61.21	0.12	0.01	65.77	4.05
Acetone	67-64-1	58	8.436	0.34	131.12	0.32	125.32	0.3	116.72	0.32	0.02	124.39	7.25
Pentane	109-66-0	72	9.643	0.27	85.37	0.28	85.9	0.24	75.77	0.26	0.02	82.35	5.7
Butanal	123-72-8	72	13.336	0.45	139.27	0.46	141.74	0.51	157.87	0.47	0.03	146.29	10.1
2-Butanone	78-93-3	72	13.543	0.32	99.54	0.33	102.96	0.31	97.97	0.32	0.01	100.16	2.55
1-Hexene	592-41-6	84	14.193	0.14	37.4	0.13	35.94	0.12	32.52	0.13	0.01	35.29	2.5
Tetrahydrofuran	109-99-9	72	15.833	0.15	46.58	0.15	46.68	0.14	42.83	0.15	0.01	45.36	2.19
1-Butanol	71-36-3	74	17.567	2.70	816.56	2.52	763.4	2.13	645.36	2.45	0.29	741.77	87.63
Pentanal	110-62-3	86	19.176	0.15	38.49	0.16	40.42	0.12	30.22	0.14	0.02	36.38	5.42
Heptane	142-82-5	100	20.517	0.34	75.43	0.32	71.12	0.27	61.37	0.31	0.04	69.31	7.2
Octane	111-65-9	114	26.016	0.22	43.12	0.21	41.63	0.2	38.44	0.21	0.01	41.06	2.39
3-Heptanone	106-35-4	114	29.514	0.45	88.68	0.43	85.31	0.35	68.38	0.41	0.05	80.79	10.88
Nonane	111-84-2	128	31.124	0.10	16.64	< 0.06	< 0.01	< 0.06	< 0.01	(e)		(e)	
Decane	124-18-5	142	35.839	1.00	157.85	0.98	154.86	0.88	138.75	0.95	0.06	150.49	10.27
Undecane	1120-21-4	156	40.203	5.04	723.62	4.99	715.87	4.62	663.48	4.88	0.23	700.99	32.71
Dodecane	112-40-3	170	44.247	6.57	865.36	6.52	859.61	6.31	831.21	6.47	0.14	852.06	18.28
Unknown C11 Ketone		170	46.538	0.10	12.8	< 0.08	< 0.01	< 0.08	< 0.01	(e)		(e)	
Unknown Alkane		170	47.136	0.10	12.66	0.11	14.82	< 0.08	< 0.01	0.11	0.01	13.74	1.53
Tridecane	629-50-5	184	48.013	6.32	769.65	6.07	738.46	6.26	762.14	6.22	0.13	756.75	16.28
Tetradecane	629-59-4	198	51.531	1.00	112.59	0.87	98.63	1.02	114.9	0.96	0.08	108.71	8.8

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

(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) Calculation is not significant with fewer than two values for mean value and fewer than three values for standard deviation value.

Table 3.3 Waste Tank C-104 OVS Sample Analyte Results (µg/sample)

WHC Sample ID	PNL LRB ID	Sample Description	Normal Paraffin Hydrocarbons					TBP
			C ₁₁	C ₁₂	C ₁₃	C ₁₄	C ₁₅	
S4004 21.C03	55409-23-01	OVS #1	<1	3	4.3	1	<1	<16.7
S4004 22.C03	55409-23-02	OVS #2	<1	<3	<3	<1	<1	<16.7
S4004 43.C03	55409-23-03	OVS #3	1	<3	<3	<1	<1	<16.7
S4004 51.C03	55409-23-04	Trip Blank #1	<1	<3	<3	<1	<1	<16.7
S4004 52.C03	55409-23-05	Trip Blank #2	<1	<3	<3	<1	<1	<16.7
S4004 53.C03	55409-23-06	Trip Blank #3	<1	<3	<3	<1	<1	<16.7
S4004 54.C03	55409-23-07	Field Surrogate #1 ^(a)	5 (5)	14.6 (15)	13.3 (15.3)	15 (15.3)	5.7 (5.3)	N/A ^(b)
S4004 55.C03	55409-23-08	Field Surrogate #2	2.8	15.7	14.3	16.3	5.7	N/A
S4004 56.C03	55409-23-09	Field Surrogate #3	5.7	13.6	12.3	13	5	N/A
LS ^(c)	55409-23-10	Lab Surrogate #1	4	14	12.3	13.6	5	N/A
LS	55409-23-11	Lab Surrogate #2	4.3	13.3	12.6	14	5	N/A
LS	55409-23-12	Lab Surrogate #3	4.3	14.3	12.3	12.7	4.7	N/A

(a) Surrogate-spike amounts are indicated in parenthesis. All surrogates were spiked with the same amount of analyte.

(b) Sample not analyzed for TBP.

(c) Samples indicated with this designation were held in the laboratory and do not have a WHC ID number.

Figure 3.1a Total Ion Chromatogram (2 - 30 min) for Hanford Waste Tank C-104
SUMMA™ Canister Sample S4004-06.C03 Collected on 3/3/94

Figure 3.1b Total Ion Chromatogram (30 - 58 min) for Hanford Waste Tank C-104
SUMMA™ Canister Sample S4004-06.C03 Collected on 3/3/94

4.0 Conclusions

The concentrations of selected inorganic and organic compounds were determined from samples of the headspace of Tank C-104. It is important to note that the inorganic samples were obtained and analyzed using procedures that were being developed, and that final procedures were not completed until later (Ligotke et al. 1994). Consequently, it is not known whether significant sampling or analytical errors occurred, and it is recommended that the headspace of Tank C-104 be sampled again using the improved methods should less qualified results be needed. The qualified results of inorganic samples were NH_3 (44 ± 0 ppmv), NO_2 (≤ 0.02 ppmv), NO (0.37 ± 0.05 ppmv), SO_x (0.4 ± 0.2 ppmv), and mass concentration (15 ± 1 mg/L). The mass concentration was expected to consist largely of water vapor. Listed uncertainties reflect repeatability; actual uncertainties were not determined.

Twenty-six TO-14 and TIC compounds were found above instrumental detection limits, dominated by four NPH n-alkanes, about 69% of all compounds observed, and 1-butanol, which is known to be a degradation product of TBP. No measurable TBP was seen in the collected OVS samples.

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.

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6.0 Further Reading

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

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