**Vapor Space Characterization of Waste
Tank 241-C-112: Results from
Samples Collected on 8/11/94**

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

Summary

This report describes organic analyses results from samples obtained from the headspace of the Hanford waste storage Tank 241-C-112 (referred to as Tank C-112). 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 (NH₃), nitrogen dioxide (NO₂), nitric oxide (NO), and water (H₂O). Sampling for hydrogen cyanide (HCN) and sulfur oxides (SO_x) was not requested. Organic compounds were also quantitatively determined. Five 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. None were observed above the 2-ppbv detection limit. The five organic analytes with the highest concentration are listed in Table 1 and account for 100% of the total organic components in Tank C-112.

Table 1. Summary Results of Inorganic and Organic Samples Collected from the Headspace of Tank C-112 on 8/11/94

<u>Category</u>	<u>Analyte</u>	<u>Vapor^(a) Concentration</u>	<u>Units</u>
Inorganic	NH ₃	22.7 ± 0.5	ppmv
	NO ₂	≤ 0.02	ppmv
	NO	0.62 ± 0.05	ppmv
	H ₂ O	26 ± 2	mg/L
Organic	Acetonitrile	1.99	mg/m ³
	Acetone	0.56	mg/m ³
	Methyl Nitrate	0.20	mg/m ³
	Acetaldehyde	0.17	mg/m ³
	Propanenitrile	0.07	mg/m ³

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

Acknowledgments

The authors gratefully acknowledge the support of other project staff at Pacific Northwest Laboratory who contributed to the successful completion of this sampling and analysis activity. Jeff Edwards served as the PNL single-point-of-contact and coordinated sample handling and communications with Westinghouse Hanford Company. K. B. Olsen assisted with the organic portion of this report. Bruce Lerner performed method development and validation work that supported the inorganic vapor sampling. Sally Slate and May-Lin Thomas analyzed inorganic samples, and Annalisa Krupsha and Gary Dennis prepared the solid-sorbent sample trains. Bonnie L. Lehrman provided word processing support.

Abbreviations

CAS	Chemical Abstracts Service
COC	chain of custody
C _v	concentration by volume
DIW	deionized water
emf	electromotive force
EPA	U.S. Environmental Protection Agency
GC/MS	gas chromatography/mass spectrometry
HP	Hewlett Packard
IC	ion chromatography
IL	impact level
IS	internal standard
MDL	minimum detection limit
NIST	National Institute for Standards and Technology
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	13
3.4 Analysis Results	15
4.0 Conclusions	17
5.0 References	17
6.0 Further Reading	17
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 Obtained from a Heated Tube Inserted into the Headspace of Tank C-112 on 8/11/94	10
2.3	Inorganic Vapor Sample Results Obtained From Samples Inserted into the Headspace of Tank C-112 on 8/11/94	11
3.1	TO-14 Analysis Results for Samples Collected from the Headspace of Tank C-112 in SUMMA™ Canisters on 8/11/94	19
3.2	Tentatively Identified Compounds and Estimated Concentrations in the Headspace of Tank C-112 SUMMA™ Canister Samples Collected on 8/11/94	21
3.3	TO-14 Analysis for Ambient Samples Collected Near Tank C-112 in SUMMA™ Canisters on 8/11/94.	22
3.4	Tentatively Identified Compounds and Estimated Concentrations in Ambient Samples Collected Near Tank C-112 on 8/11/94	23

Figures

1.1	Chain-of-Custody for Tank C-112	2
3.1	Total Ion Chromatogram of Hanford Waste Tank C-112 SUMMA™ Canister Sample S4054-A07-099 Collected on 8/11/94	24

1.0 Introduction

This report describes results of the analyses of tank-headspace samples taken from the Hanford Waste Tank 241-C-112 (referred to as Tank C-112). 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 collected near Tank C-112. The 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 S4089 and samples were collected by WHC on December 30, 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 five SUMMA™ canisters (for organic analysis) were supplied to WHC on August 9, 1994. Samples were taken (by WHC) from the tank headspace on August 11 and were returned to PNL from the field on August 12. Inorganic (sorbent trap) samples were delivered to PNL on chain of custody (COC) 007498 (see Figure 1.1a). The SUMMA™ canisters were delivered on COC 007499 (Figure 1.1b).

Project work at PNL was governed by an approved QA plan^(c). The samples were inspected upon delivery to the 326/23B laboratory and logged into PNL record book 55408 before implementation of PNL Technical Procedure PNL-TVP-07^(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 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 NH_3 or NO_2 and NO analyses). The aqueous extracts were analyzed either by selective electrode or by ion chromatography (IC). Organic analyses were performed using cryogenic preconcentration followed by gas chromatography/mass spectrometry (GC/MS).

-
- (a) Pacific Northwest Laboratory is operated for the U. S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830. TWRS Characterization Project, Pacific Northwest Laboratory, Richland, Washington.
 - (b) Letter from Mr. P. J. Melliger (PNL) to Mr. T. J. Kelley (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 Quality Assurance Plan, PNL-MCS-027, Rev. 4. August 1994. TWRS Waste Tank Safety Program, 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	WHC 007498
---------------------------------	------------------	------------

Custody Form Initiator	J. A. Edwards	Telephone (509) 373-0141
		Pager 85-3009
Company Contact	R. A. Westberg	Telephone (509) 373-5734
Project Designation/Sampling Locations	200 East Tank Farm	Collection Date 08- 1.1 -94
241-C-112 Tank	Vapor Sample SAF S4054	Preparation Date 08- 0.8 -94
Ice Chest No.	(VSS Truck)	Field Logbook No. WHC-____-__
Bill of Lading/Airbill No.	N/A	Offsite Property No. N/A
Method of Shipment	Government Truck	Sample Job _____
Shipped to	PNL	
Possible Sample Hazards/Remarks	Unknown at time of sampling	

Sample Identification

S4054 - A22 . 25W	NH ₃ /NO _x /H ₂ O (Trap # 1) Line # 8
S4054 - A23 . 26W	NH ₃ /NO _x /H ₂ O (Trap # 2) Line #10
S4054 - A24 . 27W	NH ₃ /NO _x /H ₂ O (Trap # 3) Line # 9
S4054 - A25 . 28W	NH ₃ /NO _x /H ₂ O (Trap # 4) Line #10
S4054 - A26 . 29W	NH ₃ /NO _x /H ₂ O (Trap # 5) Line # 8
S4054 - A27 . 30W	NH ₃ /NO _x /H ₂ O (Trap # 6) Line #10
S4054 - A28 . 31W	NH ₃ /NO ₂ /H ₂ O a-b-c (Trip Blank# 1)
S4054 - A29 . 32W	NH ₃ /NO ₂ /H ₂ O a-b-c (Trip Blank# 2)
S4054 - A30 . 33W	NH ₃ /NO ₂ /H ₂ O a-b-c (Trip Blank# 3)

☐ Field Transfer of Custody		☒ Chain of Possession		(Sign and Print Names)	
Relinquished By	Date	Time	Received By	Date	Time
J. A. Edwards	08-09-94		T. Utechy	08-09-94	0640
T. B. Utechy	08-11-94	0030	R. Westberg	8-11-94	0730
R. Westberg	8-11-94	0730	T. B. Utechy	8-11-94	0740
T. B. Utechy	8-12-94	1000	J. A. Edwards	8-12-94	1000

(Revised 02/28/94)

Final Sample Disposition

Disposal Method:

Disposed by:

Date/Time:

A-6000-407 (12/92) WEF061

Figure 1.1a Chain-of-Custody for Inorganic Samples

Westinghouse Hanford Company	CHAIN OF CUSTODY	WHC 007499
---------------------------------	------------------	------------

Custody Form Initiator	J. A. Edwards	Telephone (509) 373 -0141
		Pager 85-3009
Company Contact	R. A. Westberg	Telephone (509) 373-5734
Project Designation/Sampling Locations	200 East Tank Farm	Collection Date 08- <u>1</u> -94
241-C-112 Tank	Vapor Sample SAF S4054	Preparation Date 08- 0 8 -94
Ice Chest No.	(VSS Truck)	Field Logbook No. WHC-____-__
Bill of Lading/Airbill No.	N/A	Offsite Property No. N/A
Method of Shipment	Government Truck	Sample Job _____
Shipped to	PNL	

Possible Sample Hazards/Remarks Unknown at time of sampling

Sample Identification

S4054 - A01 - 080	SAP Ref _____	Ambient air SUMMA #1, <u>Upwind VSS</u> (PNL)
S4054 - A02 - 081	SAP Ref _____	Ambient air SUMMA #2, <u>Through VSS</u> (PNL)
S4054 - A05 - 088	SAP Ref _____	SUMMA #4 (PNL)
S4054 - A07 - 099	SAP Ref _____	SUMMA #6 (PNL)
S4054 - A09 - 114	SAP Ref _____	SUMMA #8 (PNL)

[X] Field Transfer of Custody		[] Chain of Possession		(Sign and Print Names)	
Relinquished By	Date	Time	Received By	Date	Time
J. A. Edwards <i>[Signature]</i>	08-08-94	1200	T. Utecht <i>[Signature]</i>	08-08-94	1300
T. Utecht / T. B. Utecht	8-11-94	0030	R. Westberg / R. A. Westberg	8-11-94	0030
R. Westberg / R. A. Westberg	8-11-94	0730	T. Utecht / T. B. Utecht	8-11-94	0740
T. B. Utecht / T. B. Utecht	8-12-94	1000	J. A. Edwards / J. A. Edwards	8-12-94	1000

(Revised 02/28/94)

Final Sample Disposition

Disposal Method:

Disposed by:

Date/Time:

A-6000-407 (12/92) WEF061

Figure 1.1b Chain-of-Custody for Organic Samples

2.0 Inorganic

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. Analytical accuracy was estimated based on procedures used. Sample preparation and analyses were performed following PNL quality assurance (QA) impact level (IL) III requirements.

2.1 Standard Sampling Methodology

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

The type and nominal quantity of sorbent material varied by application. Sorbent traps 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 adsorbed and disproportionated to equi-molar quantities of nitrite ions (NO_2^-) and nitrate ions (NO_3^-). Glass tubes containing 800 mg of an oxidant such as chromate were used to convert NO to NO_2 . The converted NO was then collected as nitrite and nitrate in an NO_2 trap. The water traps contained 300 mg of silica gel in the primary and 150 mg in the breakthrough sorbent sections.

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

The sorbent traps were prepared in multi-trap sorbent trains configured so sample flow passed in order through the traps, targeting specific analytes, and then through a desiccant trap. The specific order of traps within the various sorbent trains is described in Section 2.4. The ends of the glass-tube traps were broken, and the traps were weighed and then connected to each other using uniform lengths of 3/8-in. perfluoroalkoxy (PFA)-grade Teflon® tubing. The tubing was heated in hot air and forced over the open ends of the traps to form a tight seal. The inlets of the sorbent trains each consisted of a short section of tubing having a 3/8-in. stainless steel Swagelok® nut, sealed using a Swagelok® cap. The trailing ends of the sorbent trains (the downstream end of the traps containing silica gel) were each sealed with red-plastic end caps provided by the manufacturer. The sorbent-tube 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 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 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 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 4 or 5 samples; 5) continuing this sequence until all samples of the batch have been measured, including duplicates and spiked samples; and 6) remeasuring the complete set of calibration standards (at the end of the session). Emf signal measurements obtained for samples are compared to those for standards, either graphically or algebraically (using linear regression), to determine ammonia concentration in the samples.

2.2.2 Nitrite Analysis. The sorbent traps for NO_2 and NO were desorbed in an aqueous TEA and n-butanol solution and analyzed by suppressed-conductivity ion chromatography (SCIC) for nitrite according to PNL-ALO-212, Rev. 1 (*Determination of Inorganic Anions by Ion Chromatography*) modified to obviate interferences by concentrations of non-target analytes. Specifically, the modifications used were 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; 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-trap 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 analyzing every six samples. If the instrument response indicated that sample nitrite concentration was outside the calibration range (> 0.5 ppm nitrite), the sample was diluted with desorbing solution and reanalyzed. After all samples of a batch were analyzed, the complete set of calibration standards was remeasured to verify consistent instrument response, and the analytical session was terminated.

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

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

2.3 Quality Assurance/Quality Control

Analytical work was performed according to quality levels identified in the project QA plan and several PNL documents. The samples were analyzed following PNL QA IL III. The PNL documents include PNL-MA-70 (Part 2), PNL-MA-599, PNL-ALO-212, PNL-ALO-226, 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 NH₃).

Table 2.1 Analysis Procedures and Detection Limits of Target Inorganic Analytes

Analyte	Formula	Procedure	REL ^(a) (ppmv)	0.1 x REL ^(a) (ppmv)	MDL ^(b) (ppmv)
Ammonia	NH ₃	PNL-ALO-226	25	2.5	0.5
Nitrogen Dioxide	NO ₂	PNL-ALO-212	1	0.1	0.02
Nitric Oxide	NO	PNL-ALO-212	25	2.5	0.02
Mass (water) ^(c)	n/a ^(d)	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 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, 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 NH₃ above, the estimated maximum bias for samples derived from sampling for NO₂ is $\pm 10\%$, and for samples derived from sampling for NO, it is $\pm 5\%$ relative. The accuracy of measurements of sample mass is ± 0.05 mg, or much less than 1% of the mass changes of 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-112 on 8/11/94 using the VSS. The sample job designation number was S4054. Samples were prepared, submitted to WHC, and then analyzed to provide information on the concentrations of NH_3 , NO_2 , NO , and H_2O . Sampling and analysis for HCN and SO_x was not requested. The inorganic samples were received from WHC on 8/12/94; the sample-volume information was received on 9/12/94.

A list of samples, sampling information, sample volumes, and gravimetric results is shown in Table 2.2. The types of sample trains used, and the order of sorbent traps within each train, are also shown in the table. For example, the sorbent train $\text{NH}_3/\text{NO}_x/\text{H}_2\text{O}$ 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 22.7 ± 0.5 ppmv, based on all six samples. The blank-corrected NH_3 quantities in the sorbent traps ranged from 3.0 to 3.1 μmol in the front sorbent sections with no indication of breakthrough. Blank corrections, ≤ 0.06 μmol in front and ≤ 0.03 μmol in back sorbent sections, were based on three blanks and were not significant. Although spiked blanks were not tested, the percentage recoveries of three sets of blanks spiked with 12.2, 22.3, and 46.4 μmol NH_3 were $101 \pm 4\%$, $109 \pm 2\%$, and $104 \pm 1\%$, respectively, during related sample jobs (Clauss et al. 1994; Ligotke et al. 1994). The analysis of one sample was duplicated and yielded a repeatability of $\pm 3\%$. One sample leachate was spiked after initial analysis with roughly the quantity of NH_3 in the sample and yielded a percentage recovery of 103%. A 5-point calibration was performed over an NH_3 range of 0.1 to 1000 $\mu\text{g/mL}$.

2.4.2 Nitrogen Oxides Results. Measurements of NO_2 and NO were made using six 5-segment $\text{NH}_3/\text{NO}_x/\text{H}_2\text{O}$ sorbent-trap trains (the NO_x trains consisted of NO_2 trap, oxidizer, NO_2 trap). Related sample jobs, performed using the VSS in Tanks BY-104, -105, and -106 both with and without NO_x trains protected by a leading NH_3 trap (e.g., Clauss et al. 1994), indicated that the presence of the upstream NH_3 traps resulted in NO concentrations that were about 1.3- to 1.6-fold less than those from unprotected NO_2 traps. The NO_2 concentrations were also potentially less following an NH_3 trap.

Table 2.2 List of PNL Inorganic Samples, Controls, and Gravimetric Results Obtained From a Heated Tube Inserted into the Headspace of Tank C-112 on 8/11/94

Sample Number	Sorbent Type	Sample Port and Volume Information ^(a)				Mass Gain (g)
		Sample Port	Flow Rate (mL/min)	Duration (min)	Volume (L)	
<u>Samples:</u>						
S4054-A22-25W	NH ₃ /NO _x /H ₂ O Train	8	200	15.0	3.00	0.0825
S4054-A23-26W	NH ₃ /NO _x /H ₂ O Train	10	200	15.0	3.00	0.0717
S4054-A24-27W	NH ₃ /NO _x /H ₂ O Train	9	200	15.0	3.00	0.0764
S4054-A25-28W	NH ₃ /NO _x /H ₂ O Train	10	200	15.0	3.00	0.0758
S4054-A26-29W	NH ₃ /NO _x /H ₂ O Train	8	200	15.0	3.00	0.0836
S4054-A27-30W	NH ₃ /NO _x /H ₂ O Train	10	200	15.0	3.00	0.0774
<u>Controls:</u>						
S4054-A28-31W	NH ₃ /NO ₂ /H ₂ O Blanks	n/a ^(b)	n/a	n/a	n/a	-0.0021
S4054-A29-32W	NH ₃ /NO ₂ /H ₂ O Blanks	n/a	n/a	n/a	n/a	0.0006
S4054-A30-33W	NH ₃ /NO ₂ /H ₂ O Blanks	n/a	n/a	n/a	n/a	-0.0005

(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.

The concentrations of NO₂ and NO were ≤ 0.02 and 0.62 ± 0.05 ppmv, respectively. Blank-corrected NO₂⁻ quantities in the sorbent traps averaged ≤ 0.0015 μmol (NO₂ samples) and 0.0419 μmol (NO samples). Nitrite blank levels used to correct data were 0.0158 ± 0.0002 μmol in front and 0.0075 ± 0.0003 μmol in back sorbent sections and were based on three blanks. Although spiked blanks were not tested, blanks spiked with 0.0064 , 0.047 , 0.11 , and 0.74 μmol 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; Ligothke et al. 1994). No samples were reanalyzed to check repeatability. No sample leachates were spiked after initial analysis with quantities of NO₂⁻ to test analytical percentage recoveries. A 4-point calibration was performed over a concentration range of 0 to 0.5 μg NO₂⁻ per mL in the desorbing matrix.

2.4.3 Gravimetric Results. The mass concentration of material collected in the sorbent-trap trains, believed to be primarily water vapor, was 26 ± 2 mg/L. The result was based on an average mass gain of 78 mg from all six NH₃/NO₂/H₂O sample trains. The blank correction applied to the results was 0 ± 1 mg per sample train, based on an average per-trap mass loss of 0.2 ± 0.8 mg from nine blanks. Three traps each of NH₃, NO₂, and H₂O were prepared and analyzed as trip blanks. Although no spiked blanks were tested, the percentage recovery of mass from three blank H₂O traps spiked with 51 mg water was $103 \pm 2\%$ during a related sample job (Clauss et al. 1994).

Table 2.3 Inorganic Vapor Sample Results Obtained From a Heated Tube Inserted into the Headspace of Tank C-112 on 8/11/94

<u>Sample</u>	<u>Analytical Results (μmol)</u>			<u>Sample Volume (L)</u>	<u>Vapor^(a) Concentration (ppmv)</u>
	<u>Front Section</u>	<u>Back Section</u>	<u>Total^(b) Blank-Corrected</u>		
<u>NH₃ Samples:</u>			<u>3.05^(c)</u>	<u>3.00^(c)</u>	<u>22.7 $\pm$ 0.5^(c)</u>
S4054-A22-25W	3.09	N/A ^(d)	3.03	3.00	22.6
S4054-A23-26W	3.01	0.03	2.95	3.00	22.0
S4054-A24-27W	3.12	N/A	3.06	3.00	22.8
S4054-A25-28W	3.09	N/A	3.03	3.00	22.6
S4054-A26-29W	3.18	0.03	3.12	3.00	23.3
S4054-A27-30W	3.16	N/A	3.10	3.00	23.1
<u>NO₂ Samples:</u>			<u>≤ 0.0015</u>	<u>3.00</u>	<u>≤ 0.02</u>
S4054-A22-25W	0.0140	0.0089	n/a ^(d)	3.00	n/a
S4054-A23-26W	0.0147	0.0087	n/a	3.00	n/a
S4054-A24-27W	0.0151	0.0072	n/a	3.00	n/a
S4054-A25-28W	0.0145	0.0071	n/a	3.00	n/a
S4054-A26-29W	0.0153	0.0081	n/a	3.00	n/a
S4054-A27-30W	0.0147	0.0074	n/a	3.00	n/a
<u>NO Samples:</u>			<u>0.0419</u>	<u>3.00</u>	<u>$\leq 0.62 \pm 0.05$</u>
S4054-A22-25W	0.0552	0.0098	0.0417	3.00	0.62
S4054-A23-26W	0.0538	0.0079	0.0384	3.00	0.57
S4054-A24-27W	0.0556	0.0079	0.0402	3.00	0.60
S4054-A25-28W	0.0623	0.0087	0.0477	3.00	0.71
S4054-A26-29W	0.0573	0.0078	0.0418	3.00	0.62
S4054-A27-30W	0.0571	0.0080	0.0418	3.00	0.62
<u>Gravimetric Samples (mg/mg/L):</u>			<u>78 mg</u>	<u>3.00</u>	<u>26 $\pm$ 2 mg/L</u>
S4054-A22-25W	n/a	n/a	82	3.00	27
S4054-A23-26W	n/a	n/a	72	3.00	24
S4054-A24-27W	n/a	n/a	76	3.00	25
S4054-A25-28W	n/a	n/a	76	3.00	25
S4054-A26-29W	n/a	n/a	84	3.00	28
S4054-A27-30W	n/a	n/a	77	3.00	28

- (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 levels of analytes found in blanks are described in the subsections of Section 2.4.
- (c) Underlined values represent the average of the set of samples. 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.

3.0 Organic

3.1 SUMMA™ Canister Preparation

Before sending SUMMA™ canisters out to the field for sampling, the canisters are cleaned and verified contaminant free according to PNL Technical Procedure PNL-TVP-02^(a). The cleaning procedure uses an EnTech 3000 cleaning system that controls 1) filling the canisters with purified humid air and 2) evacuating, for several cycles with applied heat, before allowing the canister to evacuate overnight. The canister is filled a final time with purified humid air for analysis by PNL Technical Procedure PNL-TVP-01^(b), which is a modification of U.S. Environmental Protection Agency (EPA) compendium Method TO-14. If the canister is verified as clean, free of TO-14 contaminants to a level of 5 parts per billion by volume (ppbv), the canister is evacuated to 30 in. Hg, tagged, and stored for use in the field. Before sending the canisters out to the field for sampling, the canisters are prehumidified with 100 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*^(c), which is a modified version of EPA compendium Method TO-14. The method uses an EnTech cryoconcentration system interfaced with a Hewlett Packard (HP) 5971 GC/MS. The EnTech concentrator is used to pull a metered volume of sample air from the SUMMA™ canister, cryogenically concentrate the air volume, then transfer the volume to the GC/MS for analysis. A 100-mL volume of sample is measured and analyzed from the tank headspace. The organic components in the sampled air are separated on an analytical column, J&W Scientific DB-1 phase, 60-m by 0.32-mm internal diameter with 3- 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.

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

-
- (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.
 - (c) Pacific Northwest Laboratory. 8/94. *Determination of TO-14 Volatile Organic Compounds in Hanford Tank Headspace Samples Using SUMMA™ Passivated Canister Sampling and Gas Chromatographic-Mass Spectrometry Analysis* PNL-TVP-03 (Rev. 0), PNL Technical Procedure, Richland, Washington.

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 internal standard (IS) for all blank, calibration standard, and sample analyses. Analyte responses from sample components, ISs, and standards were obtained from the extracted ion plot from their selected mass ion. The calibration curve was generated by calculating the relative response ratios of the IS to calibration standard responses and plotting the ratios against the ratio of the calibration-standard concentration (in ppbv) to the IS concentration. A least-squares linear-regression routine was applied to the data set to generate the best-fit line for each compound. The equation for that line was then used to quantify the TO-14 compounds found in the tank samples.

3.3.1 Quantitation of TO-14 Results. The quantitative-analysis results for the TO-14 volatile organic compounds were calculated directly from the calibration curve generated using the IS method described above and in PNL-TVP-03. The conversion from ppbv to mg/m^3 assumes standard temperature and pressure (STP) conditions of 760 torr and 273K and was calculated directly from the following equation:

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

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 instrument operating system. Chromatographic peaks with an area count greater than, or equal to, one half of the total area count of the chlorobenzene- d_5 IS peak at the 20-ppbv calibration level are tentatively identified and quantitatively estimated. This standard was chosen to determine the integration cutoff as it is in the middle of the chromatographic range and not in a region typically affected by coelution of other compounds. The quality of the mass-spectral searches was then reviewed by the principal investigators before the identification was assigned to each chromatographic peak.

The concentration of each TIC was estimated using a relative response factor calculated using a corrected total peak area for the IS chlorobenzene- d_5 . Specifically, the total integrated area for the chlorobenzene- d_5 peak had to be corrected for possible coeluting compounds before calculating the response factor. The corrected total peak area for the IS was calculated by multiplying the IS quantitation ion by a correction factor based on the ratio of the total integrated peak area to the quantitation ion as measured in blank runs. The corrected peak area was then used to calculate a response factor using the IS concentration in mg/m^3 :

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

The calculated response factor was then multiplied by the TIC peak area to give an estimated concentration for that compound. For acetonitrile, the total peak area was multiplied by the response factor for chlorobenzene- d_5 to give an estimated concentration of $1.99 \text{ mg}/\text{m}^3$. Internal standards

(a) Nominal molecular weight.

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/m³ and the molecular weight of the analyte.

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

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-d₅. The IS concentrations were converted from ppbv to mg/m³ at STP using a molecular weight of 129.39 (g/mol) for bromochloromethane, 114.09 for 1,4-difluorobenzene, and 117.6 for chlorobenzene-d₅.

3.4 Analysis Results

The results from the GC/MS analysis of the tank-headspace samples are presented in Tables 3.1 and 3.2. The results from GC/MS analysis of the ambient air collected near the tank are presented in Tables 3.3 and 3.4. 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-112 were below the quantitation limit (2 ppb).

Table 3.2 lists the semi-quantitative results for the TICs observed in the samples. Five compounds were observed above the instrumental detection limit, with a total concentration of 3.0 mg/m³ based on the average of three samples. The analyte with the highest concentration was acetonitrile at 2.0 mg/m³, which represents about two-thirds of the TIC compounds.

Tables 3.3 and 3.4 list the analytes detected from ambient samples collected upwind of the tank and through the VSS near the tank. Only one TIC compound, acetaldehyde, was above the detection limit.

(a) Nominal molecular weight.

4.0 Conclusions

The concentrations of selected inorganic and organic compounds were determined from samples of the headspace of Tank C-112 on 8/11/94. Inorganic sampling and analysis methods followed those described by Ligotke et al. (1994) for samples obtained from C-103, a tank containing a relatively complex headspace composition. Method-validation measurements during that study did appear to validate the trapping analysis of NH_3 , but did not eliminate the possibility of interferences that could affect NO_x results. It is recommended that additional control samples be obtained if a tank is discovered in the future to contain significant quantities of NO_x . In the current sample job, NO_x samples were obtained after first passing the sample flow through an NH_3 trap. The NH_3 concentration was found to be 22.7 ± 0.5 ppmv. The concentration of NO_2 was ≤ 0.02 ppmv. The concentration of NO was 0.62 ± 0.05 ppmv. The mass concentration was 26 ± 2 mg/mL and was expected to consist largely of water vapor. All analytical results were within the target criteria $\{\pm 25\%$ precision, 70 to 130% accuracy (Carpenter 1994) $\}$ for inorganic analytes found at concentrations exceeding the lower target analytical limits (Table 2.1).

No TO-14 compounds and only six TIC compounds were found above instrumental detection limits, with acetonitrile at the highest concentration. The nitriles are probably radiolytic degradation products. Methyl nitrate is considered to be carcinogenic.

5.0 References

- Carpenter, B. C. 1994. *Tank 241-BX-104 Tank Characterization Plan, Appendix A*. Appendix A. WHC-SD-WM-TP-296, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Clauss, T. W., M. W. Ligotke, B. D. McVeety, K. H. Pool, R. B. Lucke, J. S. Fruchter, and S. C. Goheen. 1994. *Vapor Space Characterization of Waste Tank 241-BY-104: Results from Samples Collected on 6/24/94*. PNL-10208. Pacific Northwest Laboratory, Richland, Washington.
- Ligotke, M. W., K. H. Pool, and B. D. Lerner. 1994. *Vapor Space Characterization of Waste Tank 241-C-103: Inorganic Results from Sample Job 7B (5/12/94 - 5/25/94)*. PNL-10172, Pacific Northwest Laboratory, Richland, Washington.
- Mahlum, D. 1994. *Toxicological Evaluation of Analytes from Tank 241-C-103*. PNL-10189, 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 TO-14 Analysis Results for Samples Collected from the Headspace of Tank C-112 in SUMMA™ Canisters on 8/11/94

TO-14 Analyte	CAS No.	Mol Wt	S4054-A05-088 ^(a)		S4054-A06-099 ^(a)		S4054-A07-114 ^(a)		Means and	
			PNL 088 ^(b)		PNL 099 ^(b)		PNL 114 ^(b)		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	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
Methyl Chloride (Chloromethane)	74-87-3	50	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
1,2-Dichloro-1,1,2,2,-Tetrafluoroethane (FREON-114)	76-14-2	170	< 0.02	< 2	< 0.02	< 2	< 0.02	< 2	(c)	(c)
Chloroethene (Vinyl Chloride)	75-01-4	64	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
Methyl Bromide (Bromomethane)	74-83-9	94	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
Ethyl Chloride	75-00-3	62	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
Trichlorofluoromethane (FREON-11)	75-69-4	136	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
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	< 0.01	< 2	< 0.01	< 2	0.01	3.45	(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)

Table 3.1 (contd)

TO-14 Analyte	CAS No.	Mol Wt	S4054-A05-088 ^(a)		S4054-A06-099 ^(a)		S4054-A07-114 ^(a)		Means and	
			PNL 088 ^(b)		PNL 099 ^(b)		PNL 114 ^(b)		Standard Deviation	
			Concentration		Concentration		Concentration			
			(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)	(mg/m ³)	St Dev
1,1,2,2-Tetrachloroethane	79-34-5	166	< 0.02	< 2	< 0.02	< 2	< 0.02	< 2	(c)	(c)
o-Xylene (1,2-Dimethylbenzene)	95-47-6	106	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
1,3,5-Trimethylbenzene	108-67-8	120	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
1,2,4-Trimethylbenzene	95-63-6	120	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
Chloromethylbenzene, alpha (Benzyl Chloride)	100-44-7	126	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
m-Dichlorobenzene (1,3-Dichlorobenzene)	541-73-1	146	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
p-Dichlorobenzene (1,4-Dichlorobenzene)	106-46-7	146	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
o-Dichlorobenzene (1,2-Dichlorobenzene)	95-50-1	146	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
1,2,4-Trichlorobenzene	120-82-1	180	< 0.02	< 2	< 0.02	< 2	< 0.02	< 2	(c)	(c)
Hexachloro-1,3-Butadiene	87-68-3	258	< 0.02	< 2	< 0.02	< 2	< 0.02	< 2	(c)	(c)

(a) WHC sample identification number.

(b) PNL canister number.

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

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

Table 3.2 Tentatively Identified Compounds and Estimated Concentrations^(a) in the Headspace of Tank C-112 from SUMMA™ Canister Samples Collected on 8/11/94

Tentatively Identified Compound ^(d)	CAS No. ^(d)	Mol. Wt.	Ret Time	S4054-A05-088 ^(b)		S4054-A06-099 ^(b)		S4054-A07-114 ^(b)		Means and Standard Deviations			
				PNL 088 ^(c)		PNL 099 ^(c)		PNL 114 ^(c)					
				(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)	(mg/m ³)	St Dev	(ppbv)	St Dev
Acetaldehyde	75-07-0	44	5.04	0.23	117	0.1	52.0	< 0.02	< 10.0	0.17	0.09	84.3	45.8
Acetonitrile	75-05-8	41	7.82	2.07	1129	1.9	1040	2.01	1097	1.99	0.09	1088	45.1
Acetone	67-64-1	58	8.32	0.55	212	0.56	215	0.57	218	0.56	0.01	215	2.91
Methyl Nitrate	598-58-3	77	10.32	0.21	59.9	0.2	57.0	0.19	55.1	0.20	0.01	57.3	2.41
Propanenitrile	107-12-0	55	11.79	0.02	8.35	0.08	32.1	0.11	43.2	0.07	0.05	27.9	17.8

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

Table 3.3 TO-14 Analysis for Ambient Samples Collected Near Tank C-112 in SUMMA™ Canisters on 8/11/94

TO-14 Analyte	CAS No.	Mol Wt	Upwind VSS S4054-A01-080 ^(a) PNL 080 ^(b)		Through VSS S4054-A02-081 ^(a) PNL 081 ^(b)	
			Concentration		Concentration	
			(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)
Dichlorodifluoromethane (FREON-12)	75-71-8	120	< 0.01	< 2	< 0.01	< 2
Methyl Chloride (Chloromethane)	74-87-3	50	< 0.01	< 2	< 0.01	< 2
1,2-Dichloro-1,1,2,2-Tetrafluoroethane (FREON-114)	76-14-2	170	< 0.02	< 2	< 0.02	< 2
Chloroethene (Vinyl Chloride)	75-01-4	64	< 0.01	< 2	< 0.01	< 2
Methyl Bromide (Bromomethane)	74-83-9	94	< 0.01	< 2	< 0.01	< 2
Ethyl Chloride	75-00-3	62	< 0.01	< 2	< 0.01	< 2
Trichlorofluoromethane (FREON-11)	75-69-4	136	< 0.01	< 2	< 0.01	< 2
1,1-Dichloroethene (1,1-Dichloroethylene)	75-35-4	96	< 0.01	< 2	< 0.01	< 2
Dichloromethane (Methylene Chloride)	75-09-2	84	< 0.01	< 2	< 0.01	< 2
1,1,2-Trichloro-1,2,2-Trifluoroethane (FREON-113)	76-13-1	186	< 0.02	< 2	< 0.02	< 2
1,1-Dichloroethane	75-34-3	98	< 0.01	< 2	< 0.01	< 2
cis-1,2-Dichloroethene (cis-1,2-Dichloroethylene)	156-59-2	96	< 0.01	< 2	< 0.01	< 2
Trichloromethane (Chloroform)	67-66-3	118	< 0.01	< 2	< 0.01	< 2
cis 1,2-Dichloroethane	107-06-2	98	< 0.01	< 2	< 0.01	< 2
1,1,1-Trichloroethane	71-55-6	132	< 0.01	< 2	< 0.01	< 2
Benzene	71-43-2	78	< 0.01	< 2	< 0.01	< 2
Carbon Tetrachloride	56-23-5	152	< 0.01	< 2	< 0.01	< 2
1,2-Dichloropropane	78-87-5	112	< 0.01	< 2	< 0.01	< 2
Trichloroethylene	79-01-6	130	< 0.01	< 2	< 0.01	< 2
cis 1,3-Dichloropropene	61-01-5	110	< 0.01	< 2	< 0.01	< 2
trans 1,3-Dichloropropene	61-02-6	110	< 0.01	< 2	< 0.01	< 2
1,1,2-Trichloroethane	79-00-5	132	< 0.01	< 2	< 0.01	< 2
Methyl Benzene (Toluene)	108-88-3	92	< 0.01	< 2	< 0.01	< 2
1,2-Dibromoethane	106-93-4	186	< 0.02	< 2	< 0.02	< 2
Tetrachloroethene (Perchloroethylene)	127-18-4	164	< 0.02	< 2	< 0.02	< 2
Chlorobenzene	108-90-7	112	< 0.01	< 2	< 0.01	< 2
Ethylbenzene	100-41-4	106	< 0.01	< 2	< 0.01	< 2
m-Xylene (1,3-Dimethylbenzene) ^(d)	108-38-3	106	< 0.01	< 2	< 0.01	< 2
p-Xylene (1,4-Dimethylbenzene) ^(d)	106-42-3	106	< 0.01	< 2	< 0.01	< 2
Styrene	100-42-5	104	< 0.01	< 2	< 0.01	< 2
1,1,2,2-Tetrachloroethane	79-34-5	166	< 0.02	< 2	< 0.02	< 2
o-Xylene (1,2-Dimethylbenzene)	95-47-6	106	< 0.01	< 2	< 0.01	< 2
1,3,5-Trimethylbenzene	108-67-8	120	< 0.01	< 2	< 0.01	< 2
1,2,4-Trimethylbenzene	95-63-6	120	< 0.01	< 2	< 0.01	< 2
Chloromethylbenzene, alpha (Benzyl Chloride)	100-44-7	126	< 0.01	< 2	< 0.01	< 2
m-Dichlorobenzene (1,3-Dichlorobenzene)	541-73-1	146	< 0.01	< 2	< 0.01	< 2
p-Dichlorobenzene (1,4-Dichlorobenzene)	106-46-7	146	< 0.01	< 2	< 0.01	< 2
o-Dichlorobenzene (1,2-Dichlorobenzene)	95-50-1	146	< 0.01	< 2	< 0.01	< 2
1,2,4-Trichlorobenzene	120-82-1	180	< 0.02	< 2	< 0.02	< 2
Hexachloro-1,3-Butadiene	87-68-3	258	< 0.02	< 2	< 0.02	< 2

(a) WHC sample identification number.

(b) PNL canister number.

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

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

Table 3.4 Tentatively Identified Compounds and Estimated Concentrations^(a) in Ambient Samples Collected Near Tank C-112 on 8/11/94

Tentatively Identified Compound ^(d)	CAS No. ^(d)	Mol. Wt.	Ret Time	Upwind VSS S4054-A01-080 ^(b) PNL 080 ^(c)		Through VSS S4054-A02-081 ^(b) PNL 081 ^(c)	
				(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)
Acetaldehyde	75-07-0	44	5.02	0.17	89.0	0.12	60.8

- (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.

Figure 3.1a Total Ion Chromatogram (2 through 30 min) for Hanford Waste Tank C-112
SUMMA™ Canister Sample S4054-A07-099 Collected on 8/11/94

Figure 3.1b Total Ion Chromatogram (30 through 58 min) for Hanford Waste Tank C-112
SUMMATM Canister Sample S4054-A07-099 Collected on 8/11/94

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

M. F. Jarvis, S7-54
C. Babel, S7-54

Corps of Engineers

T. W. Gardner-Clayson, A5-19

10 Westinghouse Hanford Company

H. Babad, R2-78
D. R. Braitzel, S7-31 (2)
S. J. Eberlien, R2-12
T. J. Kelley, S7-30
E. R. Hewitt, R3-01
N. W. Kirch, R2-11
E. J. Lipke, S7-14
J. E. Meacham, S7-15
B. C. Simpson, R2-12

20 Pacific Northwest Laboratory

T. W. Clauss, P8-08
K. H. Pool, P8-44
B. L. Thomas, K9-25
B. D. McVeety, K6-84
K. B. Olsen, K6-96
J. S. Fruchter, K6-96
S. C. Goheen, P8-08
M. W. Ligothke P7-59 (6)
J. L. Huckaby, K6-55
K. L. Silvers, P7-27
Technical Report Files (5)