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**Vapor Space Characterization
of Waste Tank 241-C-107:
Results from Samples
Collected on 9/29/94**

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November 1995

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

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

PNL-10736

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under Contract DE-AC06-76RLO 1830

Printed in the United States of America

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Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge,
TN 37831;**

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WASTE TANK VAPOR PROGRAM

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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-107 (referred to as Tank C-107). The results described here were obtained to support safety and toxicological evaluations. A summary of the results for inorganic and organic analytes is listed in Table 1. Detailed descriptions of the results appear in the text.

Quantitative results were obtained for the inorganic compounds ammonia (NH_3), nitrogen dioxide (NO_2), nitric oxide (NO), and water (H_2O). Sampling for sulfur oxides (SO_x) was not requested. Organic compounds were also quantitatively determined. Twenty 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 55 TO-14 extended analytes. Of these, 3 were observed above the 5-ppbv detection limit. The 10 organic analytes with the highest estimated concentrations are listed in Summary Table 1 and account for approximately 96% of the total organic components in Tank C-107. Two permanent gases, carbon dioxide and nitrous oxide, were also detected.

Summary Table 1. Summary Results of Inorganic and Organic Samples Collected from the Headspace of Tank C-107 on 9/29/94

<u>Category</u>	<u>Analyte</u>	<u>Vapor^(a) Concentration</u>	<u>Units</u>
Inorganic	NH_3	84 ± 2	ppmv
	NO_2	≤ 0.02	ppmv
	NO	0.20 ± 0.01	ppmv
	H_2O	77 ± 5	mg/L
Organic	Acetone	2.17	mg/m^3
	Acetonitrile	1.18	mg/m^3
	Tridecane	1.18	mg/m^3
	Tetradecane	0.46	mg/m^3
	Dodecane	0.24	mg/m^3
	Nitric Acid, Ethyl Ester	0.23	mg/m^3
	Methyl Nitrate	0.19	mg/m^3
	Unknown Alkane	0.18	mg/m^3
	Cyclopropane	0.15	mg/m^3
	Unknown Alkane	0.12	mg/m^3

(a) Vapor concentrations were determined using sample-volume data provided by Westinghouse Hanford and are based on averaged data. The inorganic samples were obtained and analyzed using procedures that were subsequently improved.

Acknowledgments

The authors gratefully acknowledge the support of other project staff at Pacific Northwest Laboratory who contributed to the successful completion of this sampling and analysis activity. Jeff Edwards served as the PNL single-point-of-contact and coordinated sample handling and communications with Westinghouse Hanford Company. K. B. Olsen assisted in preparing the organic portion of this report. Bruce Lerner performed method development and validation work that supported the inorganic vapor sampling. Sally Slate, May-Lin Thomas, and Karen Schielke analyzed inorganic samples, and Annalisa Krupsha and Gary Dennis prepared the solid-sorbent sample trains. 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
GC/TCD	gas chromatography/thermal conductivity detection
HP	Hewlett Packard
IC	ion chromatography
IL	impact level
IS	internal standard
MDL	minimum detection limit
NIST	National Institute for Standards and Technology
NPH	normal paraffin hydrocarbon
OSHA	Occupational Safety and Health Administration
PFA	perfluoroalkoxy
PNL	Pacific Northwest Laboratory
ppbv	part per billion by volume
ppmv	part per million by volume
QA	quality assurance
REL	recommended exposure limit
SCIC	suppressed-conductivity ion chromatography
SIE	selective ion electrode
SRM	standard reference material
STP	standard temperature and pressure
TEA	triethanolamine
TIC	tentatively identified compound
VSS	vapor sampling system
WHC	Westinghouse Hanford Company

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1.0 Introduction

This report describes results of the analyses of tank-headspace samples taken from the Hanford waste Tank 241-C-107 (referred to as Tank C-107). Pacific Northwest Laboratory (PNL)^(a) contracted with Westinghouse Hanford Company (WHC) to provide sampling devices and to analyze inorganic and organic analytes collected from the tank headspace and ambient air near the tank. The organic analytes for TO-14 compounds were extended to include 15 analytes identified by the Toxicological Review Panel for Tank C-103 and reported in *Toxicological Evaluation of Analytes from Tank 241-C-103* (Mahlum et al. 1994). While these analytes (shown in Table 3.1) are only of toxicological concern for Tank C-103, program management included these analytes for future tank analyses as identified in the fiscal year work plan. This plan is attached to a letter dated 9/30/94 and addressed to Mr T. J. Kelly of WHC. The plan requires us also to analyze for the permanent gases as shown in Table 3.5. The combined TO-14 compounds and additional 15 analytes for the purpose of this report will be referred to as TO-14 extended analytes. The sample job was designated S4058, and samples were collected by WHC on August 9, 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.

Sampling devices, including six sorbent trains (for inorganic analyses), and five SUMMATM canisters (for organic analyses) were supplied to the WHC sampling staff on August 22. Samples were taken (by WHC) from the tank headspace on September 29 and returned to PNL from the field on October 5. Inorganic (sorbent trap) samples were delivered to PNL on chain of custody (COC) 007518 (see Figure 1.1a). The SUMMATM canisters were delivered on COC 007517 (see Figure 1.1b). The COCs show a sample collection date of 8/29/94. The COCs were returned to PNL with the day space empty. When a cc:mail message verifying the sampling event (Figure 1.2) was received, the sampling day was recorded on the COCs. However, the month was not changed to reflect the actual month of sampling.

The samples were inspected upon delivery to the 326/23B laboratory and logged into PNL record book 55408 before implementation of PNL Technical Procedure PNL-TVP-07^(b). Custody of the sorbent traps was transferred to PNL personnel performing the inorganic analysis and stored at refrigerated ($\leq 10^{\circ}\text{C}$) temperature until the time of analysis. The canister was stored in the 326/23B laboratory at ambient (25°C) temperature until time of analysis. Access to the 326/23B laboratory is limited to PNL personnel working on the waste-tank safety program. Analyses described in this report were performed at PNL in the 300 area of the Hanford Site. 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, nitrogen dioxide, or nitric oxide analyses). The aqueous extracts were analyzed either by selective electrode or by ion chromatography (IC). Organic analyses were performed using cryogenic preconcentration followed by gas chromatography/mass spectrometry (GC/MS).

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

(b) 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 007517
---	-------------------------	-------------------

Custody Form Initiator	J. A. Edwards	Telephone (509) 373 -0141 Pager 85-3009
Company Contact	R. A. Westberg	Telephone (509) 373-5734
Project Designation/Sampling Locations	200 East Tank Farm 241-C-107 Tank Vapor Sample SAF S4058 Ice Chest No. (VSS Truck)	Collection Date 08-29-94 Preparation Date 08-22-94 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	WHC	

Possible Sample Hazards/Remarks Unknown at time of sampling

Sample Identification

S4058 - A01 - 154 ✓ SAP Ref _____
S4058 - A02 - 163 ✓ SAP Ref _____

Ambient air SUMMA #1, Upwind VSS (PNL)
Ambient air SUMMA #2, Through VSS (PNL)

S4058 - A05 - 178 ✓ SAP Ref _____
S4058 - A07 - 179 ✓ SAP Ref _____
S4058 - A09 - 182 ✓ SAP Ref _____

SUMMA #4 (PNL)
SUMMA #6 (PNL)
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	08-22-94	1345	Tim Uechter	08-22-94	1345			
Sharon Vetter	08-22-94	1500	JP Buehler	08-22-94	1500			
JP Buehler	10-5-94	0915	BD Miskelly	10-05-94	0920			

(Revised 02/28/94)

Figure 1.1a Chain of Custody for Inorganic Samples for Tank C-107

Westinghouse Hanford Company	CHAIN OF CUSTODY	WHC 007518
---	-------------------------	-------------------

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	08-29-94
241-C-107 Tank	Vapor Sample SAF S4058	Preparation Date	08-22-94
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	WHC		

Possible Sample Hazards/Remarks Unknown at time of sampling

Sample Identification

S4058 - A22 . V13 ✓	NH ₃ /NO _x /H ₂ O (Trap # 1) Line # 8
S4058 - A23 . V14 ✓	NH ₃ /NO _x /H ₂ O (Trap # 2) Line #10
S4058 - A24 . V15 ✓	NH ₃ /NO _x /H ₂ O (Trap # 3) Line # 9
S4058 - A25 . V16 ✓	NH ₃ /NO _x /H ₂ O (Trap # 4) Line #10
S4058 - A26 . V17 ✓	NH ₃ /NO _x /H ₂ O (Trap # 5) Line # 8
S4058 - A27 . V18 ✓	NH ₃ /NO _x /H ₂ O (Trap # 6) Line #10
S4058 - A28 . V19 ✓	NH ₃ /NO ₂ /H ₂ O a-b-c (Trip Blank# 1)
S4058 - A29 . V20 ✓	NH ₃ /NO ₂ /H ₂ O a-b-c (Trip Blank# 2)
S4058 - A30 . V21 ✓	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 <i>J. A. Edwards</i>	08-22-94	1345	Tim Uecht <i>Tim Uecht</i>	08-22-94	1345	
<i>Sharon Spencer</i>	08-22-94	1500	<i>Sharon Spencer</i>	08-22-94	1500	
<i>Ed Buckler</i>	10-5-94	0915	<i>Ed Buckler</i>	10-5-94	0920	
<i>Rd M. Kelly</i>	10-5-94	1300	<i>Rd M. Kelly</i>	10-7-94	1400	

(Revised 02/28/94)

Figure 1.1b Chain of Custody for Inorganic Samples for Tank C-107

cc:Mail for: Jeffrey A Edwards

Subject: VSS sampling of C-107

From: E A (Andy) Johnson 1/17/95 13:02

To: Jerry W. Osborne at -WHC129
To: James L (Jim) Huckaby at -WHC140
To: Richard A Mezmarich at -WHC96
To: Daniel L Edwards at -WHC169
To: Shane M Brown at -WHC121
To: Neil Buechler at -WHC121
To: David K DeFord at -WHC207
To: Cindy D Hayes at -WHC121
To: E A (Andy) Johnson at -WHC225
To: Ricky D Mahon at -WHC121
To: Leonard A Jr Pingel at -WHC121
To: Robert L Ragen at -WHC225
To: Timothy B (Tim) Utecht at -WHC121
To: Rampur S Viswanath at -WHC121
To: Richard A Westberg at -WHC121
To: Kenneth L Young at -WHC343
To: Jeffrey A Edwards
To: Michael W Ligothe

The VSS crew completed vapor sampling C-107 this morning, 29 Sept. '94. The crew consisted of:

E. Johnson Field Scientist
T. Utecht Field Tech.
N. Buechler Trailer Support
E. Tampose Ops PIC

The crew entered C-Farm at 05:00 and sampling of tank vapors began at 07:30. No problems occurred during sampling. Two GC runs were made on tank vapors but neither yielded any noticeable anomalies on the graph. Sampling was completed by 10:50 and, after disconnecting from the tank and securing the VSS and Truck, the crew exited C-Farm at 11:30. Samples will be shipped after results from 222-S are received. OPS stated that we will try to move the VSS out of C-Farm and back to the weather station tomorrow, Friday, the 30th.

Andy

Figure 1.2 Verification of Sample Collection Event for Tank C-107

2.0 Inorganic Task

Solid sorbent traps, prepared in multi-trap sampling trains, were supplied to WHC for sampling the tank headspace using the VSS. Blanks, spiked blanks (when requested), and exposed samples were returned to PNL for analysis. Analyses were performed to provide information on the tank-headspace concentration of the following analytes: {ammonia (NH_3), nitrogen dioxide (NO_2), nitric oxide (NO), and water (H_2O)}. Procedures were similar to those developed previously during sample jobs performed with the VSS connected to the headspace of Tank C-107 (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 , and H_2O , (supplied by 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 tubes, having glass sealed ends, were received from the vendor.

The type and nominal quantity of sorbent material varied by application. Sorbent traps were selected for the tank sample job and included the following products. The NH_3 sorbent traps contained carbon beads impregnated with sulfuric acid; nominally, 500 mg were contained in the primary and 250 mg in the breakthrough sections. The NH_3 was chemisorbed as ammonium sulfate $\{(\text{NH}_4)_2\text{SO}_4\}$. The NO_2 traps contained a zeolite impregnated with triethanolamine (TEA), with 400 mg in the primary and 200 mg in the breakthrough sections. The NO_2 was absorbed and disproportionated to equi-molar quantities of nitrite ions (NO_2^-) and nitrate ions (NO_3^-). Glass tubes containing 800 mg of an oxidant such as chromate were used to convert NO to NO_2 . The converted NO was then collected as nitrite and nitrate in an NO_2 trap. The water traps contained 300 mg of silica gel in the primary and 150 mg in the breakthrough sections.

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

at ambient temperature, and selected oxidizer sections were returned to a freezer until completion of analyses.

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

$$C_v = \frac{75.0 \mu\text{g}}{17.0 \text{ g/mol}} \left(\frac{3.00 \text{ L}}{22.4 \text{ L/mol}} \right)^{-1} = 32.9 \text{ ppmv} \quad (2.1)$$

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 NH_3 selective sorbent traps was placed into labeled 20-mL glass scintillation vials. Vials containing front-, or primary-, section sorbent

material were treated with 10.0 mL of deionized water (DIW), and vials containing back-up-section sorbent material were treated with 5.0 mL of DIW. After extraction, the NH_3 sorbent traps were analyzed using the selective ion electrode (SIE) procedure PNL-ALO-226 {*Ammonia (Nitrogen) in Aqueous Samples*}. Briefly, this method includes 1) preparing a 1000- $\mu\text{g/mL}$ (ppm) NH_3 stock standard solution from dried reagent-grade NH_4Cl and DIW on the day analyses are performed; 2) preparing 0.1-, 0.5-, 1.0-, 10-, and 100-ppm NH_3 working calibration standards by serial dilution of the freshly made stock standard; 3) generating an initial calibration curve from the measured electromotive force (emf) signal versus NH_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 NH_3 concentration in the samples.

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

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

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

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

2.3 Quality Assurance/Quality Control

Analytical work was performed according to quality levels identified in the project QA plan and several PNL documents. The samples were analyzed following PNL IL III. The PNL documents include PNL-MA-70 (Part 2), PNL-MA-599, PNL-ALO-212, PNL-ALO-226, PNL-ALO-271, and MCS-033. A summary of the analysis procedures and limits for the target inorganic compounds is provided in Table 2.1. From the table, it can be seen that the minimum detection limit (MDL) required to resolve the analyte at one-tenth of the recommended exposure limit (REL) for each of the target analytes is achieved using current procedures and with a vapor-sample volume of 3 L and a desorption-solution volume of 3 mL (10 mL for NH₃).

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

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

(a) Target analytical limits are equal to one-tenth of the REL.

(b) MDL is defined as the vapor concentration that can be detected with an uncertainty equal to about the magnitude of the measurement. The uncertainty is expected to reduce to about one-quarter of the magnitude of the measurement at a concentration of four times the MDL. The MDLs were based on the assumption that 3 L of vapor are sampled; if greater volumes of vapor are sampled, correspondingly smaller MDLs can be achieved. The MDLs were also based on desorbing-solution volumes of 10 mL for 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.

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 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. As for NH_3 , no known NIST SRM is available for nitrite analysis (for NO_2 and NO). Based on experience in comparing nitrite working standards prepared from several different sources and factors mentioned for NH_3 above, the estimated maximum bias for samples derived from sampling for NO_2 is $\pm 10\%$, 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-107 on 9/29/94 using the VSS. The sample job designation number was S4058. Unexposed samples were prepared by PNL, 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 hydrogen cyanide (HCN) and sulfur oxides (SO_x) was not requested. The inorganic samples were received from WHC on 10/5/94; the sample-volume information was received on 10/27/94.

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 84 ± 2 ppmv, based on all six samples. The blank-corrected NH_3 quantities in the sorbent traps ranged from 10.8 to 11.7 μmol in the front sorbent sections with no indication of breakthrough. Blank corrections, ≤ 0.06 μmol in front and ≤ 0.03 μmol in back sorbent sections, were less than 1% of collected quantities and were neglected. Although spiked blanks were not tested, the percentage recoveries of three sets of blanks spiked with 12.2, 22.3, and 46.4 μmol of NH_3 were $101 \pm 4\%$, $109 \pm 2\%$, and $104 \pm 1\%$, respectively, during related sample jobs (Clauss et al. 1994; Ligothe et al. 1994). The analyses of two samples were duplicated and yielded repeatabilities of $\pm 1\%$. One sample leachate was spiked after initial analysis

Table 2.2 List of PNL Inorganic Samples, Controls, and Gravimetric Results Obtained From a Heated Tube Inserted into the Headspace of Tank C-107 on 9/29/94

<u>Sample Port and Volume Information^(a)</u>						
<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>Mass Gain</u>
Samples:						
S4058- A22-13V	NH ₃ /NO _x /H ₂ O Train	8	200	15.0	3.00	0.2448
S4058- A23-14V	NH ₃ /NO _x /H ₂ O Train	10	200	15.0	3.00	0.2638
S4058- A24-15V	NH ₃ /NO _x /H ₂ O Train	9	200	15.0	3.00	0.2426
S4058- A25-16V	NH ₃ /NO _x /H ₂ O Train	10	200	15.0	3.00	0.2199
S4058- A26-17V	NH ₃ /NO _x /H ₂ O Train	8	200	15.0	3.00	0.2309
S4058- A27-18V	NH ₃ /NO _x /H ₂ O Train	10	200	15.0	3.00	N/A ^(b)
S4058- A28-19V	NH ₃ /NO _x /H ₂ O Train	n/a ^(b)	n/a	n/a	n/a	0.0043
S4058- A29-20V	NH ₃ /NO _x /H ₂ O Train	n/a	n/a	n/a	n/a	0.0054
S4058- A30-21V	NH ₃ /NO _x /H ₂ O Train	n/a	n/a	n/a	n/a	0.0044

(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.

with roughly the quantity of NH₃ in the sample and yielded a percentage recovery of 98%. A 5-point calibration was performed over an NH₃ range of 0.1 to 1000 µg/mL.

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

The concentrations of NO₂ and NO were ≤ 0.02 and ≤ 0.20 ± 0.01 ppmv, respectively. Blank-corrected NO₂⁻ quantities in the sorbent traps averaged ≤ 0.0016 µmol (NO₂ samples) and ≤ 0.0133 µmol (NO samples). Nitrite blank levels used to correct data were 0.0124 ± 0.0005 µmol in front and 0.0066 ± 0.002 µmol in back sorbent sections and were based on three blanks. One of six samples for NO were excluded because of a handling error. Although spikes 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 ± 14%, 103 ± 4%, 106 ± 8%, and 111 ± 7%, respectively (Clauss et al. 1994; Ligotke et al. 1994). The analyses of three front-section samples were duplicated and yielded a repeatability of 2 to 5%. Two front-section sample leachates were spiked after initial analysis with roughly 1 to 2 times the quantity of NO₂⁻ in the samples and yielded percentage recoveries of 93% and 95%. A 4-point calibration was performed over a concentration range of 0 to 0.5 µg NO₂⁻ per mL in the desorbing matrix.

Table 2.3 Inorganic Vapor Sample Results Obtained From a Heated Tube Inserted into the Headspace of Tank C-107 on 9/29/94

<u>Sample</u>	<u>Analytical Results (μmol)</u>			<u>Sample Volume (L)</u>	<u>Vapor Concentration (ppmv)</u>
	<u>Front Section</u>	<u>Back Section</u>	<u>Total^(a) Blank-Corrected</u>		
<u>NH₃ Samples:</u>			<u>11.3^(c)</u>	<u>3.00^(c)</u>	<u>84 $\pm$ 2^(c)</u>
S4058- A22-13V	11.7	0.04	11.7	3.00	87
S4058- A23-14V	11.3	NA ^(d)	11.3	3.00	84
S4058- A24-15V	11.3	NA	11.3	3.00	84
S4058- A25-16V	11.2	0.03	11.2	3.00	84
S4058- A26-17V	11.5	NA	11.5	3.00	86
S4058- A27-18V	10.8	0.03	10.8	3.00	81
<u>NO₂ Samples:</u>			<u>≤ 0.0016</u>	<u>3.00</u>	<u>≤ 0.02</u>
S4058- A22-13V	0.0125	0.0065	n/a ^(d)	3.00	n/a
S4058- A23-14V	0.0121	0.0071	n/a	3.00	n/a
S4058- A24-15V	0.0118	0.0065	n/a	3.00	n/a
S4058- A25-16V	0.0118	0.0070	n/a	3.00	n/a
S4058- A26-17V	0.0118	0.0076	n/a	3.00	n/a
S4058- A27-18V	0.0124	0.0074	n/a	3.00	n/a
<u>NO Samples:</u>			<u>0.0133</u>	<u>3.00</u>	<u>$\leq 0.20 \pm 0.01$</u>
S4058- A22-13V	0.0250	0.0075	0.0126	3.00	0.19
S4058- A23-14V	0.0265	0.0075	0.0141	3.00	0.21
S4058- A24-15V	0.0253	0.0074	0.0129	3.00	0.19
S4058- A25-16V	0.0264	0.0075	0.0140	3.00	0.21
S4058- A26-17V	NA	NA	NA	3.00	NA
S4058- A27-18V	0.0253	0.0070	0.0129	3.00	0.19
<u>Gravimetric Samples (mg/mg/L):</u>			<u>233 mg</u>	<u>3.00</u>	<u>77 $\pm$ 5 mg/L</u>
S4058- A22-13V	n/a	n/a	237	3.00	79
S4058- A23-14V	n/a	n/a	256	3.00	85
S4058- A24-15V	n/a	n/a	235	3.00	78
S4058- A25-16V	n/a	n/a	212	3.00	71
S4058- A26-17V	n/a	n/a	223	3.00	74
S4058- A27-18V	n/a	n/a	NA	3.00	NA

- (a) Blank-corrected vapor concentrations were calculated using WHC-reported dry-air sample volumes (corrected to 0°C and 760 torr). In the calculation for concentration, the nitrite values (listed) were doubled to account for unanalyzed nitrate. Sample results were not corrected for percentage recovery of spiked samples or spiked blanks.
- (b) Total blank-corrected analyte masses (nitrite for NO₂ and NO) were determined, when significant, by subtracting the quantity of analyte found in blanks from that found in samples. The level of analytes found in blanks is described in the subsections of Section 2.4.
- (c) Underlined values represent the average of the set samples. Concentration uncertainty equals ± 1 standard deviation (absolute) for each set of samples. The use of " $\leq$ " is defined in Section 2.4.
- (d) NA = not analyzed; n/a = not applicable. Only selected back sorbent sections were analyzed.

2.4.3 Gravimetric Results. The mass concentration of material collected in the sorbent-trap trains, believed to be primarily water vapor, was 77 ± 5 mg/L. The result was based on an average mass gain of 233 mg from five of six $\text{NH}_3/\text{NO}_2/\text{H}_2\text{O}$ sample trains. Glass pieces from the end of one trap were lost during analysis, making its analysis unavailable. The blank correction applied to the results was 8 ± 3 mg per sample train, based on an average per-trap mass loss of 1.6 ± 0.6 mg from nine blanks. Three traps each of NH_3 , NO_2 , and H_2O were prepared and analyzed as trip blanks. Although no spiked blanks were tested, the percentage recovery of mass from three blank H_2O traps spiked with 51 mg of water was $103 \pm 2\%$ during a related sample job (Clauss et al. 1994). The quantity of mass collected in the sorbent trains was greater than usual for a tank headspace sample job. At the steady Tank C-107 headspace temperature of 48°C , the mass concentration exceeds the approximate saturated water-vapor concentration by about $8 \pm 5\%$. In addition, the capacity of the sorbent traps to effectively collect and contain this quantity of water vapor is being evaluated.

3.0 Organic Task

3.1 SUMMA™ Canister Preparation

Before sending SUMMA™ canisters out to the field for sampling, the canisters are cleaned and verified contaminant free according to PNL Technical Procedure PNL-TVP-02^(a). The cleaning procedure uses an EnTech 3000 cleaning system that controls 1) filling the canisters with purified humid air and 2) evacuating, for several cycles with applied heat, before allowing the canister to evacuate overnight. The canister is filled a final time with purified humid air for analysis by PNL Technical Procedure PNL-TVP-01^(b), which is a modification of U.S. Environmental Protection Agency (EPA) compendium Method TO-14. If the canister is verified as clean, free of TO-14 and unknown contaminants to a level of 5 parts per billion by volume (ppbv), the canister is evacuated to 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*, 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.

The TO-14 extended analytes were prepared using permeation tubes according to *Preparation of TO-14 Volatile Organic Compounds Gas Standards* PNL Technical Procedure PNL-TVP-06. The additional analytes were blended with the TO-14 standard to make a 55-component calibration gas. The standard calibration mix was analyzed using six aliquot sizes ranging from 0.3 L to 0.005 L. Depending on the concentration of each analyte in the mixture, either five or six points were used to construct the calibration curve. Butanoic acid was added to the mixture, but was not detected in the analysis. Butanal was recovered very poorly, producing a much lower than expected response. This

- (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.

results in a much higher measured amount reported in the sample analysis. This problem is currently under investigation. Detection limits for the TO-14 extended analytes have not yet been determined. Performance-based detection limits will be developed as a pool of calibration data becomes available.

The SUMMA™ canister samples were analyzed for permanent gases according to PNL Technical Procedure PNL-TVP-05, *Analysis Method for the Determination of Permanent Gases in Hanford Waste Tank Vapor Samples Collected in SUMMA™ Passivated Stainless Steel Canisters* with the exceptions listed in the following text and in the Quality Assurance/Quality Control section of this report. This method was developed in-house to analyze permanent gases defined as hydrogen (H₂), carbon dioxide (CO₂), carbon monoxide (CO), methane (CH₄), and nitrous oxide (N₂O) by gas chromatography-thermal conductivity detection (GC-TCD) and is not validated in any other laboratory. No previous work up of the sample canister is necessary before permanent gas analysis. Aliquots of sampled air are manually drawn from each canister into a 5-mL gas-tight syringe and directly injected into a GC-TCD fitted with a 0.5-mL injection loop. An aliquot of 5 mL is used to flush and fill the injection loop with sample air, ensuring that no dilution of sample concentration takes place within the injection loop. One set of GC conditions is used to analyze CO, CO₂, N₂O, and CH₄ using Helium (He) as the carrier gas. A second GC analysis is performed for H₂ using nitrogen as the carrier gas to enhance the signal sensitivity and increase the detection limit for this analyte. A total of 30 to 60 mL may be drawn from each canister sample, depending upon the number of repeat analyses performed.

3.3 Quality Assurance/Quality Control

Before the tank sample was analyzed, a diagnostic check was performed on the GC/MS instrument by running an instrument "quick tune," as described in PNL-TVP-03. Upon satisfactory completion of the instrument diagnostic check, a blank volume of purified nitrogen was analyzed to check the cleanliness of the system. The instrument was then calibrated over 6 data points ranging from 5 ppbv to 300 ppbv, using a standard gas mixture containing 40 volatile organic compounds listed in EPA compendium Method TO-14 and an additional 15 tank-related compounds (referred to as TO-14 extended analytes). A gas mixture containing bromochloromethane, 1,4-difluorobenzene, and chlorobenzene-d₃ was used as an internal standard (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.

Standards for the permanent gas analysis were blended from commercially prepared and certified standards for each of the analytes reported in Table 3.5. The instrument was calibrated over three data points for CO, CO₂, N₂O, and CH₄ using He as a carrier gas, and then the samples were analyzed. The carrier gas was changed to N₂, the calibration was performed for H₂ only, and the samples were reanalyzed. A least-squares linear-regression routine was applied to the data set to generate the best fit for each compound. Quantitation for each analyte was performed by direct comparison of sample analyte peaks to the plot generated for the compound. The lowest calibration

standard for each analyte is reported as the method detection limit. An MDL for the instrument has not been determined. A nitrogen reagent blank was not analyzed with this set of samples. The ambient air sample collected ~30 ft upwind of C-107 and the ambient air collected through the VSS were used as method blanks and used to determine the potential for analyte interferences in the samples. Continuing calibration standards for this sample set fell within $\pm 25\%$ of the expected concentrations for the analytes reported.

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

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

3.3.2 Identification and Quantitation of Tentatively Identified Compounds. The tentatively identified compounds (TICs) are determined by mass-spectral interpretation and comparison of the spectra with the EPA/NIST/WILEY Library, which is a part of the HP 5971 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 acetone, the total peak area was multiplied by the response factor for chlorobenzene- d_5 to give an estimated concentration of $2.17 \text{ mg}/\text{m}^3$. Internal standards 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 ppmv concentrations are calculated from mg/m^3 and the molecular weight of the analyte.

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

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

3.4 Analysis Results

The results from the GC/MS analysis of the tank-headspace samples are presented in Tables 3.1 and 3.2. The results from the GC/MS analysis of the ambient air near the tank are presented in Tables 3.3 and 3.4. The results for permanent gases are presented in Table 3.5. A representative total ion chromatogram showing the identity of major constituents is given in Figure 3.1.

Table 3.1 lists the quantitative results for TO-14 extended analytes. Only compounds detected in two or more canisters were averaged. The dominant TO-14 extended analytes in Tank C-107 were acetone and acetonitrile. The compound 2 butanone was detected in one sample at a relatively high concentration; while the calculation of the concentration has been verified, this apparent anomaly has not fully been explained.

Table 3.2 lists the semi-quantitative results for the TICs observed in the samples. Twenty compounds were observed above the instrumental detection limit, a total average concentration of $3.0 mg/m^3$. The normal paraffin hydrocarbons (NPH), defined as n-alkanes from C_{11} to C_{15} , present were dodecane, and tridecane, and tetradecane, which accounted for 63% of the TIC compounds. It should be noted that because the SUMMATM canisters were not heated at the time of analysis, the NPH concentrations listed after the retention time of decane may not be a true accounting of all the NPH in the sample. Similarly, polar compounds, which may adhere to the inside surface of the canister, may also be under represented in this analysis.

Tables 3.3 and 3.4 list the TO-14 extended analytes and the TICs observed in an ambient air sample collected ~30 ft upwind of Tank C-107 and an ambient air sample collected through the VSS near the tank. Normal paraffin hydrocarbons were detected as well as acetaldehyde.

Table 3.5 lists the permanent gases analysis from samples collected from the headspace of Tank C-107, ambient air collected ~30 ft upwind of the tank, and ambient air collected through the VSS. Elevated levels of N_2O and CO_2 as compared with the ambient air samples were detected in the tank headspace. A replicate analysis was performed on one of the samples collected from this tank; however, only the results from the first analysis are reported.

4.0 Conclusion

The concentrations of selected inorganic and organic compounds were determined from samples of the headspace of Tank C-107 and from the ambient air near the tank. Sampling and analysis methods followed those described by Ligothke et al. (1994) for samples obtained from C-103, a tank containing a relatively complex headspace composition. Method-validation measurements during that study did appear to validate the trapping and analysis of NH_3 , but did not eliminate the possibility of interferences that could affect NO_x results. It is recommended that additional control samples be obtained if a tank is discovered in the future to contain significant quantities of NO_x . In the current sample job, NO_x samples were obtained after first passing the sample flow through an NH_3 trap. The NH_3 concentration was found to be 84 ± 2 ppmv. The concentration of NO_2 was ≤ 0.02 ppmv. The concentration of NO was 0.02 ± 0.01 ppmv. The mass concentration was 77 ± 5 mg/L and was expected to consist largely of water vapor.

Twenty three (TO-14 extended analyte and TIC) compounds were found above instrumental detection limits, dominated by acetone, acetonitrile, and three NPH n-alkanes, about 82% of all compounds observed. The permanent gases N_2O and CO_2 were detected and averaged 41.1 and 654 ppmv, respectively.

5.0 References

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Ligothke, 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. D., et al. 1994. *Toxicological Evaluation of Analytes from Tank 241-C-103*. PNL-10189. Pacific Northwest Laboratory. Richland, Washington.

6.0 Further Reading

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

Table 3.1 Positively Identified Quantitated TO-14 and Extended Analytes Collected from the Headspace of Tank C-107 in SUMMA™ Canisters on 9/29/94

Analyte	CAS No.	Mol Wt	S4058-A05-178 ^(a)		S4058-A07-179 ^(a)		S4061-A09-182 ^(a)		Means and Standard Deviations	
			PNL 178 ^(b)		PNL 179 ^(b)		PNL 182 ^(b)			
			Concentration	Concentration	Concentration	(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)	(mg/m ³)
Dichlorodifluoromethane (FREON-12)	75-71-8	120	<0.03	<5	<0.03	<5	<0.03	<5	(c)	(c)
Methyl Chloride (Chloromethane)	74-87-3	50	<0.01	<5	<0.01	<5	<0.01	<5	(c)	(c)
1,2-Dichloro-1,1,2,2,-Tetrafluoroethane (FREON-114)	76-14-2	170	<0.04	<5	<0.04	<5	<0.04	<5	(c)	(c)
Chloroethene (Vinyl Chloride)	75-01-4	64	<0.01	<5	<0.01	<5	<0.01	<5	(c)	(c)
Methyl Bromide (Bromomethane)	74-83-9	94	<0.02	<5	<0.02	<5	<0.02	<5	(c)	(c)
Ethyl Chloride	75-00-3	62	<0.01	<5	<0.01	<5	<0.01	<5	(c)	(c)
Trichlorofluoromethane (FREON-11)	75-69-4	136	<0.03	<5	<0.03	<5	<0.03	<5	(c)	(c)
1,1-Dichloroethene (1,1-Dichloroethylene)	75-35-4	96	<0.02	<5	<0.02	<5	<0.02	<5	(c)	(c)
Dichloromethane (Methylene Chloride)	75-09-2	84	<0.02	<5	<0.02	<5	<0.02	<5	(c)	(c)
1,1,2-Trichloro-1,2,2-Trifluoroethane (FREON-113)	76-13-1	186	<0.04	<5	<0.04	<5	<0.04	<5	(c)	(c)
1,1-Dichloroethane	75-34-3	98	<0.02	<5	<0.02	<5	<0.02	<5	(c)	(c)
cis-1,2-Dichloroethene (cis-1,2-Dichloroethylene)	156-59-2	96	<0.02	<5	<0.02	<5	<0.02	<5	(c)	(c)
Trichloromethane (Chloroform)	67-66-3	118	<0.03	<5	<0.03	<5	<0.03	<5	(c)	(c)
cis 1,2-Dichloroethane	107-06-2	98	<0.02	<5	<0.02	<5	<0.02	<5	(c)	(c)
1,1,1-Trichloroethane	71-55-6	132	<0.03	<5	<0.03	<5	<0.03	<5	(c)	(c)
Benzene	71-43-2	78	<0.02	<5	<0.02	<5	<0.02	<5	(c)	(c)
Carbon Tetrachloride	56-23-5	152	<0.03	<5	<0.03	<5	<0.03	<5	(c)	(c)
1,2-Dichloropropane	78-87-5	112	<0.03	<5	<0.03	<5	<0.03	<5	(c)	(c)
Trichloroethylene	79-01-6	130	<0.03	<5	<0.03	<5	<0.03	<5	(c)	(c)
cis 1,3-Dichloropropene	61-01-5	110	<0.02	<5	<0.02	<5	<0.02	<5	(c)	(c)
trans 1,3-Dichloropropene	61-02-6	110	<0.02	<5	<0.02	<5	<0.02	<5	(c)	(c)
1,1,2-Trichloroethane	79-00-5	132	<0.03	<5	<0.03	<5	<0.03	<5	(c)	(c)
Methyl Benzene (Toluene)	108-88-3	92	<0.02	<5	<0.02	<5	<0.02	<5	(c)	(c)
1,2-Dibromoethane	106-93-4	186	<0.04	<5	<0.04	<5	<0.04	<5	(c)	(c)
Tetrachloroethene (Perchloroethylene)	127-18-4	164	<0.04	<5	<0.04	<5	<0.04	<5	(c)	(c)
Chlorobenzene	108-90-7	112	<0.03	<5	<0.03	<5	<0.03	<5	(c)	(c)
Ethylbenzene	100-41-4	106	<0.02	<5	<0.02	<5	<0.02	<5	(c)	(c)
m-Xylene (1,3-Dimethylbenzene) ^(a)	108-38-3	106	<0.02	<5	<0.02	<5	<0.02	<5	(c)	(c)
p-Xylene (1,4-Dimethylbenzene) ^(a)	106-42-3	106								
Styrene	100-42-5	104	<0.02	<5	<0.02	<5	<0.02	<5	(c)	(c)
1,1,2,2-Tetrachloroethane	79-34-5	166	<0.04	<5	<0.04	<5	<0.04	<5	(c)	(c)

Table 3.1 (Contd)

Analyte	CAS No.	Mol Wt	S4058-A05-178 ^(a)		S4058-A07-179 ^(a)		S4061-A09-182 ^(a)		Means and	
			PNL 178 ^(b)		PNL 179 ^(b)		PNL 182 ^(b)		Standard Deviations	
			Concentration		Concentration		Concentration			
			(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)	(mg/m ³)	St Dev
o-Xylene (1,2-Dimethylbenzene)	95-47-6	106	< 0.02	< 5	< 0.02	< 5	< 0.02	< 5	(c)	(c)
1,3,5-Trimethylbenzene	108-67-8	120	< 0.03	< 5	< 0.03	< 5	< 0.03	< 5	(c)	(c)
1,2,4-Trimethylbenzene	95-63-6	120	< 0.03	< 5	< 0.03	< 5	< 0.03	< 5	(c)	(c)
Chloromethylbenzene, alpha (Benzyl Chloride)	100-44-7	126	< 0.03	< 5	< 0.03	< 5	< 0.03	< 5	(c)	(c)
m-Dichlorobenzene (1,3-Dichlorobenzene)	541-73-1	146	< 0.03	< 5	< 0.03	< 5	< 0.03	< 5	(c)	(c)
p-Dichlorobenzene (1,4-Dichlorobenzene)	106-46-7	146	< 0.03	< 5	< 0.03	< 5	< 0.03	< 5	(c)	(c)
o-Dichlorobenzene (1,2-Dichlorobenzene)	95-50-1	146	< 0.03	< 5	< 0.03	< 5	< 0.03	< 5	(c)	(c)
1,2,4-Trichlorobenzene	120-82-1	180	< 0.04	< 5	< 0.04	< 5	< 0.04	< 5	(c)	(c)
Hexachloro-1,3-Butadiene	87-68-3	258	< 0.06	< 5	< 0.06	< 5	< 0.06	< 5	(c)	(c)
2-Butanone	78-93-3	72	0.04	109	0.03	8.8	0.05	14.3	0.04	0.01
Acetone	67-64-1	58	2.31	892	2.01	755	2.20	849	2.17	0.15
Acetonitrile	75-05-8	41	1.22	655	1.11	608	1.20	656	1.18	0.06
Butanal	123-72-8	72	< 0.02	< 5	< 0.02	< 5	157	48929	(c)	(c)
Heptane	142-82-5	100	< 0.02	< 5	< 0.02	< 5	< 0.02	< 5	(c)	(c)
Tetrahydrofuran	109-99-9	72	< 0.02	< 5	< 0.02	< 5	< 0.02	< 5	(c)	(c)
Pyridine	110-86-1	79	< 0.02	< 5	< 0.02	< 5	< 0.02	< 5	(c)	(c)
Butanenitrile	109-74-0	69	< 0.02	< 5	< 0.02	< 5	< 0.02	< 5	(c)	(c)
Cyclohexane	110-82-7	84	< 0.02	< 5	< 0.02	< 5	< 0.02	< 5	(c)	(c)
Decane	124-18-5	142	< 0.03	< 5	< 0.03	< 5	< 0.03	< 5	(c)	(c)
Hexane	110-54-3	86	< 0.02	< 5	< 0.02	< 5	< 0.02	< 5	(c)	(c)
4-Methyl-2-Pentanone	108-10-1	100	< 0.02	< 5	< 0.02	< 5	< 0.02	< 5	(c)	(c)
Propanenitrile	107-12-0	55	< 0.01	< 5	< 0.01	< 5	< 0.01	< 5	(c)	(c)
Cyclohexanone	108-94-1	98	< 0.02	< 5	< 0.02	< 5	< 0.02	< 5	(c)	(c)
Propanol	71-23-8	60	< 0.01	< 5	< 0.01	< 5	< 0.01	< 5	(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) from the Headspace of Tank C-107 in SUMMATM Canisters
Collected on 9/29/94

Tentatively Identified Compound ^(d)	CAS No. ^(d)	Mol. Wt.	Ret Time	S4058-A05-178 ^(b)		S4058-A07-179 ^(b)		S4058-A09-182 ^(b)		Means and Standard Deviations		
				PNL 178 ^(e) (mg/m ³)	(ppbv)	PNL 179 ^(e) (mg/m ³)	(ppbv)	PNL 182 ^(e) (mg/m ³)	(ppbv)	(mg/m ³)	St Dev	St Dev
Cyclopropane	75-19-4	42	4.77	0.15	82.2	0.14	74.6	0.15	78.5	0.15	0.01	78.4
Acetaldehyde	75-07-0	44	5.29	0.1	50.3	0.08	39.3	0.08	41.4	0.09	0.01	43.6
Methyl Nitrate	598-58-3	77	10.46	0.2	57.4	0.18	52.9	0.18	53.5	0.19	0.01	54.6
Unknown Alkane			11.9					0.12	(f)	(e)		2.5
Unknown Alkane			11.88	0.13	(f)	0.12	(f)	0.13	(f)	0.13	0.01	(f)
Unknown Alkane			13.56	0.19	(f)	0.16	(f)	0.18	(f)	0.18	0.02	(f)
Nitric Acid, Ethyl Ester	625-58-1	91	15.09	0.24	58.5	0.23	55.6	0.23	57.5	0.23	0.01	57.2
Unknown Alkane			17.03	0.12	(f)			0.11	(f)	0.12	0.01	(f)
1-Butanol	71-36-3	74	17.58	< 0.03	< 10.0	< 0.03	< 10.0	0.31	92.5	(e)	(e)	(e)
Undecane	1120-21-4	156	40.2	< 10.0	< 10.0			0.06	8.2	(e)		(e)
Dodecane	112-40-3	170	44.25	0.16	21.1	0.07	9.5	0.5	66.1	0.24	0.23	32.2
Unknown Alkane			44.88					0.05	(f)	(e)		29.9
Unknown Alkane			47.15					0.25	(f)	(e)		
Tridecane	629-50-5	184	48.01	0.61	74.5	0.3	36.7	2.62	319	1.18	1.26	143
6-Methyltridecane	13287-21-3	198	48.79	< 0.08	< 10.0	< 0.08	< 10.0	0.06	6.5	(e)	(e)	153
Pentylcyclohexane	4292-92-6	154	50.18	< 0.07	< 10.0	< 0.07	< 10.0	0.13	18.6	(e)	(e)	(e)
Unknown Alkane			50.32					0.05	(f)	(e)		
Unknown Alkane			50.91					0.36	(f)	(e)		
Tetradecane	629-59-4	198	51.55	0.12	13.5	0.05	5.9	1.2	136	0.46	0.64	51.7
Unknown Alkane			53.75					0.16	(f)	(e)		72.8

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

(b) WHC sample identification number.

(c) PNL SUMMATM canister number.

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

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

(f) No molecular weight available for calculation.

Table 3.3 Positively Identified and Quantitated TO-14 Extended Analytes for Ambient Air Collected Near Tank C-107 in SUMMA™ Canisters on 9/29/94

Analyte	CAS No.	Mol Wt	Upwind S4058-A01-154 ^(a) PNL 154 ^(b)		Through VSS S4058-A02-163 ^(a) PNL 163 ^(b)	
			Concentration		Concentration	
			(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)
Dichlorodifluoromethane (FREON-12)	75-71-8	120	<0.03	<5	<0.03	<5
Methyl Chloride (Chloromethane)	74-87-3	50	<0.01	<5	<0.01	<5
1,2-Dichloro-1,1,2,2-Tetrafluoroethane (FREON-114)	76-14-2	170	<0.04	<5	<0.04	<5
Chloroethene (Vinyl Chloride)	75-01-4	64	<0.01	<5	<0.01	<5
Methyl Bromide (Bromomethane)	74-83-9	94	<0.02	<5	<0.02	<5
Ethyl Chloride	75-00-3	62	<0.01	<5	<0.01	<5
Trichlorofluoromethane (FREON-11)	75-69-4	136	<0.03	<5	<0.03	<5
1,1-Dichloroethene (1,1-Dichloroethylene)	75-35-4	96	<0.02	<5	<0.02	<5
Dichloromethane (Methylene Chloride)	75-09-2	84	<0.02	<5	<0.02	<5
1,1,2-Trichloro-1,2,2-Trifluoroethane (FREON-113)	76-13-1	186	<0.04	<5	<0.04	<5
1,1-Dichloroethane	75-34-3	98	<0.02	<5	<0.02	<5
cis-1,2-Dichloroethene (cis-1,2-Dichloroethylene)	156-59-2	96	<0.02	<5	<0.02	<5
Trichloromethane (Chloroform)	67-66-3	118	<0.03	<5	<0.03	<5
cis 1,2-Dichloroethane	107-06-2	98	<0.02	<5	<0.02	<5
1,1,1-Trichloroethane	71-55-6	132	<0.03	<5	<0.03	<5
Benzene	71-43-2	78	<0.02	<5	<0.02	<5
Carbon Tetrachloride	56-23-5	152	<0.03	<5	<0.03	<5
1,2-Dichloropropane	78-87-5	112	<0.03	<5	<0.03	<5
Trichloroethylene	79-01-6	130	<0.03	<5	<0.03	<5
cis 1,3-Dichloropropene	61-01-5	110	<0.02	<5	<0.02	<5
trans 1,3-Dichloropropene	61-02-6	110	<0.02	<5	<0.02	<5
1,1,2-Trichloroethane	79-00-5	132	<0.03	<5	<0.03	<5
Methyl Benzene (Toluene)	108-88-3	92	<0.02	<5	<0.02	<5
1,2-Dibromoethane	106-93-4	186	<0.04	<5	<0.04	<5
Tetrachloroethene (Perchloroethylene)	127-18-4	164	<0.04	<5	<0.04	<5
Chlorobenzene	108-90-7	112	<0.03	<5	<0.03	<5
Ethylbenzene	100-41-4	106	<0.02	<5	<0.02	<5
m-Xylene (1,3-Dimethylbenzene) ^(d)	108-38-3	106	<0.02	<5	<0.02	<5
p-Xylene (1,4-Dimethylbenzene) ^(d)	106-42-3	106				
Styrene	100-42-5	104	<0.02	<5	<0.02	<5
1,1,2,2-Tetrachloroethane	79-34-5	166	<0.04	<5	<0.04	<5
o-Xylene (1,2-Dimethylbenzene)	95-47-6	106	<0.02	<5	<0.02	<5
1,3,5-Trimethylbenzene	108-67-8	120	<0.03	<5	<0.03	<5
1,2,4-Trimethylbenzene	95-63-6	120	<0.03	<5	<0.03	<5
Chloromethylbenzene, alpha (Benzyl Chloride)	100-44-7	126	<0.03	<5	<0.03	<5
m-Dichlorobenzene (1,3-Dichlorobenzene)	541-73-1	146	<0.03	<5	<0.03	<5
p-Dichlorobenzene (1,4-Dichlorobenzene)	106-46-7	146	<0.03	<5	<0.03	<5
o-Dichlorobenzene (1,2-Dichlorobenzene)	95-50-1	146	<0.03	<5	<0.03	<5
1,2,4-Trichlorobenzene	120-82-1	180	<0.02	<5	<0.02	<5
Hexachloro-1,3-Butadiene	87-68-3	258	<0.06	<5	<0.06	<5
2-Butanone	78-93-3	72	<0.02	<5	<0.02	<5
Acetone	67-64-1	58	0.08	29.6	0.08	29.6
Acetonitrile	75-05-8	41	<0.01	<5	<0.01	<5

Table 3.3 (Contd)

Analyte	CAS No.	Mol Wt	Upwind S4058-A01-154 ^(a) PNL 154 ^(b)		Through VSS S4058-A02-163 ^(a) PNL 163 ^(b)	
			<u>Concentration</u>		<u>Concentration</u>	
			(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)
Butanal	123-72-8	72	<0.02	<5	<0.02	<5
Heptane	142-82-5	100	<0.02	<5	<0.02	<5
Tetrahydrofuran	109-99-9	72	<0.02	<5	<0.02	<5
Pyridine	110-86-1	79	<0.02	<5	<0.02	<5
Butanenitrile	109-74-0	69	<0.02	<5	<0.02	<5
Cyclohexane	110-82-7	84	<0.02	<5	<0.02	<5
Decane	124-18-5	142	<0.03	<5	<0.03	<5
Hexane	110-54-3	86	<0.02	<5	<0.02	<5
4-Methyl-2-Pentanone	108-10-1	100	<0.02	<5	<0.02	<5
Propanenitrile	107-12-0	55	<0.01	<5	<0.01	<5
Cyclohexanone	108-94-1	98	<0.02	<5	<0.02	<5
Propanol	71-23-8	60	<0.01	<5	<0.01	<5

(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) of Ambient Air Samples Collected Near Tank C-107 in SUMMATM Canisters on 9/29/94

Tentatively Identified Compound ^(a)	CAS No. ^(b)	Mol. Wt.	Ret Time	Upwind S4058-A01-154 ^(b) PNL 154 ^(c)		Through VSS S4058-A02-163 ^(b) PNL 163 ^(c)	
				(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)
Acetaldehyde	75-07-0	44	5.29	<0.02	< 10.0	0.06	28.8
Dodecane	112-40-3	170	44.3	0.06	7.20	0.06	8.52
Tridecane	629-50-5	184	48.0	0.33	40.5	0.25	30.7
Tetradecane	629-59-4	198	51.5	0.10	10.9	< 0.08	< 10.0

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

(b) WHC sample identification number.

(c) PNL SUMMATM canister number.

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

Table 3.5 Permanent Gas Analysis Results for Samples Collected from the Headspace of Tank C-107 and for Ambient Air Collected Near Tank C-107 in SUMMA™ Canisters on 9/29/94.

	Ambient Air Upwind	Ambient Air Through VSS			
	S4058-A01.154 (a)	S4061-A02.163 (a)	S4061-A05.178 (a)	S4077-A05.234 (a)	S4077-A06.235 (a)
	PNL 154 (b)	PNL 163 (b)	PNL 178 (b),(c)	PNL 179 (b)	PNL 182 (b)
<u>Permanent Gas</u>	<u>Concentration</u>	<u>Concentration</u>	<u>Concentration</u>	<u>Concentration</u>	<u>Concentration</u>
	(ppmv)	(ppmv)	(ppmv)	(ppmv)	(ppmv)
Hydrogen	< 80	< 80	110	111	< 80
Methane	< 20	< 20	< 20	< 20	< 20
Carbon Dioxide	401	412	591	784	588
Carbon Monoxide	< 20	< 20	< 20	< 20	< 20
Nitrous Oxide	< 20	< 20	34.8	47.6	40.9

(a) WHC sample identification number.

(b) PNL canister number.

(c) Replicate hydrogen analysis for PNL 178 resulted in a concentration of 145.1 ppmv.

Figure 3.1a Total Ion Chromatogram (2 through 30 min) for Hanford Waste Tank C-107
SUMMA™ Canister Sample S4058-A05-179 Collected on 9/29/94

Figure 3.1b Total Ion Chromatogram (30 through 58 min) for Hanford Waste Tank C-107 SUMMATM Canister Sample S4058-A05-179 Collected on 9/29/94

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