WASTE TANK VAPOR PROGRAM

Vapor Space Characterization of Waste Tank 241-U-106 (*In Situ*): Results from Samples Collected on 8/25/94

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Summary

This report describes inorganic and organic analyses results from *in situ* samples obtained from the headspace of the Hanford waste storage Tank 241-U-106 (referred to as Tank U-106). 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 performed. In addition, we looked for the 39 TO-14 compounds plus an additional 14 target analytes. Of these, six were observed above the 5-ppbv reporting cutoff. Ten organic tentatively identified compounds (TICs) were observed above the reporting cutoff of (ca.) 10 ppbv in two or more of the three samples collected and are reported with concentrations that are semiquantitative estimates based on internal standard response factors. The 10 organic analytes with the highest estimated concentrations are listed in Table 1 and account for approximately 89% of the total organic components in Tank U-106. Methyl isocyanate, a compound of possible concern in Tank U-106, was not detected.

Table 1 Summary Results of Inorganic and Organic Samples Collected from the Headspace of Tank U-106 on 8/25/94

<u>Category</u>	<u>Analyte</u>	<u>Vapor^(a) Concentration</u>	<u>Units</u>
Inorganic	NH ₃	852 ± 8	ppmv
	NO ₂	≤ 0.1	ppmv
	NO	≤ 0.1	ppmv
	H ₂ O	16 ± 1	mg/L
Organic	Ethanol	1.47	mg/m ³
	1-Butanol	1.16	mg/m ³
	Acetone	1.16	mg/m ³
	Tridecane	0.68	mg/m ³
	Hexamethylcyclotrisiloxane	0.37	mg/m ³
	Pyridine	0.27	mg/m ³
	Isopropyl Alcohol	0.27	mg/m ³
	Toluene	0.20	mg/m ³
	Butane	0.20	mg/m ³
	Propane	0.20	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 in preparing the organic portion of this report. Sally Slate, May-Lin Thomas, and Karen Schielke analyzed inorganic samples, and Gary Dennis prepared the solid-sorbent sample trains. 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
ISS	In-Situ-Sampling System
MDL	minimum detection limit
NIST	National Institute for Standards and Technology
NPH	normal paraffin hydrocarbon
ORNL	Oak Ridge National Laboratory
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 *in situ* tank-headspace samples taken from the Hanford waste Tank 241-U-106 (referred to as Tank U-106). 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 14 analytes identified by the Toxicological Review Panel for Tank C-103 and reported by Mahlum et al. (1994). The sample job was designated S4067, and samples were collected by WHC on August 25, 1994, using the *in situ* sampling system (ISS). 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 three sorbent trains (for inorganic analyses), and four SUMMA™ canisters (for organic analyses) were supplied to the WHC sampling staff on August 16. Samples were taken (by WHC) from the tank headspace on August 25 and were returned to PNL from the field on September 20. Inorganic (sorbent trap) samples were delivered to PNL on chain of custody (COC) 007508 (see Figure 1.1a). The SUMMA™ canisters were delivered on COC 007507 (see Figure 1.1b).

The samples were inspected upon delivery to the 326/23B laboratory and logged into PNL record book 55408 before implementation of PNL Technical Procedure PNL-TVP-07^(b). Custody of the sorbent traps was transferred to PNL personnel performing the inorganic analysis on September 23 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 the time of analysis. Access to the 326/23B laboratory is limited to PNL personnel working on the waste-tank safety program. Analyses described in this report were performed at PNL in the 300 area of the Hanford Reservation. Analytical methods that were used are described in the text. In summary, sorbent traps for inorganic analyses containing sample materials were either weighed (for water analysis) or weighed and desorbed with the appropriate aqueous solutions (for ammonia, nitrogen dioxide, and nitric oxide analyses). The aqueous extracts were analyzed by either selective electrode or ion chromatography (IC). Organic analyses were performed using cryogenic preconcentration followed by gas chromatography/mass spectrometry (GC/MS).

After organic analysis, the SUMMA™ canisters were forwarded to Oak Ridge National Laboratory (ORNL). Preliminary data provided by ORNL indicated that methylisocyanate may be present in the headspace of Tank U-106. Based on this information, a detailed review of tentatively identified compounds (TICs) was conducted by PNL staff.

(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 007508	
Custody Form Initiator	J. A. Edwards	Telephone	(509) 373-0141	Pager	85-3009
Company Contact	L. A. Pingel	Telephone	(509) 373-4051		
Project Designation/Sampling Locations 200 East Tank Farm		Collection Date	08-25-94 ^{9/23}		
241-U-106 Tank	Vapor Sample SAF S4067	Preparation Date	08-15-94		
Ice Chest No.	(IN-SITU)	Field Logbook No.	WHC-N-_____		
Bill of Lading/Airbill No.	N/A	Offsite Property No.	N/A		
Method of Shipment	Government Truck				
Shipped to	WHC				
Possible Sample Hazards/Remarks Unknown at time of sampling					

Sample Identification

S4067 - .70W	NH ₃ /NO _x /H ₂ O (Sample #1)
S4067 - .71W	NH ₃ /NO _x /H ₂ O (Sample #2)
S4067 - .72W	NH ₃ /NO _x /H ₂ O (Sample #3)
S4067 - .73W	NH ₃ /NO _x /H ₂ O (Spare)

-S4067- .74W OVS/Drier (Radiological survey)
 Turned in to 2225
 LAB for Analysis
 8-25-94
 RMCL

 09/20/94 @

[X] Field Transfer of Custody			Chain of Possession (Sign and Print Names)			
Relinquished By	Date	Time	Received By	Date	Time	
J. A. Edwards	08-15-94	10:15	Andy Johnson	08-15-94	10:15	
LA Johnson	8/15/94	10:33	RM Arnold	8-24-94	10:33	
RM Arnold	8-24-94	11:00	T.B. Utter	9-20-94	11:00	
T.B. Utter	9-20-94	11:20	J.A. Edwards	9-20-94	11:20	
J.A. Edwards	9-23-94	14:20	A. Krupsha	9-23-94	10:20	

(version 02-28-94)

Final Sample Disposition

Disposal Method:

Disposed by:

Date/Time:

Comments **RAD RELEASE - NO SAMPLE DATE NOTED. (E)**
 A-6000-407 (12/92) WEF061

Figure 1.1a Chain of Custody for Inorganic Samples for Tank U-106

Westinghouse Hanford Company		CHAIN OF CUSTODY		WHC 007507	
Custody Form Initiator	J. A. Edwards	Telephone	(509) 373-0141	Pager	85-3009
Company Contact	L. A. Pingel	Telephone	(509) 373-4051		
Project Designation/Sampling Locations 200 East Tank Farm 241-U-106 Tank Vapor Sample SAF S4067 Ice Chest No. (IN-SITU)		Collection Date	08 - 25 - 94	Preparation Date	08 - 16 - 94
Bill of Lading/Airbill No.	N/A	Field Logbook No.	WHC-N-_____	Offsite Property No.	N/A
Method of Shipment	Government Truck				
Shipped to	WHC				

Possible Sample Hazards/Remarks Unknown at time of sampling

Sample Identification

S4067 - ____ .091¹ (PNL) SUMMA Ambient Air
 S4067 - ____ .092² (PNL) SUMMA Sample #1
 S4067 - ____ .093¹ (PNL) SUMMA Sample #2
 S4067 - ____ .183¹ (PNL) SUMMA Sample #3

[X] 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>	08-16-94	1015	Andy Johnson <i>S. A. Johnson</i>	08-16-94	1015			
<i>J. A. Johnson</i>	8/24/94	1035	<i>R. M. Arnold</i>	8-24-94	1035			
<i>R. M. Arnold</i>	9/20/94	1100	<i>T. B. Utter</i>	9-20-94	1100			
<i>T. B. Utter</i>	9/20/94	1120	<i>J. A. Edwards</i>	9-20-94	1120			

(version 02-28-94)

Final Sample Disposition

Disposal Method:

Disposed by:

Date/Time:

Comments *RAO RELEASED - NO SAMPLE DATE NOTED* (16)
 A-6000-407 (12/92) WEF061

Figure 1.1b Chain of Custody for Organic Samples for Tank U-106

2.0 Inorganic Task

Solid sorbent traps, prepared in multi-trap sampling trains, were supplied to WHC for sampling the tank headspace using the ISS. Controls 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 traps 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. Sorbent traps were connected end-to-end to prepare multi-trap sorbent trains for sampling.

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.

Sampling materials provided by PNL to trap inorganic compounds included 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 at $\leq 10^\circ\text{C}$, 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. Both the inlet and outlet ends of the sorbent trains (the downstream ends of the traps always contained silica gel) were each sealed with red-plastic end caps provided by the manufacturer. The leading and trailing ends of the sorbent 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 21.1°C and 760 torr), in L, by 24.1 L/mol. For example, the concentration (C_v) of a 3.00-L sample containing 75.0 μg of NH_3 equals

$$C_v = \frac{75.0 \mu\text{g}}{17 \text{ g/mol}} \left(\frac{3.00 \text{ L}}{24.1 \text{ L/mol}} \right)^{-1} = 35.4 \text{ ppmv} \quad (2.1)$$

This calculational method produces concentration results that are slightly conservative (greater than actual) because the volume of water vapor in the sample stream is neglected. The volume of water vapor is not included in the measured sampled volume because of its removal in desiccant traps upstream of the mass flowmeter. However, the bias is generally expected to be small. For a tank-headspace temperature of 35°C, the magnitude of the bias would be 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 are 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, presumed to be dominated by water vapor, was determined by dividing the combined change in mass from all traps in a sorbent train by the actual volume of gas sampled. Controls were used 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, 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).

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. 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 in the laboratory analysis of 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 10% or less of the mass change of most blanks. The analytical accuracy of measurements of the change in mass of sorbent trains is estimated to be ± 1 mg per 5-trap sorbent train; this estimate is based largely on preliminary information that unopened field-blank sorbent trains gain 0.3 ± 0.4 mg per train.

Table 2.1 Analysis Procedures and Typical Detection Limits of Target Inorganic Analytes.

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

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

(b) MDL is defined as the vapor concentration that can be detected with an uncertainty equal to about the magnitude of the measurement. The uncertainty is expected to reduce to about one-quarter of the magnitude of the measurement at a concentration of four times the MDL. The MDLs were based on the assumption that 3 L of vapor are sampled; if greater volumes of vapor are sampled, correspondingly smaller MDLs can be achieved. The MDLs were also based on desorbing-solution volumes of 10 mL for NH₃ and 3 mL for the other analytes.

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

2.4 Inorganic Sample Results

Samples were obtained by WHC from the headspace of Tank U-106 on 8/25/94 using the ISS. The sample job designation number was S4067. 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 hydrogen cyanide (HCN) and sulfur oxides (SO_x) were not requested. The exposed samples were returned to PNL on 9/20/94 and subsequently analyzed on 9/23/94 (H_2O) and 9/26/94 (NH_3 and NO_x) to provide information on the headspace concentration of selected inorganic compounds. The sample-volume information was received on 8/25/94.

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 852 ± 8 ppmv, based on all three samples. The NH_3 quantities in the sorbent traps ranged from 131 to 137 μmol . Blank corrections, ≤ 0.06 μmol in front and ≤ 0.03 in back sections, were not significant ($\leq 0.05\%$) and were neglected. Although spiked blanks were not tested, the percentage recoveries of three sets of blanks spiked with 12.2, 22.3, and 46.4 μmol of NH_3 were $101 \pm 4\%$, $109 \pm 2\%$, and $104 \pm 1\%$, respectively, during related sample jobs (Clauss et al. 1994; Ligothe et al. 1994). The analysis of one sample was duplicated and yielded a repeatability of $\pm 3\%$. One sample leachate was spiked after initial analysis with roughly the quantity of NH_3 in the sample and yielded a percentage recovery of 109%. 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 three 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, and NO_2 trap). Related sample jobs, performed using the VSS in Tanks BY-104, -105, and -106 both with and without NO_x trains protected by a leading NH_3 trap (e.g., Clauss et al. 1994), indicated that the presence of the upstream NH_3 traps resulted in NO concentrations that were about 1.3- to 1.6-fold less than those from unprotected NO_2 traps. The NO_2 concentrations were also potentially less following an NH_3 trap.

The concentrations of NO_2 and NO were both ≤ 0.1 ppmv. Blank-corrected NO_2 quantities in the sorbent traps averaged ≤ 0.008 μmol (NO_2 and NO samples). Nitrite blank levels used to correct data were 0.0152 ± 0.0023 μmol in front and 0.0068 ± 0.0008 μmol in back sorbent

Table 2.2 List of PNL Inorganic Samples, Controls, and Gravimetric Results Obtained from *In Situ* Sampling of Headspace of Tank U-106 on 8/25/94

Sample Port and Volume Information ^(a)					
<u>Sample Number</u>	<u>Sorbent Type</u>	<u>Flow Rate (mL/min)</u>	<u>Duration (min)</u>	<u>Volume (L)</u>	<u>Mass Gain (g)</u>
<u>Samples:</u>					
S4067- 067-70W	NH ₃ /NO _x /H ₂ O Sample	258	15.0	3.87	0.0648
S4067- 067-71W	NH ₃ /NO _x /H ₂ O Sample	250	15.0	3.74	0.0619
S4067- 067-72W	NH ₃ /NO _x /H ₂ O Sample	247	15.0	3.70	0.0590
S4067- 067-73W	NH ₃ /NO _x /H ₂ O Blank	n/a ^(b)	n/a	n/a	0.0017

(a) Sampling information and dry-gas sample volumes, corrected to 21°C and 760 torr, were provided by WHC. Uncertainty values were not provided with sample-volume results.

(b) n/a = not applicable.

sections, and were based on the analytical results from the spare/blank sorbent train. Although spiked blanks were not tested, blanks spiked with 0.0064, 0.047, 0.11, and 0.74 $\mu\text{mol NO}_2^-$ during a related sample job yielded percentage recoveries of $153 \pm 14\%$, $103 \pm 4\%$, $106 \pm 8\%$, and $111 \pm 7\%$, respectively (Ligotke et al. 1994; Clauss et al. 1994). No samples were reanalyzed to check repeatability. No sample leachates were spiked after initial analysis with quantities of NO_2^- to test analytical percentage recoveries. A 4-point calibration was performed over a concentration range of 0 to 0.5 $\mu\text{g NO}_2^-$ per mL in the desorbing matrix.

2.4.3 Gravimetric Results. The mass concentration of material collected in the sorbent-trap trains, believed to be primarily water vapor, was 16 ± 1 mg/L. The result was based on an average blank-corrected mass gain of 60 mg from all 3 sets of sample trains. The actual mass gains were corrected by subtracting a blank mass gain of 2 mg. The blank correction was determined as the average of blank sorbent trap trains from six related ISS sample jobs, a group from which the individual results ranged between - 1 and +4 mg. The overall measurement uncertainty was estimated based on the variability of the samples and the range of blank data. Although no spiked blanks were tested, the percentage recovery of mass from 3 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 In-Situ Sampling of the Headspace of Tank U-106 on 8/25/94

<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>133^(c)</u>	<u>3.77^(c)</u>	<u>852 $\pm$ 8^(c)</u>
S4067- 067-70W	137	≤ 0.03	137	3.87	853
S4067- 067-71W	131	≤ 0.03	131	3.74	844
S4067- 067-72W	132	≤ 0.03	132	3.70	860
<u>NO₂ Samples:</u>			<u>≤ 0.008</u>	<u>3.77</u>	<u>≤ 0.1</u>
S4067- 067-70W	0.0180	0.0066	n/a ^(d)	3.87	n/a
S4067- 067-71W	0.0133	0.0069	n/a	3.74	n/a
S4067- 067-72W	0.0185	0.0068	n/a	3.70	n/a
<u>NO Samples:</u>			<u>≤ 0.008</u>	<u>3.77</u>	<u>≤ 0.1</u>
S4067- 067-70W	0.0181	0.0064	n/a	3.87	n/a
S4067- 067-71W	0.0200	0.0066	n/a	3.74	n/a
S4067- 067-72W	0.0190	0.0066	n/a	3.70	n/a
<u>Gravimetric Samples (mg/mg/L):</u>			<u>60 mg</u>	<u>3.77</u>	<u>16 $\pm$ 1 mg/L</u>
S4067- 067-67W	n/a	n/a	63	3.87	16.3
S4067- 067-67W	n/a	n/a	60	3.74	16.0
S4067- 067-67W	n/a	n/a	57	3.70	15.4

- (a) Blank-corrected vapor concentrations were calculated using WHC-reported dry-air sample volumes (corrected to 21°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 other than mass concentration. The uncertainty in mass concentration was determined based on the added uncertainty caused by the range of results of six related blanks. The use of " $\leq$ " is defined in Section 2.0.
- (d) n/a = not applicable.

3.0 Organic Task

3.1 SUMMA™ Canister Preparation

Before sending SUMMA™ canisters out to the field for sampling, the canisters are cleaned and verified contaminant free according to PNL Technical Procedure PNL-TVP-02^(a). The cleaning procedure uses an EnTech 3000 cleaning system that controls 1) filling the canisters with purified humid air and 2) evacuating, for several cycles with applied heat, before allowing the canister to evacuate overnight. The canister is filled a final time with purified humid air for analysis by PNL Technical Procedure PNL-TVP-01^(b), which is a modification of U.S. Environmental Protection Agency (EPA) compendium Method TO-14. If the canister is verified as clean, free of TO-14 and unknown contaminants to a level of 5 parts per billion by volume (ppbv), the canister is evacuated to 5×10^{-3} torr, tagged, and stored for use in the field. Before sending the canisters out to the field for sampling, the canister vacuum is measured to determine if any leakage has occurred. If the vacuum has remained constant during storage, the canisters are prehumidified with 100 μ L of distilled water and labeled with a field-sampling identification. Canisters stored more than 30 but less than 60 days are re-evacuated and rehumidified before use. If stored more than 60 days, the canisters are recleaned and validated before use.

3.2 Sample Analysis Method

The SUMMA™ canister sample was analyzed according to PNL Technical Procedure PNL-TVP-03, *Determination of TO-14 Volatile Organic Compounds in Hanford Waste Tank Headspace Samples Using SUMMA™ Passivated Canister Sampling and Gas Chromatographic-Mass Spectrometry Analysis*, which is a modified version of EPA compendium Method TO-14. The method uses an EnTech cryoconcentration system interfaced with either a 5971 or a 5972 Hewlett Packard (HP) benchtop GC/MS. The EnTech concentrator is used to pull a metered volume of sample air from the SUMMA™ canister, cryogenically concentrate the air volume, then transfer the volume to the GC/MS for analysis. A 100-mL volume of sample is measured and analyzed from the tank headspace. The organic components in the sampled air are separated on an analytical column, J&W Scientific DB-1 phase, 60-m by 0.32-mm internal diameter with 3- μ m film thickness. The GC oven is programmed to run a temperature gradient beginning at 40°C, holding for 5 min, and ramping at 4°C per min to a final temperature of 260°C, with a 5-min hold. Twenty-four hours before the analysis, the SUMMA™ canister samples were pressurized with purified air (Aadco Instruments, Inc., 1920 Sherwood St., Clearwater, Florida 34625). The starting pressure was first measured using a calibrated diaphragm gauge (Cole Parmer) then pressurized to a level exactly twice the original pressure. For example, if the canister had a starting pressure of 740 torr, it was pressurized to 1480 torr. This dilution was an effort to improve the precision of the analysis. The sample dilution was taken into account when calculating the analysis results. The instrument calibration mixture for the TO-14 analysis consists of the standard 39 organic analytes with an additional 14 tank-related compounds.

(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.

Together, these 53 compounds that are directly quantified in this analysis make up the target analyte list (these 53 compounds will be referred to as target analytes). The calibration mixture was prepared by blending a commercially prepared 39-compound TO-14 calibration mixture with a 14-compound mixture created using a KinTech® permeation-tube standard generation system. The operation of the permeation tube system follows the method detailed in *Preparation of TO-14 Volatile Organic Compounds Gas Standards*, PNL Technical Procedure PNL-TVP-06. The standard calibration mix was analyzed using six aliquot sizes ranging from 5 mL to 300 mL. Depending on the concentration of each analyte in the mixture, either five or six points were used to construct the calibration curve. Butanoic acid was added to the mixture, but was not detected in the analysis. Butanal was recovered very poorly, producing a much lower than expected response. This results in a much higher measured amount reported in the sample analysis. This problem is currently under investigation. Performance-based detection limits for the target analytes will be developed as a pool of calibration data becomes available. Currently, the nominal detection limit of 5 ppbv is met.

3.3 Quality Assurance/Quality Control

Before the tank sample was analyzed, a diagnostic check was performed on the GC/MS instrument by running an instrument "quick tune," as described in PNL-TVP-03. Upon satisfactory completion of the instrument diagnostic check, a blank volume of purified nitrogen was analyzed to check the cleanliness of the system. The instrument was then calibrated over 5 to 6 data points ranging from 5 ppbv to 300 ppbv, using a standard gas mixture containing 39 volatile organic compounds listed in EPA compendium Method TO-14 and an additional 14 tank-related compounds (referred to as target organic analytes). 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 target organic analytes found in the tank samples.

The ambient air sample collected ~10 m upwind of Tank U-106 was used as a method blank and was used to determine the potential for analyte interferences in the samples. Continuing calibration standards for this sample set fell within $\pm 25\%$ of the expected concentrations for the analytes reported.

3.3.1 Quantitation Results of Target Organic Analytes. The quantitative-analysis results for the target organic analytes were calculated directly from the calibration curve generated using the IS method described above and in PNL-TVP-03. The conversion from ppbv to mg/m³ assumes standard temperature and pressure (STP) conditions of 760 torr and 273K and was calculated directly from the following equation:

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

3.3.2 Identification and Quantitation of Tentatively Identified Compounds. The TICs are determined by mass-spectral interpretation and comparison of the spectra with the EPA/NIST/WILEY Library, which is a part of the HP 5971/5972 instrument operating system. Chromatographic peaks with an area count greater than, or equal to, one tenth of the total area count of the nearest eluting IS are tentatively identified and quantitatively estimated. The quality of the mass-spectral searches was then reviewed by the principal investigators before the identification was assigned to each chromatographic peak. The concentration of each TIC was estimated using a relative response factor calculated using the total peak area for the nearest eluting IS. The IS peak area was used to calculate a response factor using the IS concentration in mg/m³:

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

The calculated response factor was then multiplied by the TIC peak area to give an estimated concentration for that compound.

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

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

The IS level added to all blank, standard, and sample injections was 104 ppbv for bromochloromethane, 101 ppbv for 1,4-difluorobenzene, and 98.5 ppbv for chlorobenzene-d₅. The IS concentrations were converted from ppbv to mg/m³ at STP using a molecular weight of 129.39 (g/mol) for bromochloromethane, 114.09 for 1,4-difluorobenzene, and 117.6 for chlorobenzene-d₅. All sample concentrations were multiplied by a factor of two to account for the dilution step described in Section 3.2.

3.4 Analysis Results

The results from the GC/MS analysis of the tank-headspace samples are presented in Tables 3.1 and 3.2. The results of GC/MS analysis of an ambient air sample collected upwind of Tank U-106 is 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 as target analytes. Six compounds were above the 5-ppbv detection limit. Acetone was approximately 60% of the total concentration of the target analytes.

Table 3.2 lists the semi-quantitative results for the TICs. The predominant species observed in this sample were ethanol, 1-butanol, and tridecane. Other normal paraffin hydrocarbons (NPHs), defined as n-alkanes from C₁₁ to C₁₅, were observed at trace levels in only one canister. It should be noted that because the SUMMA™ canisters were not heated at the time of analysis, the NPH concentrations listed after the retention time of decane may not be a true accounting of all the NPH in the sample. Similarly, polar compounds, which may adhere to the inside surface of the canister, may

also be under represented in this analysis. The total concentration of the TIC compounds was found to be 4.76 mg/m³.

Table 3.3 and 3.4 list results of target analyte analyses, and TIC analyses for ambient air collected upwind of Tank U-106. Pyridine and 1,2,4-trichlorobenzene were target analytes detected. The TIC compounds detected were acetaldehyde, acetone, 3-buten-2-one butanol and 2-butanone. A detailed analysis of all detected TICs was conducted to determine if there was any evidence of methylisocyanate. The presence of methylisocyanate was not confirmed.

4.0 Conclusions

The concentrations of selected inorganic and organic compounds were determined from *in situ* samples of the headspace of Tank U-106 on 8/25/94. Sampling and analysis methods for inorganics followed those described by Ligotke et al. (1994) for samples obtained from Tank C-103, a tank which contained 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 852 ± 8 ppmv. Because the concentration of NH_3 exceeded 250 ppmv, notification was provided by phone to the 200 West Area Tank Farm Shift Manager on 10/5/94. The concentration of NO_2 was ≤ 0.1 ppmv. The concentration of NO was ≤ 0.1 ppmv. The vapor mass concentration was 16 ± 1 mg/L and was expected to consist largely of water vapor. Uncertainties were based on one standard deviation of analytical results; information on sample-volume uncertainty was not provided. It is recommended that sample-volume uncertainties be evaluated and reported along with analytical uncertainties in subsequent sample jobs.

Organic analysis of the headspace samples from Tank U-106 identified six target analytes above the 5-ppbv MDL and 10 TICs above the 10-ppbv MDL in two or more of the SUMMATM samples. The concentration of target analytes accounted for 29% of the organics identified by both the target analyte and the TIC analyses. Acetone contributed 60% of the concentration of target analytes, followed by pyridine at 14%. The alcohols, ethanol, and 1-butanol were 55% of the total TIC concentration. Methylisocyanate was not observed. At least one NPH compound, tridecane, was also present in the headspace samples. Five target analytes and two TIC compounds were observed in the ambient air sample collected approximately ~ 10 m upwind of Tank U-106.

5.0 References

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- 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.

6.0 Further Reading

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

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

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

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

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

Table 3.1 Positively Identified and Quantitated Target Organic Analytes^(a) of Samples Collected from the Headspace of Tank U-106 in SUMMATM Canisters on 8/25/94

Analyte	CAS No.	Mol Wt	S4067----.092 ^(b)		S4067----.093 ^(b)		S4067----.183 ^(b)		Means and			
			PNL 092 ^(c)		PNL 093 ^(c)		PNL 183 ^(c)		Standard Deviations			
			Concentration		Concentration		Concentration		(mg/m ³)		St Dev	(ppbv)
			(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)	(mg/m ³)	St Dev	(ppbv)	St Dev
Dichlorodifluoromethane	75-71-8	121	<0.03	<5	<0.03	<5	<0.03	<5	(d)	(d)	(d)	(d)
Chloromethane	74-87-3	50	<0.01	<5	<0.01	<5	<0.01	<5	(d)	(d)	(d)	(d)
1,2-Dichloro-1,1,2,2-tetrafluoroethane	76-14-2	171	<0.04	<5	<0.04	<5	<0.04	<5	(d)	(d)	(d)	(d)
Vinyl Chloride	75-01-4	62	<0.01	<5	<0.01	<5	<0.01	<5	(d)	(d)	(d)	(d)
Bromomethane	74-83-9	95	<0.02	<5	<0.02	<5	<0.02	<5	(d)	(d)	(d)	(d)
Chloroethane	75-00-3	65	<0.01	<5	<0.01	<5	<0.01	<5	(d)	(d)	(d)	(d)
Trichlorofluoromethane	75-69-4	137	0.10	16.3	0.11	17.2	0.12	19.9	0.11	0.01	17.8	1.89
1,1-Dichloroethene	75-35-4	97	<0.02	<5	<0.02	<5	<0.02	<5	(d)	(d)	(d)	(d)
Methylene Chloride	75-09-2	85	<0.02	<5	<0.02	<5	<0.02	<5	(d)	(d)	(d)	(d)
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	187	<0.04	<5	<0.04	<5	<0.04	<5	(d)	(d)	(d)	(d)
1,1-Dichloroethane	75-34-3	99	<0.02	<5	<0.02	<5	<0.02	<5	(d)	(d)	(d)	(d)
cis-1,2-Dichloroethene	156-59-2	97	<0.02	<5	<0.02	<5	<0.02	<5	(d)	(d)	(d)	(d)
Chloroform	67-66-3	119	<0.03	<5	<0.03	<5	<0.03	<5	(d)	(d)	(d)	(d)
1,2-Dichloroethane	107-06-2	99	<0.02	<5	<0.02	<5	<0.02	<5	(d)	(d)	(d)	(d)
1,1,1-Trichloroethane	71-55-6	133	<0.03	<5	<0.03	<5	<0.03	<5	(d)	(d)	(d)	(d)
Benzene	71-43-2	78	<0.02	<5	<0.02	<5	<0.02	<5	(d)	(d)	(d)	(d)
Carbon Tetrachloride	56-23-5	154	<0.03	<5	<0.03	<5	<0.03	<5	(d)	(d)	(d)	(d)
1,2-Dichloropropane	78-87-5	113	<0.03	<5	<0.03	<5	<0.03	<5	(d)	(d)	(d)	(d)
Trichloroethene	79-01-6	131	<0.03	<5	<0.03	<5	<0.03	<5	(d)	(d)	(d)	(d)
cis-1,3-Dichloropropene	10061-01-5	111	<0.02	<5	<0.02	<5	<0.02	<5	(d)	(d)	(d)	(d)
trans-1,3-Dichloropropene	10061-02-6	111	<0.02	<5	<0.02	<5	<0.02	<5	(d)	(d)	(d)	(d)
1,1,2-Trichloroethane	79-00-5	133	<0.03	<5	<0.03	<5	<0.03	<5	(d)	(d)	(d)	(d)
Toluene	108-88-3	92	0.20	48.3	0.20	49.1	0.21	51.9	0.20	0.01	49.8	1.86
1,2-Dibromoethane	106-93-4	188	<0.04	<5	<0.04	<5	<0.04	<5	(d)	(d)	(d)	(d)
Tetrachloroethylene	127-18-4	166	<0.04	<5	<0.04	<5	<0.04	<5	(d)	(d)	(d)	(d)
Chlorobenzene	108-90-7	113	<0.03	<5	<0.03	<5	<0.03	<5	(d)	(d)	(d)	(d)
Ethyl benzene	100-41-4	106	<0.02	<5	<0.02	<5	<0.02	<5	(d)	(d)	(d)	(d)
m-Xylene ^(c)	106-42-3	106	<0.02	<5	<0.02	<5	<0.02	<5	(d)	(d)	(d)	(d)
p-Xylene ^(c)												
Styrene	100-42-5	104	<0.02	<5	<0.02	<5	<0.02	<5	(d)	(d)	(d)	(d)
1,1,2,2-Tetrachloroethane	79-34-5	168	<0.04	<5	<0.04	<5	<0.04	<5	(d)	(d)	(d)	(d)
o-Xylene	95-47-6	106	<0.02	<5	<0.02	<5	<0.02	<5	(d)	(d)	(d)	(d)

Table 3.1 (Contd)

Analyte	CAS No.	Mol Wt	S4067----.092 ^(b)		S4067----.093 ^(b)		S4067----.183 ^(b)		Means and			
			PNL 092 ^(c)		PNL 093 ^(c)		PNL 183 ^(c)		Standard Deviations			
			Concentration		Concentration		Concentration		(mg/m ³)	St Dev	(ppbv)	St Dev
			(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)				
1,3,5-Trimethylbenzene	108-67-8	120	<0.03	<5	<0.03	<5	<0.03	<5	(d)	(d)	(d)	(d)
1,2,4-Trimethylbenzene	95-63-6	120	<0.03	<5	<0.03	<5	<0.03	<5	(d)	(d)	(d)	(d)
1,3-Dichlorobenzene	541-73-1	147	<0.03	<5	<0.03	<5	<0.03	<5	(d)	(d)	(d)	(d)
1,4-Dichlorobenzene	106-46-7	147	<0.03	<5	<0.03	<5	<0.03	<5	(d)	(d)	(d)	(d)
1,2-Dichlorobenzene	95-50-1	147	<0.03	<5	<0.03	<5	<0.03	<5	(d)	(d)	(d)	(d)
1,2,4-Trichlorobenzene	120-82-1	181	<0.04	<5	<0.04	<5	<0.04	<5	(d)	(d)	(d)	(d)
Hexachloro-1,3-butadiene	87-68-3	261	<0.06	<5	<0.06	<5	<0.06	<5	(d)	(d)	(d)	(d)
2-Butanone	78-93-3	72	0.02	6.86	0.03	9.98	0.04	12.0	0.03	0.01	9.61	2.59
Acetone	67-64-1	58	1.01	388	1.07	414	1.39	535	1.16	0.20	445	78.4
Acetonitrile	75-05-8	41	<0.01	<5	<0.01	<5	<0.01	<5	(d)	(d)	(d)	(d)
Heptane	142-82-5	100	<0.02	<5	<0.02	<5	<0.02	<5	(d)	(d)	(d)	(d)
Tetrahydrofuran	109-99-9	72	0.16	50.6	0.17	54.2	0.18	57.4	0.17	0.01	54.0	3.40
Pyridine	110-86-1	79	0.27	77.3	0.28	78.4	0.27	77.1	0.27	0.01	77.6	0.75
Butanenitrile	109-74-0	69	<0.02	<5	<0.02	<5	<0.02	<5	(d)	(d)	(d)	(d)
Cyclohexane	110-82-7	84	<0.02	<5	<0.02	<5	<0.02	<5	(d)	(d)	(d)	(d)
Decane	124-18-5	142	<0.03	<5	<0.03	<5	<0.03	<5	(d)	(d)	(d)	(d)
Hexane	110-54-3	86	<0.02	<5	<0.02	<5	<0.02	<5	(d)	(d)	(d)	(d)
4-Methyl-2-pentanone	108-10-1	100	<0.02	<5	<0.02	<5	<0.02	<5	(d)	(d)	(d)	(d)
Propanenitrile	107-12-0	55	<0.01	<5	<0.01	<5	<0.01	<5	(d)	(d)	(d)	(d)
Cyclohexanone	108-94-1	98	<0.02	<5	<0.02	<5	<0.02	<5	(d)	(d)	(d)	(d)
Propanol	71-23-8	60	<0.01	<5	<0.01	<5	<0.01	<5	(d)	(d)	(d)	(d)

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

(b) WHC sample identification number.

(c) PNL canister number.

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

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

Table 3.2 Tentatively Identified Compounds and Estimated Concentrations^(a) of Samples from the Headspace of Tank U-106 in SUMMATM Canisters Collected on 8/25/94

Tentatively Identified Compound ^(e)	CAS No. ^(e)	Mol Wt	Ret Time	S4067—,092 ^(b)		S4067—,093 ^(b)		S4062—,183 ^(b)		Means and Standard Deviations			
				PNL 092 ^(c)		PNL 093 ^(c)		PNL 183 ^(c)		(mg/m ³)	St Dev	(ppbv)	St Dev
Propane	74-98-6	44	3.9	0.20	99.3	0.21	106	0.20	102	0.20	0.01	102	3.3
Dimethyl ether	115-10-6	46	4.5	0.13	63.3	0.13	63.8	0.14	67.7	0.13	0.00	64.9	2.4
Acetaldehyde	75-07-0	44	5.1	0.16	81.5	0.15	77.9	< 0.02	< 10	0.16	(e)	79.7	(e)
1-Butene	106-98-9	56	5.6	0.12	46.4	0.12	46.4	0.11	45.2	0.12	0.00	46.0	0.7
Butane	106-97-8	58	5.8	0.19	74.5	0.21	79.9	0.21	80.3	0.20	0.01	78.3	3.2
Ethanol	64-17-5	46	7.2	1.41	687	1.53	743	1.48	722	1.47	0.06	717	28.3
Isopropyl Alcohol	67-63-0	60	8.9	0.26	97.4	0.27	100	0.28	105	0.27	0.01	101	3.8
1-Butanol	71-36-3	74	17.4	1.12	340	1.20	362	1.17	354	1.16	0.04	352	11.2
Hexamethylcyclotrisiloxane	541-05-9	222	26.6	0.33	32.9	0.41	41.7	< 0.01	< 10	0.37	(e)	37.3	(e)
Dodecane	112-40-3	170	44.1	< 0.08	< 10	< 0.08	< 10	0.13	17.0	(e)	(e)	(e)	(e)
Tridecane	629-50-5	184	47.9	0.17	20.5	< 0.08	< 10	1.19	145	0.68	(e)	82.8	(e)
Tetradecane	629-59-4	198	51.4	< 0.09	< 10	< 0.09	< 10	0.38	42.9	(e)	(e)	(e)	(e)

- (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) Mean and/or standard deviation are not meaningful for this analyte.

Table 3.3 Positively Identified and Quantitated Target Organic Analytes^(a) for Ambient Air Collected Near Tank U-106 in a SUMMATM Canister on 8/25/94

<u>Analyte</u>	<u>CAS No.</u>	<u>Mol Wt</u>	S4067----091 ^(b) PNL 091 ^(c) <u>Concentration</u>	
			<u>(mg/m³)</u>	<u>(ppbv)</u>
1,2,4-Trichlorobenzene	120-82-1	181	0.10	12.3
Pyridine	110-86-1	79	0.07	18.7

(a) TO-14 plus 14 additional analytes.

(b) WHC sample identification number.

(c) PNL canister number.

Table 3.4 Tentatively Identified Compounds and Estimated Concentrations^(a) for Ambient Air Collected Near Tank U-106 in a SUMMATM Canister on 8/25/94

<u>Analyte</u>	<u>CAS No.</u>	<u>Mol Wt</u>	<u>Ret Time</u>	S4067----.091 ^(b) PNL 091 ^(c) <u>Concentration</u>	
				<u>(mg/m³)</u>	<u>(ppbv)</u>
Acetaldehyde	75-07-0	44	5.1	0.15	76.4
Acetone	67-64-1	58	8.4	0.13	51.8
3-Buten-2-one	78-94-4	70	12.9	0.19	59.2
Butanal	123-72-8	72	13.2	0.15	47.9
2-Butanone	78-93-3	72	13.5	0.05	16.8

(a) TO-14 plus 14 additional analytes.

(b) WHC sample identification number.

(c) PNL canister number.

Figure 3.1b Total Ion Chromatogram (30 - 58 min) for Hanford Waste Tank U-106 SUMMA™ Canister Sample S4067—092 Collected on 8/25/94

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