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WASTE TANK VAPOR PROGRAM

Vapor Space Characterization of Waste Tank 241-TY-101 (*In Situ*): Results from Samples Collected on 8/5/94

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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-TY-101 (referred to as Tank TY-101). The results described here were obtained to support safety and toxicological evaluations. A summary of the results for inorganic and organic analytes is listed in Summary Table 1. Detailed descriptions of the results appear in the text.

Quantitative results were obtained for the inorganic compounds ammonia (NH₃), nitrogen dioxide (NO₂), nitric oxide (NO), hydrogen cyanide (HCN), and water (H₂O). 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 reporting cutoff of (ca.) 10 ppbv. The reported concentrations for these compounds are semiquantitative estimates based on the internal standard response factor. In addition, we looked for the 40 standard TO-14 analytes. Of these, only one was observed above the 2-ppbv detection limit. The 10 organic analytes with the highest estimated concentrations are listed in Summary Table 1 and account for approximately 97% of the total organic components in Tank TY-101.

Summary Table 1. Summary Results of Inorganic and Organic Samples Collected from the Headspace of Tank TY-101 on 8/5/94

<u>Category</u>	<u>Analyte</u>	<u>Vapor^(a) Concentration</u>	<u>Units</u>
Inorganic	NH ₃	16 ± 1	ppmv
	NO ₂	≤ 0.05	ppmv
	NO	≤ 0.1	ppmv
	HCN	≤ 0.01	ppmv
	H ₂ O	9 ± 2	mg/L
Organic	3-Methylhexane	5.60	mg/m ³
	2-Methylhexane	3.74	mg/m ³
	2,3-Dimethylpentane	3.19	mg/m ³
	Methylcyclohexane	1.65	mg/m ³
	Heptane	1.52	mg/m ³
	3,3-Dimethylpentane	1.40	mg/m ³
	Unknown C ₇ Alkane	1.37	mg/m ³
	Toluene	0.73	mg/m ³
	1-Heptane	0.29	mg/m ³
	Unknown Alkane	0.28	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. Bruce Lerner performed method development and validation work that supported the inorganic vapor sampling. Sally Slate and May-Lin Thomas analyzed inorganic samples, and Annalisa Krupsha and Gary Dennis prepared the solid-sorbent sample trains. Brenda Thornton provided word processing support.

Abbreviations

CAS	Chemical Abstracts Service
COC	chain of custody
C _v	concentration by volume
DIW	deionized water
emf	electromotive force
EPA	U.S. Environmental Protection Agency
GC/MS	gas chromatography/mass spectrometry
HP	Hewlett Packard
IC	ion chromatography
IL	impact level
IS	internal standard
ISS	<i>in situ</i> sampling system
MDL	minimum detection limit
NIST	National Institute for Standards and Technology
OSHA	Occupational Safety and Health Administration
PFA	perfluoroalkoxy
PNL	Pacific Northwest Laboratory
ppbv	part per billion by volume
ppmv	part per million by volume
QA	quality assurance
REL	recommended exposure limit
SCIC	suppressed-conductivity ion chromatography
SIE	selective ion electrode
SRM	standard reference material
STP	standard temperature and pressure
TEA	triethanolamine
TIC	tentatively identified compound
WHC	Westinghouse Hanford Company

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1.0 Introduction

This report describes results of the analyses of tank-headspace *in situ* samples taken from the Hanford waste Tank 241-TY-101 (referred to as Tank TY-101). 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 the ambient air near the tank. The sample job was designated S4061, and samples were collected by WHC on August 5, 1994, using the *in situ* sampling system (ISS). While at WHC, the inorganic samples for two jobs were swapped before either tanks were sampled; consequently, although the sample job was S4061, the samples reported here are designated with identification numbers beginning with S4063.

Sampling devices, including six sorbent trains (for inorganic analyses), were supplied to WHC on August 3, 1994 and four SUMMA™ canisters (for organic analyses) were supplied on August 3, 1994. Samples were taken (by WHC) near or from the tank headspace on August 5 and were returned to PNL on August 23. Inorganic (sorbent trap) samples actually used to sample TY-101 were delivered to PNL on chain of custody (COCs) 007494 and 007370 (see Figure 1.1a, 1.1b, and 1.1c). The SUMMA™ canisters were delivered on COC 007489 (see Figure 1.1d). SUMMA™ canister sample No. S4061-----059 was sampled from ambient air collected ~ 10 m upwind of Tank TY-101.

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 canisters were stored in the 326/23B laboratory at ambient (25°C) temperature until the time of the analysis. Access to the 326/23B laboratory is limited to PNL personnel working on the waste-tank safety program. Analyses described in this report were performed at PNL in the 300 area of the Hanford Reservation. Analytical methods that were used are described in the text. In summary, sorbent traps for inorganic analyses containing sample materials were either weighed (for water analysis) or desorbed with the appropriate aqueous solutions (for NH_3 , NO_x , or HCN 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 007494
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Custody Form Initiator	J. A. Edwards	Telephone	(509) 373-0141
		Pager	85-3009

Company Contact	L. A. Pingel	Telephone	(509) 373-4051
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Project Designation/Sampling Locations 200 East Tank Farm	Collection Date 08 - 05 - 94
241-TY-104 Tank Vapor Sample SAF-S4063 S4061	Preparation Date 08 - 03 - 94
Ice Chest No. 101 ^{RDM} 2 FEB 95 (IN-SITU) ^{RDM} 2 FEB 95	Field Logbook No. WHC-N-7971

Bill of Lading/Airbill No.	N/A	Offsite Property No.	N/A
----------------------------	-----	----------------------	-----

Method of Shipment	Government Truck
--------------------	------------------

Shipped to	WHC
------------	-----

*See COC # 007370
for continuation*

Possible Sample Hazards/Remarks Unknown at time of sampling

Sample Identification			
	3 ^{RDM} 2 FEB 95		
S4062	--- .52W	NH ₃ /NO _x /H ₂ O (Sample #1)	^{RDM} 2 FEB 95 (Spare) ^{RDM} 2 FEB 95
S4062	--- .53W	NH ₃ /NO _x /H ₂ O (Sample #2)	(Set 2, Port 1)
S4062	--- .54W	NH ₃ /NO _x /H ₂ O (Sample #3)	(Set 2, Port 3)
S4062	--- .55W	HCN/H ₂ O (Sample #1)	^{RDM} 2 FEB 95 (Set 1, Port 2)
S4062	--- .56W	HCN/H ₂ O (Sample #2)	^{RDM} 2 FEB 95 (Set 1, Port 3)
S4062	--- .57W	HCN/H ₂ O (Sample #3)	(Spare)
S4062	--- .58W	OVS/Drier (Radiological survey)	(Set 1, Port 1)
S4062	--- .59W	NH ₃ /NO _x /H ₂ O (Spare)	^{RDM} 2 FEB 95 (Set 2, Port 2)
S4062	--- .60W	HCN/H ₂ O (Spare)	^{RDM} 2 FEB 95 (Set 1, Port 4)

[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>	08-03-94	1530	S. M. Brown <i>Thil Buehler</i>	08-03-94	1530
NP Buehler <i>NP Buehler</i>	8-5-94	0800	AG Rizz <i>AG Rizz</i>	8-5-94	0800
AG Rizz <i>AG Rizz</i>					

(version 02-28-94)

Final Sample Disposition

Disposal Method:

Disposed by:

Date/Time:

Comments

A-6000-407 (12/92) WEF061

Figure 1.1a Chain-of-Custody for Inorganic Samples

Figure 1.1b Chain-of-Custody for Inorganic Samples

Westinghouse Hanford Company		CHAIN OF CUSTODY/SAMPLE ANALYSIS REQUEST				Page <u>1</u> of <u>2</u>	
		007370					
Collector S.M. BROWN		Company Contact L.A. PINGEL		Telephone 373-4051			
SAF No. SAF# S4063 ^{SDM 2/28/95} 61		Project Designation 200-WEST TANK FARM 241-TY-104 ^{101 2/28/95} AM VAPOR SAMPLE		Sampling Locations 200/W 241-TY-104 TANK ^{101 RDM 2/28/95}			
Ice Chest No. N/A		Bill of Lading/Airbill No. N/A		Offsite Property No. N/A			
Method of Shipment GOV'T VEHICLE TRANSPORT				Field Logbook No. N/A			
Shipped to PNL				SPECIAL INSTRUCTION <div style="text-align: center; font-size: 1.2em;">ORIGINAL C.O.C # 007494</div>			
Possible Sample Hazards/Remarks None detected at time of sample.							
Special Handling and/or Storage Store at 4 DEG. C							
Sample Number	*	Date Collected	Time	Number and Type of Containers	Analysis Required	Preservative /	
S4063 .52W	V	8-05-94	1030	SAMPLE 1 SORBENT	VAPOR LAB SPECIFIC	Cool 4 DEG. C ^{1-2/28/95} Cool 4 Deg C	
S4063 .53W	V	8-05-94	1030	SAMPLE 2 SORBENT	VAPOR LAB SPECIFIC	Cool 4 DEG. C ^{2/28/95} Cool 4 Deg C	
S4063 .54W	V	8-05-94	1030	SAMPLE 3 SORBENT	VAPOR LAB SPECIFIC	Cool 4 DEG. C ^{ASST} Cool 4 Deg C	
S4063 .55W	V	8-05-94	1030	SAMPLE 1 SORBENT	VAPOR LAB SPECIFIC	Cool 4 DEG. C ^{ASST} Cool 4 Deg C	
S4063 .56W	V	8-05-94	1030	SAMPLE 2 SORBENT	VAPOR LAB SPECIFIC	Cool 4 DEG. C Cool 4 Deg C	
S4063 .57W	V	8-05-94	1030	SAMPLE 3 SORBENT	VAPOR LAB SPECIFIC	Cool 4 DEG. C Cool 4 Deg C	
S4063 .58W	V	8-05-94	1030	OVS/DRIER	VAPOR LAB SPECIFIC	Cool 4 DEG. C Cool 4 Deg C	
<i>Sub</i>		<i>8-23-94</i>				<i>Sub</i> <i>8/23/94</i>	

Chain of Possession Relinquished By		(Sign and Print Names)						*Matrix A = Air SE = Sediment DL = Drum Liquids SL = Sludge DS = Drum Solids SO = Solid L = Liquid T = Tissue O = Oil U = Water S = Soil VI = Wipe X = Other	
		Date	Time	Received By					
S.M. BROWN / <i>S.M. Brown</i>		8-23-94	1415	J.A. Edwards / <i>J.A. Edwards</i>		8/23-94			

Westinghouse Hanford Company		CHAIN OF CUSTODY/SAMPLE ANALYSIS REQUEST				Page <u>2</u> of <u>2</u>	
		007370					
Collector S.M. BROWN		Company Contact L.A. PINGEL ¹⁰¹		Telephone 373-4051		¹⁰¹	
SAF No. SAF# S4063- ⁵¹ 101 ^{2 FEB 95}		Project Designation 241-TY-104 TANK		Sampling Locations 200/W 241-TY-104 ¹⁰¹ ADN 2 FEB 95			
¹⁰¹ 2 FEB 95							

Sample Number	*	Date Collected	Time	Number and Type of Containers	Analysis Required	Preservative
S4063 .59	V	8-05-94	1030	SPARE	VAPOR LAB SPECIFIC	COOL 4 DEG. C
S4063 .60	V	8-05-94	1030	SPARE	VAPOR LAB SPECIFIC	COOL 4 DEG. C

Chain of Possession Relinquished By		(Sign and Print Names) Date				Time	Received By	
S.M. BROWN	<i>[Signature]</i>	8-23-94	1415	L.A. Edwards	A. Edwards	8-23-94		

LABORATORY SECTION	Received By	Title	Date/Time
Final Sample Disposition	Disposal Method:	Disposed by:	Date/Time:

Figure 1.1c Chain-of-Custody for Inorganic Samples

Westinghouse Hanford Company	CHAIN OF CUSTODY	WIIC 007489
---------------------------------	------------------	-------------

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-TY-101 Tank Vapor Sample SAF S4061
Ice Chest No. (IN-SITU)

Collection Date 08 - - - 94
Preparation Date 08 - 04 - 94
Field Logbook No. WHC-N-771-__

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

S4061 - ____ .059 (PNL) SUMMA Ambient Air

S4061 - ____ .025 (PNL) SUMMA Sample #1

S4061 - ____ .040 (PNL) SUMMA Sample #2

S4061 - ____ .057 (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>	08-04-94	1215	N. Buechler <i>N. Buechler</i>	08-04-94	1215		
<i>N. Buechler</i>	8-4-94	1245	<i>A.G. Rizzo</i>	8-5-94			
<i>A.G. Rizzo</i>							

(version 02-28-94)

Final Sample Disposition

Disposal Method:

Disposed by:

Date/Time:

Comments

A-6000-407 (12/92) WEF061

Figure 1.1d Chain-of-Custody for Organic Samples

2.0 Inorganic

Solid sorbent traps, prepared in sampling trains, were supplied to WHC for sampling the tank headspace. 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), hydrogen cyanide (HCN), 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). 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 sorbent traps consisting of glass tubes containing sorbent materials to trap the analytes of NH_3 , NO_2 , NO , HCN , 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 sections: the first section was the primary trap, and the second section provided an indication of breakthrough. In the tubes, sorbent sections are generally held in packed layers separated by glass wool. The 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 selected for the tank sample job 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 HCN traps contained soda lime, with 600 mg in the primary and 200 mg in the breakthrough sections. The water traps contained 300 mg of silica gel in the primary and 150 mg in the breakthrough sorbent sections.

Sample materials for inorganic analytes include some or all of the following: samples, spiked samples, spares, blanks, and spiked blanks. The samples of each type were prepared from same-lot batches, with the oxidizer sections of the NO_x sorbent trains having been stored previously in a freezer. After sample preparation, all samples, spiked samples, blanks, and spiked blanks were stored at $\leq 10^\circ\text{C}$. After receipt of exposed and radiologically cleared samples from WHC and disassembly of the sorbent trains, samples were provided to the analytical laboratory at ambient temperature, and selected oxidizer sections were returned to a freezer until completion of analysis.

The sorbent traps were prepared in multi-trap sorbent trains configured so sample flow passed in order through the traps, targeting specific analytes, and then through a desiccant trap. The specific

order of traps within the various sorbent trains is described in Section 2.4. The ends of the glass-tube traps were broken, and the traps were weighed and then connected to each other using uniform lengths of 3/8-in. perfluoroalkoxy (PFA)-grade Teflon® tubing. The tubing was heated in hot air and forced over the open ends of the traps to form a tight seal. Both the inlet and outlet 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 leading and trailing ends of the sorbent traps 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 compound 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 the conditions used by WHC: 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 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 herein and 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 Cyanide Analysis. The HCN samples were desorbed in 3.0 mL of 0.02 N sodium hydroxide and analyzed by amperometric detection IC according to PNL-ALO-271 (*Procedure for Analysis of Free Cyanide in Water and Soil Sample Leachates*). Calibration standards, typically 0, 20, 50, and 100 ng/mL (ppb) CN^- , were prepared from a stock 1000-ppm CN^- standard on the day of sample analysis in a 0.02 N NaOH matrix. The same analysis sequence described above in the "nitrite analysis" section was used. Instrument responses (peak height) observed for the samples were compared to those for standards to determine the CN^- concentration of the samples.

2.2.4 Mass (Water) Analysis. Sorbent traps used to make each sample train were weighed using a semi-micro mass balance after labeling and breaking the glass tube ends, without plastic end caps. After receipt of exposed samples, the sorbent traps were again weighed to determine the change in mass. Records of the measurements were documented on sample-preparation data sheets. The mass concentration, presumed to be dominated by water vapors, 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 QA 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 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
Hydrogen cyanide	HCN	PNL-ALO-271	4.8	0.48	0.01
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 (see Section 2.4.1). Sampling information, including sample volumes was provided by WHC; sample volume uncertainty was not provided. The accuracy of analytical results depends on the method used. For NH₃ analyses, the accuracy of laboratory measurements by SIE was estimated to be $\pm 5\%$ relative, independent of concentration at 1 $\mu\text{g/mL}$ or greater levels. The uncertainty includes preparation of standards, purity of the ammonium salt used to prepare standards, potential operator bias, ambient temperature variations, etc. Unfortunately, no known National Institute for Standards and Technology (NIST)-traceable standard reference material (SRM) is available against which to compare working standards. As for NH₃, no known NIST SRM is available for nitrite analysis (for NO₂ and NO). Based on experience in comparing nitrite working standards prepared from several different sources and factors mentioned for NH₃ above, the estimated maximum bias for samples derived from sampling for NO₂ is $\pm 10\%$, and for samples derived from sampling for NO, it is $\pm 5\%$ relative. For HCN analyses, an NIST SRM for uncomplexed cyanide is not available. The estimated bias (accuracy) of the free cyanide measurements is no more than 5% relative for the normal working range (which encompasses the concentration levels encountered in blanks and samples

derived from the sorbent-trap leachates). 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

Sorbent-trap trains and controls were prepared on 8/2/94, submitted to WHC on 8/3/94, and used by WHC to sample the headspace of Tank TY-101 on 8/5/94 using the ISS. The sample job designation number was S0461. The exposed samples were returned to PNL on 8/23/94 and subsequently analyzed on 8/25/94 (H_2O), 9/9/94 (NH_3), 9/15/94 (NO_x), and 9/6/94 (HCN) to provide information on the tank-headspace concentrations of selected inorganic compounds. Sampling and analysis for SO_x were not requested. The sample-volume information was received from WHC on 11/15/94.

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 each set of samples were nearly indistinguishable from those of blanks, indicating very low tank-headspace 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-headspace gas. Sample results were not corrected for the percentage recoveries of spiked blanks.

2.4.1 Ammonia Results. The concentration of NH_3 was 16 ± 1 ppmv, based on all three samples. The NH_3 quantities found in the sorbent traps ranged from 2.6 to 2.7 μmol with no indication of breakthrough. Blank corrections, ≤ 0.06 μmol in front and ≤ 0.03 μmol in back sorbent sections (Clauss et al. 1994), were not significant ($< 2\%$) 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 NH_3 were $101 \pm 4\%$, $109 \pm 2\%$, and $104 \pm 1\%$, respectively, during related sample jobs (Clauss et al. 1994; Ligothke et al. 1994). No samples were analyzed to check repeatability. No sample leachates were spiked after initial analysis to determine recovery. 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

Table 2.2 List of PNL Inorganic Samples, Blanks, and Gravimetric Results From *In Situ* Sampling of the Headspace of Tank TY-101 on 8/5/94

<u>Sample Number</u>	<u>Sorbent Train Type</u>	<u>Sample Flow Rate (mL/min)</u>	<u>Duration (min)</u>	<u>Sample Volume^(a) (L)</u>	<u>Mass Gain (g)</u>
S4063-063-59W ^(b)	NH ₃ /NO _x /H ₂ O Sample	271	15.0	3.73	0.0363
S4063-063-53W	NH ₃ /NO _x /H ₂ O Sample	265	15.0	3.98	0.0435
S4063-063-54W	NH ₃ /NO _x /H ₂ O Sample	288	15.0	4.32	0.0394
S4063-063-52W	NH ₃ /NO _x /H ₂ O Blank/Spare	n/a ^(c)	n/a	n/a	-0.0010
S4063-063-55W	HCN/H ₂ O Sample	199	14.0 ^(d)	2.8	0.312
S4063-063-56W	HCN/H ₂ O Sample	211	14.0	3.0	0.245
S4063-063-60W	HCN/H ₂ O Sample	306	14.0	4.3	0.412
S4063-063-57W	HCN/H ₂ O Blank/Spare	n/a	n/a	n/a	0.000

(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) Samples sent for TY-104 were used by WHC for TY-101. Consequently, sample identification numbers "S4063..." differ from the tank sample job number "S4061." Also, because WHC used both of the "blank/spare" sorbent trains for the samples, they were assigned to be "samples," and the unused samples were assigned to be the "blank/spare" sorbent trains for this analysis.

(c) n/a = not applicable.

(d) WHC-reported sample durations for HCN/H₂O samples was "14 to 15.5 min." For the samples, a duration of 14 min was selected for the determination of HCN concentration to be conservative.

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 ≤ 0.05 and ≤ 0.1 ppmv, respectively. Blank-corrected NO₂⁻ quantities in the sorbent traps averaged ≤ 0.004 μmol (NO₂ samples) and ≤ 0.010 μmol (NO samples). Nitrite blank levels used to correct data were 0.0156 ± 0.0022 μmol in front and 0.0080 ± 0.0009 μmol in back sorbent sections and were based on 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 μmol NO₂⁻ during a related sample job yielded percentage recoveries of $153 \pm 14\%$, $103 \pm 4\%$, $106 \pm 8\%$, and $111 \pm 7\%$, respectively (Clauss et al. 1994; Ligothke et al.). No samples were reanalyzed to check repeatability. No sample leachates were spiked after initial analysis with quantities of NO₂⁻ to test analytical percentage recoveries. A 4-point calibration was performed over a concentration range of 0 to 0.5 μg NO₂⁻ per mL in the desorbing matrix.

Table 2.3 Inorganic Vapor Sample Results Obtained From *In Situ* Samples Inserted into the Headspace of Tank TY-101 on 8/5/94

Sample	Analytical Results (μmol)			Sample Volume (L)	Vapor ^(a) Concentration (ppmv)
	Front Section	Back Section	Total ^(b) Blank-Corrected		
<u>NH₃ Samples:</u>			<u>2.7^(c)</u>	<u>4.12^(c)</u>	<u>16 $\pm$ 1^(c)</u>
S4063-063-59W	2.7	NA ^(d)	2.7	4.06	16
S4063-063-53W	2.6	NA	2.6	3.98	16
S4063-063-54W	2.7	≤ 0.03	2.7	4.32	15
<u>NO₂ Samples:</u>			<u>≤ 0.004</u>	<u>4.12</u>	<u>≤ 0.05</u>
S4063-063-59W	0.0168	0.0069	n/a ^(d)	4.06	n/a
S4063-063-53W	0.0140	0.0085	n/a	3.98	n/a
S4063-063-54W	0.0160	0.0075	n/a	4.32	n/a
<u>NO Samples:</u>			<u>≤ 0.01</u>	<u>4.12</u>	<u>≤ 0.1</u>
S4063-063-59W	0.0217	0.0083	n/a	4.06	n/a
S4063-063-53W	0.0183	0.0082	n/a	3.98	n/a
S4063-063-54W	0.0217	0.0078	n/a	4.32	n/a
<u>HCN Samples:</u>			<u>≤ 0.001</u>	<u>3.4 - 3.7</u>	<u>≤ 0.01</u>
S4056-A25-55W	0.0108	0.0043	n/a	2.8 - 3.1	n/a
S4056-A26-56W	0.0127	0.0043	n/a	3.0 - 3.3	n/a
S4056-A27-60W	0.0119	0.0039	n/a	4.3 - 4.7	n/a
<u>Gravimetric Samples (mg,mg/L):</u>			<u>38 mg</u>	<u>4.12</u>	<u>9 $\pm$ 2 mg/L</u>
S4063-063-59W	n/a	n/a	34	4.06	8.4
S4063-063-53W	n/a	n/a	42	3.98	10.6
S4063-063-54W	n/a	n/a	37	4.32	8.6
			<u>30 mg</u>	<u>3.4 - 3.7</u>	<u>7 - 10 mg/L</u>
S4063-063-55W	n/a	n/a	29	2.8 - 3.1	9 - 10
S4063-063-56W	n/a	n/a	22	3.0 - 3.3	~ 7
S4063-063-60W	n/a	n/a	39	4.3 - 4.7	8 - 9

(a) Blank-corrected vapor concentrations were calculated using WHC-reported 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 were determined, when significant, by subtracting the quantity of analyte found in blanks from that found in samples. The levels of analytes found in blanks are described in the subsections of Section 2.4.

(c) Underlined values represent the average of the set of samples. Concentrations uncertainty equals ± 1 standard deviation (absolute) for each set of samples. The uncertainty in mass concentration was determined based on the added uncertainty caused by the range of six related blanks. The use of " $\leq$ " is defined in Section 2.4.

(d) NA = not analyzed. Only selected back sorbent sections were analyzed. n/a = not applicable.

2.4.3 Hydrogen Cyanide Results. The concentration of HCN was estimated to be ≤ 0.01 ppmv. The samples contained $0.0118 \pm 0.0010 \mu\text{mol}$ in front and $0.0042 \pm 0.0002 \mu\text{mol}$ CN⁻ in back sections. The blank contained $0.0114 \mu\text{mol}$ in the front and $0.0047 \mu\text{mol}$ CN⁻ for the back section. Blanks spiked with $0.0099 \pm 0.0001 \mu\text{mol}$ CN⁻ were found previously to yield (ISS sample job

BY-111) an average blank-corrected percentage recovery of $69 \pm 10\%$ after a hold time of 11 weeks. It is possible that the poor spike recovery was related to the relatively long hold time. No samples were reanalyzed to check repeatability. No sample leachates were spiked after initial analysis with quantities of CN^- to test analytical percentage recoveries.

2.4.4 Gravimetric Results. The mass concentration of material collected in the sorbent-trap trains, believed to be primarily water vapor, was $9 \pm 2 \text{ mg/L}$. The result was based on an average mass gain of 38 mg from all three of three sets of $\text{NH}_3/\text{NO}_x/\text{H}_2\text{O}$ 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 range 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 three blank H_2O traps spiked with 51 mg of water was $103 \pm 2\%$ during a related sample job (Clauss et al. 1994).

3.0 Organic

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 clean, free of TO-14 contaminants to a level of 5 parts per billion by volume (ppbv), the canister is evacuated to 5 mtorr, tagged, and stored for use in the field. Before sending the canisters out to the field for sampling, the canisters 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 samples were 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.

3.3 Quality Assurance/Quality Control

Before the SUMMA™ tank samples were analyzed, a diagnostic check was performed on the GC/MS instrument by running an instrument "quick tune," as described in PNL-TVP-03. Upon satisfactory completion of the instrument diagnostic check, a blank volume of purified nitrogen was analyzed to check the cleanliness of the system. The instrument was then calibrated over six data points ranging from 2 ppbv to 300 ppbv, using a standard gas mixture containing 40 volatile organic compounds listed in EPA compendium Method TO-14. A gas mixture containing

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- (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.

bromochloromethane, 1,4-difluorobenzene, and chlorobenzene- d_5 was used as an internal standard (IS) for all blank, calibration standard, and sample analyses. Analyte responses from sample components, ISs, and standards were obtained from the extracted ion plot from their selected mass ion. The calibration curve was generated by calculating the relative response ratios of the IS to calibration standard responses and plotting the ratios against the ratio of the calibration-standard concentration (in ppbv) to the IS concentration. A least-squares linear-regression routine was applied to the data set to generate the best-fit line for each compound. The equation for that line was then used to quantify the TO-14 compounds found in the tank samples.

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

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

3.3.2 Identification and Quantitation of Tentatively Identified Compounds. The tentatively identified compounds (TICs) are determined by mass-spectral interpretation and comparison of the spectra with the EPA/NIST/WILEY Library, which is a part of the HP 5971/5972 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 peak at the 100-ppbv calibration level 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/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.

The ppbv concentrations are calculated from mg/m^3 and the molecular weight of the analyte.

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

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

(a) Nominal molecular weight.

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. Only compounds found to be higher than the instrumental detection limits in two or more SUMMA™ canisters were considered to be present in the headspace. A representative total ion chromatogram showing the identity of major constituents is given in Figure 3.1.

Table 3.1 lists the quantitative results for compounds listed in Method TO-14. Two compounds, methybenzene (toluene) and trichlorofluoromethane, were found to be higher than the instrumental detection limit with average concentrations of 0.73 and 0.16 mg/m³, respectively. No TO-14 analytes were found in the canister containing ambient air.

Table 3.2 lists the semiquantitative results for the TICs observed in the samples. Twenty compounds were observed above the instrumental detection limit, a total air concentration of 19.02 mg/m³ based on the average of three samples. The analyte with the highest concentration was 3-methlyhexane at 5.60 mg/m³, which represents about one third of the TIC compounds. No TIC analytes were found in the canister containing ambient air.

4.0 Conclusions

The concentrations of selected inorganic and organic compounds were determined from *in situ* samples of the headspace of Tank C-101. Sample preparation and analysis methods were similar to those described by Ligothke et al. (1994) for VSS samples obtained from Tank 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 16 ± 1 ppmv. The concentration of NO_2 was ≤ 0.05 ppmv. The concentration of NO was ≤ 0.1 ppmv. The concentration of HCN was estimated to be ≤ 0.01 ppmv. The mass concentration was 9 ± 2 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 (Section 2.3) in subsequent sample jobs.

Two TO-14 compounds (methybenzene and trichlorofluoromethane) and 20 TIC compounds were found above the 10-ppbv reporting cutoff, with methybenzene at the highest concentration. Methybenzene, the TICs, and the methylated pentanes and hexanes are gasoline-range organics.

5.0 References

Clauss, T. W., M. W. Ligothke, B. D. McVeety, K. H. Pool, R. B. Lucke, J. S. Fruchter, and S. C. Goheen. 1994. *Vapor Space Characterization of Waste Tank 241-by-104: Results from Samples Collected on 6/24/94*. PNL-10208. Pacific Northwest Laboratory, Richland, Washington.

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)*. PNL-10172, 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 TO-14 Analysis of Ambient Air Samples Collected Near Tank TY-101 and from the Headspace of Tank TY-101 from SUMMA™ Canisters on 8/5/94

TO-14 Analyte	CAS No.	Mol Wt	Ambient Air		S4061 —.025 ^(a)		S4061 —.040 ^(a)		S4061 —.057 ^(a)		Headspace Samples	
			PNL 059 ^(b)	Concentration (mg/m ³) (ppbv)	PNL 025 ^(b)	Concentration (mg/m ³) (ppbv)	PNL 040 ^(b)	Concentration (mg/m ³) (ppbv)	PNL 057 ^(b)	Concentration (mg/m ³) (ppbv)	Means and Standard Deviations (mg/m ³)	St Dev
Dichlorodifluoromethane	75-71-8	120	<0.01	<2	<0.01	<2	<0.01	<2	<0.01	<2	(c)	(c)
Methyl Chloride (Chloromethane)	74-87-3	50	<0.01	<2	<0.01	<2	<0.01	<2	<0.01	<2	(c)	(c)
1,2-Dichloro-1,1,2,2-Tetrafluoroethane	76-14-2	170	<0.02	<2	<0.02	<2	<0.02	<2	<0.02	<2	(c)	(c)
Chloroethene (Vinyl Chloride)	75-01-4	64	<0.01	<2	<0.01	<2	<0.01	<2	<0.01	<2	(c)	(c)
Methyl Bromide (Bromomethane)	74-83-9	94	<0.01	<2	<0.01	<2	<0.01	<2	<0.01	<2	(c)	(c)
Ethyl Chloride	75-00-3	62	<0.01	<2	<0.01	<2	<0.01	<2	<0.01	<2	(c)	(c)
Trichlorofluoromethane	75-69-4	136	<0.01	<2	0.16	26.4	0.16	26.4	0.16	26.4	0.16	0.00
1,1-Dichloroethene	75-35-4	96	<0.01	<2	<0.01	<2	<0.01	<2	<0.01	<2	(c)	(c)
Dichloromethane	75-09-2	84	<0.01	<2	<0.01	<2	<0.01	<2	<0.01	<2	(c)	(c)
1,1,2-Trichloro-1,2,2-Trifluoroethane	76-13-1	186	<0.02	<2	<0.02	<2	<0.02	<2	<0.02	<2	(c)	(c)
1,1-Dichloroethane	75-34-3	98	<0.01	<2	<0.01	<2	<0.01	<2	<0.01	<2	(c)	(c)
cis-1,2-Dichloroethene	156-59-2	96	<0.01	<2	<0.01	<2	<0.01	<2	<0.01	<2	(c)	(c)
Trichloromethane (Chloroform)	67-66-3	118	<0.01	<2	<0.01	<2	<0.01	<2	<0.01	<2	(c)	(c)
1,2-Dichloroethane	107-06-2	98	<0.01	<2	<0.01	<2	<0.01	<2	<0.01	<2	(c)	(c)
1,1,1-Trichloroethane	71-55-6	132	<0.01	<2	<0.01	<2	<0.01	<2	<0.01	<2	(c)	(c)
Benzene	71-43-2	78	<0.01	<2	<0.01	<2	<0.01	<2	<0.01	<2	(c)	(c)
Carbon Tetrachloride	56-23-5	152	<0.01	<2	<0.01	<2	<0.01	<2	<0.01	<2	(c)	(c)
1,2-Dichloropropane	78-87-5	112	<0.01	<2	<0.01	<2	<0.01	<2	<0.01	<2	(c)	(c)
Trichloroethylene	79-01-6	130	<0.01	<2	<0.01	<2	<0.01	<2	<0.01	<2	(c)	(c)
cis 1,3-Dichloropropene	10061-01-5	110	<0.01	<2	<0.01	<2	<0.01	<2	<0.01	<2	(c)	(c)
trans 1,3-Dichloropropene	10061-02-6	110	<0.01	<2	<0.01	<2	<0.01	<2	<0.01	<2	(c)	(c)
1,1,2-Trichloroethane	79-00-5	132	<0.01	<2	<0.01	<2	<0.01	<2	<0.01	<2	(c)	(c)
Methyl Benzene (Toluene)	108-88-3	92	<0.01	<2	0.47	114	0.96	234	0.93	226	0.79	0.27
1,2-Dibromoethane	106-93-4	186	<0.02	<2	<0.02	<2	<0.02	<2	<0.02	<2	(c)	(c)
Tetrachloroethene (Perchloroethylene)	127-18-4	164	<0.02	<2	<0.02	<2	<0.02	<2	<0.02	<2	(c)	(c)
Chlorobenzene	108-90-7	112	<0.01	<2	<0.01	<2	<0.01	<2	<0.01	<2	(c)	(c)
Ethylbenzene	100-41-4	106	<0.01	<2	<0.01	<2	<0.01	<2	<0.01	<2	(c)	(c)
m-Xylene (1,3-Dimethylbenzene) ^(d)	108-38-3	106	<0.01	<2	<0.01	<2	<0.01	<2	<0.01	<2	(c)	(c)
p-Xylene (1,4-Dimethylbenzene) ^(d)	106-42-3	106	<0.01	<2	<0.01	<2	<0.01	<2	<0.01	<2	(c)	(c)
Styrene	100-42-5	104	<0.01	<2	<0.01	<2	<0.01	<2	<0.01	<2	(c)	(c)
1,1,2,2-Tetrachloroethane	79-34-5	166	<0.02	<2	<0.02	<2	<0.02	<2	<0.02	<2	(c)	(c)
o-Xylene (1,2-Dimethylbenzene)	95-47-6	106	<0.01	<2	<0.01	<2	<0.01	<2	<0.01	<2	(c)	(c)

Table 3.1 (Contd)

TO-14 Analyte	CAS No.	Mol Wt	Ambient Air		S4061—.059 ^(a)		S4061—.025 ^(a)		S4061—.040 ^(a)		S4061—.057 ^(a)		Headspace Samples	
			S4061—.059 ^(b)		PNL 059 ^(b)		PNL 025 ^(b)		PNL 040 ^(b)		PNL 057 ^(b)		Means and	
			Concentration		Concentration		Concentration		Concentration		Concentration		Standard Deviations	
			(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)	(mg/m ³)	St Dev
1,3,5-Trimethylbenzene	108-67-8	120	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
1,2,4-Trimethylbenzene	95-63-6	120	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
Chloromethylbenzene, alpha (Benzyl Chl	100-44-7	126	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
m-Dichlorobenzene (1,3-Dichlorobenzene	541-73-1	146	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
p-Dichlorobenzene (1,4-Dichlorobenzene)	106-46-7	146	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
o-Dichlorobenzene (1,2-Dichlorobenzene)	95-50-1	146	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
1,2,4-Trichlorobenzene	120-82-1	180	< 0.02	< 2	< 0.02	< 2	< 0.02	< 2	< 0.02	< 2	< 0.02	< 2	(c)	(c)
Hexachloro-1,3-Butadiene	87-68-3	258	< 0.02	< 2	< 0.02	< 2	< 0.02	< 2	< 0.02	< 2	< 0.02	< 2	(c)	(c)

(a) WHC sample identification number.

(b) PNL canister number.

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

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

Table 3.2 Tentatively Identified Compounds and Estimated Concentrations^(a) in Headspace of Tank TY-101 from *In Situ* SUMMATM Canister Samples Collected on 8/5/94.

Tentatively Identified Compound ^(d)	C.A.S.No. ^(d)	Mol. Wt.	Ret. Time	S4061----,025 ^(b)		S4061----,040 ^(b)		S4061---,057 ^(b)		Means and Standard Deviations			
				PNL, 025 ^(c)	(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)	(mg/m ³)	(mg/m ³)	St Dev	(ppbv)	St Dev
Carbonyl sulfide	463-58-1	60	3.99	< 0.03	0.07	< 10.0	26.1	< 0.03	< 10.0	0.11	0.08	26.1	39.6
Acetaldehyde	75-07-0	44	5.325	0.168	0.058	85.5	29.5	< 0.02	< 10.0	0.27	0.02	57.5	6.2
Acetone	67-64-1	58	8.507	0.264	0.283	102.0	109.3	0.251	96.9	0.12	0.03	102.7	7.8
2-Butanone	78-93-3	72	13.61	0.092	0.142	28.6	44.2	0.12	37.3	0.06	0.01	36.7	(e)
Unknown Alkane			13.96		0.068	(f)	(f)	0.056	(f)	0.23	0.05	(e)	(e)
Unknown Alkane			16.31	0.184	0.279	(f)	(f)	0.216	(f)	0.28	0.06	(e)	(e)
Unknown Alkane			16.62	0.219	0.341	(f)	(f)	0.281	(f)	0.09	0.02	(e)	(e)
Unknown Alkane			17.08	0.071	0.108	(f)	(f)	0.086	(f)	1.40	0.29	313.8	65.6
3,3-dimethylpentane	562-49-2	100	18.22	1.108	1.694	248.2	379.5	1.401	313.8	3.74	0.73	838.4	163.2
2-Methylhexane	591-76-4	100	18.76	2.966	4.411	664.4	988.1	3.852	862.8	3.19	0.62	713.6	138.2
2,3-Dimethylpentane	565-59-3	100	18.98	2.531	566.9	566.9	841.3	3.27	732.5	5.60	0.94	1254.5	210.5
3-Methylhexane	589-34-4	100	19.3	4.576	1025.0	1025.0	1438.8	5.802	1299.6	1.37	0.30	307.4	67.6
Unknown C7 Alkane		100	19.91	1.046	234.3	367.6	1.43	320.3	0.29	0.07	66.5	15.4	
1-Heptene	592-76-7	98	20.18	0.22	50.3	80.9	0.354	0.299	68.3	1.52	0.36	339.7	81.2
Heptane	142-82-5	100	20.61	1.107	248.0	402.3	1.796	1.646	368.7	0.10	0.02	(e)	(e)
Unknown Alkane			21.91	0.074	(f)	(f)	(f)	0.104	(f)	1.65	0.39	376.2	88.6
Methylcyclohexane	108-87-2	98	22.19	1.21	276.6	446.2	1.952	1.776	405.9	0.10	0.03	19.8	5.2
Unknown C8 Alkane		114	22.58	0.072	14.1	24.4	0.124	0.107	21.0	0.25	0.17	30.1	20.2
Tridecane	629-50-5	184	48.07	0.434	52.8	23.1	0.19	0.117	14.2	0.26	0.14	29.6	16.2
Tetradecane	629-59-4	198	51.59	0.389	44.0	32.6	0.288	0.107	12.1				

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

Figure 3.1a Total Ion Chromatogram (2 - 30 min) for Hanford Waste Tank TY-101
In Situ SUMMA™ Canister Sample S4061—025 Collected on 8/6/94

Figure 3.1b Total Ion Chromatogram (30 - 58 min) for Hanford Waste Tank TY-101
In Situ SUMMA™ Canister Sample S4061—025 Collected on 8/6/94

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