**Vapor Space Characterization of Waste
Tank 241-BY-109 (*In Situ*): Results from
Samples Collected on 9/22/94**

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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-BY-109 (referred to as Tank BY-109). 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), and water (H₂O). Sampling for hydrogen cyanide (HCN) and sulfur oxides (SO_x) was not requested. Organic compounds were also quantitatively determined. Twenty-three organic tentatively identified compounds (TICs) were observed above the detection limit of (ca.) 10 ppbv, but standards for most of these were not available at the time of analysis, and the reported concentrations are semiquantitative estimates. In addition, we looked for the 40 standard TO-14 analytes. We observed 38. Of these, only a few were observed above the 2-ppbv calibrated instrument detection limit. The ten organic analytes with the highest estimated concentrations are listed in Summary Table 1. The ten analytes account for approximately 84% of the total organic components in Tank BY-109.

Summary Table 1. Summary Results of Inorganic and Organic Samples Collected from the Headspace of Tank BY-109 on 9/22/94

Category	Analyte	Vapor ^(a) Concentration	Units
Inorganic	NH ₃	46 ± 2	ppmv
	NO ₂	≤ 0.03	ppmv
	NO	≤ 0.04	ppmv
	H ₂ O	15 ± 1	mg/L
Organic	Tridecane	2.62	mg/m ³
	Dodecane	2.49	mg/m ³
	Toluene	2.08	mg/m ³
	Undecane	1.76	mg/m ³
	1-Butanol	1.16	mg/m ³
	Decane	0.565	mg/m ³
	Acetone	0.497	mg/m ³
	Trichlorotrifluoromethane	0.218	mg/m ³
	Nonane	0.204	mg/m ³
	Octane	0.178	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 and May-Lin Thomas analyzed inorganic samples, and Gary Dennis prepared the solid-sorbent sample trains. Georgia K. Ruebsamen 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
NPH	normal paraffin hydrocarbon
OSHA	Occupational Safety and Health Administration
PFA	perfluoroalkoxy
PNL	Pacific Northwest Laboratory
ppbv	part per billion by volume
ppmv	part per million by volume
QA	quality assurance
REL	recommended exposure limit
SCIC	suppressed-conductivity ion chromatography
SIE	selective ion electrode
SRM	standard reference material
STP	standard temperature and pressure
TEA	triethanolamine
TIC	tentatively identified compound
VSS	vapor sampling system
WHC	Westinghouse Hanford Company

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1.0 Introduction

This report describes results of the analyses of *in situ* samples taken from the headspace of the Hanford waste Tank 241-BY-109 (referred to as Tank BY-109). 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. The sample job was designated S4071, and samples were collected by WHC on September 22, 1994, using the *in situ* sampling system (ISS).

Sampling devices, including four sorbent trains (for inorganic analyses), were supplied to WHC on August 31, 1994. Four SUMMATM canisters (for organic analyses) were supplied to the WHC sampling staff on August 29. Samples were taken (by WHC) from the tank headspace on September 22 and were returned to PNL from the field on September 26. Inorganic (sorbent trap) samples were delivered to PNL on chain of custody (COC) 007522 (see Figure 1.1a). The SUMMATM canisters were delivered on COC No. 007521 (see Figure 1.1b). SUMMATM canister sample No. S4071-----209 was sampled from ambient air near the tank. The canister was analyzed, and results are described in Table 3.3.

The samples were inspected upon delivery to the 326/23B laboratory and logged into PNL record book 55408 before implementation of PNL Technical Procedure PNL-TVP-07^(b). Custody of the sorbent traps was transferred to PNL personnel performing the inorganic analysis and stored at refrigerated ($\leq 10^{\circ}\text{C}$) temperature until the time of analysis. The canister was stored in the 326/23B laboratory at ambient (25°C) temperature until 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 desorbed with the appropriate aqueous solutions (for NH_3 or NO_x 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).

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- (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 007522
---	-------------------------	-------------------

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-BY-109 Tank Vapor Sample SAF S4071
 Ice Chest No. (IN-SITU)

Collection Date 09 - 22 - 94 22 / 24 / 94
 Preparation Date 08 - 31 - 94
 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

S4071 -	---	.31V-	NH ₃ /NO _x /H ₂ O (Sample #1)
S4071 -	---	.32V-	NH ₃ /NO _x /H ₂ O (Sample #2)
S4071 -	---	.33V-	NH ₃ /NO _x /H ₂ O (Sample #3)
S4071 -	---	.34V-	NH ₃ /NO _x /H ₂ O (Spare)

S4071 - 35V - OVS/Drier (Radiological survey) 22 09/26/94

[X] Field Transfer of Custody			Chain of Possession (Sign and Print Names)		
Relinquished By	Date	Time	Received By	Date	Time
J. A. Edwards	08-31-94	1245	Shannon Spencer	08-31-94	1245
Shannon L. Spencer	08-31-94	1445	Shannon L. Spencer	08-31-94	1445
Shannon L. Spencer	09-22-94	1000	Shannon L. Spencer	09-22-94	1000
Shannon L. Spencer	09-22-94	1140	Shannon L. Spencer	09-22-94	1140
Shannon L. Spencer	09-27-94	1145	Shannon L. Spencer	09-27-94	1145

(version 02-28-94)

Final Sample Disposition

Disposal Method:

Disposed by:

Date/Time:

Comments NO RAD - RELEASE, NO TAMPER TAPE ON PACKAGE. ACTIVITY REPORT OK 22
 A-6000-407 (12/92) WEP061

Figure 1.1a Chain-of-Custody for Inorganic Samples from Tank BY-109

Westinghouse Hanford Company	CHAIN OF CUSTODY	WHC 007521
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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
-----------------	--------------	-----------	----------------

Project Designation/Sampling Locations 200 East Tank Farm
 241-BY-109 Tank Vapor Sample SAF S4071
 Ice Chest No. (IN-SITU)

Collection Date 09-22-94 (16) 9/26
 Preparation Date 08-29-94
 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

S4071 - - - - .209 ✓	(PNL) SUMMA Ambient Air
S4071 - - - - .210 ✓	(PNL) SUMMA Sample #1
S4071 - - - - .211 ✓	(PNL) SUMMA Sample #2
S4071 - - - - .212 ✓	(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>[Signature]</i>	08-29-94	1400	Tim Utecht <i>[Signature]</i>	08-29-94	1400			
T. B. Utecht <i>[Signature]</i>	09-26-94	1300	J. A. Edwards <i>[Signature]</i>	09-26-94	1400			

(version 02-28-94)

Final Sample Disposition

Disposal Method:

1b Organic

Disposed by:

Date/Time:

Comments TAMPER TAPE ON MAIN BOX, NO RAD-RELEASE TAPE (P)
 A-6000-407 (12/92) WEP061 ACTIVITY REPORT (OK)

Figure 1.1b Chain-of-Custody for Organic Samples from Tank BY-109

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), and water (H_2O). Procedures were similar to those developed previously during sample jobs performed with the vapor sampling system (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 , 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 received from the vendor having glass sealed ends. 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 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 a temperature of $\leq 10^\circ\text{C}$. 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 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 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 ammonia 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 ammonia-selective sorbent traps was placed into labeled 20-mL glass scintillation vials. Vials containing front-, or primary-, section sorbent material were treated with 10.0 mL of deionized water (DIW), and vials containing back-up-section sorbent material were treated with 5.0 mL of DIW. After extraction, the NH_3 sorbent traps were analyzed using the selective ion electrode (SIE) procedure PNL-ALO-226 {Ammonia (Nitrogen) in Aqueous Samples}. Briefly, this method includes 1) preparing a 1000- $\mu\text{g/mL}$ (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 ammonia concentration in the samples.

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

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

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

2.2.3 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 included to provide information on uncertainty.

2.3 Quality Assurance/Quality Control

Analytical work was performed according to quality levels identified in the project QA plan and several PNL documents. The samples were analyzed following PNL IL III. The PNL documents include some or all of the following: 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

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

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 ^(d)	n/a	n/a	n/a	n/a

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

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

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

(d) n/a = not applicable

each of the target analytes is achieved using current procedures and with a vapor-sample volume of 3 L and a desorption-solution volume of 3 mL (10 mL for ammonia).

The accuracy of concentration measurements depends on errors associated with both sampling and analysis (see Section 2.4). Sampling information, including sample volume, was provided by WHC; sample volume uncertainty was not provided. The accuracy of analytical results depends on the method used. For ammonia analyses, the accuracy of laboratory measurements by SIE was estimated to be $\pm 5\%$ relative, 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 ammonia, 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 ammonia 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 sorbent-trap leachates). The accuracy of measurements of sample mass is ± 0.05 mg, or much less than 1% of the mass changes of samples, and roughly 5% or less of the mass change of blanks.

2.4 Inorganic Sample Results

Sorbent-trap trains and controls were prepared on 8/29/94, submitted to WHC on 8/31/94, and used by WHC to sample the headspace of Tank BY-109 on 9/22/94 using the ISS. The sample job

designation number was S4071. The exposed samples were returned to PNL on 9/26/94 and subsequently analyzed on 9/27/94 (H₂O), 10/15/94 (NH₃), and 9/29/94 (NO_x) to provide information on the tank-headspace concentrations of selected inorganic compounds. Sampling and analysis for HCN and SO_x were not requested. The sample-volume information was received from WHC on 11/5/94.

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 NH₃/NO_x/H₂O contained an ammonia 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 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.

Table 2.2 List of PNL Inorganic Samples, Blanks, and Gravimetric Results From *In Situ* Sampling of the Headspace of Tank BY-109 on 9/22/94

Sample Number	Sorbent Train Type	Sample Flow Rate (mL/min)	Duration (min)	Sample Volume ^(a) (L)	Mass Gain (g)
S4071-071-31V	NH ₃ /NO _x /H ₂ O Sample	245	15.0	3.67	0.0571
S4071-071-32V	NH ₃ /NO _x /H ₂ O Sample	239	15.0	3.58	0.0540
S4071-071-34V	NH ₃ /NO _x /H ₂ O Sample	245	15.0	3.68	0.0574
S4071-071-33V	NH ₃ /NO _x /H ₂ O Blank	n/a ^(b)	n/a	n/a	0.0042

(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.

2.4.1 Ammonia Results. The concentration of NH₃ was 46 ± 2 ppmv, based on all three samples. The blank-corrected NH₃ quantities in the sorbent traps ranged from 6.8 to 7.2 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%). 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 NH₃ were 101 ± 4%, 109 ± 2%, and 104 ± 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 ± 9%. One sample leachate was spiked after initial analysis with roughly the quantity of NH₃ in the sample and yielded a percentage recovery of 86%. A 5-point calibration was performed over an NH₃ range of 0.1 to 1000 μg/mL.

Table 2.3 Inorganic Vapor-Sample Results Obtained from *In Situ* Samples Inserted into the Headspace of Tank BY-109 on 9/22/94

Sample	Analytical Results (μmol)			Sample Volume (L)	Vapor ^(a) Concentration (ppmv)
	Front Section	Back Section	Total ^(b) Blank-Corrected		
<u>NH₃ Samples:</u>			<u>7.0^(c)</u>	<u>3.64^(c)</u>	<u>46 $\pm$ 2^(c)</u>
S4071-071-31V	7.2	≤ 0.03	7.2	3.67	47
S4071-071-32V	6.9	≤ 0.03	6.9	3.58	46
S4071-071-34V	6.8	≤ 0.03	6.8	3.68	44
<u>NO₂ Samples:</u>			<u>≤ 0.002</u>	<u>3.64</u>	<u>≤ 0.03</u>
S4071-071-31V	0.0119	0.0070	n/a ^(d)	3.67	n/a
S4071-071-32V	0.0122	0.0071	n/a	3.58	n/a
S4071-071-34V	0.0124	0.0065	n/a	3.68	n/a
<u>NO Samples:</u>			<u>≤ 0.014</u>	<u>3.64</u>	<u>≤ 0.04</u>
S4071-071-31V	0.0134	0.0025	n/a	3.67	n/a
S4071-071-32V	0.0125	0.0063	n/a	3.58	n/a
S4071-071-34V	0.0135	0.0063	n/a	3.68	n/a
<u>Gravimetric Samples (mg. mg/L):</u>			<u>54 mg</u>	<u>3.64</u>	<u>15 $\pm$ 1 mg/L</u>
S4071-071-31V	n/a	n/a	55	3.67	15.0
S4071-071-32V	n/a	n/a	52	3.58	14.5
S4071-071-34V	n/a	n/a	55	3.68	14.9

- (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 Section 2.4.
- (c) Underlined values represent the average of the set of samples. Concentration uncertainty equals ± 1 standard deviation (absolute) for each set of samples. The use of " $\leq$ " is defined in Section 2.0.
- (d) n/a = not applicable.

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

The concentrations of NO₂ and NO were ≤ 0.03 and ≤ 0.04 ppmv, respectively. Blank-corrected NO₂⁻ quantities in the sorbent traps averaged ≤ 0.002 μmol (NO₂ samples) and ≤ 0.003 μmol (NO samples). Nitrite blank levels used to correct data were 0.0119 ± 0.0003 μmol in front and 0.0062 ± 0.0003 μmol in back sorbent 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 15 ± 1 mg/L. The result was based on an average blank-corrected mass gain of 54 g from all three of three 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 three blank H_2O traps spiked with 51 mg 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 as clean, free of TO-14 contaminants to a level of 5 parts per billion by volume (ppbv), the canister is evacuated to 30 in. Hg, tagged, and stored for use in the field. Before sending the canisters out to the field for sampling, the canisters are prehumidified with 100 µL of distilled water and labeled with a field-sampling identification. Canisters stored more than 30 but less than 60 days are re-evacuated and rehumidified before use. If stored more than 60 days, the canisters are recleaned and validated before use.

3.2 Sample Analysis Method

The SUMMA™ canister sample was analyzed according to PNL Technical Procedure PNL-TVP-03, *Determination of TO-14 Volatile Organic Compounds in Hanford Waste Tank Headspace Samples Using SUMMA™ Passivated Canister Sampling and Gas Chromatographic-Mass Spectrometry Analysis*, which is a modified version of EPA compendium Method TO-14. The method uses an EnTech cryoconcentration system interfaced with a Hewlett Packard (HP) 5971 GC/MS. The EnTech concentrator is used to pull a metered volume of sample air from the SUMMA™ canister, cryogenically concentrate the air volume, then transfer the volume to the GC/MS for analysis. A 100-mL volume of sample is measured and analyzed from the tank headspace. The organic components in the sampled air are separated on an analytical column, J&W Scientific DB-1 phase, 60-m by 0.32-mm internal diameter with 3-µm 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.

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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.

3.3 Quality Assurance/Quality Control

Before the tank sample was analyzed, a diagnostic check was performed on the GC/MS instrument by running an instrument "quick tune," as described in PNL-TVP-03. Upon satisfactory completion of the instrument diagnostic check, a blank volume of purified nitrogen was analyzed to check the cleanliness of the system. The instrument was then calibrated over 6 data points ranging from 2 ppbv to 100 ppbv, using a standard gas mixture containing 40 volatile organic compounds listed in EPA compendium Method TO-14. A gas mixture containing bromochloromethane, 1,4-difluorobenzene, and chlorobenzene- d_5 was used as an internal standard (IS) for all blank, calibration standard, and sample analyses. Analyte response from sample components, ISs, and standards were obtained from the extracted ion plot from their selected mass ion. The calibration curve was generated by calculating the relative response ratios of the IS to calibration standard responses and plotting the ratios against the ratio of the calibration-standard concentration (in ppbv) to the IS concentration. A least-squares linear-regression routine was applied to the data set to generate the best-fit line for each compound. The equation for that line was then used to quantify the TO-14 compounds found in the tank samples.

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

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

3.3.2 Identification and Quantitation of Tentatively Identified Compounds. The tentatively identified compounds (TICs) are determined by mass-spectral interpretation and comparison of the spectra with the EPA/NIST/WILEY Library, which is a part of the HP 5971 instrument operating system. Chromatographic peaks with an area count greater than, or equal to, one half of the total area count of the chlorobenzene- d_5 IS peak at the 20-ppbv calibration level are tentatively identified and quantitatively estimated. This standard was chosen to determine the integration cutoff as it is in the middle of the chromatographic range and not in a region typically affected by coelution of other compounds. The quality of the mass-spectral searches was then reviewed by the principal investigators before the identification was assigned to each chromatographic peak.

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

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

The calculated response factor was then multiplied by the TIC peak area to give an estimated concentration for that compound. For butane, the total peak area was multiplied by the response factor for chlorobenzene-d₅ to give an estimated concentration of 0.087 mg/m³. Internal standards bromochloromethane and difluorobenzene were not used to quantitate the TICs because previous tank-sample matrices appeared to have greatly altered the signal of the quantitation ions for those two ISs. By pressurizing the samples as described in Section 3.2 and increasing the relative amount of IS used in sample analysis, the quantitation ions of these two ISs are less suppressed.

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

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

The IS level added to all blank, standard, and sample injections was 91.5 ppbv for bromochloromethane, 101.5 ppbv for 1,4-difluorobenzene, and 91.0 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 sample 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. 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. Table 3.3 presents data found by GC/MS analysis of the canister containing ambient air. 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. Six compounds were found to be higher than the instrumental detection limit with a total average concentration of 2.43 mg/m³. Toluene had the highest concentration, an average 2.08 mg/m³, more than 85% of the six TO-14 compounds detected.

Table 3.2 lists the semi-quantitative results for the TICs. Twenty-three compounds were detected. The predominant species observed in this sample were tridecane, dodecane, undecane, butanol, decane, acetone, nonane, and octane. Of the normal paraffin hydrocarbons (NPH), defined as n-alkanes from C₁₁ to C₁₅, undecane, dodecane, and tridecane (C₁₁ to C₁₃), were seen in a significant amount in the sample. The total concentration of the TIC compounds was 11.52 mg/m³. A substantial amount of toluene was also detected in the BY-109 sample, but its concentration is reported in Table 3.1 where it is traceable to a standard gas mixture. 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. No TO-14 constituents were found above the instrumental detection limits in the ambient sample. Table 3.3 lists the semi-quantitative results for the TICs found in the ambient air near Tank BY-109. FREON-113 (1,1,2-trichloro-1,2,2-trifluoroethane) was above the detection limit.

4.0 Conclusions

The concentrations of selected compounds were determined from *in situ* samples of the headspace of Hanford waste Tank BY-109 on 9/22/94. Sample preparation and analysis methods for inorganic samples 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 ammonia, 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 ammonia trap. The ammonia concentration was found to be 46 ± 2 ppmv. The concentration of NO_2 was ≤ 0.03 ppmv. The concentration of NO was ≤ 0.04 ppmv. The mass concentration was 15 ± 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.

The concentration of toluene was approximately 12% of the total estimated concentration of all organic analytes identified. The total concentration of TO-14 analytes observed (2.43 mg/m^3) accounted for 17% of the total estimated concentration. NPHs were observed. FREON-113 (1,1,2-trichloro-1,2,2-trifluoroethane) was detected in the ambient air sample, but this compound is a contaminant in the EnTech GC/MS system and may not have been present in the ambient air.

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 - 5/25/94)*. 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 Results for *In Situ* Samples Collected from the Headspace of Tank BY-109 in SUMMA™ Canisters on 9/22/94.

TO-14 Analyte	CAS #	Mol Wt	S4071-210 ^(a) PNL 210 ^(b) Concentration		S4071-211 ^(a) PNL 211 ^(b) Concentration		S4071-212 ^(a) PNL 212 ^(b) Concentration		Means and Standard Deviations			
			ppbv	mg/m ³	ppbv	mg/m ³	ppbv	mg/m ³	(ppbv)	St Dev	(mg/m ³)	St Dev
Dichlorodifluoromethane	75-71-8	120.9	< 2	< 0.01	< 2	< 0.01	< 2	< 0.01	(c)	(c)	(c)	(c)
Chloromethane	74-87-3	50.5	< 2	< 0.005	< 2	< 0.005	< 2	< 0.005	(c)	(c)	(c)	(c)
1,2-Dichloro-1,1,2,2-tetrafluoroethane	76-14-2	170.9	< 2	< 0.02	< 2	< 0.02	< 2	< 0.02	(c)	(c)	(c)	(c)
Vinyl Chloride	75-01-4	62.5	< 2	< 0.01	< 2	< 0.01	< 2	< 0.01	(c)	(c)	(c)	(c)
Bromomethane	74-83-9	94.9	< 2	< 0.01	< 2	< 0.01	< 2	< 0.01	(c)	(c)	(c)	(c)
Chloroethane	75-00-3	64.5	< 2	< 0.01	< 2	< 0.01	< 2	< 0.01	(c)	(c)	(c)	(c)
Trichlorofluoromethane	75-69-4	137.4	31.2	0.19	23.2	0.14	52.3	0.32	35.6	15.0	0.22	0.09
1,1-Dichloroethene	75-35-4	96.9	< 2	< 0.01	< 2	< 0.01	< 2	< 0.01	(c)	(c)	(c)	(c)
Methylene Chloride	75-09-2	84.9	< 2	< 0.01	< 2	< 0.01	< 2	< 0.01	(c)	(c)	(c)	(c)
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	187.4	< 2	< 0.02	< 2	< 0.02	< 2	< 0.02	(c)	(c)	(c)	(c)
1,1-Dichloroethane	75-34-3	99.0	< 2	< 0.01	< 2	< 0.01	< 2	< 0.01	(c)	(c)	(c)	(c)
cis-1,2-Dichloroethene	156-59-2	96.9	< 2	< 0.01	< 2	< 0.01	< 2	< 0.01	(c)	(c)	(c)	(c)
Chloroform	67-66-3	119.4	< 2	< 0.01	< 2	< 0.01	< 2	< 0.01	(c)	(c)	(c)	(c)
1,2-Dichloroethane	107-06-2	99.0	< 2	< 0.01	< 2	< 0.01	< 2	< 0.01	(c)	(c)	(c)	(c)
1,1,1-Trichloroethane	71-55-6	133.4	< 2	< 0.01	< 2	< 0.01	< 2	< 0.01	(c)	(c)	(c)	(c)
Benzene	71-43-2	78.1	< 2	< 0.01	< 2	< 0.01	3.0	0.01	(c)	(c)	(c)	(c)
Carbon Tetrachloride	56-23-5	153.8	< 2	< 0.01	< 2	< 0.01	< 2	< 0.01	(c)	(c)	(c)	(c)
1,2-Dichloropropane	78-87-5	113.0	< 2	< 0.01	< 2	< 0.01	< 2	< 0.01	(c)	(c)	(c)	(c)
Trichloroethene	79-01-6	131.4	< 2	< 0.01	< 2	< 0.01	< 2	< 0.01	(c)	(c)	(c)	(c)
cis-1,3-Dichloropropene	10061-01-5	111.0	< 2	< 0.01	< 2	< 0.01	< 2	< 0.01	(c)	(c)	(c)	(c)
trans-1,3-Dichloropropene	10061-02-6	111.0	< 2	< 0.01	< 2	< 0.01	< 2	< 0.01	(c)	(c)	(c)	(c)
1,1,2-Trichloroethane	79-00-5	133.4	< 2	< 0.01	< 2	< 0.01	< 2	< 0.01	(c)	(c)	(c)	(c)
Toluene	108-88-3	92.1	384	1.58	358	1.47	774	3.18	505	233	2.08	0.96
1,2-Dibromoethane	106-93-4	187.9	< 2	< 0.02	< 2	< 0.02	< 2	< 0.02	(c)	(c)	(c)	(c)
Tetrachloroethylene	127-18-4	165.8	< 2	< 0.02	< 2	< 0.02	5.0	0.04	(c)	(c)	(c)	(c)
Chlorobenzene	108-90-7	112.6	< 2	< 0.01	< 2	< 0.01	< 2	< 0.01	(c)	(c)	(c)	(c)
Ethylbenzene	100-41-4	106.2	< 2	< 0.01	< 2	< 0.01	< 2	< 0.01	(c)	(c)	(c)	(c)
p/m-Xylene	106-42-3	106.2	< 2	< 0.01	< 2	< 0.01	< 2	< 0.01	(c)	(c)	(c)	(c)
Styrene	100-42-5	104.2	< 2	< 0.01	< 2	< 0.01	< 2	< 0.01	(c)	(c)	(c)	(c)
1,1,2,2-Tetrachloroethane	79-34-5	167.9	< 2	< 0.02	< 2	< 0.02	< 2	< 0.02	(c)	(c)	(c)	(c)
o-Xylene	95-47-6	106.2	< 2	< 0.01	< 2	< 0.01	< 2	< 0.01	(c)	(c)	(c)	(c)
1,3,5-Trimethylbenzene	108-67-8	120.2	< 2	< 0.01	< 2	< 0.01	5.5	0.03	(c)	(c)	(c)	(c)
1,2,4-Trimethylbenzene	95-63-6	120.2	5.8	0.03	3.6	0.02	22.0	0.12	10.5	10.0	0.06	0.05
Chloromethylbenzene, alpha (Benzyl Chloride)	108-67-8	126.6	< 2	< 0.01	< 2	< 0.01	< 2	< 0.01	(c)	(c)	(c)	(c)
1,3-Dichlorobenzene	541-73-1	147.0	< 2	< 0.01	< 2	< 0.01	< 2	< 0.01	(c)	(c)	(c)	(c)
1,4-Dichlorobenzene	106-46-7	147.0	< 2	< 0.01	< 2	< 0.01	< 2	< 0.01	(c)	(c)	(c)	(c)
1,2-Dichlorobenzene	95-50-1	147.0	< 2	< 0.01	< 2	< 0.01	< 2	< 0.01	(c)	(c)	(c)	(c)
1,2,4-Trichlorobenzene	120-82-1	181.5	< 2	< 0.02	< 2	< 0.02	< 2	< 0.02	(c)	(c)	(c)	(c)
Hexachloro-1,3-butadiene	87-68-3	260.8	< 2	< 0.02	< 2	< 0.02	< 2	< 0.02	(c)	(c)	(c)	(c)

(a) WHC sample identification number.

(b) PNL canister number.

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

Table 3.2 Tentatively Identified Compounds and Estimated Concentrations^(a) in Tank BY-109 from *In Situ* SUMMATM Canister Samples Collected on 9/22/94

Tentatively Identified Compound ^(d)	CAS No. ^(d)	Mol Wt	Ret Time	S4030-----210 ^(b) PNL210 ^(c)		S4030-----211 ^(b) PNL211 ^(c)		S4030-----212 ^(b) PNL212 ^(c)		Mean and Standard Deviation			
				(mg/m ³)	(ppmv)	(mg/m ³)	(ppmv)	(mg/m ³)	(ppmv)	(mg/m ³)	St Dev	ppm	St Dev
Carbon Dioxide	124-38-9	44	3.19	(e)	(e)	(e)	(e)	(e)	(e)	(e)	(e)	(e)	(e)
Propene	115-07-1	42	4.035	<0.019	<0.01	<0.019	<0.01	0.071	0.038	0.071	(h)	0.038	
Propane	74-98-6	44	4.117	<0.02	<0.01	<0.02	<0.01	0.078	0.040	0.078	(h)	0.040	
Acetaldehyde	75-07-0	44	5.414	<0.02	<0.01	<0.02	<0.01	0.066	0.034	0.066	(h)	0.034	
2-Methyl-1-Propene	115-11-7	56	5.857	0.060	0.024	0.061	0.025	0.134	0.054	0.085	0.042	0.034	0.017
Butane	106-97-8	58	6.125	<0.026	<0.01	<0.026	<0.01	0.087	0.034	0.087	(h)	0.034	
Ethanol	64-17-5	46	7.535	0.099	0.048	0.086	0.042	0.195	0.095	0.127	0.060	0.062	0.029
Acetone	67-64-1	58	8.606	0.407	0.157	0.362	0.140	0.722	0.279	0.497	0.196	0.192	0.076
2-Propanol	67-63-0	60	9.224	0.109	0.041	0.091	0.034	0.185	0.069	0.128	0.049	0.048	0.018
Pentane	109-66-0	72	9.811	<0.032	<0.01	<0.032	<0.01	0.055	0.017	0.055	(h)	0.017	
1,1,2 Trichloro-1,2,2- Trifluoroethane	76-13-1	187	11.194	0.051	0.006	<0.083	<0.01	0.000	(g)	0.026	0.036	(g)	
Butanal	123-72-8	72	13.518	0.085	0.026	0.078	0.024	0.167	0.052	0.110	0.050	0.034	0.015
2-Butanone	78-93-3	72	13.703	0.093	0.029	0.080	0.025	0.174	0.054	0.116	0.051	0.036	0.016
Unknown			14.352	(g)	(g)	(g)	(g)	0.051	(g)	0.051	(h)	(g)	
Bromochloromethane (IS)	74-97-5		14.969	(f)	(f)	(f)	(f)	(f)	(f)	(f)	(f)	(f)	(f)
Tetrahydrofuran	109-99-9	72	15.989	0.056	0.018	0.053	0.016	0.121	0.038	0.077	0.038	0.024	0.012
1-Butanol	71-36-3	74	17.739	1.017	0.308	0.882	0.267	1.567	0.474	1.155	0.363	0.350	0.110
Unknown			18.336	(g)	(g)	(g)	(g)	0.065	(g)	0.065	(h)	(f)	
1,4-Difluorobenzene (IS)	540-36-3		18.686	(f)	(f)	(f)	(f)	(f)	(f)	(f)	(f)	(f)	(f)
Unknown			19.345	(g)	(g)	(g)	(g)	0.098	(g)	0.098	(h)	(g)	
Heptane	142-82-5	100	20.684	0.156	0.035	0.143	0.032	0.311	0.070	0.203	0.094	0.046	0.021
Methyl Cyclohexane	108-87-2	98	22.269	<0.044	<0.01	<0.044	<0.01	0.058	0.013	0.058	(h)	0.007	0.009
Toluene	108-88-3	92	24.113	1.231	0.300	1.213	0.295	2.505	0.610	1.650	0.741	0.402	0.180
Unknown			24.38	(g)	(g)	(g)	(g)	0.064	(g)	0.064	(h)	(g)	
2-hexanone	591-78-6	100	24.494	<0.045	<0.01	<0.045	<0.01	0.063	0.014	0.063	(h)	0.007	0.010
hexanal	66-25-1	98	25.07	<0.044	<0.01	<0.044	<0.01	0.069	0.016	0.069	(h)	0.016	
octane	111-65-9	114	26.172	0.134	0.026	0.124	0.024	0.277	0.054	0.178	0.086	0.035	0.017
d5-chlorobenzene (IS)	3114-55-4		28.231	(f)	(f)	(f)	(f)	(f)	(f)	(f)	(f)	(f)	(f)
Unknown			28.808	(g)	(g)	0.053	(g)	0.096	(g)	0.074	(h)	(g)	
3-Heptanone	106-35-4	114	29.673	0.077	0.015	0.072	0.014	0.166	0.033	0.105	0.053	0.021	0.010
N-butyl ether	142-96-1	130	30.012	<0.058	<0.01	<0.058	<0.01	0.078	0.013	0.078	(h)	0.013	
Heptanal	111-71-7	114	30.393	<0.051	<0.01	<0.051	<0.01	0.079	0.015	0.079	(h)	0.015	
Unknown			30.764	0.058	(g)	0.055	(g)	0.065	(g)	0.059	0.005	(g)	
Nonane	111-84-2	128	31.279	0.154	0.027	0.135	0.024	0.323	0.056	0.204	0.103	0.036	0.018
2,4-Dimethyl pyridine	108-47-4	108	32.185	<0.048	<0.01	<0.048	<0.01	0.151	0.031	0.151	(h)	0.031	
Unknown			32.617	(g)	(g)	(g)	(g)	0.052	(g)	0.052	(h)	(g)	
3-Methylnonane	5911-04-6	142	33.06	<0.063	<0.01	<0.063	<0.01	0.102	0.016	0.102	(h)	0.016	
c3-Cyclohexane		126	33.287	<0.056	<0.01	<0.056	<0.01	0.106	0.019	0.106	(h)	0.019	

Table 3.2 Contd

Tentatively Identified Compound ^(d)	CAS No. ^(d)	Mol Wt	Ret Time	S4030-----210 ^(b) PNL210 ^(c)		S4030-----211 ^(b) PNL211 ^(c)		S4030-----212 ^(b) PNL212 ^(c)		Mean and Standard Deviation			
				(mg/m ³)	(ppmv)	(mg/m ³)	(ppmv)	(mg/m ³)	(ppmv)	(mg/m ³)	St Dev	(ppm)	St Dev
c3-Benzene		120	34.162	0.059	0.011	<0.054	<0.01	0.132	0.025	0.095	(h)	0.018	0.010
c3-Benzene		120	34.296	<0.054	<0.01	<0.054	<0.01	0.061	0.011	0.061	(h)	0.011	
c3-Benzene		120	34.533	<0.054	<0.01	<0.054	<0.01	0.095	0.018	0.095	(h)	0.018	
c10-Alkane		142	34.749	<0.063	<0.01	<0.063	<0.01	0.056	0.009	0.056	(h)	0.009	
c10-Alkene		140	34.903	<0.063	<0.01	<0.063	<0.01	0.055	0.009	0.055	(h)	0.009	
c3-Benzene		120	35.119	<0.054	<0.01	<0.054	<0.01	0.052	0.010	0.052	(h)	0.010	
Unknown			35.336	(g)	(g)	(g)	(g)	0.095	(g)	0.095	(h)	(g)	
c3-Benzene		120	35.799	0.090	0.017	0.076	0.014	0.205	0.038	0.124	0.071	0.023	0.013
Decane	124-18-5	142	35.995	0.431	0.068	0.382	0.060	0.882	0.139	0.565	0.275	0.089	0.043
2-Ethyl-1-Hexanol	104-76-7	130	36.633	0.088	0.015	0.079	0.014	0.154	0.027	0.107	0.041	0.020	0.009
c11-Alkane		156	37.138	0.061	0.009	0.052	0.007	0.143	0.020	0.085	0.050	0.012	0.007
Unknown alkane			37.354	(g)	(g)	(g)	(g)	0.073	(g)	0.073	(h)	(g)	
Unknown alkane			38.208	0.076	(g)	0.064	(g)	0.161	(g)	0.101	0.053	(g)	
Unknown			38.579	(g)	(g)	(g)	(g)	0.050	(g)	0.050	(h)	(g)	
Unknown alkane			39.073	(g)	(g)	(g)	(g)	0.078	(g)	0.078	(h)	(g)	
c11-Alkane			39.856	0.051	(g)	(g)	(g)	0.103	(g)	0.077	(h)	(g)	
Undecane	1120-21-4	156	40.35	1.436	0.206	1.322	0.190	2.533	0.364	1.764	0.668	0.253	0.096
Dodecane	112-40-3	170	44.396	2.066	0.272	1.982	0.261	3.414	0.450	2.487	0.803	0.328	0.106
c13 Alkane		184	45.014	0.076	0.009	0.076	0.009	0.112	0.014	0.088	0.021	0.011	0.003
c13 Alkene		182	46.445	<0.082	<0.01	(g)	(g)	0.056	0.007	0.056	(h)	0.007	
Unknown alkane			47.29	0.070	(g)	0.072	(g)	0.123	(g)	0.088	0.030	(g)	
Tridecane	629-50-5	184	48.165	2.165	0.264	2.145	0.261	3.547	0.432	2.619	0.804	0.319	0.098
Tetradecane	629-59-4	198	51.676	0.394	0.045	0.419	0.047	0.705	0.080	0.506	0.173	0.057	0.020

(a) Semi-quantitative estimate calculated using IS

(b) WHC sample number

(c) PNL SUMMA™ canister number

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

(e) Carbon dioxide cannot be determined by the analytical method used.

(f) Concentration information for ISs are determined by direct calibration.

(g) Concentration cannot be calculated because molecular weight and/or compound is unknown.

(h) Calculation is not significant with fewer than three values.

Table 3.3 Tentatively Identified Compounds and Estimated Concentrations^(a) from Sampling Ambient Air Near Tank BY-109 Collected in a SUMMATM Canister on 9/22/94

Tentatively Identified Compounds ^(d)	CAS No. ^(d)	Mol Wt.	Retention Time (min)	S4071-----209 ^(b) PNL209 ^(c)	
				(mg/m ³)	(ppmv)
Carbon dioxide	124-38-9	44.0	3.2	(e)	(e)
1,1,2 Trichloro-1,2,2-trifluoroethane	76-13-1	187.0	11.2	0.028	0.003
Bromochloromethane (IS)	74-97-5	129.5	15.0	(f)	(f)
1,4-Difluorobenzene (IS)	540-36-3	114.0	18.7	(f)	(f)
d5-Chlorobenzene (IS)	3114-55-4	117.5	28.3	(f)	(f)

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

(b) WHC sample number.

(c) PNL SUMMATM canister number.

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

(e) Carbon Dioxide cannot be determined by the analytical method used.

(f) Concentration information for ISs are determined by direct calibration.

Figure 3.1 GC/MS Chromatogram of Hanford Tank BY-109 In Situ SUMMA™ Canister Sample S4071 -----211
Collected on 9/22/94

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