PNL-10597
UC-606

Vapor Space Characterization of Waste Tank 241-TY-103 (*In Situ*): Results from Samples Collected on 8/5/94

K. H. Pool
B. D. McVeety
T. W. Clauss
J. S. Young
J. S. Fruchter
R. B. Lucke
G. S. Klinger
M. W. Ligotke
M. McCulloch
S. C. Goheen

June 1995

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

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

Battelle

PNL-10597

PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE MEMORIAL INSTITUTE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC06-76RLO 1830

Printed in the United States of America

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831; prices available from (615) 576-8401. FTS 626-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161.

The contents of this report were printed on recycled paper

PNL-10597
UC-606

Vapor Space Characterization of Waste Tank 241-TY-103 (*In Situ*): Results from Samples Collected on 8/5/94

K. H. Pool
R. B. Lucke
B. D. McVeety
G. S. Klinger
T. W. Clauss
M. W. Ligotke
J. S. Young
M. McCulloch
J. S. Fruchter
S. C. Goheen

June 1995

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

Pacific Northwest Laboratory
Richland, Washington 99352

DISCLAIMER

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-103 (referred to as Tank TY-103). The results described here were obtained to support safety and toxicological evaluations. A summary of the results for inorganic and organic analytes is listed in Table 1. Detailed descriptions of the results appear in the text.

Quantitative results were obtained for the inorganic compounds ammonia (NH_3), nitrogen dioxide (NO_2), nitric oxide (NO), hydrogen cyanide (HCN), and water (H_2O). Sampling for sulfur oxides (SO_X) was not requested. In addition, quantitative results were obtained for the 39 TO-14 target analytes. Of these, four were observed above the 5-ppbv reporting cutoff. Eighteen organic tentatively identified compounds were observed above the reporting cutoff of (ca.) 10 ppbv in two or more of the three samples collected and an additional seven in only one of the three samples. Tentatively identified compounds are reported with concentrations that are semiquantitative estimates based on internal-standard response factors. The 10 organic analytes with the highest estimated concentrations are listed in Summary Table 1 and account for approximately 92% of the total organic components in Tank TY-103.

Summary Table 1. Summary Results of Inorganic and Organic Samples Collected from the Headspace of Tank TY-103 on 8/5/94

Category	Analyte	Vapor[(a)] Concentration	Units
Inorganic	NH_3	31 ± 6	ppmv
	NO_2	≤ 0.02	ppmv
	NO	≤ 0.06	ppmv
	HCN	≤ 0.01	ppmv
	H_2O	12 ± 2	mg/L
Organic			
	Tridecane	18.50	mg/m^3
	Tetradecane	5.84	mg/m^3
	Dodecane	5.20	mg/m^3
	3-Methylhexane	2.67	mg/m^3
	2-Methylhexane	1.59	mg/m^3
	2,3-Dimethlypentane	1.49	mg/m^3
	Trichlorofluoromethane	0.84	mg/m^3
	Toluene	0.82	mg/m^3
	Methylcyclohexane	0.80	mg/m^3
	1-Butanol	0.77	mg/m^3

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

Acknowledgments

The authors gratefully acknowledge the support of other project staff at Pacific Northwest Laboratory who contributed to the successful completion of this sampling and analysis activity. Jeff Edwards served as the PNL single-point-of-contact and coordinated sample handling and communications with Westinghouse Hanford Company. K. B. Olsen assisted in preparing the organic portion of this report. Sally Slate, May-Lin Thomas, and Karen Schielke analyzed inorganic samples, and Gary Dennis prepared the solid-sorbent sample trains. Brenda M. 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	In-Situ-Sampling
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
RPD	relative percent difference
SCIC	suppressed-conductivity ion chromatography
SIE	selective ion electrode
SRM	standard reference material
STP	standard temperature and pressure
TEA	triethanolamine
TIC	tentatively identified compound
VSS	Vapor Sampling System
WHC	Westinghouse Hanford Company

Contents

Tables

Figures

1.0 Introduction

This report describes results of the analyses of *in situ* tank-headspace samples taken from the Hanford waste Tank 241-TY-103 (referred to as Tank TY-103). Pacific Northwest Laboratory (PNL)[a] contracted with Westinghouse Hanford Company (WHC) to provide sampling devices and to analyze inorganic and organic analytes collected from the tank headspace and ambient air near the tank. The sample job was designated S4062, and samples were collected by WHC on August 5, 1994, using the *in situ* sampling system (ISS). The results of the analyses are expected to be used to estimate the potential toxicity of tank-headspace gas as described in *Data Quality Objectives for Generic In-Tank Health and Safety Vapor Issue Resolution*, WHC-SD-WM-DQO-002, Rev. 0.

Sampling devices, including six sorbent trains (for inorganic analyses), and five SUMMA™ canisters (for organic analyses) were supplied to the WHC sampling staff on August 3. Samples were taken (by WHC) from the tank headspace on August 5 and were returned to PNL from the field on August 23. Inorganic (sorbent trap) samples were delivered to PNL on chain of custody (COC)/sample analysis request 007492 (see Figure 1.1a). The SUMMA™ canisters were submitted to WHC on COC 007491 (see Figure 1.1b). However, the SUMMA™ canisters were delivered on COC 007369 (see Figure 1.1c).

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 tubes was transferred to PNL personnel performing the inorganic analysis and stored at refrigerated ($\leq$ 10°C) temperature until the time of analysis. The canisters were stored in the 326/23B laboratory at ambient (25°C) temperature until the time of analysis. Access to the 326/23B laboratory is limited to PNL personnel working on the waste-tank safety program. Analyses described in this report were performed at PNL in the 300 area of the Hanford Reservation. Analytical methods that were used are described in the text. In summary, sorbent tubes for inorganic analyses containing sample materials were either weighed (for water analysis) or weighed and desorbed with the appropriate aqueous solutions (for ammonia, nitrogen dioxide, nitric oxide, and hydrogen cyanide analyses). The aqueous extracts were analyzed by either selective electrode or ion chromatography (IC). Organic analyses were performed using cryogenic preconcentration followed by gas chromatography/mass spectrometry (GC/MS).

(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 007492

Custody Form Initiator	J. A. Edwards	Telephone Pager	(509) 373-0141 85-3009
Company Contact	L. A. Pingel	Telephone	(509) 373-4051
Project Designation/Sampling Locations	200 East Tank Farm 241-TY-103 Tank Vapor Sample SAF S4062 (IN-SITU)	Collection Date Preparation Date Field Logbook No.	08 - 0 5 - 94 08 - 0 3 - 94 WHC-N-797-1 2Feb95
Ice Chest No.			
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

S4062 - ___ .43W	$NH_3/NO_x/H_2O$ ~~(Sample #1)~~	(Set 2, Port 1)
S4062 - ___ .44W	$NH_3/NO_x/H_2O$ ~~(Sample #2)~~	(Set 2, Port 2)
S4062 - ___ .45W	$NH_3/NO_x/H_2O$ ~~(Sample #3)~~	(Set 2, Port 3)
S4062 - ___ .46W	HCN/H_2O ~~(Sample #1)~~	(Set 1, Port 2)
S4062 - ___ .47W	HCN/H_2O ~~(Sample #2)~~	(Set 1, Port 4)
S4062 - ___ .48W	HCN/H_2O (Sample #3)	(Set 1, Port 3)
~~S4062 - ___ .49W~~ SMB 8/23/94	~~OVS/Drier (Radiological survey)~~	(Set 1, Port 1)
S4062 - ___ .50W	$NH_3/NO_x/H_2O$ (Spare)	
S4062 - ___ .51W	HCN/H_2O (Spare)	

[X] Field Transfer of Custody [ ] Chain of Possession (Sign and Print Names)

Relinquished By	Date	Time	Received By	Date	Time
J. A. Edwards	08-03-94	1530	~~S. M. Brown~~ NP Buechler	08-03-94	1530
NP Buechler	8-5-94	Open	AR Rizzo	8-5-94	Open
AR Rizzo	8-23-94	1415	SM Brown	8-23-94	1415
SM Brown	8-23-94	1415	AEDMARDS	8-23-94	1415

(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

Westinghouse Hanford Company	CHAIN OF CUSTODY	WHC 007491

Custody Form Initiator	J. A. Edwards	Telephone Pager	(509)	373-0141 85-3009
Company Contact	L. A. Pingel	Telephone	(509)	373-4051

Project Designation/Sampling Locations 200 East Tank Farm
241-TY-103 Tank Vapor Sample SAF S4062
Ice Chest No. (IN-SITU)

Collection Date 08 - _ _ - 94
Preparation Date 08 - 0 3 - 94
Field Logbook No.WHC-N-797-1

Bill of Lading/Airbill No. N/A

Offsite Property No. N/A 2Feb95

Method of Shipment Government Truck

Shipped to WHC

Possible Sample Hazards/Remarks Unknown at time of sampling

Sample Identification

2/2/95

S4061 - ___ . 020 (PNL) SUMMA Ambient Air

S4061 - ___ . 028 (PNL) SUMMA Sample #1
S4061 - ___ . 165 (PNL) SUMMA Sample #2
S4061 - ___ . 166 (PNL) SUMMA Sample #3

S4061 - ___ . 167 (PNL) SUMMA Surrogate

[X] Field Transfer of Custody			[ ] Chain of Possession	(Sign and Print Names)	
Relinquished By	Date	Time	Received By	Date	Time
J. A. Edwards ~~J. A. Edwards~~	08-03-94	1530	~~S. M. Brown~~	08-03-94	1530
NP Buckler	8-5-94	0800	A G Rizzo	8-5-94	0800
A. G. Rizzo					

(version 02-28-94)

Final Sample Disposition

Disposal Method: See COC 007369

Disposed by:

Date/Time: 2Feb95

Comments

A-6000-407 (12/92) WEF061

Figure 1.1b Chain-of-Custody for Organic Samples

1

Westinghouse Hanford Company	CHAIN OF CUSTODY/SAMPLE ANALYSIS REQUEST	Page 1 of 1 007369

Collector S.M. BROWN
Company Contact L.A.PINGEL
Telephone 373-4051

SAF No. SAF# S4062
Project Designation 200-WEST TANK FARM 241-TY-103 VAPOR SAMPLE
Sampling Locations 200/W 241-TY-103 TANK

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

Possible Sample Hazards/Remarks None detected at time of sample.

Special Handling and/or Storage Store at 4 DEG. C

SPECIAL INSTRUCTION
Original C.O.C # 007491

Sample Number	*	Date Collected	Time	Number and Type of Containers	Analysis Required	Preservative
S4062___.20	V	8-05-94	1020	PNL SUMMA AMBIENT AIR	VAPOR LAB SPECIFIC	~~Cool 4 DEG. C~~ 2Feb95
S4062___.028	V	8-05-94	1020	PNL SUMMA SAMPLE # 1	VAPOR LAB SPECIFIC	~~Cool 4 DEG. C~~ 2Feb95
S4062___.165	V	8-05-94	1020	PNL SUMMA SAMPLE # 2	VAPOR LAB SPECIFIC	~~COOL 4 DEG. C~~ 2Feb95
S4062___.166	V	8-05-94	1020	PNL SUMMA SAMPLE # 3	VAPOR LAB SPECIFIC	2Feb95 ~~Cool 4 DEG. C~~
S4062___.167	V	8-05-94	1020	PNL SUMMA SURROGATE	VAPOR LAB SPECIFIC	2Feb95 ~~Cool 4 DEG. C~~

Chain of Possession Relinquished By (Sign and Print Names)	Date	Time	Received By
S.M. BROWN [signature]	8/23/94	1415	H Edwards [signature] 8-23-94

*Matrix
A = Air
DL = Drum Liquids
DS = Drum Solids
L = Liquid
O = Oil
S = Soil
√ = VAPOR
SE = Sediment
SL = Sludge
SO = Solid
T = Tissue
W = Water
WI = Wipe
X = Other

Figure 1.1c Chain-of-Custody for Organic Samples

2.0 Inorganic

Solid sorbent traps, prepared in multi-trap sampling trains, were supplied to WHC for sampling the tank headspace using the ISS. Controls and exposed samples were returned to PNL for analysis. Analyses were performed to provide information on the tank-headspace concentration of the following analytes: ammonia (NH_3), nitrogen dioxide (NO_2), nitric oxide (NO), 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 glass traps containing sorbent materials to trap vapors of selected analytes of NH_3, NO_2, NO, and H_2O (SKC Inc., Eighty Four, Pennsylvania) were obtained, prepared, and submitted for use by WHC. The sorbent traps were selected based on their use by the Occupational Safety and Health Administration (OSHA) to perform workplace monitoring, and because of available procedures and verification results associated with that particular application. The typical sorbent traps used consisted of a glass tube containing a sorbent material specific to the compound of interest. In general, the tubes contained two sorbent layers, or sections; the first layer was the primary trap, and the second layer provided an indication of breakthrough. In the tubes, sorbent layers are generally held in packed layers separated by glass wool. The sorbent traps, having glass-sealed ends, were received from the vendor. Sorbent traps were connected end-to-end to prepare multi-trap sorbent trains for sampling.

The type and nominal quantity of sorbent material varied by application. Sorbent traps were selected for the tank sample job and included the following products. The NH_3 sorbent traps contained carbon beads impregnated with sulfuric acid; nominally, 500 mg were contained in the primary and 250 mg in the breakthrough sections. The NH_3 was chemisorbed as ammonium sulfate $\{(NH_4)_2SO_4\}$. 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 sections.

Sampling materials provided by PNL to trap inorganic compounds include all or some of the following: samples, spiked samples, spares, single trap blanks, and spiked blanks. The samples of each were prepared from same-lot batches, with the oxidizer sections of the NO_x sorbent trains having been stored previously in a freezer. After sample preparation, all samples, spiked samples, blanks, and spiked blanks were stored at $\leq$ 10°C, primarily because of handling recommendations for the oxidizer tubes attached to some samples. After receipt of exposed and radiologically cleared samples from WHC and disassembly of the sorbent trains, samples were provided to the analytical laboratory at ambient temperature, and selected oxidizer sections were returned to a freezer until completion of analyses.

The sorbent traps were prepared in multi-trap sorbent trains configured so sample flow passed in order through the traps, targeting specific analytes, and then through a desiccant trap. The specific order of traps within the various sorbent trains is described in Section 2.4. The ends of the glass-tube traps were broken, and the traps were weighed and then connected to each other using uniform lengths of 3/8-in. perfluoroalkoxy (PFA)-grade Teflon® tubing. The tubing was heated in hot air and forced over the open ends of the traps to form a tight seal. Both the inlet and outlet ends of the sorbent trains (the downstream ends of the traps always contained silica gel) were each sealed with red-plastic end caps provided by the manufacturer. The leading and trailing ends of the sorbent trains remained sealed other than during the actual sampling periods. C-Flex® tubing was provided by WHC to connect the downstream ends of the sorbent trains to the sampling exhaust manifold connections.

2.1.1 Concentration Calculations. The concentrations of target compounds in the tank headspace were determined from sample results, assuming effective sample transport to the sorbent traps. Concentration, in parts per million by volume (ppmv), was determined by dividing the mass of the compound, in μmol, by the volume of the dried tank air sampled in mol. The micromolar sample mass was determined by dividing the compound mass, in μg, by the molecular weight of the compound, in g/mol. The molar sample volume was determined, excluding water vapor, by dividing the standard sample volume (at 21.1°C and 760 torr), in L, by 24.1 L/mol. For example, the concentration (C_v) of a 3.00-L sample containing 75.0 μg of NH_3 equals

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

This calculational method produces concentration results that are slightly conservative (greater than actual) because the volume of water vapor in the sample stream is neglected. The volume of water vapor is not included in the measured sampled volume because of its removal in desiccant traps upstream of the mass flowmeter. However, the bias is generally expected to be small. For a tank-headspace temperature of 35°C, the magnitude of the bias would be about 1 to 6%, assuming tank-headspace relative humidities of 20 to 100%, respectively. The concentration of mass (determined gravimetrically) was also per dry-gas volume at standard conditions.

2.2 Analytical Procedures

The compounds of interest were trapped using solid sorbents and chemisorption (adsorption of water vapor). Analytical results were based on extraction and analysis of selected ions. Analytical procedures used are specified in the text. All are compiled in PNL-MA-599.

2.2.1 Ammonia Analysis. The sorbent material from the NH_3-selective sorbent traps was placed into labeled 20-mL glass scintillation vials. Vials containing front-, or primary-, section sorbent material were treated with 10.0 mL of deionized water (DIW), and vials containing back-up-section sorbent material were treated with 5.0 mL of DIW. After extraction, the NH_3 sorbent traps were analyzed using the selective ion electrode (SIE) procedure PNL-ALO-226 {*Ammonia (Nitrogen) in Aqueous Samples*}. Briefly, this method includes 1) preparing a 1000-μg/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 the Analysis of Free Cyanide in Water and Soil Sample Leachates*). Calibration standards, typically 0, 20, 50, and 100 ppb CN^-, were prepared from a stock 1000 ppm CN^- standard on the day of sample analysis in 0.02 N NaOH matrix. The same analysis sequence described above in the "nitrite analysis" section was used. Instrument responses (peak height) observed for 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 vapor, was determined by dividing the combined change in mass from all traps in a sorbent train by the actual volume of gas sampled. Controls were used to provide information on uncertainty.

2.3 Quality Assurance/Quality Control

Analytical work was performed according to quality levels identified in the project QA plan and several PNL documents. The samples were analyzed following PNL IL III. The PNL documents include PNL-MA-70 (Part 2), PNL-MA-599, PNL-ALO-212, PNL-ALO-226, 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 NH_3).

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

Analyte	Formula	Procedure	REL[a] (ppmv)	0.1 x REL[a] (ppmv)	MDL[b] (ppmv)
Ammonia	NH_3	PNL-ALO-226	25	2.5	0.5
Nitrogen Dioxide	NO_2	PNL-ALO-212	1	0.1	0.02
Nitric oxide	NO	PNL-ALO-212	25	2.5	0.02
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 NH_3 and 3 mL for the other analytes.
(c) The vapor-mass concentration, thought to be largely water vapor, is determined gravimetrically.

The accuracy of concentration measurements depends on errors associated with both sampling and analysis. Sampling information was provided by WHC. The accuracy of analytical results depends on the method used. For NH_3 analyses, the accuracy of laboratory measurements by SIE was estimated to be $\pm$ 5% relative, independent of concentration at 1 μg/mL or greater levels. The uncertainty includes preparation of standards, purity of the ammonium salt used to prepare standards, potential operator bias, ambient temperature variations, etc. Unfortunately, no known National Institute for Standards and Technology (NIST)-traceable standard reference material (SRM) is available against which to compare working standards. Similarly, no known NIST SRM is available for nitrite analysis (for NO_2 and NO). Based on experience in comparing nitrite working standards prepared from several different sources and factors mentioned for NH_3 above, the estimated maximum bias in the laboratory analysis of samples derived from sampling for NO_2 is ± 10%, and for samples derived from sampling for NO, it is ± 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 a 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 most samples, and roughly 5% or less of the mass change of most blanks. The analytical accuracy of measurements of the change in mass of sorbent trains is estimated to be ± 1 mg per 5-trap sorbent train; this estimate is based largely on preliminary information that unopened field-blank sorbent trains gain 0.3 ± 0.4 mg per train.

2.4 Inorganic Sample Results

Sorbent trap trains and controls were prepared on 8/3/94, submitted to WHC on 8/3/94, and used by WHC to sample the tank headspace of Tank TY-103 on 8/5/94 using the ISS. The sample job designation number was S4062. 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 vapor-space concentrations of selected inorganic compounds. Sampling for sulfur oxides was not performed by WHC. 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 $NH_3/NO_x/H_2O$ contained an NH_3 trap at the inlet end, an NO_x series in the middle (Section 2.4.2), and a desiccant trap at the outlet end. Analytical mass and concentration results are shown in Table 2.3. Sample volumes were provided by WHC; sample-volume uncertainty was not provided. Tank-headspace concentration results (Table 2.3) are based on this information, and the listed uncertainties equal plus-or-minus one standard deviation of the individual results from each set of samples. Where analytical results from samples were nearly indistinguishable from those of blanks, indicating very low vapor concentrations of the analyte, the concentration results (Table 2.3) are listed as "less than or equal to" a probable maximum value determined by subtracting the average of the blanks less one standard deviation from the average of the samples plus one standard deviation. Results of control samples, such as spiked blanks, are discussed in this section. Spiked blanks, when used, were transported to the field but not opened. Spiked samples, when used, were opened in the field and used to collect tank vapors. Sample results were not corrected for the percentage recoveries of spiked blanks.

2.4.1 Ammonia Results. The concentration of NH_3 was 31 ± 6 ppmv, based on all three samples. The NH_3 quantities in the sorbent traps ranged from 4.0 to 6.0 μmol. Blank corrections, ≤ 0.06 μmol in front sections and ≤ 0.06 μmol in back sorbent sections, were ≤ 2% of collected quantities and were neglected. Although spiked blanks were not tested, the percentage recoveries of three sets of blanks spiked with 12.2, 22.3, and 46.4 μmol of NH_3 were 101 ± 4%, 109 ± 2%, and 104 ± 1%, respectively, during related sample jobs (Clauss et al. 1994; Ligotke et al. 1994). The analysis of one sample was duplicated and yielded a repeatability of ± 1%. One sample leachate was spiked after initial analysis with roughly the quantity of NH_3 in the sample and yielded a percentage recovery of 104%. A 5-point calibration was performed over an NH_3 range of 0.1 to 1000 μg/mL.

Table 2.2 List of PNL Inorganic Samples, Controls, and Gravimetric Results Obtained From *In Situ* Sampling of Headspace of Tank TY-103 on 8/5/94

		Sample Port and Volume Information[a]			
Sample Number	Sorbent Type	Flow Rate (mL/min)	Duration (min)	Volume (L)	Mass Gain (g)
Samples:					
S4062-062-43W	$NH_3/NO_x/H_2O$ Sample	269	15.0	4.03	0.0420
S4062-062-44W	$NH_3/NO_x/H_2O$ Sample	286	15.0	4.30	0.0522
S4062-062-45W	$NH_3/NO_x/H_2O$ Sample	254	15.0	3.80	0.0441
S4062-062-50W	$NH_3/NO_x/H_2O$ Blank/Spare	n/a[b]	n/a	n/a	-0.0001
S4062-062-46W	HCN/H_2O Sample	326	15.0	4.89	0.0557
S4062-062-47W	HCN/H_2O Sample	273	15.0	4.10	0.0567
S4062-062-48W	HCN/H_2O Sample	258	15.0	3.87	0.0481
S4062-062-51W	HCN/H_2O Blank/Spare	n/a	n/a	n/a	0.0006

(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.

2.4.2 Nitrogen Oxides Results. Measurements of NO_2 and NO were made using three 5-segment $NH_3/NO_x/H_2O$ sorbent-trap trains (the NO_x trains consisted of NO_2 trap, oxidizer, and NO_2 trap). Related sample jobs, performed using the vapor sampling system (VSS) in Tanks BY-104, -105, and -106 both with and without NO_x trains protected by a leading NH_3 trap (e.g., Clauss et al. 1994), indicated that the presence of the upstream NH_3 traps resulted in NO concentrations that were about 1.3- to 1.6-fold less than those from unprotected NO_2 traps. The NO_2 concentrations were also potentially less following an NH_3 trap.

The concentrations of NO_2 and NO were $\leq$ 0.02 and $\leq$ 0.06 ppmv, respectively. Blank-corrected NO_2^- quantities in the sorbent traps averaged $\leq$ 0.001 μmol (NO_2 samples) and $\leq$ 0.005 μmol (NO samples). Nitrite blank levels used to correct data were 0.0144 $\pm$ 0.0004 μmol in front and 0.0064 $\pm$ 0.0004 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 μmol of NO_2^- during related sample jobs yielded percentage recoveries of 153 $\pm$ 14%, 103 $\pm$ 4%, 106 $\pm$ 8%, and 111 $\pm$ 7%, respectively (Clauss et al. 1994; Ligotke 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 μg NO_2^- per mL in the desorbing matrix.

2.4.3 Hydrogen Cyanide Results. The concentration of HCN was estimated to be $\leq$ 0.01 ppmv. The samples contained 0.0106 $\pm$ 0.0008 μmol in front and 0.0043 $\pm$ 0.0004 μmol CN^- in back sections. The blank contained 0.0107 μmol in the front and 0.0039 μmol CN^- in the back section.

Table 2.3 Inorganic Vapor Sample Results Obtained From *In Situ* Sampling of the Headspace of Tank TY-103 on 8/5/94

Sample	Analytical Results (μmol) Front Section	Back Section	Total[b] Blank-Corrected	Sample Volume (L)	Vapor[a] Concentration (ppmv)
NH_3 Samples:			5.2[c]	4.04[c]	31 ± 6[c]
S4062-062-43W	4.0	≤0.06	4.0	4.03	24
S4062-062-44W	6.0	≤0.06	6.0	4.30	34
S4062-062-45W	5.7	≤0.06	5.7	3.80	36
NO_2 Samples:			≤0.001	4.04	≤ 0.02
S4062-062-43W	0.0143	0.0063	n/a[d]	4.03	n/a
S4062-062-44W	0.0144	0.0062	n/a	4.30	n/a
S4062-062-45W	0.0146	0.0059	n/a	3.80	n/a
NO Samples:			≤0.005	4.04	≤ 0.06
S4062-062-43W	0.0158	0.0061	n/a	4.03	n/a
S4062-062-44W	0.0185	0.0065	n/a	4.30	n/a
S4062-062-45W	0.0178	0.0063	n/a	3.80	n/a
HCN Samples:			≤ 0.002	4.29	≤ 0.01
S4062-062-46W	0.0107	0.0048	n/a	4.89	n/a
S4062-062-47W	0.0096	0.0041	n/a	4.10	n/a
S4062-062-48W	0.0113	0.0039	n/a	3.87	n/a
Gravimetric Samples (mg.mg/L):			48 mg	4.16	12 ± 2 mg/L
S4062-062-43W	n/a	n/a	40	4.03	9.9
S4062-062-44W	n/a	n/a	50	4.30	11.6
S4062-062-45W	n/a	n/a	42	3.80	11.1
S4062-062-46W	n/a	n/a	54	4.89	11.0
S4062-062-47W	n/a	n/a	55	4.10	13.4
S4062-062-48W	n/a	n/a	46	3.87	11.9

(a) Blank-corrected vapor concentrations were calculated using WHC-reported dry-air sample volumes (corrected to 21°C and 760 torr). In the calculation for concentration, the nitrite values (listed) were doubled to account for unanalyzed nitrate. Sample results were not corrected for percentage recovery of spiked samples or spiked blanks.

(b) Total blank-corrected analyte masses (nitrite for NO_2 and NO) were determined, when significant, by subtracting the quantity of analyte found in blanks from that found in samples. The level of analytes found in blanks is described in the subsections of Section 2.4.

(c) Underlined values represent the average of the set samples. Concentration uncertainty equals ± 1 standard deviation (absolute) for each set of samples other than mass concentration. The uncertainty in mass concentration was determined based on the added uncertainty caused by the range of results of six related blanks. The use of "≤" is defined in Section 2.0.

(d) n/a = not applicable.

Blanks spiked with 0.0099 ± 0.0001 μmol CN^- were found previously to yield an average blank-corrected percentage recovery of 69 ± 10% after a hold time of 11 weeks (ISS sample job in BY-111). It is possible that the relatively 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.

2.4.3 Gravimetric Results. The mass concentration of material collected in the sorbent-trap trains, believed to be primarily water vapor, was 12 ± 2 mg/L. The result was based on an average blank-corrected mass gain of 48 mg from all six sets of sample trains. The actual mass gains were corrected by subtracting a blank mass gain of 2 mg from the change in mass of each train. 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 for the $NH_3/NO_x/H_2O$ trains and -1 to +6 mg for the HCN/H_2O trains. 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 ± 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 and unknown contaminants to a level of 5 parts per billion by volume (ppbv), the canister is evacuated to 5×10^{-3} torr, tagged, and stored for use in the field. Before sending the canisters out to the field for sampling, the canister vacuum is measured to determine if any leakage has occurred. If the vacuum has remained constant during storage, the canisters are prehumidified with 100 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 either a 5971 or a 5972 Hewlett Packard (HP) benchtop GC/MS. The EnTech concentrator is used to pull a metered volume of sample air from the SUMMA™ canister, cryogenically concentrate the air volume, then transfer the volume to the GC/MS for analysis. A 100-mL volume of sample is measured and analyzed from the tank headspace. The organic components in the sampled air are separated on an analytical column, J&W Scientific DB-1 phase, 60-m by 0.32-mm internal diameter with 3-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. The instrument calibration mixture for the TO-14 analysis consists of the standard 39 organic analytes.

(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.

The calibration mixture was a commercially prepared 39-compound TO-14 calibration mixture. The standard calibration mix was analyzed using six aliquot sizes ranging from 5 mL to 300 mL. Depending on the concentration of each analyte in the mixture, either five or six points were used to construct the calibration curve. Performance-based detection limits for the target analytes will be developed as a pool of calibration data becomes available. Currently, the nominal detection limit of 5 ppbv is met.

3.3 Quality Assurance/Quality Control

Before the tank sample was analyzed, a diagnostic check was performed on the GC/MS instrument by running an instrument "quick tune," as described in PNL-TVP-03. Upon satisfactory completion of the instrument diagnostic check, a blank volume of purified nitrogen was analyzed to check the cleanliness of the system. The instrument was then calibrated over 5 to 6 data points ranging from 5 ppbv to 300 ppbv, using a standard gas mixture containing 39 volatile organic compounds listed in EPA compendium Method TO-14. A gas mixture containing bromochloromethane, 1,4-difluorobenzene, and chlorobenzene-d_5 was used as an internal standard (IS) for all blank, calibration standard, and sample analyses. Analyte responses from sample components, ISs, and standards were obtained from the extracted ion plot from their selected mass ion. The calibration curve was generated by calculating the relative response ratios of the IS to calibration standard responses and plotting the ratios against the ratio of the calibration-standard concentration (in ppbv) to the IS concentration. A least-squares linear-regression routine was applied to the data set to generate the best-fit line for each compound. The equation for that line was then used to quantify the target organic analytes found in the tank samples.

The ambient air sample collected ~10 m upwind of TY-103 was used as a method blank and was used to determine the potential for analyte interferences in the samples. Continuing calibration standards for this sample set fell within ± 25% of the expected concentrations for the analytes reported.

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

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

3.3.2 Identification and Quantitation of Tentatively Identified Compounds. The tentatively identified compounds (TICs) are determined by mass-spectral interpretation and comparison of the spectra with the EPA/NIST/WILEY Library, which is a part of the HP 5971/5972 instrument operating system. Chromatographic peaks with an area count greater than, or equal to, one tenth of the total area count of the nearest eluting IS are tentatively identified and quantitatively estimated. The quality of the mass-spectral searches was then reviewed by the principal investigators before the identification was assigned to each chromatographic peak. The concentration of each TIC was estimated using a relative response factor calculated using the total peak area for the nearest eluting IS. The IS peak area was used to calculate a response factor using the IS concentration in mg/m^3:

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

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.

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

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. All sample concentrations were multiplied by a factor of two to account for the dilution step described in Section 3.2.

3.4 Analysis Results

The results from the GC/MS analysis of the tank-headspace samples are presented in Tables 3.1 and 3.2. The results of replicate analyses of a single sample are presented in Table 3.3 and 3.4 The results of GC/MS analysis of an ambient air sample collected upwind of Tank TY-103 is presented in Table 3.5. A representative total ion chromatogram showing the identity of major constituents is given in Figure 3.1.

Table 3.1 lists the quantitative results for the target analytes. Four analytes were above the 5-ppbv detection limit. Trichlorofluoromethane (0.84 mg/m^3) and Toluene (0.82 mg/m^3) were approximately 89% of the total concentration of target analytes. Table 3.2 lists the semi-quantitative results for the TICs. The total concentration of the TIC compounds was found to be 41.88 mg/m^3. The predominant species observed were tridecane, tetradecane, and dodecane. Other normal paraffin hydrocarbons (NPHs), defined as n-alkanes from C_{11} to C_{15}, were observed. 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.

SUMMA™ canister PNL 165 was analyzed in replicate for target analytes and TICs to determine precision. The analytical and relative percent difference (RPD) results are presented in Tables 3.3 and 3.4. The RPD was calculated for analytes detected above the detection limit and found in both replicates. All four of the analytes had an RPD of less than 10%. Five of the 19 TICs detected had RPDs of less than 10%.

Table 3.5 lists semi-quantitative results for the TIC analytes in the ambient air sample collected ~10 m upwind of Tank TY-103. Acetaldehyde, acetone, and butanal were observed in the upwind sample.

4.0 Conclusions

The concentrations of selected inorganic and organic compounds were determined from *in situ* samples of the headspace of Tank TY-103 on 8/5/94. Sampling and analysis methods followed those described by Ligotke et al. (1994) for samples obtained from Tank C-103 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 average and standard deviation of the concentration results from inorganic sorbent trains were 31 $\pm$ 6 ppmv (NH_3), $\leq$0.02 ppmv (NO_2), $\leq$0.06 ppmv (NO), $\leq$0.01 ppmv (HCN), and 12 $\pm$ 2 mg/L (vapor-mass concentration). The vapor-mass concentration is 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.

Organic analysis of the tank-headspace samples from Tank TY-103 identified four target analytes above the 5-ppbv MDL and 25 TICs above the 10-ppbv detection limit. Eighteen TICs were identified in two or more of the SUMMA™ samples. The total target analyte concentration accounted for 4% of the total compounds identified by both the target analyte and the TIC analyses. Trichlorofluoromethane and toluene accounted for 89% of the target analytes and 4% of the total compounds identified by both analyses. The highest concentration TIC was tridecane; it accounted for 46% of the total TIC concentration. The results of the TIC analysis identified numerous NPH type compounds as the predominant species (by number) present in the tank-headspace samples. Results of replicate analysis of a single SUMMA™ canister observed none of the target analytes, and five TICs have an RPD of less than 10%. The results of the ambient air sample collected ~10 m upwind of Tank TY-103 identified three TIC analytes, acetaldehyde, acetone, and butanal, and no target analytes.

5.0 References

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

Ligotke, M. W., K. H. Pool, and B. D. Lerner. 1994. *Vapor Space Characterization of Waste Tank 241-C-103: Inorganic Results from Sample Job 7B (5/12/94 - 5/25/94).* PNL-10172, Pacific Northwest Laboratory, Richland, Washington.

6.0 Further Reading

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

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

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

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

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

Table 3.1 Positively Identified and Quantitated Target Organic Analytes[a] of Samples Collected from the Headspace of Tank TY-103 in SUMMA™ Canisters on 8/5/94

Analyte	CAS No.	Mol Wt	S4062—.028[b] PNL 028[d] Concentration (mg/m^3)	(ppbv)	S4062—.165[b],[c] PNL 165[d] Concentration (mg/m^3)	(ppbv)	S4062—.166[b] PNL 166[d] Concentration (mg/m^3)	(ppbv)	Means and Standard Deviation (mg/m^3)	St Dev
Dichlorodifluoromethane	75-71-8	120	< 0.03	< 5	< 0.03	< 5	< 0.03	< 5	(e)	(e)
Chloromethane	74-87-3	50	< 0.01	< 5	< 0.01	< 5	< 0.01	< 5	(e)	(e)
1,2-Dichloro-1,1,2,2,-Tetrafluoroethane	76-14-2	170	< 0.04	< 5	< 0.04	< 5	< 0.04	< 5	(e)	(e)
Vinyl Chloride	75-01-4	64	< 0.01	< 5	< 0.01	< 5	< 0.01	< 5	(e)	(e)
Bromomethane	74-83-9	94	< 0.02	< 5	< 0.02	< 5	< 0.02	< 5	(e)	(e)
Chloroethane	75-00-3	62	< 0.01	< 5	< 0.01	< 5	< 0.01	< 5	(e)	(e)
Trichlorofluoromethane	75-69-4	136	0.73	120	0.81	133	0.98	161.2	0.84	0.13
1,1-Dichloroethene	75-35-4	96	< 0.02	< 5	< 0.02	< 5	< 0.02	< 5	(e)	(e)
Methylene Chloride	75-09-2	84	< 0.02	< 5	< 0.02	< 5	< 0.02	< 5	(e)	(e)
1,1,2-Trichloro-1,2,2-Trifluoroethane	76-13-1	186	< 0.04	< 5	< 0.04	< 5	< 0.04	< 5	(e)	(e)
1,1-dichloroethane	75-34-3	98	< 0.02	< 5	< 0.02	< 5	< 0.02	< 5	(e)	(e)
cis-1,2-dichloroethene	156-59-2	96	< 0.02	< 5	< 0.02	< 5	< 0.02	< 5	(e)	(e)
Chloroform	67-66-3	118	< 0.02	< 5	< 0.02	< 5	< 0.02	< 5	(e)	(e)
1,2-Dichloroethane	107-06-2	98	< 0.02	< 5	< 0.02	< 5	< 0.02	< 5	(e)	(e)
1,1,1-Trichloroethane	71-55-6	132	< 0.03	< 5	< 0.03	< 5	< 0.03	< 5	(e)	(e)
Benzene	71-43-2	78	< 0.02	< 5	< 0.02	< 5	< 0.02	< 5	(e)	(e)
Carbon Tetrachloride	56-23-5	152	0.16	23.8	0.08	11.8	0.14	19.8	0.13	0.04
1,2-Dichloropropane	78-87-5	112	< 0.03	< 5	< 0.03	< 5	< 0.03	< 5	(e)	(e)
Trichloroethylene	79-01-6	130	< 0.03	< 5	< 0.03	< 5	< 0.03	< 5	(e)	(e)
cis 1,3-Dichloropropene	61-01-5	110	< 0.02	< 5	< 0.02	< 5	< 0.02	< 5	(e)	(e)
trans 1,3-Dichloropropene	61-02-6	110	< 0.02	< 5	< 0.02	< 5	< 0.02	< 5	(e)	(e)
1,1,2-Trichloroethane	79-00-5	132	< 0.03	< 5	< 0.03	< 5	< 0.03	< 5	(e)	(e)
Toluene	108-88-3	92	0.75	183	0.63	154	1.08	260	0.82	0.23
1,2-Dibromoethane	106-93-4	186	< 0.04	< 5	< 0.04	< 5	< 0.04	< 5	(e)	(e)
Tetrachloroethylene	127-18-4	164	0.08	10.8	0.09	12.0	0.08	10.6	0.08	0.01
Chlorobenzene	108-90-7	112	< 0.03	< 5	< 0.03	< 5	< 0.03	< 5	(e)	(e)
Ethylbenzene	100-41-4	106	< 0.02	< 5	< 0.02	< 5	< 0.02	< 5	(e)	(e)
m-Xylene[f]	108-38-3	106	< 0.02	< 5	< 0.02	< 5	< 0.02	< 5	(e)	(e)
p-Xylene[f]	106-42-3	106								
Styrene	100-42-5	104	< 0.02	< 5	< 0.02	< 5	< 0.02	< 5	(e)	(e)
1,1,2,2-Tetrachloroethane	79-34-5	166	< 0.02	< 5	< 0.02	< 5	< 0.02	< 5	(e)	(e)
o-Xylene	95-47-6	106	< 0.02	< 5	< 0.02	< 5	< 0.02	< 5	(e)	(e)

Table 3.1 (Contd)

Analyte	CAS No.	Mol Wt	S4062—.028[b] PNL 028[d] Concentration (mg/m^3)	(ppbv)	S4062—.165[b],[c] PNL 165[d] Concentration (mg/m^3)	(ppbv)	S4062—.166[b] PNL 166[d] Concentration (mg/m^3)	(ppbv)	Means and Standard Deviation (mg/m^3)	St Dev
1,3,5-Trimethylbenzene	108-67-8	120	< 0.03	< 5	< 0.03	< 5	< 0.03	< 5	(e)	(e)
1,2,4-Trimethylbenzene	95-63-6	120	< 0.03	< 5	< 0.03	< 5	< 0.03	< 5	(e)	(e)
Chloromethylbenzene, alpha	100-44-7	126	< 0.03	< 5	< 0.03	< 5	< 0.03	< 5	(e)	(e)
1,3-Dichlorobenzene	541-73-1	146	< 0.03	< 5	< 0.03	< 5	< 0.03	< 5	(e)	(e)
1,4-Dichlorobenzene	106-46-7	146	< 0.03	< 5	< 0.03	< 5	< 0.03	< 5	(e)	(e)
1,2-Dichlorobenzene	95-50-1	146	< 0.03	< 5	< 0.03	< 5	< 0.03	< 5	(e)	(e)
1,2,4-Trichlorobenzene	120-82-1	180	< 0.04	< 5	< 0.04	< 5	< 0.04	< 5	(e)	(e)
Hexachloro-1,3-Butadiene	87-68-3	258	< 0.60	< 5	< 0.60	< 5	< 0.60	< 5	(e)	(e)

(a) TO-14 analytes.
(b) WHC sample identification number.
(c) Replicates of this sample are found in Table 3.3
(d) PNL canister number.
(e) Mean and standard deviation are not meaningful for this analyte.
(f) m-Xylene and p-Xylene coelute; the reported concentration is the sum of these two compounds.

Table 3.2 Tentatively Identified Compounds and Estimated Concentrations[a] of Samples from the Headspace of Tank TY-103 in SUMMA™ Canisters Collected on 8/5/94

Tentatively Identified Compound[e]	CAS No.[e]	Mol Wt	Ret Time	S4062—.028[b] PNL 028[d] (mg/m³)	(ppbv)	S4062—.165[b],[c] PNL 165[d] (mg/m³)	(ppbv)	S4062—.166[b] PNL 166[d] (mg/m³)	(ppbv)	Means and Standard Deviations (mg/m³)	St Dev	(ppbv)	St Dev
Acetaldehyde	75-07-0	44	5.4	0.28	141	0.50	253	0.26	134.4	0.35	0.13	176	66.5
Butane	106-97-8	58	6.3	0.16	63.3	0.12	47.1	0.15	59.5	0.15	0.02	56.6	8.5
2-Methyl-1-propene	115-11-7	56	7.0	< 0.03	< 10	< 0.03	< 10	< 0.03	< 10	(f)	(f)	(f)	(f)
Acetone	67-64-1	58	8.7	0.46	176	0.80	311	0.46	177.7	0.57	0.20	221	77
Pentane	109-66-0	72	10.0	< 0.03	< 10	< 0.03	< 10	< 0.03	< 10	(f)	(f)	(f)	(f)
Butanal	123-72-8	72	13.6	0.13	40.1	0.25	79.0	0.14	44.8	0.18	0.07	54.7	21.2
2-Butanone	78-93-3	72	13.8	0.14	43.6	0.19	58.5	0.26	79.6	0.19	0.06	60.6	18.1
Unknown C8 Alkane		114	16.5	< 0.05	< 10	0.15	30.3	0.13	25.5	0.14		27.9	
2,4-Dimethylpentane	108-08-7	100	16.8	< 0.04	< 10	0.13	28.2	< 0.04	< 10	(f)	(f)	(f)	(f)
1-Butanol	71-36-3	74	17.8	0.82	247	0.73	221	0.77	232	0.77	0.04	234	13.2
2-Methylhexane	591-76-4	100	18.9	1.56	350	1.61	360	1.60	358	1.59	0.02	356	5
2,3-Dimethylpentane	565-59-3	100	19.2	1.50	336	1.50	336	1.47	330	1.49	0.01	334	3.2
3-Methylhexane	589-34-4	100	19.5	2.65	594	2.68	600	2.67	598	2.67	0.01	597	3
Unknown C7 Alkane		100	20.1	0.57	127	0.63	141	0.58	130.8	0.59	0.03	133	7.3
Unknown C7 Alkene/Cycloalkane		100	20.4	0.13	29.1	0.14	30.5	0.14	32.3	0.14	0.01	30.6	1.6
Heptane	142-82-5	100	20.8	0.60	134	0.58	129	0.68	152.8	0.62	0.06	139	12.4
Methylcyclohexane	108-87-2	98	22.4	0.78	177	0.85	194	0.79	180.1	0.80	0.04	184	8.9
Hexanal	66-25-1	100	25.1	< 0.04	< 10	0.09	19.3	< 0.04	< 10	(f)	(f)	(f)	(f)
Heptanal	111-71-7	114	30.5	0.07	13.4	< 0.05	< 10	< 0.05	< 10	(f)	(f)	(f)	(f)
Undecane	1120-21-4	156	40.4	0.23	33.3	0.22	31.3	0.22	31.6	0.22	0.01	32	1.1
Dodecane	112-40-3	170	44.5	6.09	802	4.75	625	4.76	627	5.20	0.77	685	102
Tridecane	629-50-5	184	48.2	27.22	3313	12.84	1563	15.45	1880	18.5	7.7	2252	932
Unknown Ketone			50.4	0.14			< 10		< 10	(f)	(f)	(f)	(f)
Tetradecane	629-59-4	198	51.7	8.04	910	3.29	372	6.19	700	5.84	2.40	661	271
Pentadecane	629-62-9	212	55.0	0.12	12.5		< 10		< 10	(f)	(f)	(f)	(f)
Unknown Alkane			56.7	0.08			< 10		< 10	(f)	(f)	(f)	(f)
Unknown Alkane			57.0	0.09			< 10		< 10	(f)	(f)	(f)	(f)

(a) Semi-quantitative estimate calculated using concentration of closest eluting IS.
(b) WHC sample identification number.
(c) Replicates of this sample are found in Table 3.4
(d) PNL SUMMA™ canister number.
(e) Obtained by mass spectral interpretation amd comparison with the EPA/NIST/WILEY Library.
(f) Mean and standard deviation are not meaningful for this analyte.

Table 3.3 Positively Identified and Quantitated Target Organic Analytes[a] of Replicate Analyses of a Single SUMMA™ Canister Collected from the Headspace of Tank TY-103 on 8/5/94

Analyte	CAS No.	Mol Wt	S4062—.165[b] PNL 165[c] Concentration (mg/m^3)	(ppbv)	S4062—.165[b] PNL 165[c] Concentration (mg/m^3)	(ppbv)	Relative Percent Differenc %
Dichlorodifluoromethane	75-71-8	120	< 0.03	< 5	< 0.03	< 5	
Chloromethane	74-87-3	50	< 0.01	< 5	< 0.01	< 5	
1,2-Dichloro-1,1,2,2,-Tetrafluoroethane	76-14-2	170	< 0.04	< 5	< 0.04	< 5	
Vinyl Chloride	75-01-4	64	< 0.01	< 5	< 0.01	< 5	
Bromomethane	74-83-9	94	< 0.02	< 5	< 0.02	< 5	
Chloroethane	75-00-3	62	< 0.01	< 5	< 0.01	< 5	
Trichlorofluoromethane	75-69-4	136	0.81	133	1.11	181	31.3
1,1-Dichloroethene	75-35-4	96	< 0.02	< 5	< 0.02	< 5	
Methylene Chloride	75-09-2	84	< 0.02	< 5	< 0.02	< 5	
1,1,2-Trichloro-1,2,2-Trifluoroethane	76-13-1	186	< 0.04	< 5	< 0.04	< 5	
1,1-dichloroethane	75-34-3	98	< 0.02	< 5	< 0.02	< 5	
cis-1,2-dichloroethene	156-59-2	96	< 0.02	< 5	< 0.02	< 5	
Chloroform	67-66-3	118	< 0.02	< 5	< 0.02	< 5	
1,2-Dichloroethane	107-06-2	98	< 0.02	< 5	< 0.02	< 5	
1,1,1-Trichloroethane	71-55-6	132	< 0.03	< 5	< 0.03	< 5	
Benzene	71-43-2	78	< 0.02	< 5	< 0.02	< 5	
Carbon Tetrachloride	56-23-5	152	0.08	11.8	0.09	13.8	11.8
1,2-Dichloropropane	78-87-5	112	< 0.03	< 5	< 0.03	< 5	
Trichloroethylene	79-01-6	130	< 0.03	< 5	< 0.03	< 5	
cis 1,3-Dichloropropene	61-01-5	110	< 0.02	< 5	< 0.02	< 5	
trans 1,3-Dichloropropene	61-02-6	110	< 0.02	< 5	< 0.02	< 5	
1,1,2-Trichloroethane	79-00-5	132	< 0.03	< 5	< 0.03	< 5	
Toluene	108-88-3	92	0.63	154	0.7	170	10.5
1,2-Dibromoethane	106-93-4	186	< 0.04	< 5	< 0.04	< 5	
Tetrachloroethylene	127-18-4	164	0.09	12.0	0.1	13.4	10.5
Chlorobenzene	108-90-7	112	< 0.03	< 5	< 0.03	< 5	
Ethylbenzene	100-41-4	106	< 0.02	< 5	< 0.02	< 5	
m-Xylene[f]	108-38-3	106	< 0.02	< 5	< 0.02	< 5	
p-Xylene[f]	106-42-3	106					
Styrene	100-42-5	104	< 0.02	< 5	< 0.02	< 5	
1,1,2,2-Tetrachloroethane	79-34-5	166	< 0.02	< 5	< 0.02	< 5	
o-Xylene	95-47-6	106	< 0.02	< 5	< 0.02	< 5	

Table 3.3 (Contd)

Analyte	CAS No.	Mol Wt	S4062—.165[b] PNL 165[c] Concentration		S4062—.165[b] PNL 165[c] Concentration		Relative Percent Differenc
			(mg/m^3)	(ppbv)	(mg/m^3)	(ppbv)	%
1,3,5-Trimethylbenzene	108-67-8	120	< 0.03	< 5	< 0.03	< 5	
1,2,4-Trimethylbenzene	95-63-6	120	< 0.03	< 5	< 0.03	< 5	
Chloromethylbenzene, alpha	100-44-7	126	< 0.03	< 5	< 0.03	< 5	
1,3-Dichlorobenzene	541-73-1	146	< 0.03	< 5	< 0.03	< 5	
1,4-Dichlorobenzene	106-46-7	146	< 0.03	< 5	< 0.03	< 5	
1,2-Dichlorobenzene	95-50-1	146	< 0.03	< 5	< 0.03	< 5	
1,2,4-Trichlorobenzene	120-82-1	180	< 0.04	< 5	< 0.04	< 5	
Hexachloro-1,3-Butadiene	87-68-3	258	< 0.60	< 5	< 0.60	< 5	

(a) TO-14 analytes.
(b) WHC sample identification number.
(c) PNL canister number.
(d) m-Xylene and p-Xylene coelute; the reported concentration is the sum of these two compounds.

Table 3.4 Tentatively Identified Compounds and Estimated Concentrations[a] of Replicate Analyses of a Single SUMMA™ Canister Collected from the Headspace of Tank TY-103 on 8/5/94

Tentatively Identified Compound[d]	CAS No.[d]	Mol Wt	Ret Time	S4062----.165[b] PNL 165[c] (mg/m^3)	(ppbv)	S4062----.165[b] PNL 165[c] (mg/m^3)	(ppbv)	Relative Percent Difference %
Acetaldehyde	75-07-0	44	5.4	0.50	253	0.63	320	23.5
Butane	106-97-8	58	6.3	0.12	47.1	0.20	76.5	47.5
2-Methyl-1-propene	115-11-7	56	7.0	< 0.03	< 10	0.11	44.8	
Acetone	67-64-1	58	8.7	0.80	311	0.88	341	9.5
Pentane	109-66-0	72	10.0	< 0.03	< 10	0.12	36.4	
Butanal	123-72-8	72	13.6	0.25	79.0	0.32	98.0	21.4
2-Butanone	78-93-3	72	13.8	0.19	58.5	0.21	64.7	10.1
Unknown C8 Alkane		114	16.5	0.15	30.3	0.20	39.7	27.0
2,4-Dimethylpentane	108-08-7	100	16.8	0.13	28.2	< 0.04	< 10	
1-Butanol	71-36-3	74	17.8	0.73	221	0.82	247	11.0
2-Methylhexane	591-76-4	100	18.9	1.61	360	1.83	409	12.8
2,3-Dimethylpentane	565-59-3	100	19.2	1.50	336	1.71	382	13.0
3-Methylhexane	589-34-4	100	19.5	2.68	600	3.07	687	13.5
Unknown C7 Alkane		100	20.1	0.63	141	0.66	148	4.7
Unknown C7 Alkene/Cycloalkane		100	20.4	0.14	30.5	0.16	36.3	17.4
Heptane	142-82-5	100	20.8	0.58	129	0.67	149	14.3
Methylcyclohexane	108-87-2	98	22.4	0.85	194	0.91	209	7.3
Hexanal	66-25-1	100	25.1	0.09	19.3	0.10	22.4	15.1
Heptanal	111-71-7	114	30.5	< 0.05	< 10	< 0.05	< 10	
Undecane	1120-21-4	156	40.4	0.22	31.3	0.23	32.9	4.9
Dodecane	112-40-3	170	44.5	4.75	625	4.91	647	3.4
Tridecane	629-50-5	184	48.2	12.84	1563	15.53	1891	19.0
Unknown Ketone			50.4	(e)	< 10	(e)	< 10	

Table 3.4 (Contd)

Tentatively Identified Compound[d]	CAS No.[d]	Mol Wt	Ret Time	S4062—.165[b] PNL 165[c] (mg/m^3)	(ppbv)	S4062—.165[b] PNL 165[c] (mg/m^3)	(ppbv)	Relative Percent Difference %
Tetradecane	629-59-4	198	51.7	3.29	372	4.08	462	21.6
Pentadecane	629-62-9	212	55.0	(e)	< 10	(e)	< 10	
Unknown Alkane			56.7	(e)	< 10	(e)	< 10	
Unknown Alkane			57.0	(e)	< 10	(e)	< 10	

(a) Semi-quantitative estimate calculated using concentration of closest eluting IS.
(b) WHC sample identification number.
(c) PNL SUMMA™ canister number.
(d) Obtained by mass spectral interpretation amd comparison with the EPA/NIST/WILEY Library.
(e) No molecular weight available for calculation.

Table 3.5 Tentatively Identified Compounds and Estimated Concentrations in Samples of Ambient Air Collected in SUMMA™ Canisters Near Tank TY-103 on 8/5/94

			S4062----.020[(a)] PNL 020[(b)] Concentration	
Analyte	CAS No.	Mol Wt	(mg/m^3)	(ppbv)
Acetaldehyde	75-07-0	44	0.46	234
Acetone	67-64-1	58	0.43	165
Butanal	123-72-8	72	0.14	42.0

(a) WHC sample identification number.
(b) PNL canister number.

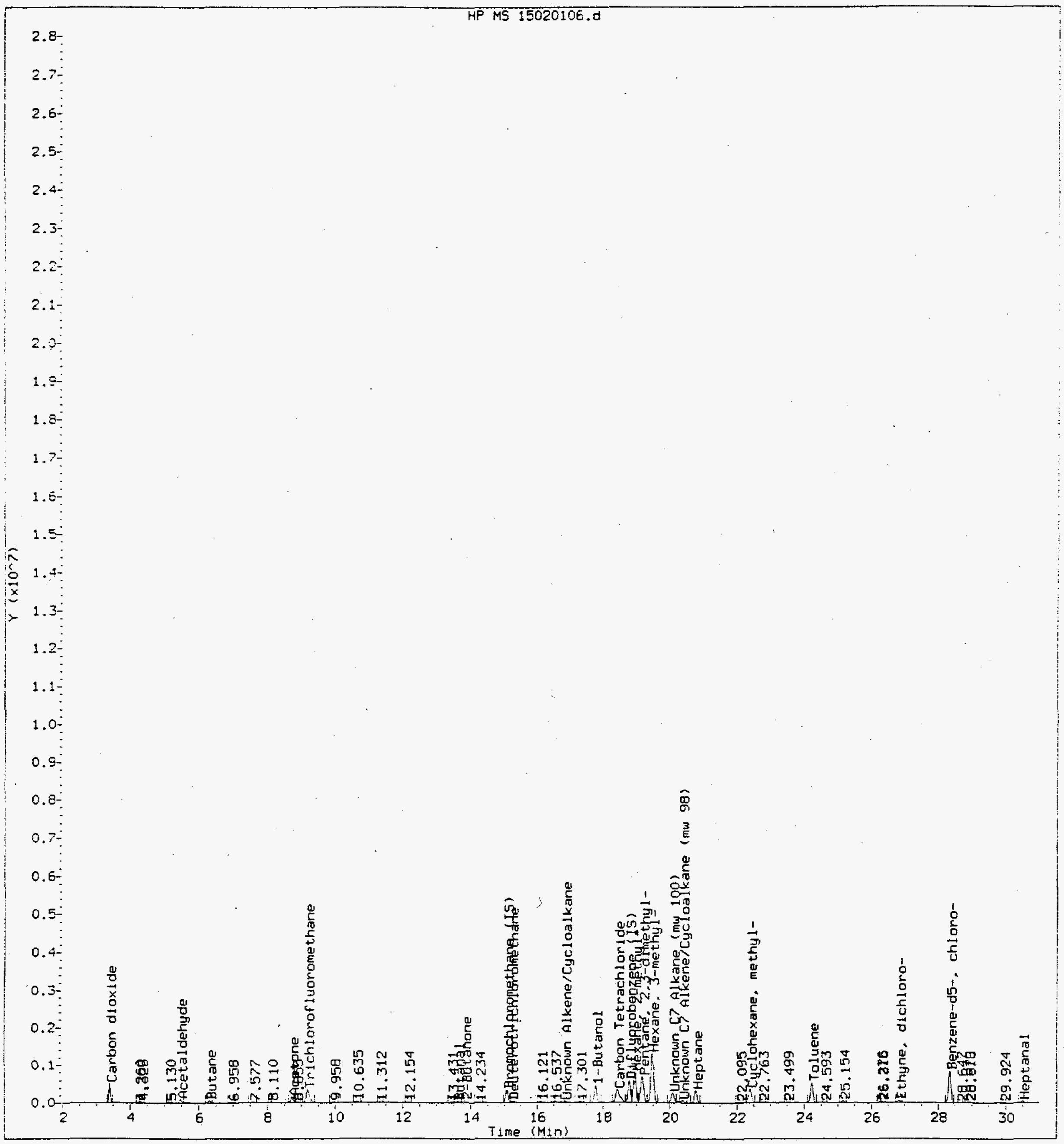

Figure 3.1a Total Ion Chromatogram (2 - 30 min) for Hanford Waste Tank TY-103 *In Situ* SUMMA™ Canister Sample S-4062---.028 Collected on 8/5/94

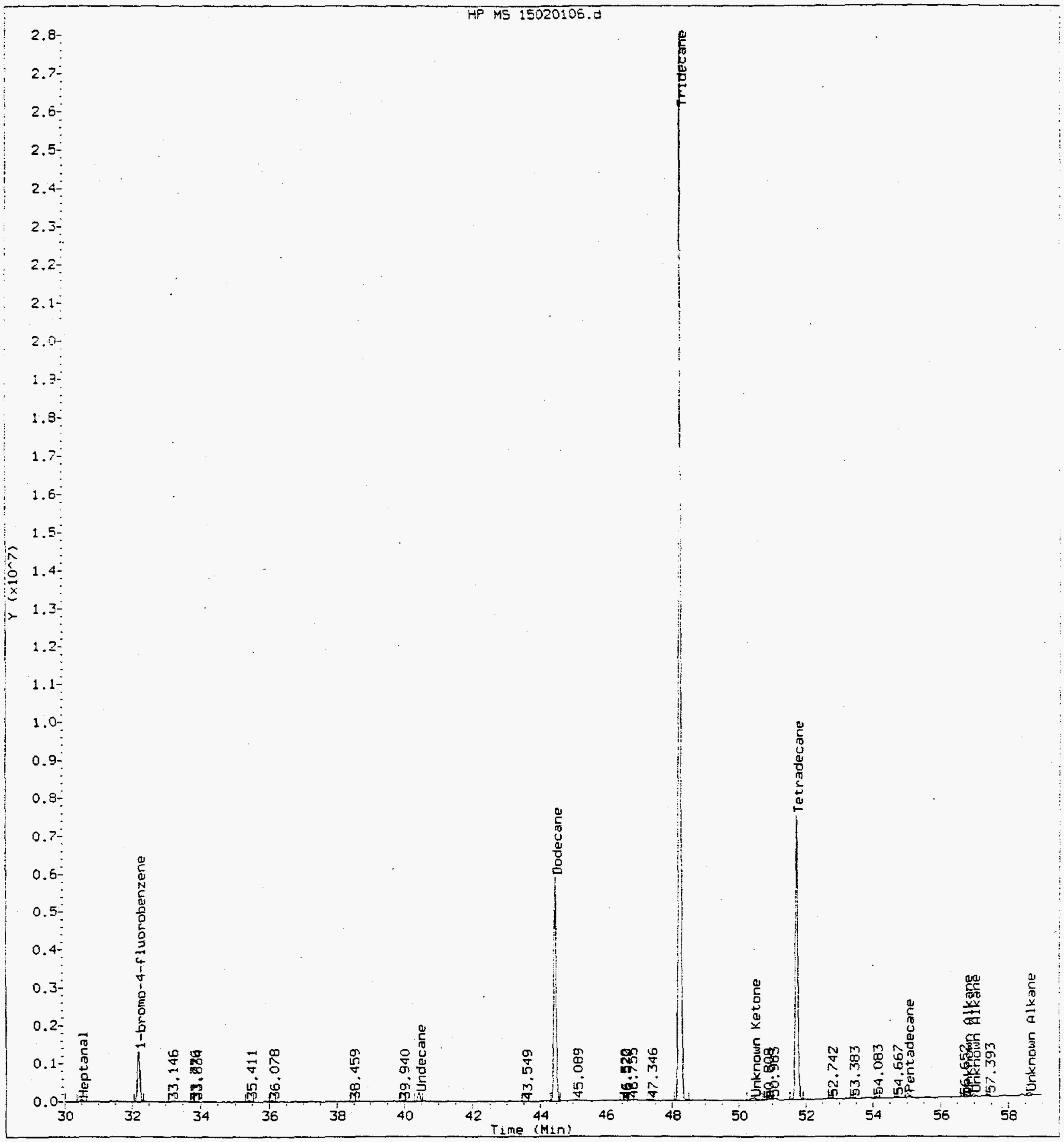

Figure 3.1b Total Ion Chromatogram (30 - 58 min) for Hanford Waste Tank TY-103 *In Situ* SUMMA™ Canister Sample S-4062---.028 Collected on 8/5/94

Distribution

No. of Copies

Offsite

2 DOE/Office of Scientific and Technical Information

R. A. Jenkins
Oak Ridge National Laboratory
P.O. Box 2008
Building 4500-5, MS 6120
Oak Ridge, Tennessee 37831-6120

No. of Copies

Onsite

2 DOE Richland Operations Office

J. M. Clark, S7-54
T. Noble, S7-54

Corps of Engineers

T. W. Gardner-Clayson, A5-19

3 Westinghouse Hanford Company

H. Babad, R2-78
D. R. Bratzel, S7-31
J. E. Meacham, S7-15

27 Pacific Northwest Laboratory

S. C. Goheen, P8-08 (20)
J. L. Huckaby, K6-55
M. W. Ligotke, P7-59
Technical Report Files (5)