

**Vapor Space Characterization of Waste
Tank 241-BY-106: Results from
Samples Collected Through the Vapor
Sampling System on 7/8/94**

R. B. Lucke
K. H. Pool, Ph.D.
M. W. Ligothke
T. W. Clauss
B. D. McVeety, Ph.D.
J. S. Fruchter, Ph.D.
S. C. Goheen, Ph.D.

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Pacific Northwest Laboratory
Richland, Washington 99352

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Summary

This report describes organic and inorganic analyses results from tank-headspace samples collected from the Hanford single-shell waste storage Tank 241-BY-106 (referred to as Tank BY-106). Quantitative results were obtained for NH₃, NO_x, and H₂O. A summary of the results for inorganic analytes is listed in Summary Table 1.

Summary Table 1. Summary Results of Inorganic Analytes from Samples Collected from the Tank Headspace of Tank BY-106 on 7/7/94

<u>Analyte</u>	<u>Concentration</u>
NH ₃	74 ± 2 ppmv ^(a)
NO	0.16 ± 0.06 ppmv ^(a)
NO ₂	0.05 ± 0.04 ppmv ^(a)
H ₂ O	17 ± 2 mg/L ^(a)

(a) See Section 2.4. NO_x values are from sorbent-trap sections that were not protected by NH₃ sorbent traps.

Organic analytes that are listed in U.S. Environmental Protection Agency (EPA) compendium Method TO-14 were quantitatively determined. Of these only a few were observed above the 2-ppbv detection limits. These are summarized in Table 3.1. Approximately 50 tentatively identified compounds (TICs) not listed in EPA compendium Method TO-14 were observed above the detection limit of (ca.) 10 ppbv. Standards for the TICs were not available at the time of analysis. The tentative identification of these analytes and their estimated semi-quantitative concentrations in the samples are provided in Table 3.2, which shows quantities of all TICs above the concentration of ca. 10 ppbv. This consists of more than 50 organic analytes. The 7 organic analytes with the highest estimated concentrations are shown in Summary Table 2. These 7 analytes account for approximately 50% of the total organic components in Tank BY-106 and are reported from the average of three SUMMA™ canister samples. Detailed descriptions of the results appear in the text. Unlike tanks previously studied, normal paraffin hydrocarbons did not contribute significantly to the total organic concentration of the tank headspace of Tank BY-106. The total concentration of TICs detected in the tank-headspace samples was also much lower than that seen in other tanks^(a). The average of three SUMMA™ canister samples was 130 mg/m³. This concentration is approximately 10% of the concentration of organic material in the vapor of Tank C-103 (Huckaby and Story 1994).

(a) Analysis reports for Tanks BY-104, BY-108, and BY-107 are presently being prepared for Pacific Northwest Laboratory clearance.

Summary Table 2. Summary Results of Selected Organic Analytes

<u>Selected Organic Analytes (TIC)</u>	<u>Average Concentrations (mg/m³)</u>
Propene	1
2-Methyl-1-propene	1
n-Butane	1
Acetone	1
n-Pentane	1
1-Butanol	1
Trichlorofluoromethane	1

Reference

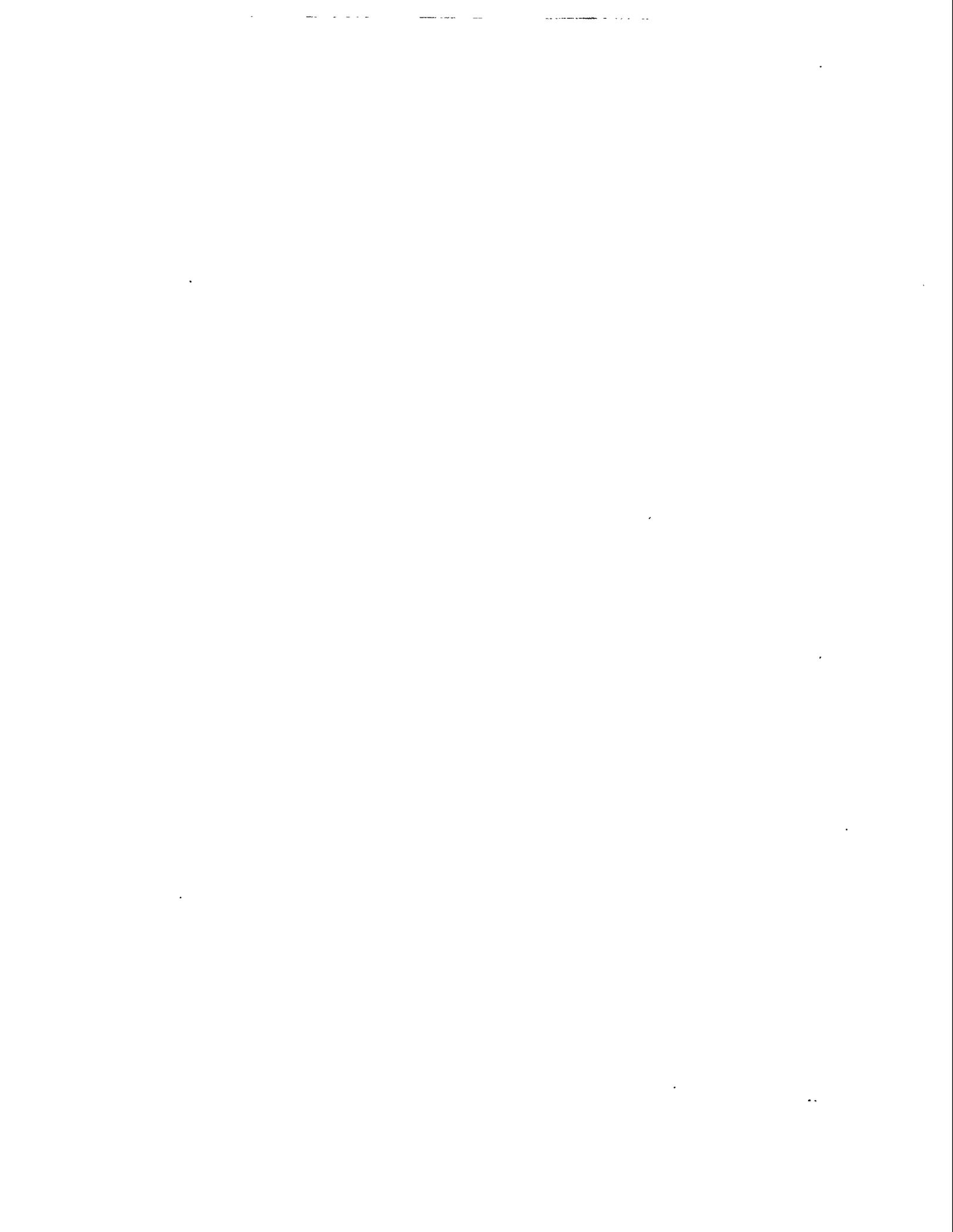
Huckaby, J. L. and M. S. Story. 1994. *Vapor Characterization of Tank 241-C-103*. WHC-EP-0780. Westinghouse Hanford Company, Richland, Washington.

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Abbreviations

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
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 analysis of tank headspace samples taken from the Hanford waste Tank 241-BY-106 (referred to as Tank BY-106) on July 8, 1994. The samples were collected using the Westinghouse Hanford Company (WHC) vapor sampling system (VSS). The WHC sample job number was S4021 (Figure 1). These results 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 sorbent tubes (for inorganic analyses), and SUMMA™ canisters (for organic analysis) were supplied to the WHC sampling staff on June 20, 1994. Samples were taken (by WHC) on July 8 and were returned from the field on July 11. Inorganic (sorbent tube) samples delivered to Pacific Northwest Laboratory (PNL)^(a) on chain of custody (COC) 006895 (Figure 1.1a) included 16 multi-sorbent trap samples as described in Tables 2.2, 2.3, and 2.4. Five SUMMA™ samples delivered to PNL on COC 006898 (Figure 1.1b), included one ambient-air sample through the VSS, one ambient-air sample without the VSS and three tank-headspace SUMMA™ canister samples through the VSS.

The samples were inspected upon delivery to the 326/23B laboratory and logged into PNL record book 55408 as per 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 (4°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 desorbed with water (for ammonia or NO_x analyses). The water extracts were analyzed either by selective electrode or by ion chromatography (IC). Organic analyses were performed using 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), 2/94, Sample Shipping and Receiving Procedure for PNL Waste Tank Samples, PNL Technical DRAFT Procedure, Pacific Northwest Laboratory, Richland, Washington.

Westinghouse Hanford Company	CHAIN OF CUSTODY	WHC 006895
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Custody Form Initiator	J. A. Edwards	Telephone	(509)373 -0141
		Pager	85-3009
Company Contact	R. Westberg	Telephone	(509) 373-5734
Project Designation/Sampling Locations	200 East Tank Farm	Collection Date	06-__-94
BY 106 Tank Vapor Sample SAF S4021		Preparation Date	06-15-94
Ice Chest No. (VSS Truck)		Field Logbook No.	WHC-N-__-
Bill of Lading/Airbill No.	N/A	Offsite Property No.	N/A
Method of Shipment	Government Truck	Sample Job #	_____
Shipped to	PNL?		
Possible Sample Hazards/Remarks	Unknown at time of sampling		

Sample Identification

S4021 - A16 . W64	NH ₃ /NO _x /H ₂ O (Sample #1)
S4021 - A17 . W65	NH ₃ /NO _x /H ₂ O (Sample #2)
S4021 - A18 . W66	NH ₃ /NO _x /H ₂ O (Sample #3)
S4021 - A19 . W67	NH ₃ /NO _x /H ₂ O (Sample #4)
S4021 - A20 . W68	NH ₃ /NO _x /H ₂ O (Sample #5)
S4021 - A21 . W69	NH ₃ (Blank)
S4021 - A22 . W70	NH ₃ (Spiked Blank)
S4021 - A23 . W71	NO _x /H ₂ O (Sample #1)
S4021 - A24 . W72	NO _x /H ₂ O (Sample #2)
S4021 - A25 . W73	NO _x /H ₂ O (Sample #3)
S4021 - A26 . W74	NO _x /H ₂ O (Sample #4)
S4021 - A27 . W75	NO _x /H ₂ O (Sample #5)
S4021 - A28 . W76	NO _x (Blank)
S4021 - A29 . W77	NO _x (Spiked Blank)
S4021 - A30 . W78	H ₂ O (Blank)
S4021 - A31 . W79	H ₂ O (Spiked Blank)

<input checked="" type="checkbox"/> Field Transfer of Custody		<input type="checkbox"/> Chain of Possession		(Sign and Print Names)		
Relinquished By	Date	Time	Received By	Date	Time	
J. A. Edwards	06-20-94	1015	SM BROWN	6-20-94	1015	
SM BROWN	07-8-94	0200	RA Westberg	7-8-94	0200	
RA Westberg	7-8-94	0415	SM BROWN	7-8-94	0415	
SM BROWN	7-11-94	1130	J.A. Edwards	7-11-94	1130	

(Revised 02/28/94)

Final Sample Disposition

Disposal Method:

A-6000-407 (12/92) WEP061

June 20, 1994 @ 9:01

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

Westinghouse Hanford Company	CHAIN OF CUSTODY	WHC 006898
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Custody Form Initiator	J. A. Edwards	Telephone	(509)373 -0141
		Pager	85-3009
Company Contact	R. A. Westberg	Telephone	(509) 373-5734
Project Designation/Sampling Locations	200 East Tank Farm	Collection Date	0 6- __ -9 4
241-BY-106 Tank	Vapor Sample SAF S4021	Preparation Date	0 6- 1 9 -9 4
Ice Chest No.	(VSS Truck)	Field Logbook No.	WHC-N-__-
Bill of Lading/Airbill No.	N/A	Offsite Property No.	N/A
Method of Shipment	Government Truck	Sample Job #	_____
Shipped to	PNL ¹		
Possible Sample Hazards/Remarks	Unknown at time of sampling		

Sample Identification

S4021 - A01 . S023 ✓	Ambient Air SUMMA (PNL)
S4021 - A02 . S024 ✓	Ambient . SUMMA #1 (PNL)
S4021 - A05 . S027 ✓	Sample SUMMA #3 (PNL)
S4021 - A07 . S102 ✓	Sample SUMMA #5 (PNL)
S4021 - A09 . S103 ✓	Sample SUMMA #7 (PNL)

<input checked="" type="checkbox"/> Field Transfer of Custody		<input type="checkbox"/> Chain of Possession		(Sign and Print Names)		
Relinquished By	Date	Time	Received By	Date	Time	
J. A. Edwards	06-20-94	1015	SM Brown	6/20/94	1015	
SM Brown	7-8-94	0200	RA Westberg	7/8/94	0200	
RA Westberg	7-8-94	0415	SM Brown	7-8-94	0415	
SM Brown	7-11-94	1130	J.A. Edwards	7/11/94	1130	

(Revised 02/28/94)

Final Sample Disposition

Disposal Method:

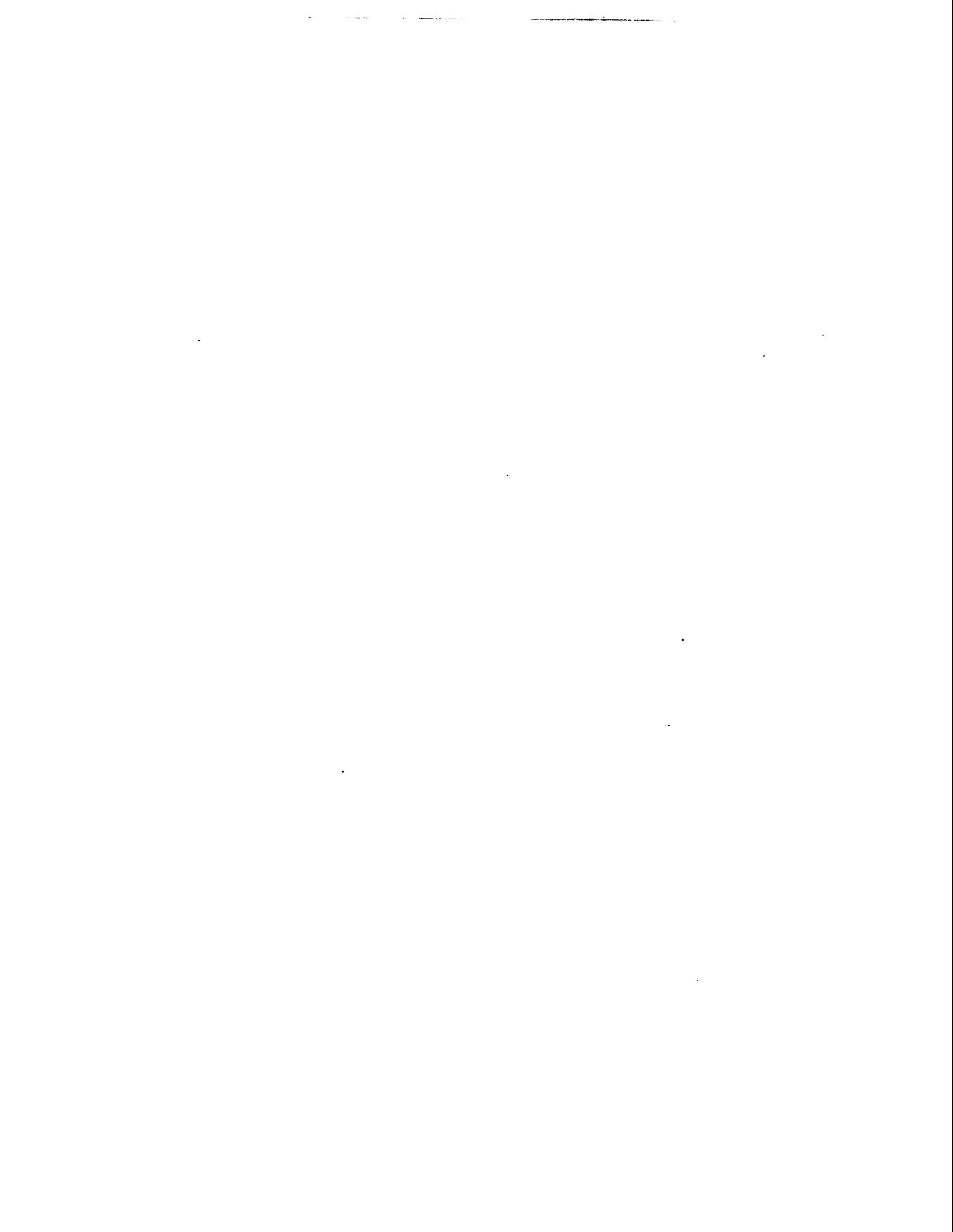
Disposed by:

Date/Time:

A-6000-407 (12/92) WEF061

June 20, 1994 @ 7:46

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



2.0 Inorganic Task

Solid sorbent traps, prepared in sampling trains, were supplied to WHC for sampling from the tank headspace using the VSS. Blanks, spiked blanks, 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, nitrogen dioxide, nitric oxide, and water. Procedures were similar to those developed previously during sample jobs performed with the VSS connected to the tank headspace of Tank C-103 (Ligothke 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 tubes containing sorbent materials to trap vapors of selected analytes from the group of NH_3 , NO_x , 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 tubes were received from the vendor having glass-sealed ends.

The type and nominal quantity of sorbent material varied by application. Sorbent traps selected for the tank sample job included the following. 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. 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 oxidized 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 a NO_2 trap. The water traps contained 300 mg of silica gel in the primary and 150 mg in the breakthrough sorbent sections.

Samples provided by PNL to trap inorganic compounds include the following: samples, single-tube 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 in a freezer, primarily because of handling recommendations for the oxidizer tubes attached to some samples. After receipt of exposed and radiologically cleared samples from WHC and disassembly of the sorbent trains, samples were provided to the analytical laboratory at ambient temperature, and selected oxidizer sections were returned to a freezer for possible subsequent use in laboratory method-validation studies.

The sorbent traps were prepared in 2-, 4-, or 5-trap sorbent trains configured so sample flow passed in order through the traps, targeting specific analytes, and then through a desiccant trap. The ends of the glass-tube traps were broken, and the traps were weighed and then connected to each other using uniform lengths of 3/8-in. perfluoroalkoxy (PFA)-grade Teflon[®] tubing. The tubing was heated in hot air and forced over the open ends of the traps to form a tight seal. The inlets of the sorbent trains each consisted

of a short section of tubing having a 3/8-in. stainless steel Swagelok nut, sealed using a cap. The trailing ends of the sorbent trains (the downstream end of the silica-gel tubes) were each sealed with red-plastic end caps provided by the manufacturer. The sorbent-tube trains remained sealed other than during the actual sampling periods. C-Flex tubing was provided by WHC to connect the downstream ends of the sorbent trains to the sampling exhaust-manifold connections.

2.1.1 Concentration Calculations. The concentrations of target compounds in the tank headspace were determined from sample results, assuming effective sample transport to the sorbent traps. Concentration, in parts-per-million by volume (ppmv), was determined by dividing the μ moles of the compound by the moles of the sample. The micromolar compound mass was determined by dividing the compound mass, in μ g, by the molecular weight of the compound, in g/mol. The molar sample was determined, excluding water vapor, by dividing the standard sample volume (at 0°C and 760 torr), in L, by 22.4 L/mol. For example, the concentration (C_v) of a 3.00-L sample containing 75.0 μ g of ammonia equals

$$C_v = \frac{75.0 \mu\text{g}}{17 \text{ g/mol}} \times \left(\frac{3.00 \text{ L}}{22.4 \text{ L/mol}} \right)^{-1} = 32.9 \text{ ppmv} \quad (2.1)$$

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

2.2 Analytical Procedures

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

2.2.1 Ammonia Analysis. The sorbent material from the ammonia-selective sorbent tubes 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 aqueous solutions 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- μ 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 NO₂ 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 Na₂CO₃ + 1.8 mM NaHCO₃ 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- μ m 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 NO₂ and NO converted to NO₂ were collected on the sorbent as equal quantities of nitrite and nitrate, and the analysis was specific for nitrite, the molar masses of NO₂ and NO were determined by doubling the analytically determined molar mass of nitrite.

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

2.3 Quality Assurance/Quality Control

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

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

Analyte	Formula	Procedure	REL ^(a) (ppmv)	0.1 x REL ^(a) (ppmv)	MDL ^(b) (ppmv)
Ammonia	NH ₃	PNL-ALO-226	25	2.5	0.5
Nitrogen dioxide	NO ₂	PNL-ALO-212	1	0.1	0.02
Nitric oxide	NO	PNL-ALO-212	25	2.5	0.02
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 obtained. 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.

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 ammonia analyses, the accuracy of laboratory measurements by selective ion electrode 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. 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

Samples were obtained from the tank headspace of Tank BY-106 on 7/8/94 using the VSS. The sample job designation number was S4021. Samples were prepared, submitted to WHC, and then analyzed to provide information on the concentrations of ammonia, nitrogen dioxide, nitric oxide, and water. Sampling and analysis for hydrogen cyanide and sulfur oxides was not requested. Blank and spiked-blank samples were pooled with those provided for similar sampling jobs associated with Tank BY-104 (S4019) and Tank BY-105 (S4020). The inorganic samples were received from WHC on 7/11/94; the sample volume information was also received on 7/11/94.

A list of samples, sampling information, sample volumes, and gravimetric results is shown in Table 2.2. Percentage recovery results from spiked blanks are shown in Table 2.3. Analytical mass and concentration results are shown in Table 2.4. Sample volumes (Table 2.2) were provided by WHC; sample-volume uncertainty was not provided. Tank-headspace concentration results (Table 2.4) are based

Table 2.2. List of PNL Inorganic Samples and Gravimetric Results Obtained From a Heated Tube Inserted in the Tank Headspace of Tank BY-106 on 7/8/94. Blanks and spiked blanks were included from three similar sample jobs. Estimated sample information was provided by WHC.

Sample	Type	Sample Port	Planned Flow Rate (mL/min)	Actual Duration (min)	Sample Volume ^(a) (L)	Mass Gain (g)
S4021-A16-W64	NH ₃ /NO _x /H ₂ O Sample	8	200	15.0	3.00	0.0509
S4021-A17-W65	NH ₃ /NO _x /H ₂ O Sample	10	200	15.0	3.00	0.0490
S4021-A18-W66	NH ₃ /NO _x /H ₂ O Sample	9	200	15.0	3.00	0.0516
S4021-A19-W67	NH ₃ /NO _x /H ₂ O Sample	10	200	15.0	3.00	0.0501
S4021-A20-W68	NH ₃ /NO _x /H ₂ O Sample	8	200	15.0	3.00	0.0530
S4021-A23-W71	NO _x /H ₂ O Sample	10	200	15.0	3.00	0.0478
S4021-A24-W72	NO _x /H ₂ O Sample	9	200	15.0	3.00	0.0566
S4021-A25-W73	NO _x /H ₂ O Sample	10	200	15.0	3.00	0.0343 ^(b)
S4021-A26-W74	NO _x /H ₂ O Sample	8	200	15.0	3.00	0.0516
S4021-A27-W75	NO _x /H ₂ O Sample	10	200	15.0	3.00	0.0473
S4019-A21-W37	NH ₃ Blank	n/a	n/a	n/a	n/a	0.0004
S4020-A21-W53	NH ₃ Blank	n/a	n/a	n/a	n/a	0.0022
S4021-A21-W69	NH ₃ Blank	n/a	n/a	n/a	n/a	0.0013
S4019-A28-W44	NO ₂ ⁻ Blank	n/a	n/a	n/a	n/a	-0.0008
S4020-A28-W60	NO ₂ ⁻ Blank	n/a	n/a	n/a	n/a	0.0025
S4021-A28-W76	NO ₂ ⁻ Blank	n/a	n/a	n/a	n/a	0.0008
S4019-A30-W46	H ₂ O Blank	n/a	n/a	n/a	n/a	0.0005
S4020-A30-W62	H ₂ O Blank	n/a	n/a	n/a	n/a	0.0016
S4021-A30-W78	H ₂ O Blank	n/a	n/a	n/a	n/a	-0.0001
S4019-A22-W38	NH ₃ Spiked Blank	n/a	n/a	n/a	n/a	0.0008
S4020-A22-W54	NH ₃ Spiked Blank	n/a	n/a	n/a	n/a	0.0025
S4021-A22-W70	NH ₃ Spiked Blank	n/a	n/a	n/a	n/a	0.0015
S4019-A29-W45	NO ₂ ⁻ Spiked Blank	n/a	n/a	n/a	n/a	0.0006
S4020-A29-W61	NO ₂ ⁻ Spiked Blank	n/a	n/a	n/a	n/a	0.0023
S4021-A29-W77	NO ₂ ⁻ Spiked Blank	n/a	n/a	n/a	n/a	0.0010
S4019-A31-W47	H ₂ O Spiked Blank	n/a	n/a	n/a	n/a	0.0005
S4020-A31-W63	H ₂ O Spiked Blank	n/a	n/a	n/a	n/a	0.0020
S4021-A31-W79	H ₂ O Spiked Blank	n/a	n/a	n/a	n/a	0.0013

(a) Sample volumes were provided by WHC and were for dry gas at 0°C and 760 torr. Uncertainty values were not provided with sample volume results.

(b) Values excluded from the analysis of mass concentration. Loss of broken glass tube ends was the probable cause of less-than-typical mass results. Mass change of spiked blanks does not include the added mass of the spikes.

on this information, and the listed uncertainties equal plus-or-minus one standard deviation of the individual results from each set of samples. Sample results were not corrected for the percentage recoveries of spiked blanks.

2.4.1 Ammonia Results. The concentration of NH₃ was 74 ± 2 ppmv, based on all five samples. The mass of NH₃ ranged from 9.7 to 10.5 μmol in the front sorbent sections and was 0.03 in the two back sections that were analyzed. The MDL was ≤ 0.06 μmol and was equivalent to a vapor concentration of ≤ 0.5 ppmv. The mass of NH₃ on the front and back sections of three blanks was ≤ 0.06 μmol , and thus, a blank correction was not significant. The percentage recovery of three blanks spiked with 12.2 μmol NH₃ was $101 \pm 4\%$. Past blanks spiked with 22.3 and 46.4 μmol yielded percentage recoveries of 109 ± 2 and $104 \pm 1\%$, respectively (Ligotke et al. 1994). One sample leachate was spiked after initial analysis with

Table 2.3. Percentage Recovery Results of Inorganic Spiked Blanks Sent to the Field but not Opened During Sampling of Tanks BY-104, -105, and -106 in June and July, 1994. Spikes were applied to the center of front sorbent sections. Analysis of selected back sections yielded levels comparable to those found in the blanks.

Sample Identifier	Tank	Compound	Spike Added ^(a) (μmol)	Analytical Result ^(b) (μmol)	Percentage Recovery	
					Sample (%)	Average ^(c) (%)
S4019-A22-W38	BY-104	NH ₃	12.4	13.2	106	101 \pm 4
S4020-A22-W54	BY-105	NH ₃	12.1	12.0	99	
S4021-A22-W70	BY-106	NH ₃	12.2	12.0	98	
S4019-A29-W45	BY-104	NO ₂ ⁻	0.0472	0.0465	99	103 \pm 4
S4020-A29-W61	BY-105	NO ₂ ⁻	0.0463	0.0484	105	
S4021-A29-W77	BY-106	NO ₂ ⁻	0.0480	0.0508	106	
S4019-A31-W47	BY-104	H ₂ O	2811 ^(d)	2839	101	103 \pm 2
S4020-A31-W63	BY-105	H ₂ O	2856	2967	104	
S4021-A31-W79	BY-106	H ₂ O	2878	2950	103	

- (a) The NH₃ spike solutions were 20 μL of 10,000 ppm (3.142 g NH₄Cl per 100 mL). The NO₂ spike solutions were 20 μL of 100 ppm nitrite. The H₂O spike was 50 μL of distilled water. The μmol of spiked material added were determined gravimetrically (e.g., 0.021 g \times 10,000 μg NH₃/mL \div 17 g/mol = 12.4 μmol).
- (b) Blank corrections for NH₃ analytical results were not significant. Analytical results for NO₂⁻ were corrected for blank levels, with each result corrected by the single blank associated with the tank.
- (c) Summary results are listed as average recovery \pm 1 standard deviation.
- (d) Water measured in μg and converted to μmol by dividing by the molecular weight of water (18).

roughly twice the mass of NH₃ in the sample and yielded a percentage recovery of 98%. The analysis of one sample was duplicated and yielded a repeatability of \pm 1%. A 5-point calibration was performed over an NH₃ range of 0.1 to 1000 $\mu\text{g}/\text{mL}$. The NH₃ concentrations from samples from Ports 8 and 9 were not significantly different from those from Port 10.

2.4.2 Nitrogen Oxides Results. Measurements of NO₂ and NO were made using NH₃/NO_x/H₂O and NO_x/H₂O sorbent-trap trains (the NO_x trains consisted of NO₂ trap, oxidizer, NO₂ trap). Five samples of each sample-train type were obtained. The presence of the upstream NH₃ traps resulted in NO concentrations that were about 1.6-fold less than those from unprotected NO₂ traps. The NO₂ concentrations were also potentially less following an NH₃ trap.

The concentration of NO₂ was \leq 0.04 ppmv (the MDL) from sorbent traps downstream of NH₃ traps and 0.05 \pm 0.04 ppmv from sorbent traps leading the sample trains. The concentration of NO was 0.10 \pm 0.05 ppmv from sorbent traps downstream of NH₃ traps and 0.16 \pm 0.06 ppmv from sorbent traps leading the sample trains. Uncorrected NO₂⁻ quantities in the traps ranged from 0.014 to 0.029 μmol in the front sorbent sections and 0.007 to 0.009 μmol in the back sections. The MDL of NO₂⁻ was about 0.001 μmol . The NO₂⁻ content of three front and back blank sorbent sections was 0.016 \pm 0.002 and 0.0087 \pm 0.0007 μmol , respectively, and these values were used to correct the quantity of NO₂⁻ measured in the samples. The percentage recovery of three blanks spiked with 0.047 μmol NO₂⁻ was 103 \pm 4%. Past blanks spiked with 0.0064, 0.11, and 0.74 μmol NO₂⁻ yielded percentage recoveries of 153 \pm 14, 106

± 8 , and $111 \pm 7\%$, respectively (Ligotke et al. 1994). No sample leachates were spiked after initial analysis with quantities of NO_2^- to test analytical percentage recoveries. No samples were reanalyzed to check repeatability. 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 $17 \pm 2 \text{ mg/L}$. The result was based on an average mass gain of $0.509 \pm 0.028 \text{ g}$ from 9 of 10 sets of $\text{NH}_3/\text{NO}_2/\text{H}_2\text{O}$ and $\text{NO}_x/\text{H}_2\text{O}$ sample trains. The percentage recovery of mass from three blank silica-gel traps spiked with $51 \mu\text{g}$ water was $103 \pm 2\%$. The six blank and spiked-blank traps generally gained mass, and ranged between -0.001 and 0.001 g gained per trap. Based on four traps per sample train, a blank correction would result in an additional uncertainty of $\pm 1 \text{ mg/L}$. Although no blank correction was made, the total measurement uncertainty was determined as the sum of one standard deviation and the blank uncertainty. The mass gains of the samples obtained from Ports 8 and 9 averaged 8% greater than those of samples from Port 10 (the range was 1 to 16% more mass in samples from Ports 8 and 9).

Table 2.4. Inorganic Vapor Sample Results Obtained From a Heated Tube Inserted in the Tank Headspace of Tank BY-106 on 7/8/94

Sample	Tank if Other Than BY-106	Port	Mass Collected		Estimated ^(a) Concentration (ppmv)
			Front (μmol)	Back (μmol)	
NH ₃ Samples:					74 ± 2 ^(b)
S4021-A16-W64		8	10.5	0.03	
S4021-A17-W65		10	10.0	NA ^(c)	
S4021-A18-W66		9	9.7	0.03	
S4021-A19-W67		10	9.7	NA	
S4021-A20-W68		8	9.9	0.03	
S4019-A21-W37	BY-104	blank	≤ 0.06	≤ 0.03	n/a
S4020-A21-W53	BY-105	blank	≤ 0.06	0.03	n/a
S4021-A21-W69		blank	≤ 0.06	≤ 0.06	n/a
NO ₂ ⁻ Blanks:					
S4019-A28-W44	BY-104	blank	0.0182	0.0095	n/a
S4020-A28-W60	BY-105	blank	0.0148	0.0082	n/a
S4021-A28-W76		blank	0.0148	0.0085	n/a
NO ₂ Samples (Protected by NH ₃ sorbent trap):					<u>≤ 0.04</u>
S4021-A16-W64		8	0.0145	0.0069	
S4021-A17-W65		10	0.0143	0.0078	
S4021-A18-W66		9	0.0162	0.0073	
S4021-A19-W67		10	0.0168	0.0081	
S4021-A20-W68		8	0.0159	0.0081	
NO ₂ Samples (Not Protected by NH ₃ sorbent trap):					<u>0.05 ± 0.04</u>
S4021-A23-W71		10	0.0191	0.0072	
S4021-A24-W72		9	0.0187	0.0078	
S4021-A25-W73		10	0.0198	0.0067	
S4021-A26-W74		8	0.0192	0.0074	
S4021-A27-W75		10	0.0196	0.0076	
NO Samples (Protected by NH ₃ sorbent trap):					<u>0.10 ± 0.05</u>
S4021-A16-W64		8	0.0235	0.0078	
S4021-A17-W65		10	0.0225	0.0069	
S4021-A18-W66		9	0.0215	0.0072	
S4021-A19-W67		10	0.0215	0.0068	
S4021-A20-W68		8	0.0247	0.0069	
NO Samples (Not Protected by NH ₃ sorbent trap):					<u>0.16 ± 0.06</u>
S4021-A23-W71		10	0.0252	0.0077	
S4021-A24-W72		9	0.0248	0.0069	
S4021-A25-W73		10	0.0264	0.0071	
S4021-A26-W74		8	0.0274	0.0086	
S4021-A27-W75		10	0.0290	0.0081	
Gravimetric Samples:					<u>17 ± 2 mg/L</u>

(a) Blank-corrected concentrations were calculated using WHC-reported sample volumes at standard temperature and pressure (STP) (0°C and 760 torr), neglecting the 1 to 2% volume contribution of water vapor (condensed and collected before flow-rate measurement). Listed nitrite values were corrected for blank levels and doubled to account for unanalyzed nitrate. Mass concentration was determined per L of dry air at STP, based on 10 of 10 samples; no blank correction was made.

(b) Underlined values represent the average ± 1 standard deviation for each set of samples.

(c) NA = not analyzed. Only selected back sorbent sections were analyzed.

3.0 Organic Task

3.1 SUMMA™ Canister Preparation

Before sending SUMMA™ canisters out to the field for sampling, the canisters are cleaned and verified contaminant free according to PNL Technical Procedure PNL-TVP-02^(a). The cleaning procedure uses an EnTech 3000 cleaning system that controls 1) filling the canisters with purified humid air and 2) evacuating, for several cycles with applied heat, before allowing the canister to evacuate overnight. The canister is filled a final time with purified humid air for analysis by PNL Technical Procedure PNL-TVP-01^(b), which is a modification of U.S. Environmental Protection Agency (EPA) Compendium Method TO-14. If the canister is verified as clean, free of TO-14 contaminants to a level of 5 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 not used after 30 days of storage are recleaned and validated before use.

3.2 Sample Analysis Method

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

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-d₅ 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

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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.

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 determine the concentration of positively identified compounds (PICs) seen 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 273°K and was calculated directly from the following equation:

$$\text{mg}/\text{m}^3 = \frac{\text{ppmv} \times \text{molecular weight of compound}}{22.4} \quad (3.1)$$

3.3.2 Identification and Quantitation of Tentatively Identified Compounds. The TICs are determined by mass spectral interpretation and comparison of the spectra with the EPA/NIST/WILEY Library, which is a part of the HP 5971 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- d_5 to give an estimated concentration of $1.26 \text{ mg}/\text{m}^3$ (for PNL 027). Internal standards bromochloromethane and difluorobenzene were not used to quantitate the TICs because coeluting compounds appeared to have greatly altered the signal of the quantitation ions for those two ISs.

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

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

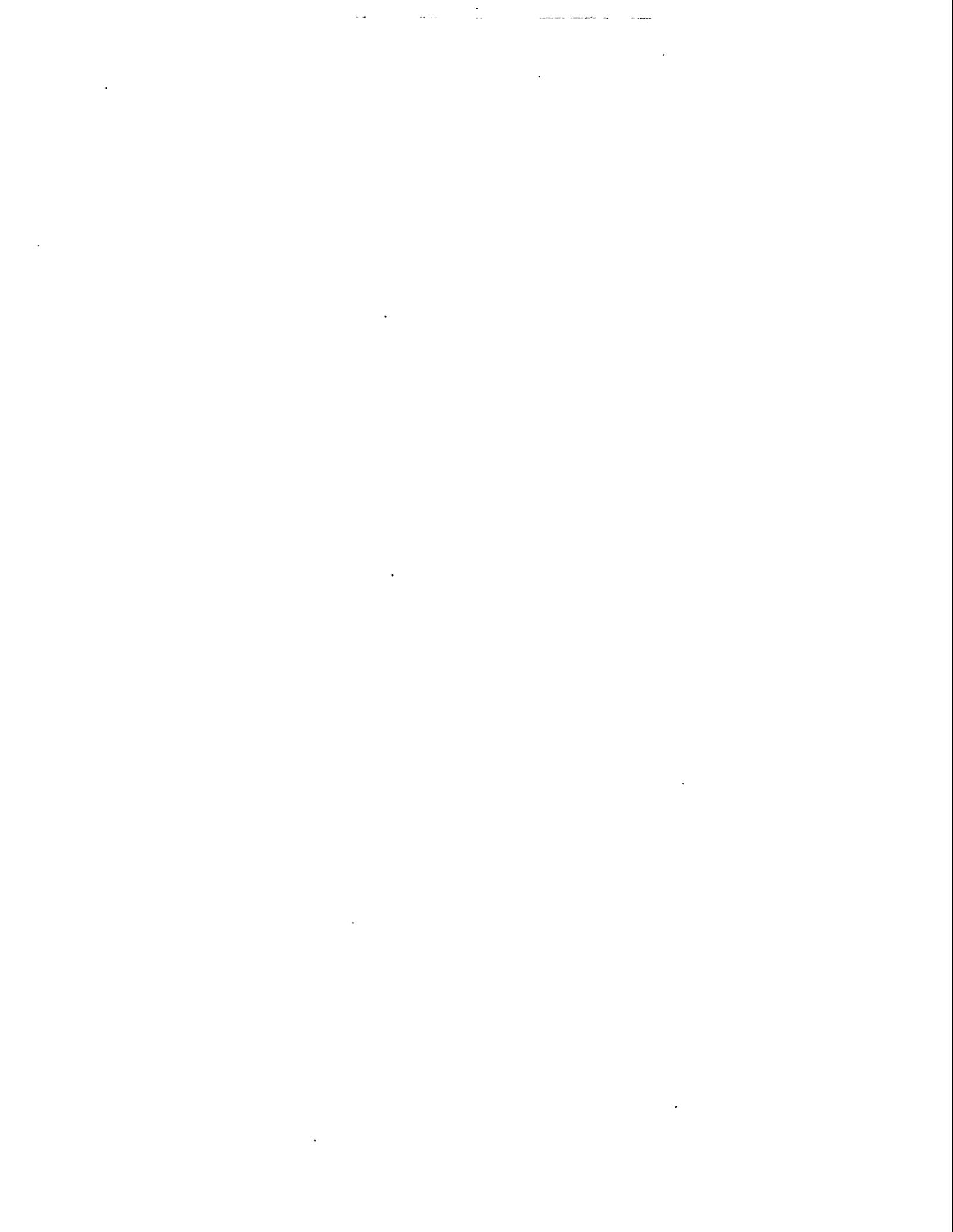
The IS level added to all blank, standard, and sample injections was 18.3 ppbv for bromochloromethane, 20.3 ppbv for 1,4-difluorobenzene, and 18.2 ppbv for chlorobenzene-d₅. The IS concentrations were converted from ppbv to mg/m³ at STP using a molecular weight of 129.39 (g/mol) for bromochloromethane, 114.09 for 1,4-difluorobenzene, and 117.6 for chlorobenzene-d₅.

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. 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. The levels of TO-14 analytes observed in the samples collected from Tank BY-106 were similar to those seen in Tank BY-107. The most predominant TO-14 species seen in this sample were freon-11 (209 ppbv), freon 12 (14 ppbv), and toluene (7.5 ppbv). The other TO-14 compounds were at 4 ppbv or less.

Table 3.2 lists the semi-quantitative results for the TICs. The predominant species observed in these samples were 1-propene, 2-methyl-1-propene, butane, acetone, pentane, and butanol. As in previous tanks, the normal paraffin hydrocarbons (NPH) defined as n-alkanes from C₁₁ to C₁₅ were present in the sample. However, in Tank BY-106, the NPH did not constitute the major portion of organic components seen. However, it should be noted that because the SUMMA™ canisters were not heated at the time of analysis, the NPH concentrations listed after the retention time of decane may not be a true accounting of all the NPH in the sample. Similarly, polar compounds, which may adhere to the inside surface of the canister, may also be under represented in this analysis. The total concentration of the TICs averaged 13.0 mg/m³ for three canisters analyzed. The estimated TIC concentration for one canister, S4021-A05-S027, totaled 17.6 mg/m³ while the estimated concentrations for the other two canisters amounted to 10.83 and 10.55 mg/m³. To date, nothing in the analytical procedure followed can account for this anomaly. The two SUMMA™ samples that were used to check VSS cleanliness were S4021-A01-S023 (ambient air SUMMA™) and S4021-A02-S024 (ambient SUMMA™ No. 1). Comparison of the total ion chromatograms from the two samples showed the presence of minor constituents and no major differences. Minor constituents present were acetaldehyde, acetone, acetophenone, and benzothiazole. Table 3.3 shows the estimated concentration of these components. Further comparison with instrument blanks (high purity nitrogen) showed that benzothiazole was also present in the blanks. The source of this artifact may have come from the laboratory building since workers were re-tarring the roof at the time of analysis.



4.0 Conclusions

The concentrations of selected inorganic compounds were determined from samples of the tank headspace of Tank BY-106. The ammonia concentration was found to be 74 ± 2 ppmv. The concentration of NO_2 was 0.05 ± 0.04 ppmv. The concentration of NO was 0.16 ± 0.06 ppmv. The presence of an upstream NH_3 sorbent trap resulted in samples yielding NO concentrations 1.6-fold less than those from unprotected samples. The NO_2 concentrations were also potentially less following an NH_3 trap. The vapor mass concentration, assumed to be largely water vapor, was 17 ± 2 mg/L. Although a slight difference was observed from mass change results, the more reliable ammonia measurements indicated the quantity of material collected in samples connected to Ports 8 and 9 was not significantly different from those connected to Port 10.

The concentration of selected organic compounds was determined from samples of the tank headspace of Tank BY-106. The total tentatively identified organic concentration for this tank was approximately 55% of the total seen in Tank BY-104. The decahydronaphthalene compounds seen in Tanks BY-107 and BY-108 were not observed in Tank BY-106. It should also be noted that while some NPH compounds were seen in this tank, the concentrations estimated were considerably lower than what has been calculated in other tank samples. See Figure 3.1 for the GC/MS chromatogram for Tank BY-106.

5.0 Reference

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.

Table 3.1 TO-14 Analysis Results for Samples Collected from Hanford Waste Tank BY-106 in SUMMA™ Canisters on 7/8/94

TO-14 Analytes	Cas. No.	S4021-A05-S027 ^(a) PNL 027 ^(b)		S4021-A07-S102 ^(a) PNL 102 ^(b)		S4021-A09-S103 ^(a) PNL 103 ^(b)	
		(ppbv)	(mg/m ³) ^(c)	(ppbv)	(mg/m ³)	(ppbv)	(mg/m ³)
Dichlorodifluoromethane (FREON-12)	75-71-8	13.50	0.07	10.26	0.06	9.86	0.05
Methyl chloride (chloromethane)	74-87-3	3.50	0.01	2.52	0.01	2.50	0.01
1,2-Dichloro-1,1,2,2-tetrafluoroethane (FREON-114)	76-14-2	<2	<.02	<2	<.02	<2	<.02
Chloroethene (vinyl chloride)	75-01-4	<2	<.006	<2	<.006	<2	<.006
Methyl bromide (bromomethane)	74-83-9	<2	<.009	<2	<.009	<2	<.009
Ethyl chloride	75-00-3	<2	<.006	<2	<.006	<2	<.006
Trichlorofluoromethane (FREON-11)	75-69-4	209.18	1.28	180.12	1.10	176.70	1.08
1,1-Dichloroethene (1,1-Dichloroethylene)	75-35-4	<2	<.009	<2	<.009	<2	<.009
Dichloromethane	75-09-2	<2	<.01	<2	<.01	<2	<.01
1,1,2-Trichloro-1,2,2-trifluoroethane (FREON-113)	76-13-1	<2	<.02	<2	<.02	<2	<.02
1,1-Dichloroethane	75-34-3	<2	<.009	<2	<.009	<2	<.009
cis-1,2-Dichloroethene	156-60-5	<2	<.009	<2	<.009	<2	<.009
Trichloromethane (chloroform)	67-66-3	<2	<.01	<2	<.01	<2	<.01
cis 1,2-Dichloroethane	107-06-2	<2	<.009	<2	<.009	<2	<.009
1,1,1-Trichloroethane	71-55-6	<2	<.01	<2	<.01	<2	<.01
Benzene	71-43-2	2.72	0.01	2.00	0.01	2.00	0.01
Carbon Tetrachloride	56-23-5	<2	<.01	<2	<.01	<2	<.01
1,2-Dichloropropane	78-87-5	<2	<.01	<2	<.01	<2	<.01
Trichloroethylene	79-01-6	<2	<.01	<2	<.01	<2	<.01
cis 1,3-Dichloropropene	10061-01-5	<2	<.01	<2	<.01	<2	<.01
trans 1,3-Dichloropropene	10061-02-6	<2	<.01	<2	<.01	<2	<.01
1,1,2-Trichloroethane	79-00-5	<2	<.01	<2	<.01	<2	<.01
Methyl benzene (toluene)	108-88-3	7.47	0.03	6.83	0.03	7.00	0.03
1,2-Dibromoethane	106-93-4	<2	<.02	<2	<.02	<2	<.02
Tetrachloroethene	127-18-4	3.75	0.03	2.00	0.01	4.00	0.03
Chlorobenzene	108-90-7	<2	<.01	<2	<.01	<2	<.01
Ethylbenzene	100-41-4	1.33	0.01	<2	<.01	<2	<.01
m-Xylene (1,3-dimethylbenzene)	108-38-3	3.55	0.02	2.75	0.01	3.00	0.01
p-Xylene (1,4-Dimethylbenzene)	106-42-3	3.55	0.02	2.75	0.01	3.00	0.01
Styrene	100-42-5	<2	<.01	<2	<.01	<2	<.01
1,1,2,2-Tetrachloroethane	79-34-5	<2	<.01	<2	<.01	<2	<.01
o-Xylene (1,2-dimethylbenzene)	95-47-6	<2	<.01	<2	<.01	<2	<.01
1,3,5-Trimethylbenzene	108-67-8	<2	<.01	<2	<.01	<2	<.01
1,2,4-Trimethylbenzene	95-63-6	<2	<.01	<2	<.01	<2	<.01
Chloromethylbenzene	100-44-7	<2	<.01	<2	<.01	<2	<.01
m-Dichlorobenzene	541-73-1	<2	<.01	<2	<.01	<2	<.01
p-Dichlorobenzene	106-46-7	<2	<.01	<2	<.01	<2	<.01
o-Dichlorobenzene	95-50-1	<2	<.01	<2	<.01	<2	<.01
1,2,4-Trichlorobenzene	120-82-1	<2	<.02	<2	<.02	<2	<.02
Hexachloro-1,3-butadiene	87-68-3	<2	<.02	<2	<.02	<2	<.02

(a) WHC ID number.

(b) PNL SUMMA™ canister number.

(c) Calculated from ppbv using molecular weight of compound, 760 mm torr, and 0°C.

Table 3.2 Table of Tentatively Identified Compounds and Estimated Concentrations in Hanford Waste Tank BY-106
SUMMA™ Canister Samples Collected on 7/8/94

TIC Analytes ^(c)	Retention Time	S4021-A05-S027(a) PNL 027(R) (mg/m ³) ^(d)	(ppmv)	S4021-A07-S102 PNL 102 (mg/m ³)	(ppmv)	S4021-A09-S103(a) PNL 103(R) (mg/m ³)	(ppmv)	Average (mg/m ³)	Std. Dev. (mg/m ³)
Carbon dioxide	3.41	(f)	(f)	(f)	(f)	(f)	(f)	(f)	(f)
Carbon dioxide	3.52	(f)	(f)	(f)	(f)	(f)	(f)	(f)	(f)
1-Propene	4.29	1.16	0.59	0.83	0.42	1.14	0.58	1.04	0.18
n-Propane	4.39	0.84	0.43	0.61	0.31	0.59	0.30	0.68	0.14
1-Propyne	4.74	0.08	0.04	0.06	0.03	0.05	0.03	0.06	0.01
Cyclopropane	5.19	0.22	0.11	0.15	0.08	0.14	0.07	0.17	0.04
2-Methyl-propane	5.52	0.83	0.32	0.47	0.18	0.37	0.14	0.56	0.24
2-Methyl-1-propene	6.11	1.05	0.41	0.60	0.23	0.55	0.21	0.73	0.27
n-Butane	6.37	1.26	0.49	0.68	0.26	0.63	0.24	0.86	0.35
2-Butene	7.01	0.23	0.09	0.13	0.05	0.12	0.05	0.16	0.07
Ethanol	7.66	0.11	0.04	<0.1	<0.04	<0.1	<0.04	(g)	(g)
C4 Alkene ^(e)	8.21	0.13	0.05	0.07	0.03	0.06	0.02	0.09	0.04
Acetone	8.80	1.41	0.55	0.64	0.25	0.59	0.23	0.88	0.46
C5 Alkane ^(e)	8.93	0.56	0.22	0.23	0.09	<0.1	<0.03	(g)	(g)
1-Pentene	9.51	0.38	0.15	0.19	0.07	0.17	0.07	0.25	0.11
n-Pentane	10.01	1.25	0.39	0.53	0.16	0.47	0.14	0.75	0.44
C5 Alkene ^(e)	10.93	0.06	0.02	<0.06	<0.02	<0.08	<0.02	(g)	(g)
C6 Alkene ^(e)	12.77	0.08	0.02	<0.08	<0.02	<0.06	<0.02	(g)	(g)
1-Propanol	13.32	0.07	0.02	<0.07	<0.02	<0.07	<0.02	(g)	(g)
2-Methylpentane	13.44	0.77	0.24	0.69	0.22	0.65	0.20	0.71	0.06
Butanal	13.65	0.21	0.07	0.15	0.05	0.14	0.04	0.17	0.04
2-Butanone	13.84	0.21	0.06	0.17	0.05	0.15	0.05	0.17	0.03
3-Methyl pentane	14.25	0.15	0.04	0.13	0.03	0.13	0.03	0.14	0.01
1-Hexene	14.51	0.17	0.04	0.14	0.04	0.13	0.03	0.15	0.02
Bromochloromethane	15.13								
n-Hexane		0.64	0.17	0.51	0.13	0.48	0.13	0.54	0.08
Tetrahydrofuran	16.14	0.19	0.06	0.17	0.05	0.15	0.05	0.17	0.02
2-Methyl-1-pentene	16.86	0.09	0.02	0.07	0.02	0.07	0.02	0.07	0.01
1-Butanol	17.83	1.13	0.35	0.96	0.30	0.89	0.28	0.99	0.13
1,4-Difluorobenzene	18.83								
2-Pentanone	18.95	0.16	0.04	0.13	0.03	0.11	0.03	0.13	0.02
C7 Alkane ^(e)	19.49	0.29	0.07	0.22	0.05	0.20	0.05	0.24	0.05
1-Heptene	20.16	0.07	0.01	0.06	0.01	0.05	0.01	0.06	0.01
n-Heptane	20.80	0.38	0.09	0.32	0.07	0.30	0.07	0.33	0.04
C7 Alkene ^(e)	22.41	0.07	0.02	0.05	0.01	0.06	0.01	0.06	0.01
C8-Alkane ^(e)	24.48	0.14	0.03	0.11	0.03	0.11	0.02	0.12	0.02
Hexanal	25.20	0.07	0.01	<0.07	<0.01	<0.07	<0.01	(g)	(g)
Octane	26.27	0.13	0.03	0.11	0.02	0.10	0.02	0.11	0.02

Table 3.2 Contd

TIC Analytes ^(c)	Retention Time	S4021-A05-S027 ^(a) PNL 027 ^(b) (mg/m ³) ^(d) (ppmv)	S4021-A07-S102 PNL 102 (mg/m ³) (ppmv)	S4021-A09-S103 ^(a) PNL 103 ^(b) (mg/m ³) (ppmv)	Average (mg/m ³)	Std. Dev. (mg/m ³)
Chlorobenzene-d5	28.36					
2-Butoxyethanol	30.93	0.06	< 0.06	< 0.06	(g)	(g)
C10 Alkane ^(e)	31.37	0.07	0.06	0.05	0.06	0.01
C10 Alkane ^(e)	33.15	0.05	< 0.1	< 0.1	(g)	(g)
Phenol	33.79	0.05	< 0.1	< 0.1	(g)	(g)
C11 Alkane ^(e)	36.08	0.05	< 0.05	< 0.05	(g)	(g)
n-Undecane	40.41	0.06	0.05	< 0.1	0.06	0.00
n-Dodecane	44.44	0.09	0.09	0.08	0.09	0.01
C12 Alkane ^(e)	45.07	0.08	0.07	0.07	0.07	0.01
Benzothiazole (impurity)	45.67	0.06	< 0.05	< 0.05	(g)	(g)
C7 Cyclohexane ^(e)	46.52	0.06	< 0.05	< 0.05	(g)	(g)
C13 Alkane ^(e)	47.33	0.06	0.07	0.06	0.06	0.01
n-Tridecane	48.18	0.11	0.08	0.09	0.09	0.01
C13 Alkane ^(e)	51.06	0.07	0.05	0.05	0.06	0.01
C13 Alkane ^(e)	51.69	0.06	< 0.05	< 0.05	(g)	(g)

- (a) WHC sample number.
- (b) PNL SUMMA™ canister number.
- (c) Obtained by mass spectral interpretation and comparison with the EPA/NIST/WILEY Library.
- (d) Semi-quantitative estimate calculated using concentration of the chlorobenzene-d5.
- (e) Other structural isomers should be considered.
- (f) Carbon dioxide is not quantifiable due to the analytical method used.
- (g) Molecular weight information is not available for this TIC.

Table 3.3 Estimated Concentrations in Ambient SUMMA™ Canister Samples Taken for VSS Cleanliness Comparison

<u>TIC Analytes</u>	<u>Mol Wt (gram/mole)</u>	<u>S4021-A01-S024 Ambient Air ppmv</u>	<u>S4021-A02-S023 VSS SUMMA™ No. 1 (ppmv)</u>	<u>Nitrogen Instrument (ppmv)</u>
Acetaldehyde	44	0.031	0.058	(a)
Acetone	58	0.041	0.072	(a)
Acetophenone	120	0.005	0.011	(a)
Benzothiazole	135	0.009	0.006	0.002

(a) Below detection limit of 0.001 ppmv

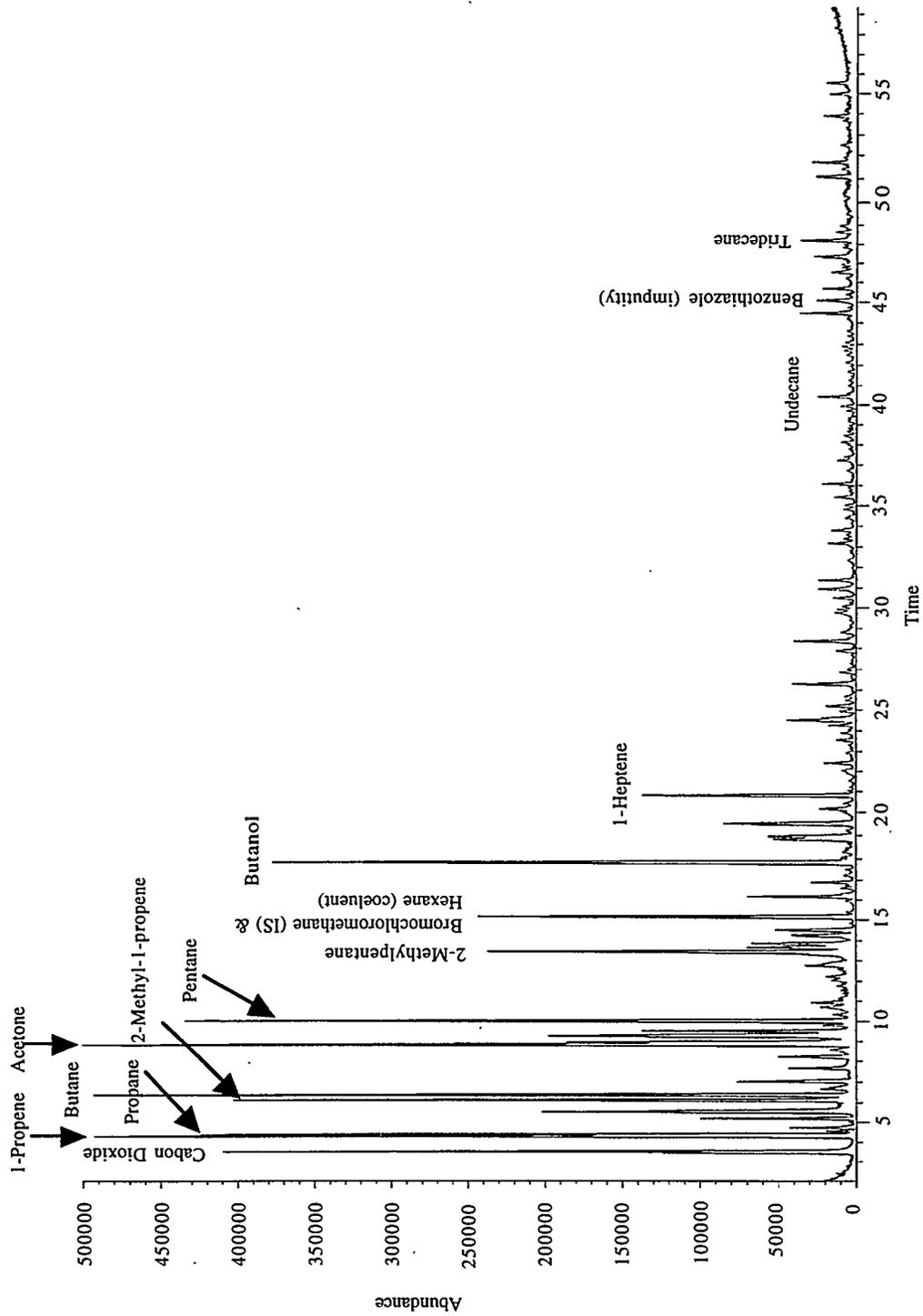


Figure 3.1 GC/MS Chromatogram of Hanford Waste Tank BY-106 SUMMA™ Canister Vapor Sample S4021-A05-027 Collected Through the WHC Vapor Sampling System on 7/8/94

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