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

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June 1995

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under a Related Services Agreement
with the U.S. Department of Energy
Contract DE-AC06-76RLO 1830**

**Pacific Northwest Laboratory
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Pacific Northwest Laboratory
Richland, Washington 99352

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Summary

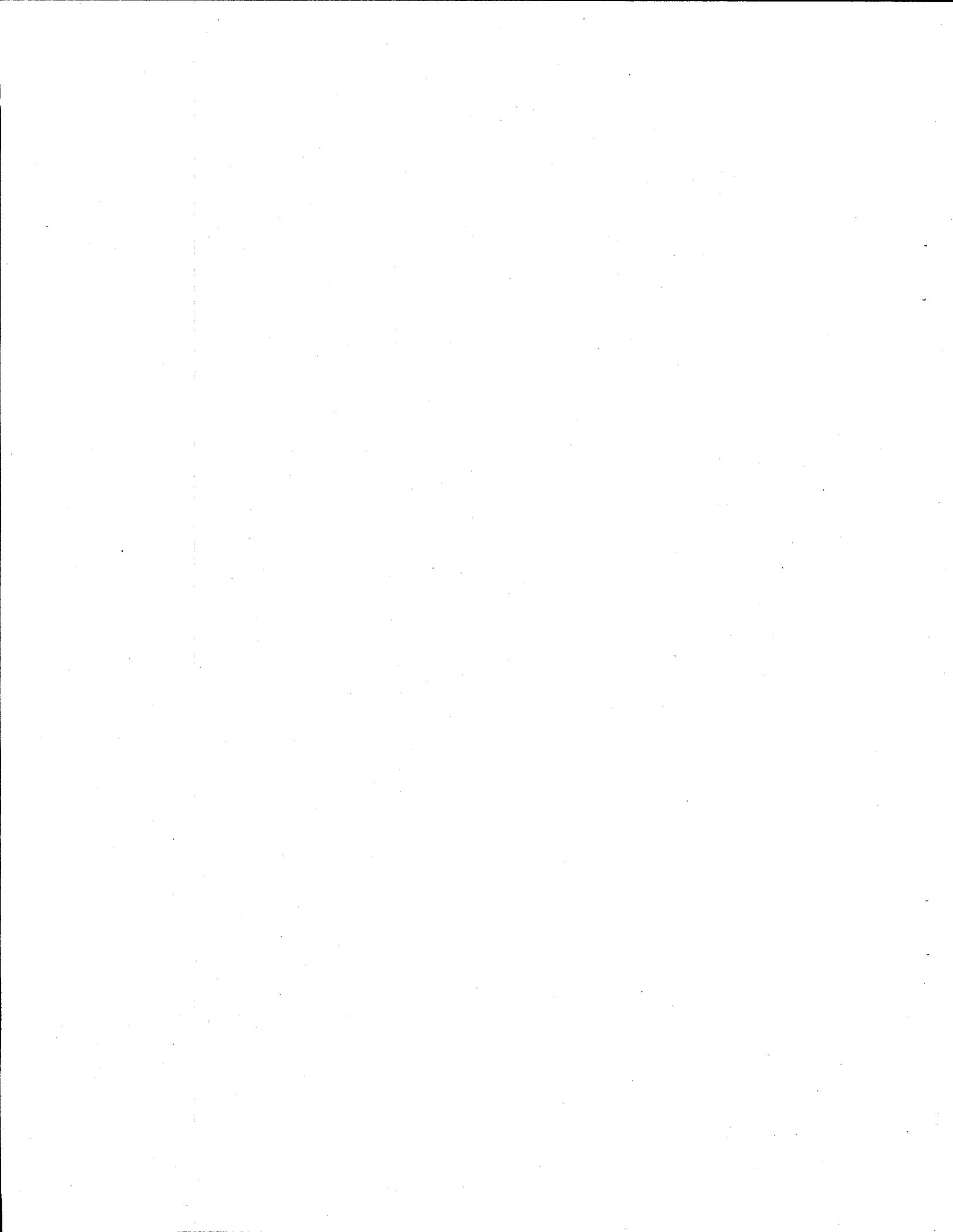
This report describes inorganic and organic analyses results from *in situ* samples obtained from the tank headspace of the Hanford waste storage Tank 241-BY-103 (referred to as Tank BY-103). The results described here were obtained to support safety and toxicological evaluations. A summary of the results 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 NH_3 , NO_2 , NO , HCN , and H_2O . Sampling for sulfur oxides was not requested. Organic compounds were also quantitatively determined. Twenty-three tentatively identified organic analytes were observed above the detection limit of (ca.) 10 ppbv, but standards for most of these were not available at the time of analysis, and their quantitation is beyond the scope of this study. In addition, we looked for the 41 standard TO-14 analytes. Of these, only a few were observed above the 2-ppbv detection limit. The 11 organic analytes with the highest estimated concentrations are listed in Table 1. The 11 analytes account for approximately 76% of the total organic components in Tank BY-103. The remaining 24% is made up of the other tentatively identified compounds listed in Table 3.2.

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

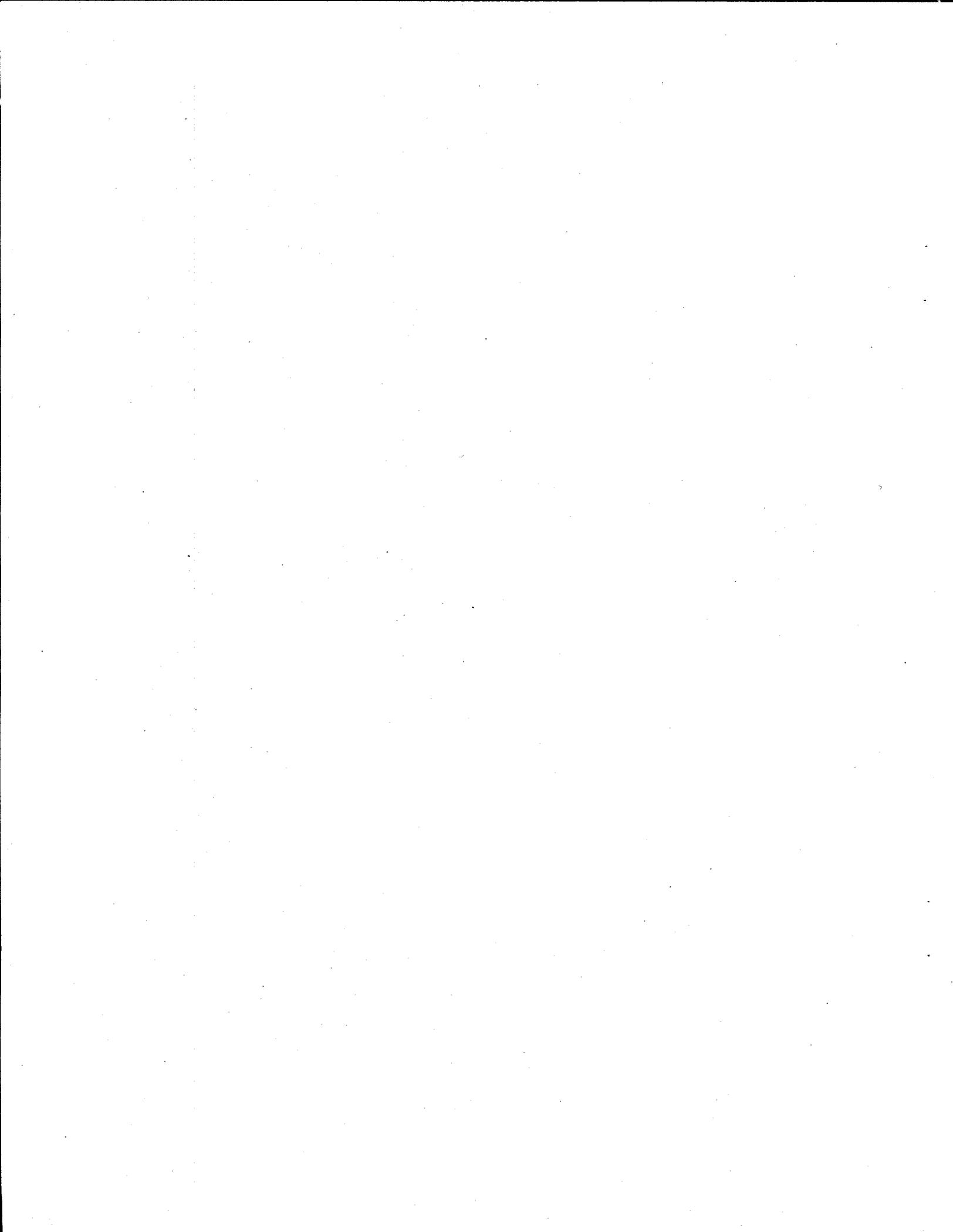
Category	Analyte	Vapor ^(a) Concentration	Units
Inorganic	NH_3	30.7 ± 0.4	ppmv
	NO_2	≤ 0.1	ppmv
	NO	≤ 0.2	ppmv
	HCN	≤ 0.005	ppmv
	H_2O	8.9 ± 1.0	mg/L
Organic	Acetone	0.59	mg/m^3
	2-Butanone	0.10	mg/m^3
	n-Butanol	0.13	mg/m^3
	C7 alkanes	0.17	mg/m^3
	3-Methylhexane	0.24	mg/m^3
	n-Heptane	0.14	mg/m^3
	Methylcyclohexane	0.31	mg/m^3
	2-Butoxyethanol	0.14	mg/m^3
	n-Decane	0.23	mg/m^3
	n-Tridecane	0.45	mg/m^3
	n-Tetradecane	0.10	mg/m^3

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



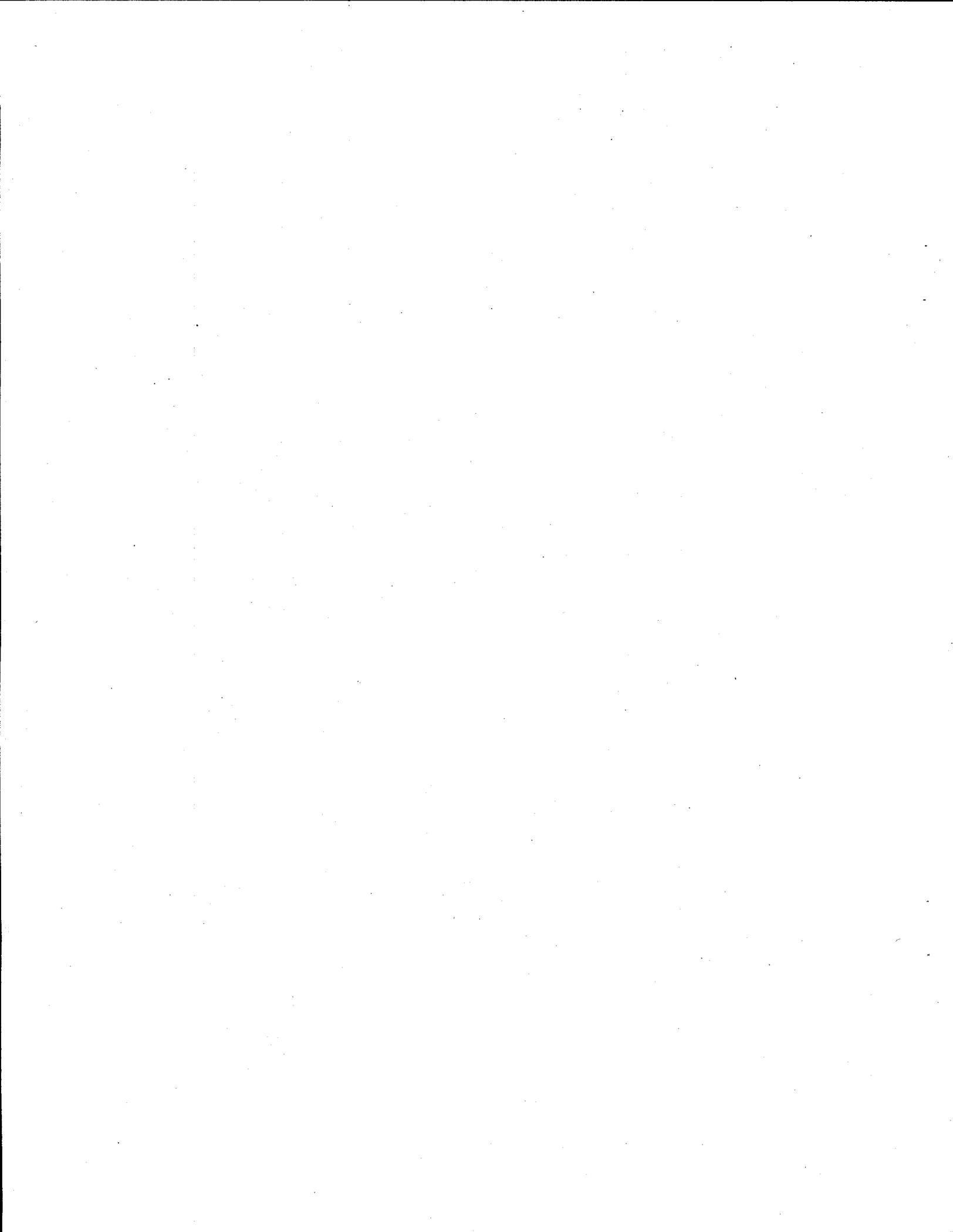
Acknowledgments

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. Bruce Lerner performed method development and validation work that supported the inorganic vapor sampling. Sally Slate and May-Lin Thomas analyzed inorganic samples, and Annalisa Krupsha and Gary Dennis prepared the solid-sorbent sample trains. Therese Clauss assisted in preparing this report. Georgia Ruebsamen provided word processing support.



Abbreviations

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



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1.0 Introduction

This report describes results of the analyses of *in situ* tank-headspace samples taken from the Hanford waste Tank 241-BY-103 (referred to as Tank BY-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. The sample job was designated S4026, and samples were collected by WHC on May 5, 1994, using the *in situ* sampling system (ISS).

Sampling devices, including six sorbent trains (for inorganic analyses), were supplied to WHC on May 5, 1994. One SUMMA™ canister (for organic analyses) was supplied to the WHC sampling staff on March 23. Samples were taken (by WHC) from the tank headspace on May 5 and were returned to PNL from the field on May 12. Inorganic (sorbent trap) samples were delivered to PNL on chain of custody (COC)/sample analysis request 006864. One SUMMA™ canister was delivered on COC/sample analysis request No. 006854 (see Figure 1).

The samples were inspected upon delivery to the 326/23B laboratory and logged into PNL record book 55408 before implementation of PNL Technical Procedure PNL-TVP-07^(b). Custody of the sorbent traps was transferred to PNL personnel performing the inorganic analysis and stored at refrigerated ($\leq 10^{\circ}\text{C}$) temperature until the time of analysis. The canister was stored in the 326/23B laboratory at ambient (25°C) temperature until the time of analysis. Access to the 326/23B laboratory is limited to PNL personnel working on the waste-tank safety program. Analyses described in this report were performed at PNL in the 300 area of the Hanford Reservation. Analytical methods that were used are described in the text. In summary, sorbent traps for inorganic analyses containing sample materials were either weighed (for water analysis) or desorbed with the appropriate aqueous solutions (for NH_3 , NO_x , or HCN analyses). The aqueous extracts were analyzed either by selective electrode or by ion chromatography (IC). Organic analyses were performed using cryogenic preconcentration followed by gas chromatography/mass spectrometry (GC/MS).

-
- (a) Pacific Northwest Laboratory is operated for the U. S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.
- (b) PNL-TVP-07, Rev. 0, October 1994, *Sample Shipping and Receiving Procedure for PNL Waste Tank Samples*, PNL-Technical Procedure, Tank Vapor Project, Richland, Washington.

Westinghouse Hanford Company		CHAIN OF CUSTODY/SAMPLE ANALYSIS REQUEST										Page 1 of 2
Collector S. R. Brown	Company Contact L.A. P. Inge	Telephone No. (509) 373-4051	Data Turnaround <input type="checkbox"/> Priority <input checked="" type="checkbox"/> Normal									
Project Designation 241-BY-103	Sampling Location 200 EAST TANK FARM: VAPOR SAMPLE	SAF No. S4026	COC # 006864 (P)									
Ice Chest No. N/A	Field Logbook No. N/A	Method of Shipment GOVERNMENT TRUCK	Bill of Lading/AR Bill No. N/A									
Shipped To UIC--PHL	Offsite Property No. N/A											
Possible Specific Hazards/Remarks UNKNOWN AT TIME OF SAMPLING	Preservative NONE	None										
	Type of Container SORBANT SUMMA											
	No. of Containers 1	1										
	Volume ---	---										
Special Handling and/or Storage			IMORG DRG									
SAMPLE ANALYSIS												
Sample No.	Matrix*	Date Sampled	Date Sampled	Time Sampled	Matrix*	Significant Names	Date/Time	Date/Time	Date/Time	Date/Time	Date/Time	Matrix*
26 S4034-026-X45 ✓	VAPOR	05/05/94	05/05/94	1430	X		5/5/94 @ 1040	5/5/94 @ 1040	5/5/94 @ 1040	5/5/94 @ 1040	5/5/94 @ 1040	S SE SO SL WO O A DS DL T WI L V X
26 S4034-026-X46 ✓	VAPOR	05/05/94	05/05/94	1430	X		5/5/94 @ 1040	5/5/94 @ 1040	5/5/94 @ 1040	5/5/94 @ 1040	5/5/94 @ 1040	S SE SO SL WO O A DS DL T WI L V X
26 S4034-026-X47 ✓	VAPOR	05/05/94	05/05/94	1430	X		5/5/94 @ 1040	5/5/94 @ 1040	5/5/94 @ 1040	5/5/94 @ 1040	5/5/94 @ 1040	S SE SO SL WO O A DS DL T WI L V X
26 S4034-026-X48 ✓	VAPOR	05/05/94	05/05/94	1430	X		5/5/94 @ 1040	5/5/94 @ 1040	5/5/94 @ 1040	5/5/94 @ 1040	5/5/94 @ 1040	S SE SO SL WO O A DS DL T WI L V X
26 S4034-026-X49 ✓	VAPOR	05/05/94	05/05/94	1430	X		5/5/94 @ 1040	5/5/94 @ 1040	5/5/94 @ 1040	5/5/94 @ 1040	5/5/94 @ 1040	S SE SO SL WO O A DS DL T WI L V X
26 S4034-026-X50 ✓	VAPOR	05/05/94	05/05/94	1430	X		5/5/94 @ 1040	5/5/94 @ 1040	5/5/94 @ 1040	5/5/94 @ 1040	5/5/94 @ 1040	S SE SO SL WO O A DS DL T WI L V X
CHAIN OF POSSESSION												
Relinquished By J. Edwards	Received By S. R. Brown	Date/Time 5/5/94 @ 1040	Date/Time 5/5/94 @ 1040	Date/Time 5/5/94 @ 1040	Date/Time 5/5/94 @ 1040	Date/Time 5/5/94 @ 1040	Date/Time 5/5/94 @ 1040	Date/Time 5/5/94 @ 1040	Date/Time 5/5/94 @ 1040	Date/Time 5/5/94 @ 1040	Date/Time 5/5/94 @ 1040	Date/Time 5/5/94 @ 1040
Relinquished By S. R. Brown	Received By J. Edwards	Date/Time 5/5/94 @ 1445	Date/Time 5/5/94 @ 1445	Date/Time 5/5/94 @ 1445	Date/Time 5/5/94 @ 1445	Date/Time 5/5/94 @ 1445	Date/Time 5/5/94 @ 1445	Date/Time 5/5/94 @ 1445	Date/Time 5/5/94 @ 1445	Date/Time 5/5/94 @ 1445	Date/Time 5/5/94 @ 1445	Date/Time 5/5/94 @ 1445
Relinquished By	Received By	Date/Time	Date/Time	Date/Time	Date/Time	Date/Time	Date/Time	Date/Time	Date/Time	Date/Time	Date/Time	Date/Time
LABORATORY SECTION												
FINAL SAMPLE DISPOSITION												
DISTRIBUTION: Original - Sample Yellow - Sampler												

Figure 1.1a. Chain-of-Custody for Inorganic Samples from Tank BY-103

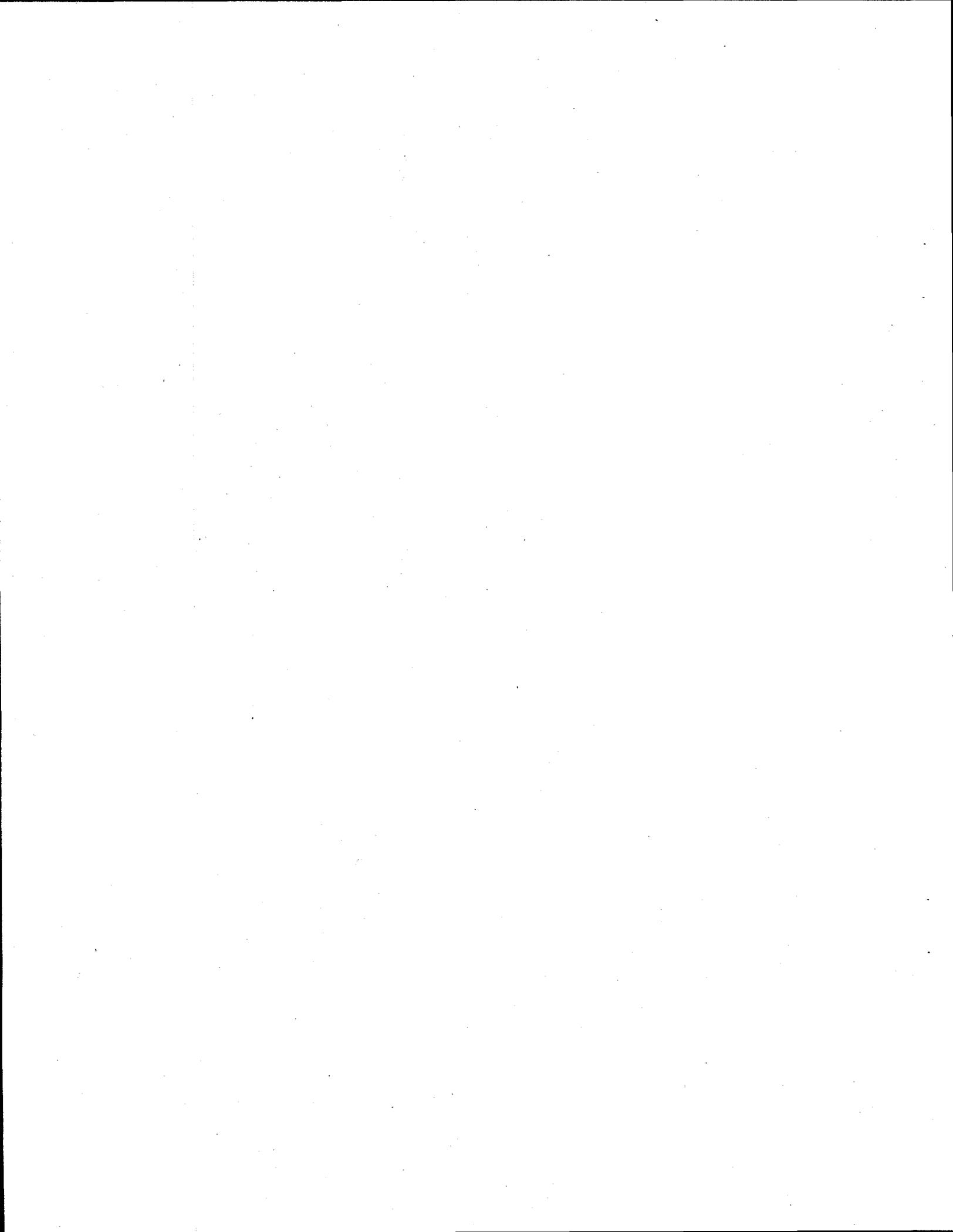
Page 1 of 1
Data Turnaround
 Priority
 Normal

CHAIN OF CUSTODY/SAMPLE ANALYSIS REQUEST

Westinghouse Hanford Company		Company Contact L.A. P. Dingl		Telephone No. (509) 373-4051	
Collector S.H. Brown		Sampling Location 200 EAST TANK FARM; VAPOR SAMPLE		SAF No. S4026	
Project Designation 241-BY-103		Field Logbook No. UNC-11-797		Method of Shipment GOVERNMENT TRUCK	
Job Sheet No. N/A		Offsite Property No. N/A		Bill of Lading/Air Bill No.	
Shipped To UNC--PHL		Preservative NONE		NONE	
Possible Sample Hazard/Remarks UNKNOWN AT TIME OF SAMPLING		Type of Container SORBANT SUMMA		SORBANT SUMMA	
		No. of Containers 1		1	
		Volume --		--	
		THORG DNG		DNG	
SAMPLE ANALYSIS					
Sample No. 26 S4011-026-077	Matrix* VAPOR	Date Sampled 05/03/94	Time Sampled 1430		
CHAIN OF POSSESSIONS					
Relinquished By J. Edwards	Date/Time 5/3/94 845	Received By S.M. Lewis	Date/Time 3/23/94 0805		
Relinquished By S.H. Brown	Date/Time 5/12/94 1445	Received By J.A. Edwards	Date/Time 5/12/94 1445		
Relinquished By	Date/Time	Received By	Date/Time		
Relinquished By	Date/Time	Received By	Date/Time		
SPECIAL INSTRUCTIONS					
This					
LABORATORY SECTIONS		Received By		Date/Time	
FIELD SAMPLE DISPOSITION		Disposal Method		Disposed By	

8C-0000-028 (12/93)

Figure 1.1b. Chain-of-Custody for Organic Samples from Tank BY-103



2.0 Inorganic

Solid sorbent traps, prepared in sampling trains, were supplied to WHC for sampling the tank headspace. Blanks, spiked blanks (when requested), 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. Procedures were similar to those developed previously during sample jobs performed with the vapor sampling system (VSS) connected to the tank headspace of Tank C-103 (Ligotke et al. 1994). Analytical accuracy was estimated based on procedures used. Sample preparation and analyses were performed following PNL quality assurance (QA) impact level (IL) III requirements.

2.1 Standard Sampling Methodology

Standard sorbent traps consisting of glass tubes containing sorbent materials to trap the analytes of NH_3 , NO_2 , NO, HCN, and H_2O (SKC Inc., Eighty Four, Pennsylvania) were obtained, prepared, and submitted for use by WHC. The sorbent traps were selected based on their use by the Occupational Safety and Health Administration (OSHA) to perform workplace monitoring, and because of available procedures and verification results associated with that particular application. The typical sorbent traps used consisted of a glass tube containing a sorbent material specific to the compound of interest. In general, the tubes contained two sections; the first section was the primary trap, and the second section provided an indication of breakthrough. In the tubes, sorbent sections are generally held in packed layers separated by glass wool. The sorbent tubes were connected end-to-end to prepare multi-trap sorbent trains for sampling.

The type and nominal quantity of sorbent material varied by application. Sorbent traps selected for the tank sample job included the following products. The NH_3 sorbent traps contained carbon beads impregnated with sulfuric acid; nominally, 500 mg were contained in the primary and 250 mg in the breakthrough sections. The NH_3 was chemisorbed as ammonium sulfate $\{(\text{NH}_4)_2\text{SO}_4\}$. The NO_2 traps contained a zeolite impregnated with triethanolamine (TEA), with 400 mg in the primary and 200 mg in the breakthrough sections. The NO_2 was absorbed and disproportionated to equi-molar quantities of nitrite ions (NO_2^-) and nitrate ions (NO_3^-). Glass tubes containing 800 mg of an oxidant such as chromate were used to convert NO to NO_2 . The converted NO was then collected as nitrite and nitrate in a NO_2 trap. The HCN traps contained soda lime, with 600 mg in the primary and 200 mg in the breakthrough sections. The water traps contained 300 mg of silica gel in the primary and 150 mg in the breakthrough sorbent sections.

Sample materials for inorganic analytes include some or all of the following: samples, spiked samples, spares, blanks, and spiked blanks. The samples of each type were prepared from same-lot batches, with the oxidizer sections of the NO_x sorbent trains having been stored previously in a freezer. After sample preparation, all samples, spiked samples, blanks, and spiked blanks were stored 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 until completion of analyses.

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

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

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

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

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

2.2 Analytical Procedures

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

2.2.1 Ammonia Analysis. The sorbent material from the ammonia-selective sorbent traps was placed into labeled 20-mL glass scintillation vials. Vials containing front-, or primary-, section sorbent material were treated with 10.0 mL of deionized water (DIW), and vials containing back-up-section sorbent material were treated with 5.0 mL of DIW. After extraction, the NH_3 sorbent traps were analyzed using the selective ion electrode (SIE) procedure PNL-ALO-226 {Ammonia (Nitrogen) in Aqueous Samples}. Briefly, this method includes 1) preparing a 1000-ppm NH_3 stock standard solution from dried reagent-grade NH_4Cl and DIW on the day analyses are performed; 2) preparing 0.1-, 0.5-, 1.0-, 10-, and 100-ppm NH_3 working calibration standards by serial dilution of the freshly made stock standard; 3) generating an initial calibration curve from the measured electromotive force (emf) signal versus NH_3 concentration data obtained for the set of working standards; 4) performing a calibration-verification check, using one of the midrange standards, after analyzing every four or five samples; 5) continuing this sequence until all samples of the batch have

been measured, including duplicates and spiked samples; and 6) remeasuring the complete set of calibration standards at the end of the session. Emf signal measurements obtained for samples are compared to those for standards, either graphically or algebraically (using linear regression) to determine ammonia concentration in the samples.

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

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

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

2.2.3 Cyanide Analysis. The HCN samples were desorbed in 3.0 mL of 0.02 N sodium hydroxide and analyzed by amperometric detection ion chromatography according to PNL-ALO-271^(b). 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 the samples were compared to those for standards to determine CN^- the 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

(a) Pacific Northwest Laboratory. *Determination of Inorganic Anions by Ion Chromatography*, Richland Washington.

(b) Pacific Northwest Laboratory. *Procedure for Analysis of Free cyanide in Water and Soil Sample Leachates*, Richland Washington.

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. The samples were analyzed following PNL IL III. The PNL documents include some or all of the following: PNL-MA-70 (Part 2), PNL-MA-599, PNL-ALO-212, PNL-ALO-226, 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 Typical Detection Limits of Target Inorganic Analytes. Not all analytes are included in every sample job.

Analyte	Formula	Procedure	REL ^(a) (ppmv)	0.1 x REL ^(a) (ppmv)	MDL ^(b) (ppmv)
Ammonia	NH ₃	PNL-ALO-226	25	2.5	0.5
Nitrogen dioxide	NO ₂	PNL-ALO-212	1	0.1	0.02
Nitric oxide	NO	PNL-ALO-212	25	2.5	0.02
Sulfur oxide	SO _x	PNL-ALO-212	2	0.2	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 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 (see Section 2.4). Sampling information, including sample volumes, was provided by WHC; sample volume uncertainty was not provided. The accuracy of analytical results depends on the method used. For ammonia analyses, the accuracy of laboratory measurements by SIE was estimated to be $\pm 5\%$ relative, independent of concentration at 1 $\mu\text{g/mL}$ or greater levels. The uncertainty includes preparation of standards, purity of the ammonium salt used to prepare standards, potential operator bias, ambient temperature variations, etc. Unfortunately, no known National Institute for Standards and Technology (NIST)-traceable standard reference material (SRM) is available against which to compare working standards. As for ammonia, no known NIST SRM is available for nitrite analysis (for NO₂ and NO). Based on experience in comparing nitrite working standards prepared from several different sources and factors mentioned for ammonia above, the estimated maximum bias for samples derived from sampling for NO₂ is $\pm 10\%$, and for samples

derived from sampling for NO, it is $\pm 5\%$ relative. For SO_x analysis, the IC determination of sulfate derived from SO_x trapped in sorbent traps is judged to be biased no more than 10% even at the very low concentrations of solutions actually analyzed. Comparison of working standards to an NIST standard reference material (SRM) solution for sulfate exhibit no more than a 2 to 3% difference at concentrations of 2 ppm or greater. 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 normal working range (which encompasses the concentration levels encountered in blanks and samples derived from sorbent-trap leachates). The accuracy of measurements of sample mass is ± 0.05 mg, or much less than 1% of the mass changes of samples, and roughly 5% or less of the mass change of blanks.

2.4 Inorganic Sample Results

Sorbent-trap trains and controls were prepared on 3/28/94 and submitted to WHC. They were used by WHC to sample the tank headspace of Tank BY-103 on 5/5/94 using the ISS. The sample job designation number was S4026. The exposed samples were returned to PNL on 5/12/94 and subsequently analyzed on 6/8/94 (H₂O), 6/14/94 (NH₃ and HCN), and 7/1/94 (NO_x) to provide information on the tank-headspace concentrations of selected inorganic compounds. Sampling and analysis for sulfur oxides were not requested. Blank and spiked-blank samples associated with this sample job were those sent for the related ISS sample job in Tank BY-111 (S4028) or related sample jobs. The sample volume information for the current sample job was received from WHC on 8/2/94.

A list of samples, sampling information, sample volumes, and gravimetric results is shown in Table 2.2. The types of sample trains used and the order of sorbent traps within each train are also shown in the table. For example, the sorbent train NH₃/NO_x/H₂O contained an ammonia trap at the inlet end, a NO_x series in the middle (section 2.4.2), and a desiccant trap at the outlet end. Analytical mass and concentration results are shown in Table 2.3. Sample volumes were provided by WHC; sample-volume uncertainty was not provided. Tank-headspace concentration results (Table 2.3) are based on this information, and the listed uncertainties equal plus-or-minus one standard deviation of the individual results from each set of samples. Where analytical results from samples were nearly indistinguishable from those of blanks, indicating very low tank-headspace concentrations of the analyte, the concentration results (Table 2.3) are listed as "less-than-or-equal-to" a probable maximum value determined by subtracting the average of the blanks less one standard deviation from the average of the samples plus one standard deviation. Results of control samples, such as spiked blanks, are discussed in this section. Spiked blanks, when used, were transported to the field but not opened. Spiked samples, when used, were opened in the field and used to collect tank-headspace gas. Sample results were not corrected for the percentage recoveries of spiked blanks.

2.4.1 Ammonia Results. The concentration of NH₃ was 30.7 ± 0.4 ppmv, based on all three samples. The blank-corrected NH₃ quantities in the sorbent traps ranged from 5.2 to 5.8 μmol with no indication of breakthrough. Blank corrections, ≤ 0.06 μmol in front and ≤ 0.03 μmol in back sorbent sections (Clauss et al. 1994), were not significant ($<2\%$). Although spiked blanks were not tested, the percentage recoveries of three sets of blanks spiked with 12.2, 22.3, and 46.4 μmol NH₃ were $101 \pm 4\%$, $109 \pm 2\%$, and $104 \pm 1\%$, respectively, during related sample jobs (Clauss et al. 1994; Ligothke et al. 1994). The analysis of one sample was duplicated and yielded a repeatability of $\pm 2\%$. One sample leachate was spiked after initial analysis with 2.5 times the mass of NH₃ in the sample and yielded a percentage recovery of 96%. A 5-point calibration was performed over an NH₃ range of 0.1 to 1000 $\mu\text{g/mL}$. Minor differences between the individual results of the three NH₃ samples matched closely the differences in the quantities of dry air sampled during each sample.

Table 2.2. List of PNL Inorganic Samples, Blanks, and Gravimetric Results From *In Situ* Sampling of the Headspace of Tank BY-103 on 5/5/94

Sample Number	Sorbent Train Type	Sample Flow Rate (mL/min)	Duration (min)	Sample Volume ^(a) (L)	Mass Gain (g)
S4026-026-X48	NH ₃ /NO _x /H ₂ O Sample	285	15.0	4.28	NA ^(b)
S4026-026-X49	NH ₃ /NO _x /H ₂ O Sample	277	15.0	4.15	NA
S4026-S026-X50	NH ₃ /NO _x /H ₂ O Sample	308	15.0	4.62	NA
S4026-026-X45	HCN/H ₂ O Sample	279	15.0	4.19	0.0405
S4026-026-X46	HCN/H ₂ O Sample	286	15.0	4.28	0.0371
S4026-026-X47	HCN/H ₂ O Sample	241	15.0	3.61	0.0391
S4028-028-X66	HCN/H ₂ O Blank (BY-111)	n/a	n/a	n/a	0.0031
S4028-028-X67	HCN/H ₂ O Blank (BY-111)	n/a	n/a	n/a	0.0033
S4028-028-X68	HCN/H ₂ O Blank (BY-111)	n/a	n/a	n/a	0.0033

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

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

The concentrations of NO₂ and NO were ≤ 0.1 and ≤ 0.2 ppmv, respectively. The concentrations exceeded the usual MDL (Table 2.1) for the analytes largely because of a lack of detailed blank information. Blank-corrected NO₂⁻ quantities in the sorbent traps averaged ≤ 0.0085 μmol (NO₂ samples) and ≤ 0.014 μmol (NO samples). Nitrite blank levels used to correct data were 0.016 ± 0.002 μmol in front and 0.0087 ± 0.0007 μmol in back sorbent sections, and were based on typical values such as those reported by Clauss et al. (1994). Although spiked blanks were not tested, blanks spiked with 0.0064, 0.047, 0.11, and 0.74 μmol NO₂⁻ during a related sample job yielded percentage recoveries of 153 ± 14%, 103 ± 4%, 106 ± 8%, and 111 ± 7%, respectively (Ligothke et al. 1994; Clauss et al. 1994). No samples were reanalyzed to check repeatability. No sample leachates were spiked after initial analysis with quantities of NO₂⁻ to test analytical percentage recoveries. A 4-point calibration was performed over a concentration range of 0 to 0.5 μg NO₂⁻ per mL in the desorbing matrix.

2.4.3 Hydrogen Cyanide Results. The concentration of HCN was ≤ 0.005 ppmv, based on all three samples. Blank-corrected sample results averaged ≤ 0.0009 μmol. Blank corrections were based on the results of three blanks from a related sample job (Tank BY-111) which averaged 0.0128 ± 0.0005 μmol for the front and 0.0049 ± 0.0002 μmol for the back sorbent section. Three spiked-blank sorbent traps were prepared by adding 50 μL of 5-ppm CN⁻ in water, confirmed

Table 2.3. Inorganic Vapor Sample Results Obtained from *In Situ* Samples Inserted into the Headspace of Tank BY-103 on 5/5/94

Sample	Analytical Results (μmol)			Sample Volume (L)	Vapor (a) Concentration (ppmv)
	Front Section	Back Section	Total ^(b) Blank-Corrected		
<u>NH₃ Samples:</u>			<u>5.54</u> (c)	<u>4.35</u> (c)	<u>30.7 ± 0.4</u> (c)
S4026-026-X48	5.6	NA ^(d)	5.5	4.28	31.2
S4026-026-X49	5.3	NA	5.2	4.15	30.5
S4026-026-X50	5.9	≤ 0.03	5.8	4.62	30.5
<u>NO₂ Samples:</u>			<u>≤0.0085</u>	<u>4.35</u>	<u>≤0.1</u>
S4026-026-X48	0.0156	0.0079	n/a	4.28	n/a
S4026-026-X49	0.0210	0.0076	n/a	4.15	n/a
S4026-026-X50	0.0181	0.0098	n/a	4.62	n/a
<u>NO Samples:</u>			<u>≤0.014</u>	<u>4.35</u>	<u>≤ 0.2</u>
S4026-026-X48	0.0211	0.0076	n/a	4.28	n/a
S4026-026-X49	0.0208	0.0094	n/a	4.15	n/a
S4026-026-X50	0.0272	0.0090	n/a	4.62	n/a
<u>HCN Samples:</u>			<u>≤0.0009</u>	<u>4.03</u>	<u>≤0.005</u>
S4026-026-X45	0.0130	0.0047	n/a	4.19	n/a
S4026-026-X46	0.0120	0.0046	n/a	4.28	n/a
S4026-026-X47	0.0123	0.0046	n/a	3.61	n/a
<u>Gravimetric Samples (mg, mg/L):</u>			<u>35.7 mg</u>	<u>4.03</u>	<u>8.9 ± 1.0 mg/L</u>
S4026-026-X45	n/a	n/a	37.3	4.19	8.90
S4026-026-X46	n/a	n/a	33.9	4.28	7.92
S4026-026-X47	n/a	n/a	35.9	3.61	9.94

- (a) Blank-corrected vapor concentrations were calculated using WHC-reported air sample volumes (corrected to 21°C and 760 torr). In the calculation for concentration, the nitrite values (listed) were doubled to account for unanalyzed nitrate. Sample results were not corrected for percentage recovery of spiked samples or spiked blanks.
- (b) Total blank-corrected analyte masses were determined, when significant, by subtracting the quantity of analyte found in blanks from that found in samples. The levels of analytes found in blanks are described in section 2.4.
- (c) Underlined values represent the average of the set of samples. Concentration uncertainty equals ± 1 standard deviation (absolute) for each set of samples. The use of "≤" is defined in section 2.0.
- (d) NA = not analyzed. Only selected back sorbent sections were analyzed. n/a = not applicable.

gravimetrically to average $0.0099 \pm 0.0001 \mu\text{mol CN}^-$ {e.g., $0.0520 \text{ g} \times 1.00 \text{ mL/g} \times 5.00 \mu\text{g CN}^-/\text{mL} \div 26 \text{ g/mol} = 0.0100 \mu\text{mol}$ }, and sent to WHC with samples for a related job in Tank BY-111. The spikes, sample numbers S4028-SOR-X66, -X67, and -X68, were applied to the center of front sorbent sections, and levels of CN^- in the back sections were equal to blank levels which indicated that no migration of CN^- occurred. The spiked blanks were analyzed and yielded an average blank-corrected percentage recovery of $69 \pm 10\%$ after a hold time of 11 weeks. It is possible that the poor spike recovery was related to the relatively long hold time. No samples were reanalyzed to check

repeatability. No sample leachates were spiked after initial analysis with quantities of CN^- to test analytical percentage recoveries.

2.4.4 Gravimetric Results. The mass concentration of material collected in the sorbent-trap trains, believed to be primarily water vapor, was 8.9 ± 1.0 mg/L. The result was based on an average mass gain of 0.036 ± 0.002 g from three of three sets of $\text{HCN}/\text{H}_2\text{O}$ sample trains. The $\text{NH}_3/\text{NO}_2/\text{H}_2\text{O}$ sample trains were not weighed. Blank corrections for the weighed sample trains were 0.0032 ± 0.0001 g, based on the results of three blank sorbent trains sent to WHC with samples for Tank BY-111. Although no spiked blanks were tested, the percentage recovery of mass from three blank H_2O traps spiked with 51 mg water was $103 \pm 2\%$ during a related sample job (Clauss et al. 1994).

3.0 Organic

3.1 SUMMA™ Canister Preparation

Before sending SUMMA™ canisters out to the field for sampling, the canisters are cleaned and verified contaminant free according to PNL Technical Procedure PNL-TVP-02^(a). The cleaning procedure uses an EnTech 3000 cleaning system that controls 1) filling the canisters with purified humid air and 2) evacuating, for several cycles with applied heat, before allowing the canister to evacuate overnight. The canister is filled a final time with purified humid air for analysis by PNL Technical Procedure PNL-TVP-01^(b), which is a modification of U.S. Environmental Protection Agency (EPA) Compendium Method TO-14. If the canister is verified as clean, free of TO-14 contaminants to a level of 5 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

The SUMMA™ canister sample was analyzed according to PNL Technical Procedure PNL-TVP-03^(c), 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

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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.
 - (c) Pacific Northwest Laboratory. *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. PNL Technical Procedure, Richland, Washington.

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

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

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

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 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 :

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

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 mg/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.

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

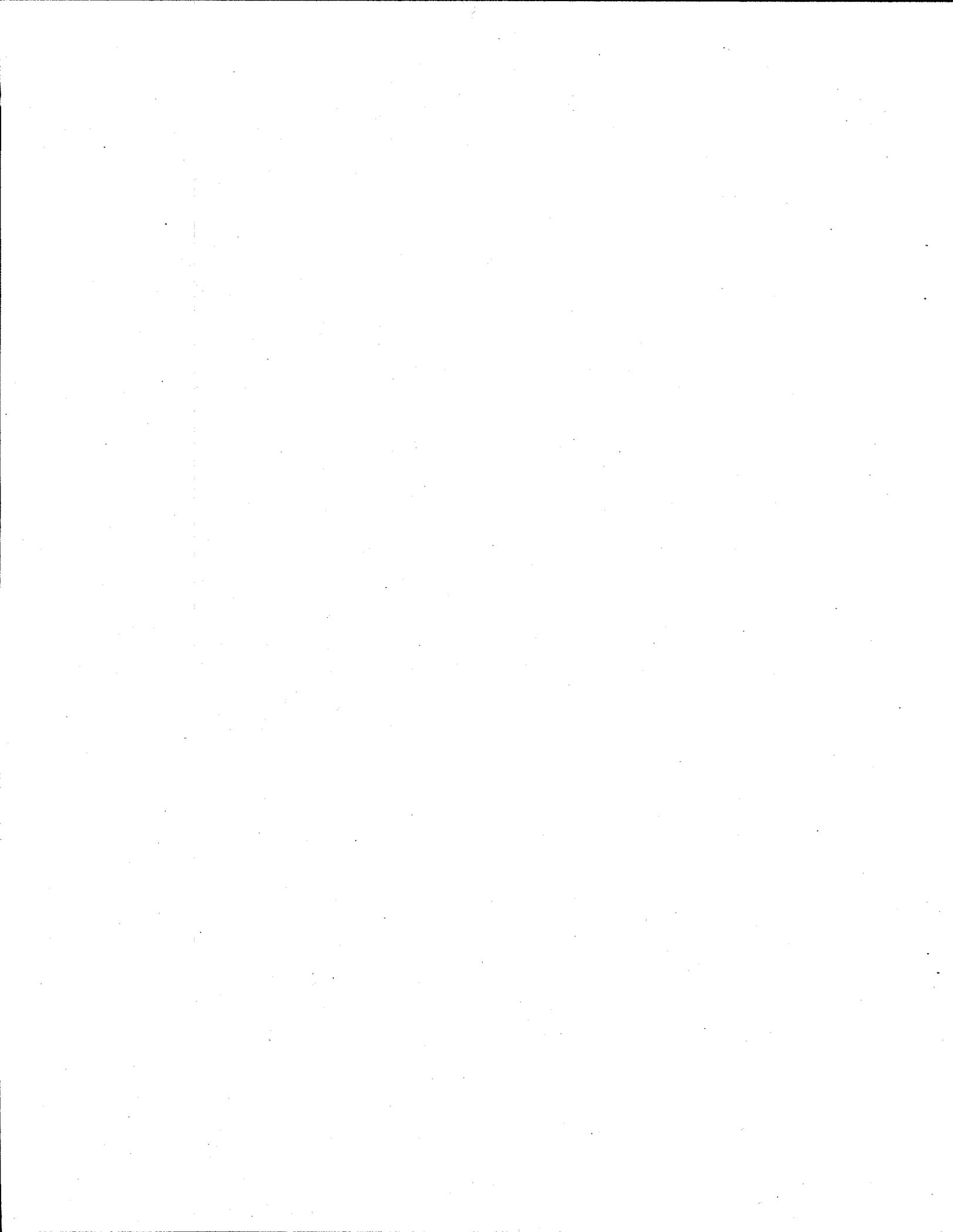
The IS level added to all blank, standard, and sample injections was 18.3 ppbv for bromochloromethane, 20.3 ppbv for 1,4-difluorobenzene, and 18.2 ppbv for chlorobenzene-d₅. The IS concentrations were converted from ppbv to mg/m³ at STP using a molecular weight of 129.39 (g/mol) for bromochloromethane, 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-103 were significantly low, close to the quantitation limit (2 ppb).

Table 3.2 lists the semi-quantitative results for the TICs. The predominant species observed in this sample were acetone, 3-methylhexane, butanol, methylcyclohexane, decane, and normal paraffin hydrocarbons (NPHs). The NPHs defined as n-alkanes from C₁₁ to C₁₅ were present in the sample. However, it should be noted that because the SUMMA™ canister was 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 was 3.42 mg/m³ for the canister analyzed. A significant amount (0.6 mg/m³) of acetone was observed in the sample. In addition, the amount of NPH and alkanes present in the TIC tables were approximately 25% of the total analytes identified.



4.0 Conclusions

The concentrations of selected inorganic and organic compounds were determined from *in situ* samples of the tank headspace of Tank BY-103. The average and standard deviation of the concentration results from inorganic sorbent trains were 30.7 ± 0.4 ppmv (NH_3), ≤ 0.1 ppmv (NO_2), ≤ 0.2 ppmv (NO), ≤ 0.005 ppmv (HCN), and 8.90 ± 1.0 mg/L (vapor mass concentration). The vapor mass concentration is expected to consist largely of water vapors. Minor differences between the individual results of the three NH_3 samples matched closely the differences in the quantities of dry air sampled during each sample.

Acetone was found to make up about 18% of the total concentration of all the organic compounds identified. Contrary to the VSS samples from Tank BY-106, ISS samples from Tank BY-103 had a significant amount of NPH and decane present (25% of the total concentration of all the identified analytes). The estimated concentration of all the analytes identified in the ISS sample of Tank BY-103 was found to be below the 1-ppmv level.

5.0 References

- Clauss, T. W., M. W. Ligothke, B. D. McVeety, K. H. Pool, R. B. Lucke, J. S. Fruchter, and S. C. Goheen. 1994. *Vapor Space Characterization of Waste Tank 241-BY-104: Results from Samples Collected on 6/24/94*. PNL-10208. Pacific Northwest Laboratory, Richland, Washington.
- Ligothke, M. W., K. H. Pool, and B. D. Lerner. 1994. *Vapor Space Characterization of Waste Tank 241-C-103: Inorganic Results from Sample Job 7B (5/12/94 - 5/25/94)*. PNL-10172, Pacific Northwest Laboratory, Richland, Washington.

6.0 Further Reading

- Pacific Northwest Laboratory. Analytical Laboratory Procedure Compendium. Procedures PNL-ALO-212, -226, -271. PNL-MA-599, Richland, Washington.
- Pacific Northwest Laboratory. Quality Assurance Manual, Part 2: Good Practices Standard. PNL-MA-70, Part 2, Richland, Washington.
- Pacific Northwest Laboratory. Quality Assurance Plan for Activities Conducted by the Analytical Chemistry Laboratory (ACL). MCS-033, Analytical Chemistry Laboratory, Richland, Washington.
- Pacific Northwest Laboratory. 1994. Determination of TO-14 Volatile Organic Compounds in Hanford Waste Tank Headspace Samples Using SUMMA™ Passivated Canister Sampling and Gas Chromatographic-Mass Spectrometry Analysis, PNL-TVP-03 (Rev. 0), PNL Technical Procedure, Richland, Washington.
- Pacific Northwest Laboratory. 1994. Sample Shipping and Receiving Procedure - DRAFT for PNL Waste Tank Samples. PNL-TVP-07 (Rev. 0), PNL Technical Procedure, Richland, Washington.

Table 3.1. TO-14 Analysis Results for *In Situ* Samples Collected from the Headspace of Tank BY-103 in SUMMA™ Canisters on 5/5/94.

TO-14 Analyte	CAS #	Mol Wt	S4026-A05-079 ^(a) PNL 79 ^(b) Concentration	
			ppbv	mg/m ³
Dichlorodifluoromethane	75-71-8	120.9	< 2	<0.01
Chloromethane	74-87-3	50.5	< 2	<0.005
1,2-Dichloro-1,1,2,2-tetrafluoroethane	76-14-2	170.9	< 2	< 0.02
Vinyl Chloride	75-01-4	62.5	< 2	< 0.01
Bromomethane	74-83-9	94.9	< 2	< 0.01
Chloroethane	75-00-3	64.5	< 2	< 0.01
Trichlorofluoromethane	75-69-4	137.4	143	0.88
1,1-Dichloroethene	75-35-4	96.9	< 2	< 0.01
Methylene Chloride	75-09-2	84.9	< 2	< 0.01
1,1,2-Trichloro-1,1,2,2-trifluoroethane	76-13-1	187.4	< 2	< 0.02
1,1-Dichloroethane	75-34-3	99.0	< 2	< 0.01
cis-1,2-Dichloroethene	156-59-2	96.9	< 2	< 0.01
Chloroform	67-66-3	119.4	< 2	< 0.01
1,2-Dichloroethane	107-06-2	99.0	< 2	< 0.01
1,1,1-Trichloroethane	71-55-6	133.4	< 2	< 0.01
Benzene	71-43-2	78.1	2.3	0.01
Carbon Tetrachloride	56-23-5	153.8	< 2	< 0.01
1,2-Dichloropropane	78-87-5	113.0	< 2	< 0.01
Trichloroethene	79-01-6	131.4	< 2	< 0.01
cis-1,3-Dichloropropene	10061-01-5	111.0	< 2	< 0.01
trans-1,3-Dichloropropene	10061-02-6	111.0	< 2	< 0.01
1,1,2-Trichloroethane	79-00-5	133.4	< 2	< 0.01
Toluene	108-88-3	92.1	57.2	0.24
1,2-Dibromoethane	106-93-4	187.9	< 2	< 0.02
Tetrachloroethylene	127-18-4	165.8	< 2	< 0.02
Chlorobenzene	108-90-7	112.6	< 2	< 0.01
Ethylbenzene	100-41-4	106.2	< 2	< 0.01
p/m-Xylene	106-42-3	106.2	< 2	< 0.01
Styrene	100-42-5	104.2	< 2	< 0.01
1,1,2,2-Tetrachloroethane	79-34-5	167.9	< 2	< 0.02
o-Xylene	95-47-6	106.2	< 2	< 0.01
1,3,5-Trimethylbenzene	108-67-8	120.2	< 2	< 0.01
1,2,4-Trimethylbenzene	95-63-6	120.2	< 2	< 0.01
Chloromethylbenzene, alpha (Benzyl Chloride)	108-67-8	126.6	< 2	< 0.01
1,3-Dichlorobenzene	541-73-1	147.0	< 2	< 0.01
1,4-Dichlorobenzene	106-46-7	147.0	< 2	< 0.01
1,2-Dichlorobenzene	95-50-1	147.0	< 2	< 0.01
1,2,4-Trichlorobenzene	120-82-1	181.5	< 2	< 0.02
Hexachloro-1,3-butadiene	87-68-3	260.8	< 2	< 0.02

(a) WHC sample identification number.

(b) PNL canister number.

Table 3.2 Tentatively Identified Compounds and Estimated Concentrations in the Headspace of Tank BY-103 *In Situ* SUMMA™ Canister Sample S4026-SUM-079^(a) Collected on 5/5/94

Tentatively Identified Compounds ^(c)	Mol. Wt.	Retention Time (min)	PNL 079 ^(b)	
			Estimated Concentration ^(d)	
			mg/m ³	ppmv
Carbon dioxide	44	5.94	(f)	(f)
Carbon dioxide	44	6.11	(f)	(f)
n-Butane	58	8.19	0.06	0.02
Acetone	58	10.26	0.59	0.23
n-Pentane	72	11.20	0.05	0.02
2-Methyl-pentane	84	14.25	0.06	0.02
2-Butanone	72	14.62	0.10	0.03
Chlorobromomethane (IS)		15.78		
n-Hexane (coeluent)	86		0.06	0.02
1-Butanol	74	18.28	0.13	0.04
1,4-Difluorobenzene (IS)		19.33		
C7 Alkane ^(e) (coeluent)	100		0.17	0.04
2,3-Dimethylpentane	100	19.56	0.09	0.02
3-Methylhexane	100	19.84	0.24	0.05
C7 Alkane ^(e)	100	20.71	0.06	0.01
n-Heptane	100	21.10	0.14	0.03
Methylcyclohexane	100	22.65	0.31	0.07
Chlorobenzene-d5 (IS)		28.45		
3-Heptanone	114	29.82	0.07	0.01
2-Butoxyethanol	118	30.95	0.14	0.03
n-Decane	142	44.39	0.23	0.04
Alkane	(g)	45.02	0.08	(g)
C13 Alkene ^(e)	182	46.46	0.05	0.01
Alkane	(g)	47.28	0.14	(g)
n-Tridecane	184	48.14	0.45	0.05
Alkane	(g)	51.02	0.10	(g)
n-Tetradecane	198	51.64	0.10	0.01

(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 closest eluting internal standard.

(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.

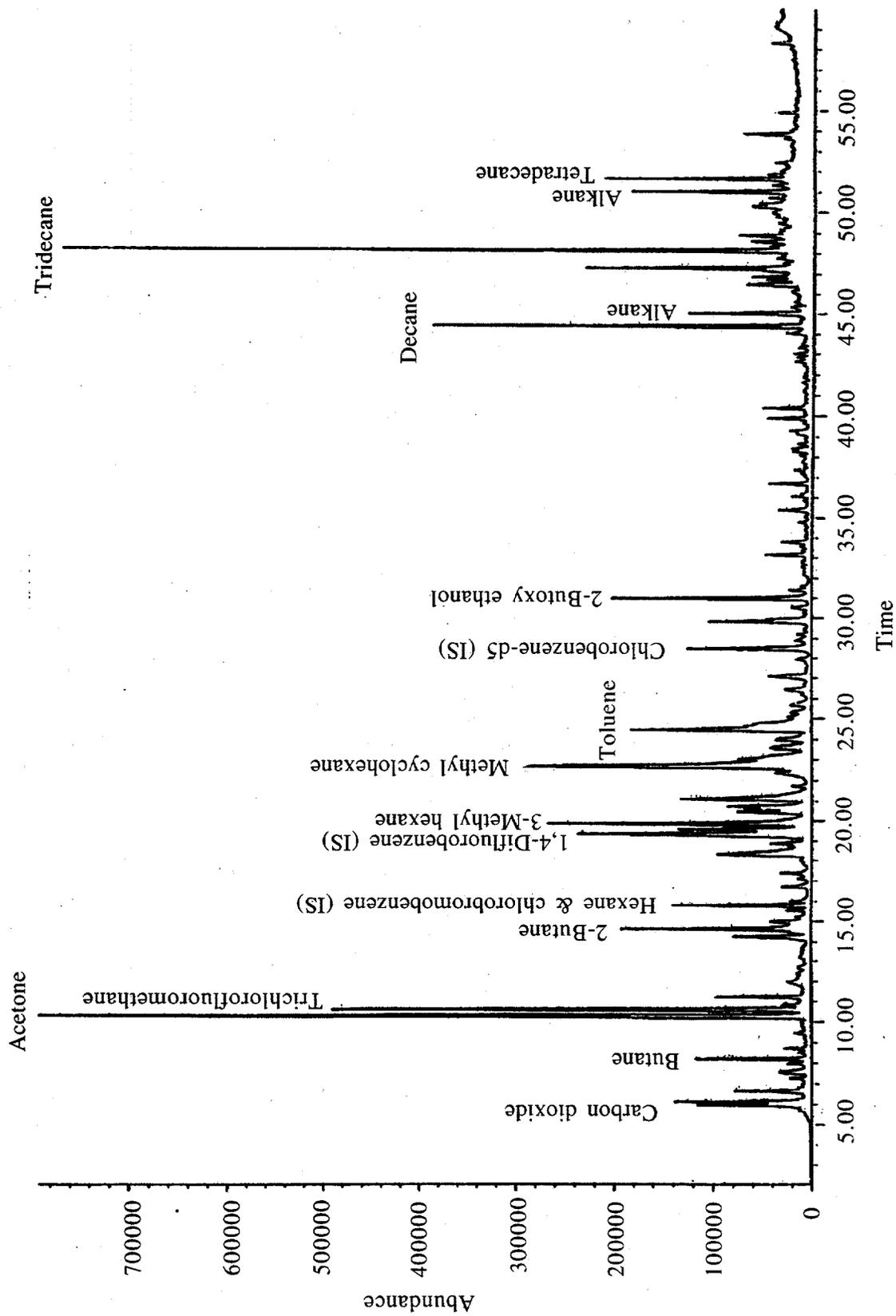


Figure 3.1 GC/MS Chromatogram of Hanford Waste Tank BY-103 In Situ SUMMA™ Canister Vapor Sample S4026-026-079 Collected on 5/5/94

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