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Vapor Space Characterization of Waste Tank 241-BY-105: Results from Samples Collected on 7/7/94

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May 1995

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Summary

This report describes organic and inorganic results from vapors of the Hanford single-shell waste storage Tank 241-BY-105 (referred to as Tank BY-105). The results described here were obtained to support safety and toxicological evaluations. Quantitative results were obtained for the inorganic compounds ammonia (NH_3), nitrogen dioxide (NO_2), nitric oxide (NO), and water (H_2O). Sampling for hydrogen cyanide (HCN) and sulfur oxides (SO_x) was not requested.

Several organic analytes were quantitatively determined, but quantities of non-TO-14 analytes were only estimated. Approximately 40 tentatively identified organic analytes were observed above the detection limit of (ca.) 10 ppb, but standards for most of these were not available at the time of analysis, and their quantitative determination is beyond the scope of this study. The SUMMA™ canisters were also analyzed for components listed in U.S. Environmental Protection Agency (EPA) compendium Method TO-14. Of these only a few were observed above the 2-ppb detection limits. These are summarized in Table 3.1. Estimated quantitations also determined were of tentatively identified compounds (TICs). A summary of these results (Table 3.2) shows quantities of all TICs above the concentration of ca. 10 ppb. This consists of more than 40 organic analytes. The 6 organic analytes with the highest estimated concentrations are shown in Table 1. These 6 analytes account for approximately 45% of the total organic components in Tank BY-105. Detailed descriptions of the results appear in the text. Unlike tanks previously studied, normal paraffin hydrocarbons (NPHs) did not contribute significantly to the total organic concentration of the vapor headspace of Tank BY-105. The total concentration of TICs detected in the tank headspace samples was also much lower than that seen in other reported tanks averaging 6.5 mg/m^3 for all three canisters collected.

Table 1. Summary Results of Inorganic and Organic Samples Collected from the Tank Headspace of Tank BY-105 on 7/7/94

	Analyte	Vapor Concentration	Units
Inorganic			
	NH_3	43 ± 1	ppmv[(a)]
	NO_2	≤ 0.04	ppmv[(a)]
	NO	0.12 ± 0.05	ppmv[(a)]
	H_2O	17 ± 1	mg/L[(a)]
Organic			
	1-propene	1	mg/m^3
	2-methyl-1-propene	0.4	mg/m^3
	2-methylpentane	0.5	mg/m^3
	hexane	0.4	mg/m^3
	1-butanol	0.6	mg/m^3
	trichlorofluoromethane	0.3	mg/m^3

(a) See section 2.4. NO_x values from sorbent-trap sections not protected by NH_3 sorbent traps.

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. Jeff also supported work in the organic analytical laboratory. Amit Sharma assisted in the organic analytical laboratory and assisted in preparing this report. Sally Slate and May-Lin Thomas analyzed inorganic samples, and Gary Dennis prepared the solid-sorbent sample trains. Georgia K. Ruebsamen provided word processing support.

Abbreviations

COC	chain of custody
DIW	deionized water
emf	electromotive force
EPA	U.S. Environmental Protection Agency
HP	Hewlett Packard
IC	ion chromatography
IL	impact level
IS	internal standard
MDL	minimum detection limit
NIST	National Institute for Standards and Technology
NPH	normal paraffin hydrocarbon
OSHA	Occupational Safety and Health Administration
PFA	perflouroalkoxy
ppb	parts per billion
ppm	parts per million
ppmv	parts 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 compounds
VSS	vapor sampling system
WHC	Westinghouse Hanford Company

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1.0 Introduction

This report describes results of the analysis of vapor samples taken from the Hanford waste Tank 241-BY-105 (referred to as Tank BY-105) on July 7, 1994. The Westinghouse Hanford Company (WHC) sample job number was S4020 (see Figure 1).

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 7 and were returned from the field on July 11. Inorganic (sorbent tube) samples delivered to Pacific Northwest Laboratory (PNL)[(a)] on COC 006894 (see Figure 1a) included 16 samples as described in Tables 2.2, 2.3, and 2.4. SUMMA™ samples delivered to PNL on chain of custody (COC) 006897 (see Figure 1b), included one ambient-air sample through the vapor sampling system (VSS), one ambient-air sample without the vapor sampling system and three tank-headspace SUMMA™ canister samples.

The samples were inspected upon delivery to the 326/23B laboratory and logged into PNL laboratory record book BNW 55408 before implementation of PNL Technical Procedure PNL-TVP-07[(b)]. Custody of the sorbent tubes was transferred to PNL personnel performing the inorganic analyses 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.

Methods used for organic and inorganic analyses are described in the text of this report. In summary, sorbent tubes for inorganic analyses containing sample materials were either weighed (for water analysis) or desorbed with water (for ammonia) or an aqueous triethanolamine solution (for NO_x) analyses. The extracts were analyzed either by selective electrode or by ion chromatography (IC). Organic analyses were performed using 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), 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 006894

Custody Form Initiator	J. A. Edwards	Telephone Pager	(509)373 -0141 85-3009
Company Contact	R. Westberg	Telephone	(509) 373-5734
Project Designation/Sampling Locations BY 105 Tank Vapor Sample SAF S4020 Ice Chest No. (VSS Truck)	200 East Tank Farm	Collection Date Preparation Date Field Logbook No.	0 6- _ _ -9 4 0 6- 1 5 -9 4 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

S4020 - A16 . W48	$NH_3/NO_X/H_2O$ (Sample #1)
S4020 - A17 . W49	$NH_3/NO_X/H_2O$ (Sample #2)
S4020 - A18 . W50	$NH_3/NO_X/H_2O$ (Sample #3)
S4020 - A19 . W51	$NH_3/NO_X/H_2O$ (Sample #4)
S4020 - A20 . W52	$NH_3/NO_X/H_2O$ (Sample #5)
S4020 - A21 . W53	NH_3 (Blank)
S4020 - A22 . W54	NH_3 (Spiked Blank)
S4020 - A23 . W55	NO_X/H_2O (Sample #1)
S4020 - A24 . W56	NO_X/H_2O (Sample #2)
S4020 - A25 . W57	NO_X/H_2O (Sample #3)
S4020 - A26 . W58	NO_X/H_2O (Sample #4)
S4020 - A27 . W59	NO_X/H_2O (Sample #5)
S4020 - A28 . W60	NO_X (Blank)
S4020 - A29 . W61	NO_X (Spiked Blank)
S4020 - A30 . W62	H_2O (Blank)
S4020 - A31 . W63	H_2O (Spiked Blank)

[X] Field Transfer of Custody [ ] 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	07-07-94	0930	RA Westberg	7-7-94	0930
RA Westberg	7-7-94	1200	SM Brown	7-07-94	1200
SM Brown	7-11-94	1130	JA Edwards	7/11/94	1130

(Revised 02/28/94)

Final Sample Disposition

Disposal Method:

A-6000-407 (12/92) WEF061 June 20, 1994 @ 9:01

Figure 1a. Chain-of-Custody for Inorganic Samples from Tank BY-105

Westinghouse Hanford Company	CHAIN OF CUSTODY	WHC 006897

Custody Form Initiator	J. A. Edwards	Telephone Pager	(509)373 -0141 85-3009
Company Contact	R. A. Westberg	Telephone	(509) 373-5734
Project Designation/Sampling Locations 241-BY-105 Tank Ice Chest No.	200 East Tank Farm Vapor Sample SAF S4020 (VSS Truck)	Collection Date Preparation Date Field Logbook No.	0 6- _ _ -9 4 0 6- 1 6 -9 4 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

S4020 - A01 . S007	Ambient Air SUMMA	(PNL)
S4020 - A02 . S009	Ambient	SUMMA #1 (PNL)
S4020 - A05 . S010	Sample	SUMMA #3 (PNL)
S4020 - A07 . S021	Sample	SUMMA #5 (PNL)
S4020 - A09 . S022	Sample	SUMMA #7 (PNL)

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

Relinquished By	Date	Time	Received By	Date	Time
J. A. Edwards / J A Edwards	06-10-94	1910	SM BROWN / Sm Brown	6/10/94	1010
SM Brown / Sm Brown	7-7-94	0700	RA Westberg / RA Westberg	7-7-94	0700
RA Westberg / RA Westberg	7-7-94	1200	SM Brown / Sm Brown	7-7-94	1200
SM Brown / Sm Brown	7-11-94	1130	JA EDWARDS / 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 18, 1994 @ 15:20

Figure 1b. Chain-of-Custody for Organic Samples from Tank BY-105

2.0 Inorganic Results

Solid sorbent traps, prepared in sampling trains, were supplied to WHC for sampling from the tank headspace using the VSS. 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 oxide (NO_2), nitric oxide (NO), and water (H_2O). Procedures were similar to those developed previously during sample jobs performed with the 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 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 traps, having glass-sealed ends, were received from the vendor.

The type and nominal quantity of sorbent material varied by application. Sorbent traps were selected for the tank sample job and included the following products. The NH_3 sorbent traps contained carbon beads impregnated with sulfuric acid; nominally, 500 mg were contained in the primary and 250 mg in the breakthrough sections. The NH_3 was chemisorbed as ammonium sulfate. 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 adsorbed 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 all or some of 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 NOx sorbent trains having been stored previously in a freezer. After sample preparation, all 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. perflouroalkoxy (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 mass of the compound, in µmol, by the volume of the sample, in mol. The micromolar sample mass was determined by dividing the compound mass, in µg, by the molecular weight of the compound, in g/mol. The volume of the sample was determined, excluding water vapor, by dividing the standard sample volume (at 0°C and 760 torr), in L, by 22.41 L/mol. For example, the concentration of a 3.00-L sample containing 75.0 µg of ammonia equals

$$C_v = \left(\frac{75.0\ \mu g}{17\ g/mol} \times \frac{3L}{25.52\ L/mol} \right)^{-1} = 33.0\ ppmv \qquad (1)$$

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. Target compounds included those described in this section. 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 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 NH3 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 NH3 working calibration standards by serial dilution of the freshly made stock standard; 3) generating an initial calibration curve from the measured emf signal versus NH3 concentration data obtained for the set of working standards; 4) performing a calibration-verification check, using one of the midrange standards, after analyzing every 4 or 5 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 triethanolamine (TEA) and n-butanol solution and analyzed by suppressed-conductivity ion chromatography (SCIC) for nitrite according to PNL-ALO-212, Rev. 1 (*Determination of Inorganic Anions by Ion Chromatography*) modified to obviate interferences by concentrations of non-target analytes. Specifically, the modifications used were 1) eluent 1.44 mM Na_2CO_3 + 1.8 mM $NaHCO_3$ at 2.0 mL/min; 2) one guard column (AG4A) and two separator columns (AS4A) in series instead of just one separator column; 3) all standards, samples, and blanks injected into the ion chromatograph 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 analyzing 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 mass of NO_2 and NO were determined by doubling the analytically determined molar mass of nitrite.

2.2.3 Mass (Water) Analysis. Sorbent traps used to make each sample train were weighed using a semi-micro mass balance after labeling and breaking the glass tube ends, without plastic end caps. After receipt of exposed samples, the sorbent traps were again weighed to determine the change in mass. Records of the measurements were documented on sample-preparation data sheets. The mass concentration, 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 PNL quality impact level was IL III. The PNL documents include PNL-MA-70 (Part 2), PNL-MA-599, PNL-ALO-212, PNL-ALO-226, and MCS-033. A summary of the analysis procedures and limits for the target inorganic compounds is provided in Table 2.1. From the table, it can be seen that the minimum detection limit (MDL) required to resolve the analyte at one-tenth of the recommended exposure limit (REL) for 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 MDL can be obtained. The MDL 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 selective ion electrode was estimated to be ± 5% relative, independent of concentration at 1 μg/mL or greater levels. The uncertainty includes preparation of standards, purity of the ammonium salt used to prepare standards, potential operator bias, ambient temperature variations, etc. Unfortunately no known National Institute for Standards and Technology (NIST)-traceable standard reference material (SRM) is available against which to compare working standards. As for ammonia, no known NIST SRM is available for nitrite analysis (for NO_2 and NO). Based on experience in comparing nitrite working standards prepared from several different sources and factors mentioned for ammonia above, the estimated maximum bias for samples derived from sampling for NO_2 is ± 10%, and for samples derived from sampling for NO, it is ± 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 BY-105 on 7/7/94 using the VSS. The sample job designation number was S4020. Samples were prepared, submitted to WHC, and then analyzed to provide information on the concentrations of ammonia, nitrogen dioxide, nitric oxide, and water. Blank and spiked-blank samples were pooled with those provided for similar sampling jobs associated with Tank BY-104 (S4019) and Tank BY-106 (S4021). 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 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.

Table 2.2. List of PNL Inorganic Samples and Gravimetric Results Obtained From a Heated Tube Inserted in the Tank Headspace of Tank BY-105 on 7/7/94. 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)
S4020-A16-W48	$NH_3/NO_x/H_2O$ Sample	8	200	15.0	3.00	0.0516
S4020-A17-W49	$NH_3/NO_x/H_2O$ Sample	10	200	15.0	3.00	0.0509
S4020-A18-W50	$NH_3/NO_x/H_2O$ Sample	9	200	15.0	3.00	0.0523
S4020-A19-W51	$NH_3/NO_x/H_2O$ Sample	10	200	15.0	3.00	0.0509
S4020-A20-W52	$NH_3/NO_x/H_2O$ Sample	8	200	15.0	3.00	0.0507
S4020-A23-W55	NO_x/H_2O Sample	10	200	15.0	3.00	0.0494
S4020-A24-W56	NO_x/H_2O Sample	9	200	15.0	3.00	0.0528
S4020-A25-W57	NO_x/H_2O Sample	10	200	15.0	3.00	0.0503
S4020-A26-W58	NO_x/H_2O Sample	8	200	15.0	3.00	0.0524
S4020-A27-W59	NO_x/H_2O Sample	10	200	15.0	3.00	0.0496
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_2O Blank	n/a	n/a	n/a	n/a	0.0005
S4020-A30-W62	H_2O Blank	n/a	n/a	n/a	n/a	0.0016
S4021-A30-W78	H_2O 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_2O Spiked Blank	n/a	n/a	n/a	n/a	0.0005
S4020-A31-W63	H_2O Spiked Blank	n/a	n/a	n/a	n/a	0.0020
S4021-A31-W79	H_2O 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.

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 (%)	Percentage Recovery Average[c] (%)
S4019-A22-W38	BY-104	NH_3	12.4	13.2	106	101 ± 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 ± 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_2O	2811[d]	2839	101	103 ± 2
S4020-A31-W63	BY-105	H_2O	2856	2967	104	
S4021-A31-W79	BY-106	H_2O	2878	2950	103	

(a) The NH_3 spike solutions were 20 μL of 10,000 ppm (3.142 g NH_4Cl per 100 mL). The NO_2 spike solutions were 20 μL of 100 ppm nitrite. The H_2O spike was 50 μL of distilled water. The μmol of spiked material added were determined gravimetrically (e.g., 0.021g x 10,000 μg NH_3/mL ÷ 17 g/mol = 12.4 μmol).
(b) Blank corrections for NH_3 analytical results were not significant. Analytical results for NO_2^- 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 ± 1 standard deviation.
(d) Water measured in μg and converted to μmol by dividing by the molecular weight of water (18).

2.4.1 Ammonia Results. The concentration of NH_3 was 43 ± 1 ppmv, based on all five samples. The mass of NH_3 ranged from 5.5 to 5.9 μmol in the front sorbent sections and was ≤ 0.04 μmol 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 NH_3 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 NH_3 was 101 ± 4%. Past blanks spiked with 22.3 and 46.4 μmol yielded percentage recoveries of 109 ± 2% and 104 ± 1%, respectively (Ligotke et al. 1994). One sample leachate was spiked after initial analysis with roughly the mass of the mass of NH_3 in the sample and yielded a percentage recovery of 100%. The analysis of one sample was duplicated and yielded a repeatability of ± 1%. A 5-point calibration was performed over an NH_3 range of 0.1 to 1000 μg/mL. The NH_3 concentrations from samples from Ports 8 and 9 were 5 ± 2% greater than those from Port 10.

2.4.2 Nitrogen Oxides Results. Measurements of NO_2 and NO were made using $NH_3/NO_x/H_2O$ and NO_x/H_2O sorbent trap trains (the NO_x trains consisted of NO_2 trap, oxidizer, and NO_2 trap). Five samples of each sample-train type were obtained. The presence of the upstream NH_3 traps resulted in NO concentrations that were about 1.4-fold less than those from unprotected NO_2 traps. The NO_2 concentrations were also potentially less following an NH_3 trap.

Table 2.4. Inorganic Vapor Sample Results Obtained From a Heated Tube Inserted in the Tank Headspace of Tank BY-105 on 7/7/94

Sample	Tank if Other Than BY-105	Port	Mass Collected Front (μmol)	Mass Collected Back (μmol)	Estimated[a] Concentration (ppmv)
NH_3 Samples:					43 ± 1[b]
S4020-A16-W48		8	5.9	NA[c]	
S4020-A17-W49		10	5.7	0.04	
S4020-A18-W50		9	5.9	NA	
S4020-A19-W51		10	5.5	0.03	
S4020-A20-W52		8	5.9	NA	
S4019-A21-W37	BY-104	blank	≤ 0.06	≤ 0.03	n/a
S4020-A21-W53		blank	≤ 0.06	0.03	n/a
S4021-A21-W69	BY-106	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		blank	0.0148	0.0082	n/a
S4021-A28-W76	BY-106	blank	0.0148	0.0085	n/a
NO_2 Samples (Protected by NH_3 sorbent trap):					≤ 0.02
S4020-A16-W48		8	0.0137	0.0076	
S4020-A17-W49		10	0.0130	0.0076	
S4020-A18-W50		9	0.0134	0.0073	
S4020-A19-W51		10	0.0146	0.0076	
S4020-A20-W52		8	0.0144	0.0092	
NO_2 Samples (Not Protected by NH_3 sorbent trap):					≤ 0.04
S4020-A23-W55		10	0.0159	0.0076	
S4020-A24-W56		9	0.0156	0.0078	
S4020-A25-W57		10	0.0148	0.0078	
S4020-A26-W58		8	0.0155	0.0078	
S4020-A27-W59		10	0.0170	0.0075	
NO Samples (Protected by NH_3 sorbent trap):					0.08 ± 0.05
S4020-A16-W48		8	0.0209	0.0076	
S4020-A17-W49		10	0.0238	0.0073	
S4020-A18-W50		9	0.0208	0.0081	
S4020-A19-W51		10	0.0208	0.0074	
S4020-A20-W52		8	0.0219	0.0078	
NO Samples (Not Protected by NH_3 sorbent trap):					0.12 ± 0.05
S4020-A23-W55		10	0.0216	0.0078	
S4020-A24-W56		9	0.0230	0.0074	
S4020-A25-W57		10	0.0232	0.0082	
S4020-A26-W58		8	0.0262	0.0081	
S4020-A27-W59		10	0.0246	0.0080	
Gravimetric Samples:					17 ± 1 mg/L

(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 prior to 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.

The concentration of NO_2 was ≤ 0.02 ppmv (the MDL) from sorbent traps downstream of NH_3 traps, and ≤ 0.04 ppmv from sorbent traps leading the sample trains. The concentration of NO was 0.08 ± 0.05 ppmv from sorbent traps downstream of NH_3 traps, and 0.12 ± 0.05 ppmv from sorbent traps leading the sample trains. Uncorrected NO_2^- quantities in the traps ranged from 0.013 to 0.026 μmol in the front sorbent sections and 0.007 to 0.008 μmol in the back sections. The MDL of NO_2^- was about 0.001 μmol. The NO_2^- content of three front and back blank sorbent sections were 0.016 ± 0.002 and 0.0087 ± 0.0007 μmol, respectively, and these values were used to correct the quantity of NO_2^- measured in the samples. The percentage recovery of three blanks spiked with 0.047 μmol NO_2^- was 103 ± 4%. Past blanks spiked with 0.0064, 0.11, and 0.74 μmol NO_2^- yielded percentage recoveries of 153 ± 14%, 106 ± 8%, and 111 ± 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 μg 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 ± 1 mg/L. The result was based on an average mass gain of 0.511 ± 0.012 g from all 10 sets of NH_3/NO_2/H2O and NO_x/H_2O sample trains. The percentage recovery of mass from three blank silica -gel traps spiked with 51 μg water was 103 ± 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 ± 1 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 five samples obtained from Ports 8 and 9 averaged 3.5% greater than those of the five samples from Port 10 (the range was 0.6 to 6.2% more mass in samples from Ports 8 and 9).

3.0 Organic Analysis

3.1 Sample Analysis Method

The SUMMA™ canister sample was analyzed according to PNL Technical Procedure PNL-TVP-03, *Determination of TO-14 Volatile Organic Compounds in Hanford Waste Tank Headspace Samples Using SUMMA™ Passivated Canister Sampling and Gas Chromatographic-Mass Spectrometry Analysis*, which is a modified version of U.S. Environmental Protection Agency (EPA) compendium Method TO-14. The method uses an EnTech cryoconcentration system that is 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, and then transfer the volume to the GC/MS for analysis. A 100-mL volume of air is measured and analyzed from the tank headspace sample. 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 inside diameter with 3-µm film thickness. The GC column is programmed for a temperature gradient beginning at 40°C, holding for 5 min, and ramping at 4°C /min to a final temperature of 260°C with a 5-min hold.

3.2 Quality Assurance and 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 the PNL-TVP-03. Upon satisfactory completion of the instrument diagnostic check, a blank volume of purified nitrogen was analyzed to check the cleanliness of the system. The instrument was then calibrated over 6 data points ranging from 2 ppbv to 100 ppbv, using a standard gas mixture containing 40 volatile organic compounds listed in EPA compendium Method TO-14. A gas mixture containing bromochloromethane, 1,4-difluorobenzene, and chlorobenzene-d_5 was used as an internal standard (IS) or all blank, calibration standard, and sample analyses. 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 determine the concentration of TIC seen in the tank samples.

3.2.1 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/m3 assumes STP conditions of 760 torr and 273°K and was calculated directly from the following equation:

$$mg/m^3 = \frac{\text{ppmv x molecular weight of compound}}{22.4}$$

3.2.2 Identification and Quantitation of Tentatively Identified Compounds. The TICs are determined by performing a mass spectral library search on each integrated peak using 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 an 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-d5. 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:

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

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 5.05 mg/m^3. Internal standards bromochloromethane and difluorobenzene were not used to quantitate the TIC because coeluting compounds appeared to have greatly altered the signal of the quantitation ions for those two ISs.

The ppmv concentrations reported for TIC are estimates determined by using the calculated concentration in mg/m3 and the molecular weight of the n-alkane eluting closest to the TIC of interest on the chromatogram.

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

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/m^3 at STP using a molecular weight of 129.39 (g/mol) for bromochloromethane, 114.09 for 1,4-difluorobenzene, and 117.6 for chlorobenzene-d_5.

3.3 Analysis Results

The results from the GC/MS analysis of the tank headspace are presented in Tables 3.1 and 3.2. Representative total ion chromatographs showing identity of major constituents are shown in Figures 3.1 through 3.3.

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-105 were at or near the 2-ppbv detection limit. The predominant TO-14 species seen in these samples were Freon-11 (trichlorofluoromethane 44 ppbv), toluene (2.4 ppbv), and p/m-xylene (2.3 ppbv). The levels of TO-14 compounds seen in Tank BY-105 are much lower than those previously reported in samples from other BY tanks.

Table 3.1 TO-14 Analysis Results for Samples Collected from Hanford Waste Tank BY-105 in SUMMA™ Canisters on 7/7/94

TO-14 Analytes	S4020-A05-S010[a] PNL 010[b] (ppbv)	(mg/m^3)[c]	S4020-A07-S021 PNL 021 (ppbv)	(mg/m^3)	S4020-A09-S022 PNL 022 (ppbv)	(mg/m^3)
dichlorodifluoromethane (FREON-12)	2.00	0.01	< 2	< .01	2.00	0.01
methyl chloride (chloromethane)	< 2	< .01	< 2	< .01	< 2	< .01
1,2-dichloro-1,1,2,2,-tetrafluoroethane (FREON-114)	< 2	< .02	< 2	< .02	< 2	< .02
chloroethene (vinyl chloride)	< 2	< .006	< 2	< .006	< 2	< .006
methyl bromide (bromomethane)	< 2	< .009	< 2	< .009	< 2	< .009
ethyl chloride	< 2	< .006	< 2	< .006	< 2	< .006
trichlorofluoromethane (FREON-11)	50.00	0.31	39.00	0.24	42	0.26
1,1-dichloroethene (1,1-dichloroethylene)	< 2	<.009	< 2	<.009	< 2	<.009
dichloromethane	< 2	< .01	< 2	< .01	< 2	< .01
1,1,2-trichloro-1,2,2-trifluoroethane (FREON-113)	< 2	< .02	< 2	< .02	< 2	< .02
1,1-dichloroethane	< 2	< .009	< 2	< .009	< 2	< .009
1,2-dichloroethene	< 2	< .009	< 2	< .009	< 2	< .009
trichloromethane (chloroform)	< 2	< .01	< 2	< .01	< 2	< .01
1,2-dichloroethane	< 2	<.009	< 2	<.009	< 2	<.009
1,1,1-trichloroethane	< 2	< .01	< 2	< .01	< 2	< .01
benzene	< 2	< .01	< 2	< .01	< 2	< .01
carbon tetrachloride	< 2	< .01	< 2	< .01	< 2	< .01
1,2-dichloropropane	< 2	< .01	< 2	< .01	< 2	< .01
trichloroethylene	< 2	< .01	< 2	< .01	< 2	< .01
cis 1,3-dichloropropene	< 2	< .01	< 2	< .01	< 2	< .01
trans 1,3-dichloropropene	< 2	< .01	< 2	< .01	< 2	< .01
1,1,2-trichloroethane	< 2	< .01	< 2	< .01	< 2	< .01
methyl benzene (toluene)	2.53	0.01	2.20	0.01	2.60	0.01
1,2-dibromoethane	< 2	< .02	< 2	< .02	< 2	< .02
tetrachloroethene)	< 2	< .02	< 2	< .02	< 2	< .02
chlorobenzene	< 2	< .01	< 2	< .01	< 2	< .01
ethylbenzene	< 2	< .01	< 2	< .01	< 2	< .01
p/m-xylene (1,3-dimethylbenzene & 1,4-dimethylbenzene)	2.31	0.01	2.20	0.01	2.30	0.01
styrene	< 2	< .01	< 2	< .01	< 2	< .01
1,1,2,2-tetrachloroethane	< 2	< .01	< 2	< .01	< 2	< .01
o-xylene (1,2-dimethylbenzene)	< 2	< .01	< 2	< .01	< 2	< .01
1,3,5-trimethylbenzene	< 2	< .01	< 2	< .01	< 2	< .01
1,2,4-trimethylbenzene	< 2	< .01	< 2	< .01	< 2	< .01
chloromethylbenzene	< 2	< .01	< 2	< .01	< 2	< .01
m-dichlorobenzene	< 2	< .01	< 2	< .01	< 2	< .01
p-dichlorobenzene	< 2	< .01	< 2	< .01	< 2	< .01
o-dichlorobenzene	< 2	< .01	< 2	< .01	< 2	< .01
1,2,4-trichlorobenzene	< 2	< .02	< 2	< .02	< 2	< .02
hexachloro-1,3-butadiene	< 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 lists the semi-quantitative results for the TICs. The predominant species observed in these samples were 1-propene, 2-methyl-1-propene, 2-methylpentane, hexane, and butanol. The normal paraffin hydrocarbons (NPH) defined as n-alkanes from C11 to C15 were present in the samples at low

concentrations, similar to that seen in the Tank BY-106 samples. 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 that may adhere to the inside surface of the canister may also be under represented in this analysis. The total concentration of the TICs averaged 6.5 mg/m^3 with a standard deviation of 1.4 mg/m^3 for all three canisters analyzed.

4.0 Conclusions

The concentrations of selected inorganic and organic compounds were determined from samples obtained from the headspace of Hanford Tank BY-105 on 7/7/94. The average and standard deviation of the concentration results from inorganic sorbent trains were 43± 1 ppmv (NH_3), ≤ 0.04 ppmv (NO_2), 0.12 ± 0.05 ppmv (NO), and 17 ± 1 mg/l (vapor mass concentration). The vapor mass concentration is expected to consist largely of water vapor. The presence of an upstream NH3 sorbent trap resulted in samples yielding NO concentrations 1.4-fold less than those from unprotected samples. The NO_2 concentrations were also potentially less following an NH_3 trap. Ammonia and mass-change measurements indicated samples connected to Ports 8 and 9 collected on average 5 and 3% more mass than samples connected to Port 10, respectively. The total tentatively identified organic concentration for this tank was the lowest level seen of all BY tank samples previously reported, approximately 30% of the total seen in Tank BY-106. The decahydronaphthalene compounds observed in the headspace samples from Tanks BY-107 and BY-108 were not observed in the headspace of Tank BY-105. 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 headspace samples.

5.0 Reference

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6.0 Further Reading

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Table 3.2 Table of Tentatively Identified Compounds and Estimated Concentrations in Hanford Waste Tank BY-105 SUMMA™ Canister Samples Collected on 7/7/94.

TIC Analytes[c]	Retention Time	S4020-A05-S010 PNL 010		S4020-A07-S021 PNL 021		S4020-A09-S022[a] PNL 022[b]		Average	Std. Dev.
		(mg/m^3)[d]	(ppmv)	(mg/m^3)	(ppmv)	(mg/m^3)	(ppmv)	(mg/m^3)	(ppmv)
carbon dioxide[f]	3.44	(f)	(f)	(f)	(f)	(f)	(f)	(f)	(f)
carbon dioxide[f]	3.51	(f)	(f)	(f)	(f)	(f)	(f)	(f)	(f)
propene	4.31	1.16	0.62	0.77	0.41	0.95	0.51	0.96	0.19
propane	4.40	0.33	0.17	0.24	0.12	0.28	0.14	0.28	0.04
cyclopropane	5.20	0.08	0.04	< 0.08	< 0.04	0.06	0.03	(g)	(g)
2-methylpropane	5.52	0.20	0.08	0.12	0.04	0.17	0.06	0.16	0.04
2-methyl-1-propene	6.11	0.41	0.16	0.27	0.11	0.33	0.13	0.34	0.07
n-butane	6.37	0.31	0.12	0.20	0.08	0.25	0.10	0.25	0.05
C4 alkene[e]	7.02	0.08	0.03	0.05	0.02	0.06	0.02	0.06	0.01
2-methyl-1-butene	8.22	0.05	0.02	< 0.05	< 0.02	< 0.05	< 0.02	(g)	(g)
acetone	8.80	0.19	0.07	0.12	0.05	0.18	0.07	0.16	0.04
2-methylbutane	8.94	0.11	0.03	0.07	0.02	0.09	0.03	0.09	0.02
2-pentene	9.51	0.14	0.04	0.09	0.03	0.12	0.04	0.12	0.02
C5 alkane[e]	10.02	0.23	0.07	0.15	0.05	0.19	0.06	0.19	0.04
2-methylpentane	13.46	0.54	0.17	0.39	0.12	0.47	0.15	0.47	0.07
2-butanone	13.85	0.08	0.02	0.06	0.02	0.08	0.02	0.07	0.01
3-methylpentane	14.25	0.10	0.03	0.07	0.02	0.09	0.02	0.09	0.01
1-hexene	14.52	0.16	0.04	0.12	0.03	0.14	0.04	0.14	0.02
bromochloromethane	15.14								
hexane (coeluent)		0.40	0.10	0.28	0.07	0.35	0.09	0.34	0.06
unknown	16.15	0.14	0.04	0.10	0.03	0.13	0.04	0.12	0.02
C6 alkene[e]	16.87	0.06	0.01	< 0.05	< 0.01	0.05	0.01	(g)	(g)
1-butanol	17.85	0.61	0.19	0.45	0.13	0.53	0.16	0.53	0.08
1,4-difluorobenzene	18.82								
C7 alkane[e]	18.96	0.08	0.02	0.06	0.01	0.08	0.02	0.07	0.01
C7 alkane[e]	19.50	0.15	0.03	0.13	0.03	0.15	0.03	0.14	0.01
1-heptene	20.16	0.06	0.01	0.06	0.01	0.07	0.02	0.06	0.01
n-heptane	20.81	0.24	0.05	0.19	0.04	0.22	0.05	0.22	0.03
2-methylheptane	24.49	0.09	0.02	0.06	0.01	0.08	0.01	0.08	0.01
2,4-dimethylhexane	26.29	0.08	0.02	0.07	0.01	0.08	0.02	0.08	0.01
siloxane	27.03	0.14	0.02	< 0.1	< 0.02	< 0.1	< 0.02	(g)	(g)
chlorobenzene-d5	28.37								

Table 3.2 Contd

TIC Analytes[c]	Retention Time	S4020-A05-S010 PNL 010		S4020-A07-S021 PNL 021		S4020-A09-S022[a] PNL 022[b]		Average	Std. Dev.
		(mg/m^3)[d]	(ppmv)	(mg/m^3)	(ppmv)	(mg/m^3)	(ppmv)	(mg/m^3)	(ppmv)
2-butoxyethanol	30.93	0.06	0.01	< 0.05	< 0.01	0.05	0.01	(g)	(g)
siloxane	35.41	0.07	0.01	< 0.05	< 0.01	< 0.05	< 0.01	(g)	(g)
n-dodecane	44.44	0.10	0.01	0.07	0.01	0.09	0.01	0.09	0.01
C13 alkane[e]	45.07	0.08	0.01	0.06	0.01	0.07	0.01	0.07	0.01
C13 alkane[e]	47.33	0.11	0.01	0.07	0.01	0.09	0.01	0.09	0.02
n-tridecane	48.19	0.16	0.02	0.11	0.01	0.16	0.02	0.14	0.03
C14 alkane[e]	51.07	0.14	0.02	0.09	0.01	0.13	0.02	0.12	0.02
n-tetradecane	51.69	0.15	0.02	0.10	0.01	0.14	0.02	0.13	0.03
unknown	53.90	0.07	0.01	0.06	0.01	0.09	0.01	0.08	0.02
unknown	54.97	< 0.05	< 0.01	< 0.05	< 0.01	0.05	0.01	(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-d_5 IS.
(e) Other structural isomers should be considered.
(f) Carbon dioxide was observed as a split peak.

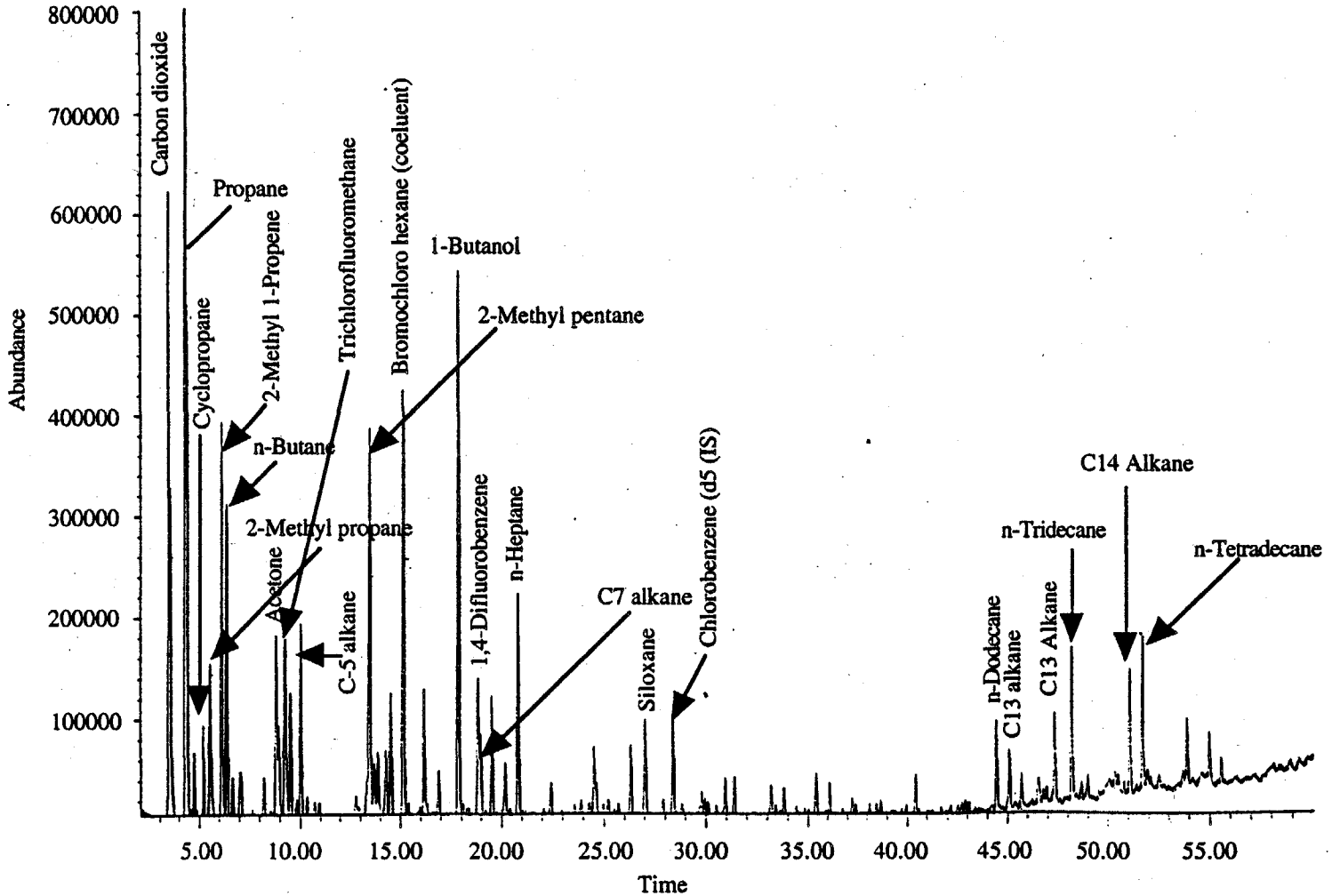

Figure 3.1 GC/MS Chromatogram of Hanford Waste Tank BY-105 SUMMA™ Canister Vapor Sample S4020-A05-S010 Collected Through the WHC Vapor Sampling System on 7/7/94

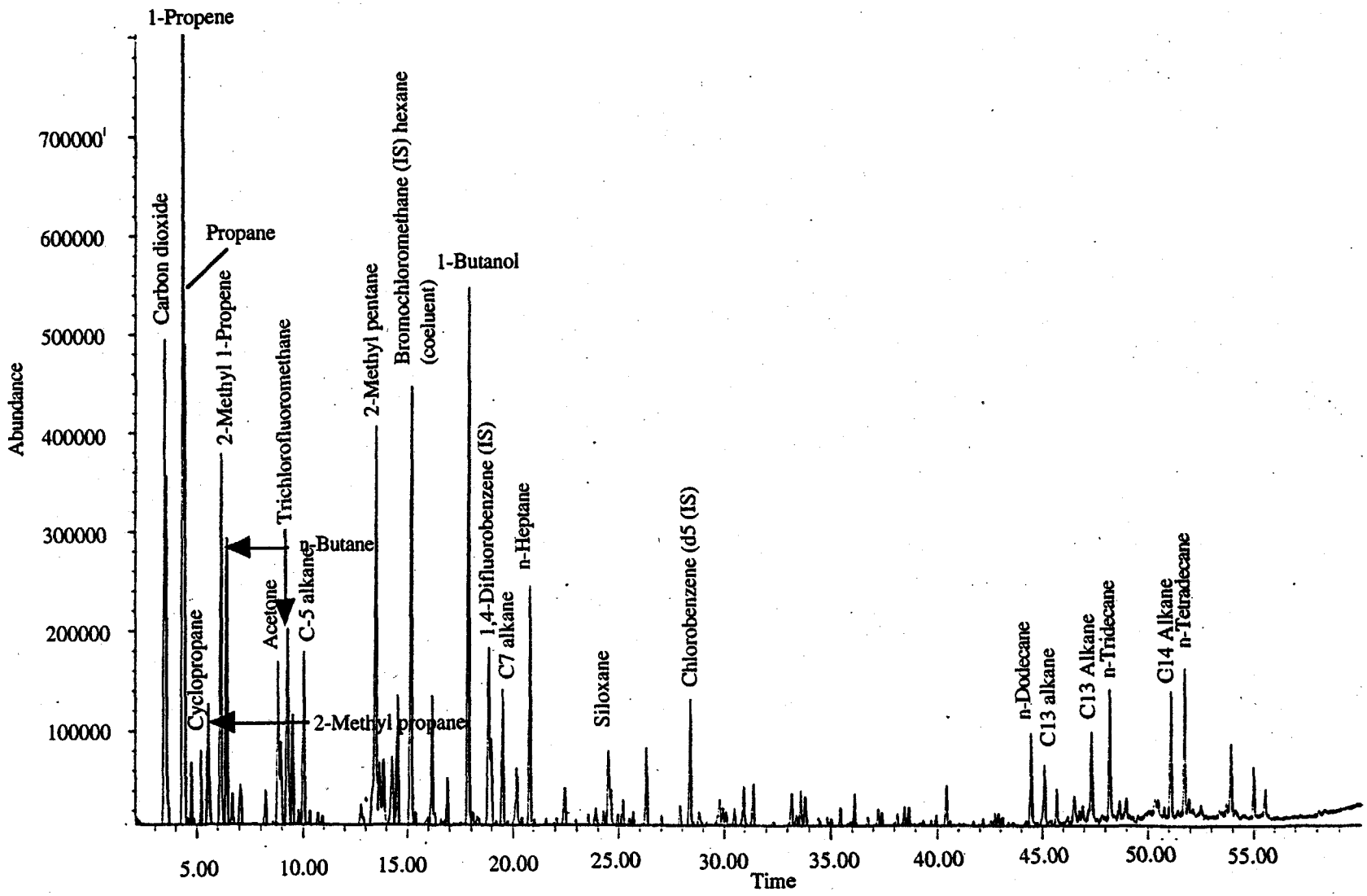

Figure 3.2 GC/MS Chromatogram of Hanford Waste Tank BY-105 SUMMA™ Canister Vapor Sample S4020-A07-S021 Collected Through the WHC Vapor Sampling System on 7/7/94

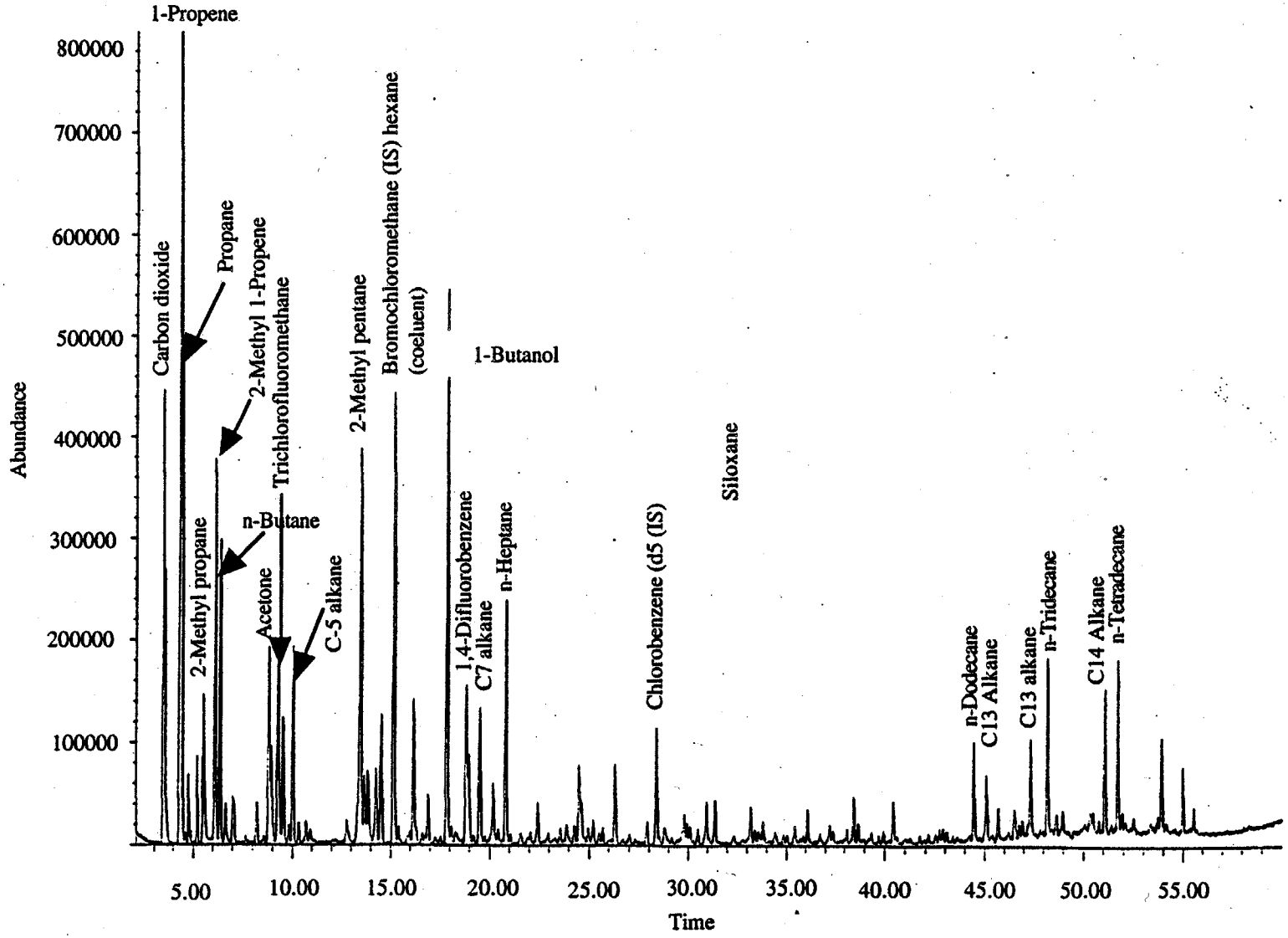

Figure 3.3 GC/MS Chromatogram of Hanford Waste Tank BY-105 SUMMA™ Canister Vapor Sample S4020-A09-S022 Collected Through the WHC Vapor Sampling System on 7/7/94

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