PNL-10466
UC-606

Vapor Space Characterization of Waste Tank 241-C-105: Results from Samples Collected on 2/16/94

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July 1995

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

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DISCLAIMER

Summary

This report describes inorganic and organic analyses results from samples obtained from the headspace of the Hanford waste storage Tank 241-C-105 (referred to as Tank C-105). The results described here were obtained to support safety and toxicological evaluations. A summary of the results for inorganic and organic analytes is listed in Summary Table 1. Detailed descriptions of the results appear in the text.

Quantitative results were obtained for the inorganic compounds ammonia (NH_3) nitrogen dioxide (NO_2), nitric oxide (NO), water (H_20). Organic compounds were also quantitatively determined. Five organic tentatively identified compounds (TICs) were observed above the detection limit of (ca.) 10 ppbv, but standards for most of these were not available at the time of analysis, and the reported concentrations are semiquantitative estimates. In addition, we looked for the 40 standard TO-14 analytes. None were observed above the 2-ppbv detection limit. The five TIC's are listed in Table 1 and account for 100% of the total organic components in Tank C-105.

Table 1. Summary Results of Inorganic and Organic Samples Collected from the Headspace of Tank C-105 on 2/16/94

Category	Analyte	Vapor[a] Concentration	Units
Inorganic	NH_3	2.4 ± 0.3	ppmv
	NO_2	≤ 0.1	ppmv
	H_2O	7.5 ± 0.9	mg/L
Organic	Dodecane	0.29	mg/m^3
	Tridecane	0.27	mg/m^3
	Undecane	0.22	mg/m^3
	1-Butanol	0.18	mg/m^3
	Propene	0.05	mg/m^3

(a) Vapor concentrations were determined using sample-volume data provided by Westinghouse Hanford Company and are based on averaged data. The inorganic samples were obtained and analyzed using procedures that were subsequently improved.

Acknowledgments

The authors gratefully acknowledge the support of other project staff at Pacific Northwest Laboratory who contributed to the successful completion of this sampling and analysis activity. Jeff Edwards served as the PNL single-point-of-contact and coordinated sample handling and communications with Westinghouse Hanford Company. K. B. Olsen assisted in preparing the organic portion of this report. Sally Slate and May-Lin Thomas analyzed inorganic samples, and Gary Dennis prepared the solid-sorbent sample trains. Bonnie L. Lehrman, Trina Buruss and Rose Nipper, provided word processing support.

Abbreviations

CAS	Chemical Abstracts Service
COC	chain of custody
Cv	concentration by volume
DIW	deionized water
emf	electromotive force
EPA	U.S. Environmental Protection Agency
GC/MS	gas chromatography/mass spectrometry
HP	Hewlett Packard
IC	ion chromatography
IL	impact level
IS	internal standard
MDL	minimum detection limit
NIST	National Institute for Standards and Technology
NPH	normal paraffin hydrocarbon
OSHA	Occupational Safety and Health Administration
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 tank-headspace samples taken from the Hanford waste Tank 241-C-105 (referred to as Tank C-105). Pacific Northwest Laboratory (PNL) contracted with Westinghouse Hanford Company (WHC) to provide sampling devices and to analyze inorganic and organic analytes collected from the tank headspace. Jerry Osborne sent a letter of instruction to S. C. Goheen on February 15, 1994, requesting that SUMMA™ canisters and sorbent traps be analyzed by PNL quality assurance (QA) impact level (IL) III. The sample job was designated S4005, and samples were collected by WHC on February 16, 1994, using the vapor sampling system (VSS).

No chain of custody (COC) forms are available for inorganic samples, so for the purpose of this report, all samples analyzed are identified by numbers affixed to each sample by WHC before transfer to PNL. For organic analyses, six SUMMA™ canisters were delivered to WHC on COC 006111 on 2/14/94 (Figure 1.1a). At the request of WHC, an additional six SUMMA™ canisters were supplied on COC 005127 (Figure 1.1b) on 2/16/94. Samples were collected by WHC from the headspace of Tank C-105 through the VSS on 2/16/94, but only three SUMMA™ canisters were returned to PNL using COC 006111 (Figure 1.1c) on 2/18/94.

The samples were inspected upon delivery to the 326/23B laboratory and logged into PNL record book 55408 before analyses. Custody of the sorbent traps was transferred to PNL personnel performing the inorganic analysis and stored at refrigerated (≤ 10°C) temperature until the time of analysis. The canisters were stored in the 326/23B laboratory at ambient (25°C) temperature until the time of the 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. 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).

Westinghouse Hanford Company	CHAIN OF CUSTODY	PNL 006111	FIG. 1.1a

Custody Form Initiator C. M. Jones/ J. E. Darling

Company Contact J. L. Huckaby

Telephone (509) 373-3443

Project Designation/Sampling Locations 200 East Tank Farm: Tank 241-C-105 vapor sample SAF S4005, 241-C-105

Collection Date 02-16-94

Ice Chest No.

Field Logbook No. WHC-N-647-4

Bill of Lading/Airbill No. N/A

Offsite Property No. N/A

Method of Shipment

Shipped to PNL

Possible Sample Hazards/Remarks Unknown at tine of sampling

Sample Identification

S4005- 04 .B16	SAP Ref	9A	PNL summa	PNL# 073
S4005- 05 .B16	SAP Ref	9B	PNL summa	PNL# 063
S4005- 06 .B16	SAP Ref	19	PNL summa	PNL# 054
S4005- 07 .B16	SAP Ref	15A	PNL surrogate	PNL# 055
S4005- 08 .B16	SAP Ref	---	PNL surrogate	PNL# 062
S4005- 09 .B16	SAP Ref	---	PNL surrogate	PNL# 066

☐ Field Transfer of Custody — Chain of Possession — (Sign and Print Names)

Relinquished By	Date	Time	Received By	Date	Time
[illegible] Clauss	2/14/94	16:29			

Final Sample Disposition

Disposal Method:	Disposed by:	Date/Time:

Comments:
WHC purchased canisters are returned from PNL to WHC. PNL # above can be removed. PNL will not receive canister samples for this tank sample job. [illegible] Clauss 2/14/94

Figure 1.1a Chain of Custody for Organic samples

Westinghouse Hanford Company	CHAIN OF CUSTODY	005127

Custody Form Initiator J.E. Darling   FIG. 1.1 b

Company Contact J.L. Huckaby   Telephone 373-3443

Project Designation/Sampling Locations C-135 Tank Vapor Sampling SAF #S4005   Collection Date 2-16-94

Ice Chest No. N-A   Field Logbook No. WHC-N-

Bill of Lading/Airbill No. N-A   Offsite Property No.

Method of Shipment Government Truck

Shipped to N-A

Possible Sample Hazards/Remarks N-A

Sample Identification

PNL Summa Cans (6)
PNL Can 048
" " 050
049
051
052
053

☒ Field Transfer of Custody   **CHAIN OF POSSESSION**   (Sign and Print Name)

Relinquished By	Date	Time	Received By	Date	Time
Therese Clauss	2/16/94	10:40	J.E. Darling	2-16-94	1039

Final Sample Disposition

Disposal Method:	Disposed by:	Date/Time:

Comments:

Figure 1.1b Chain of Custody for Organic samples

Westinghouse Hanford Company	CHAIN OF CUSTODY	PNL 006111	FIG. 1.1C

Custody Form Initiator C. M. Jones/ J. E. Darling

Company Contact J. L. Huckaby

Telephone (509) 373-3443

Project Designation/Sampling Locations 200 East Tank Farm: Tank 241-C-105 vapor sample SAF S4005, 241-C-105

Collection Date 02-16-94

Ice Chest No.

Field Logbook No. WHC-N-647-4

Bill of Lading/Airbill No. N/A

Offsite Property No. N/A

Method of Shipment Government Truck

Shipped to PNL

Possible Sample Hazards/Remarks Unknown at tine of sampling

Sample Identification

S4005- 04 .B~~17~~ 16 JLH 2-18-94 SAP Ref 9A PNL summa PNL# PNL ~~051~~ 048 2/16/94

S4005- 05 .B~~17~~ 16 JLH 2-18-94 SAP Ref 9B PNL summa PNL# PNL ~~052~~ 049 2/16/94

S4005- 06 .B~~17~~ 16 JLH 2-18-94 SAP Ref 19 PNL summa PNL# PNL ~~053~~ 050 2/16/94

~~S4005- 07 .B17 SAP Ref 15A PNL surrogate PNL#~~ JLH 2-16-94

~~S4005- 08 .B17 SAP Ref --- PNL surrogate PNL#~~ JLH 2-16-94

~~S4005- 09 .B17 SAP Ref --- PNL surrogate PNL#~~ JLH 2-16-94

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

Relinquished By	Date	Time	Received By	Date	Time
CM Jones	2-16-94	1825	L GUERRA	2-16-94	1830
L. GUERRA	2-17-94	14:38	J.E. Darling	2-17-94	1438
J.E. Darling	2-18-94	0830	B.	2-18-94	1310

Final Sample Disposition

Disposal Method:	Disposed by:	Date/Time:

Comments:

See COC #005127 for Custody Transfer from PNL Custody to WHC Custody.

Figure 1.1c Chain of Custody for Organic samples

2.0 Inorganic

Solid sorbent traps were supplied to WHC for sampling the headspace of Tank C-105 using the VSS. Samples were returned to PNL for analysis. Analyses were performed to provide information on the tank-headspace concentration of the following analytes: ammonia (NH_3), nitrogen dioxide (NO_2), nitric oxide (NO), and water (H_20). It is important to note that both sampling and analytical procedures were developmental as Tank C-105 was one of the first four trial sample jobs. Differences in sample preparation, sampling, and sample handling, compared with subsequent jobs, varied from those used after April 1994 (Ligotke et al. 1994). Analytical accuracy was estimated based on procedures used. Sample preparation and analyses were performed following PNL QA IL III requirements.

2.1 Standard Sampling Methodology

Standard glass tubes containing sorbent materials to trap vapors of selected analytes of NH_3, NO_x, and H_2O (SKC Inc., Eighty Four, Pennsylvania) were obtained, prepared, and submitted for use by WHC. The sorbent traps were selected based on their use by the Occupational Safety and Health Administration (OSHA) to perform workplace monitoring, and because of available procedures and verification results associated with that particular application. The typical sorbent traps used consisted of a glass tube containing a sorbent material specific to the compound of interest. In general, the tubes contained two sorbent layers, or sections: the first layer was the primary trap, and the second layer provided an indication of breakthrough. In the tubes, sorbent layers are generally held in packed layers separated by glass wool. The sorbent tubes, having glass-sealed ends, were received from the vendor.

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 $\{(NH_4)_2SO_4\}$. The NO_2 traps contained a zeolite impregnated with triethanolamine (TEA), with 200 mg in the primary and 100 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^-). The water trap 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 included samples and single-trap blanks. The samples of each type were prepared from same-lot batches, with the NO_x sorbent traps having been stored previously in a freezer. 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.

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

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

This calculational method produces concentration results that are slightly conservative (greater than actual) because the volume of water vapor in the sample stream is neglected. The volume of water vapor is not included in the measured sampled volume because of its removal in desiccant traps upstream of the mass 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-μg/mL (ppm) NH_3 stock standard solution from dried reagent-grade NH_4Cl and DIW on the day analyses are performed; 2) preparing 0.1-, 0.5-, 1.0-, 10-, and 100-ppm NH_3 working calibration standards by serial dilution of the freshly made stock standard; 3) generating an initial calibration curve from the measured electromotive force (emf) signal versus NH_2 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 TEA and n-butanol solution and analyzed by suppressed-conductivity ion chromatography (SCIC) for nitrite according to PNL-ALO-212, Rev. 1 (*Determination of Inorganic Anions by Ion Chromatography*) modified to obviate interferences by concentrations of non-target analytes. Specifically, the modifications used were 1) eluent 1.44 mM Na_2CO_3 + 1.8 mM $NaHCO_3$ at 2.0 mL/min, 2) one guard column (AG4A) and two separator columns (AS4A) in series instead of just one separator column, and 3) all standards, samples, and blanks injected into the IC sample loop through 0.45-μm syringe filters.

For the analysis, the sorbent materials were placed into labeled 20-mL glass scintillation vials. To each vial, 3.0 mL of desorbing solution (15 g TEA + 1 mL n-butanol in 1.0 L DIW) was added.

Primary sorbent-tube sample materials and back-up (breakthrough) sorbent-trap materials were analyzed separately using identical procedures. Each analytical session was conducted as follows. Working nitrite standards (0, 0.1, 0.25, and 0.5 ppm) were prepared by diluting a stock nitrite standard with desorbing solution. An initial calibration curve was prepared from the instrument response (chromatographic peak height) versus nitrite standard concentration data for the set of working standards. A calibration verification check using one of the midrange standards was performed after the analysis of every six samples. If the instrument response indicated that sample nitrite concentration was outside the calibration range (> 0.5 ppm nitrite), the sample was diluted with desorbing solution and reanalyzed. After all samples of a batch were analyzed, the complete set of calibration standards was remeasured to verify consistent instrument response, and the analytical session was terminated.

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

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

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 ± 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 NH_3, no known NIST SRM is available for nitrite analysis (for NO_2 and NO). Based on experience in comparing nitrite working standards prepared from several different sources and factors mentioned for NH_3 above, the estimated maximum bias 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 most samples, and roughly 5% or less of the mass change of most blanks.

Table 2.1 Analysis Procedures and Detection Limits of Target Inorganic Analytes

Analyte	Formula	Procedure	REL[a] (ppmv)	0.1 x REL[a] (ppmv)	MDL[b] (ppmv)
Ammonia	NH_3	PNL-ALO-226	25	2.5	0.5
Nitrogen Dioxide	NO_2	PNL-ALO-212	1	0.1	0.02
Nitric oxide	NO	PNL-ALO-212	25	2.5	0.02
Mass (water)[c]	n/a	n/a	n/a	n/a	n/a

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

(b) MDL is defined as the vapor concentration that can be detected with an uncertainty equal to about the magnitude of the measurement. The uncertainty is expected to reduce to about one quarter of the magnitude of the measurement at a concentration of four times the MDL. The MDLs were based on the assumption that 3 L of vapor are sampled; if greater volumes of vapor are sampled, correspondingly smaller MDLs can be achieved. The MDLs were also based on desorbing-solution volumes of 10 mL for NH_3 and 3 mL for the other analytes.

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

2.4 Inorganic Sample Results

Samples were obtained by WHC from the headspace of Tank C-105 on 2/16/94 using VSS. The sample job designation number was S4005. Samples were prepared, submitted to WHC, and then analyzed to provide information on the concentrations of NH_3, NO_2, NO and H_2O. Sampling and analysis for SO_x and HCN was not requested. The inorganic samples were received from WHC on 3/4/94; the sample-volume information was received on 3/25/95.

A list of samples, sampling information, and sample volumes is shown in Table 2.2. The types of solid sorbent traps used are also shown in the table. 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 each set of samples were nearly indistinguishable from those of blanks, indicating very low vapor concentrations of the analyte, the concentration results (Table 2.3) are listed as "less than or equal to" a probable maximum value determined be subtracting the blank result from the sample result. Sample results were not corrected for the percentage recoveries of spiked samples.

2.4.1 Ammonia Results. The concentration of NH_3 was 2.4 ± 0.3 ppmv, based on all six samples. The NH_3 quantities found in the exposed sorbent traps were 0.32 to 0.42 μmol in the front sorbent sections and <0.06 μmol in the back sections (indicating no breakthrough). Blank corrections,

Table 2.2 List of PNL Inorganic Samples, Controls, and Gravimetric Results Obtained From a Heated Tube Inserted into the Headspace of Tank C-105 on 2/16/94

Sample Number	Sorbent Type	Sample Port and Volume Information[a]			
		Sample Port	Flow Rate (mL/min)	Duration (min)	Volume (L)
Samples:					
S4005- 23-B16	NH_3 Trap	1	200	15.0	3.00
S4005- 24-B16	NH_3 Trap	10	200	15.0	3.00
S4005- 37-B16	NH_3 Trap	3	200	15.0	3.00
S4005- 38-B16	NH_3 Trap	10	200	15.0	3.00
S4005- 46-B16	NH_3 Trap	1	200	15.0	3.00
S4005- 47-B16	NH_3 Trap	10	200	15.0	3.00
S4005- 19-B16	NO_x Trap	1	200	15.0	3.00
S4005- 20-B16	NO_x Trap	10	200	15.0	3.00
S4005- 35-B16	NO_x Trap	1	200	15.0	3.00
S4005- 36-B16	NO_x Trap	10	200	15.0	3.00
S4005- 44-B16	NO_x Trap	1	200	15.0	3.00
S4005- 45-B16	NO_x Trap	10	200	15.0	3.00
S4005- 21-B16	H_2O Trap	3	200	15.0	3.10
S4005- 25-B16	H_2O Trap	3	200	15.0	3.00
S4005- 26-B16	H_2O Trap	10	200	15.0	3.00
S4005- 39-B16	H_2O Trap	1	200	15.0	3.00
S4005- 40-B16	H_2O Trap	10	200	15.0	3.00
Controls:					
S4005- 50-B16	NH_3 Spare	n/a[b]	n/a	n/a	n/a
S4005- 54-B16	NH_3 Blank	n/a	n/a	n/a	n/a
S4005- 51-B16	NO_2 Blank	n/a	n/a	n/a	n/a
S4005- 52-B16	NO_2 Spare	n/a	n/a	n/a	n/a
S4005- 53-B16	H_2O Blank	n/a	n/a	n/a	n/a

(a) Sampling information and dry-gas sample volumes, corrected to 0°C and 760 torr, were provided by WHC. Uncertainty values were not provided with sample-volume results.

(b) n/a = not applicable.

≤ 0.06 μmol per section, were used to correct the results. Although spiked blanks were not tested, the percentage recoveries of three sets of blanks spiked with 12.2, 22.3, and 46.4 μmol NH_3 were 101 ± 4% and 109 ± 1%, respectively, during related sample jobs (Clauss et al. 1994; Ligotke et al. 1994). Two sample analyses were duplicated after initial analysis and yielded repeatibilities of 111 and 119%; the relatively poor repeatability was attributed to the very low quantities of NH_3 found in the sorbent traps. No sample leachates were spiked after initial analysis to check percentage recovery.

Table 2.3 Inorganic Vapor Sample Results Obtained From a Heated Tube Inserted into the Headspace of Tank C-105 on 2/16/94

Sample	Analytical Results (μmol) Front Section	Back Section	Total[a] Blank-Corrected	Sample Volume (L)	Vapor Concentration (ppmv)
NH_3 Samples:			0.33[c]	3.00[c]	2.4 ± 0.3[c]
S4005- 23-B16	0.42	0.06	0.36	3.00	2.7
S4005- 24-B16	0.32	0.06	0.26	3.00	1.9
S4005- 37-B16	0.42	0.06	0.36	3.00	2.7
S4005- 38-B16	0.41	0.06	0.35	3.00	2.6
S4005- 46-B16	0.41	0.06	0.35	3.00	2.6
S4005- 47-B16	0.35	0.06	0.29	3.00	2.2
NO_2 Samples:			≤0.006	3.00	≤ 0.1
S4005- 23-B16	0.0157	NA[d]	n/a	3.00	n/a
S4005- 20-B16	0.0191	NA	n/a	3.00	n/a
S4005- 35-B16	0.0212	NA	n/a	3.00	n/a
S4005- 36-B16	0.0200	NA	n/a	3.00	n/a
S4005- 44-B16	0.0265	NA	n/a	3.00	n/a
S4005- 45-B16	0.0185	NA	n/a	3.00	n/a
NO Samples:			≤0.008	3.00	≤0.1
S4005- 19-B16	0.0154	NA	n/a	3.00	n/a
S4005- 20-B16	0.0163	NA	n/a	3.00	n/a
S4005- 35-B16	0.0145	NA	n/a	3.00	n/a
S4005- 36-B16	0.0172	NA	n/a	3.00	n/a
S4005- 44-B16	0.0293	NA	n/a	3.00	n/a
S4005- 45-B16	0.0190	NA	n/a	3.00	n/a
Gravimetric Samples (mg.mg/L):			22.7 mg	3.20	7.5 ± 0.9 mg/L
S4005- 21-B16	n/a	n/a	18.8	3.10	6.1
S4005- 25-B16	n/a	n/a	22.9	3.00	7.6
S4005- 26-B16	n/a	n/a	23.7	3.00	7.9
S4005- 39-B16	n/a	n/a	21.9	3.00	7.3
S4005- 40-B16	n/a	n/a	26.1	3.00	8.7

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

(b) Blank-corrected vapor concentrations as per Section 2.1.1. In the calculation for concentration, the nitrite values (listed) were doubled to account for unanalyzed nitrate.

(c) Underlined values represent the average of the set of samples. Concentrations uncertainty equals ± 1 standard deviation (absolute) for each set of samples. The use of "≤" is defined in Section 2.4.

(d) NA = not analyzed; n/a = not applicable; x = not included in determination of average concentration.

2.4.2 Nitrogen Oxides Results. Measurements of NO_2 and NO were made using six NO_x sorbent-trap trains (the NO_x trains consisted of NO_2 trap, oxidizer, and NO_2 trap). The concentrations of NO_2 and NO were each ≤ and NO were each ≤0.1 ppmv. Blank-corrected NO_2^- quantities in the sorbent traps averaged ≤ 0.006 μmol (NO_2 samples) and ≤ 0.008 μmol (NO samples). One nitrite blank was analyzed and used to correct data for each analyte: 0.0145 μmol for NO_2 and 0.0107 μmol for NO. Although spiked blanks were not tested, blanks spiked with 0.0064, 0.047, 0.11, and 0.74 μmol NO_2^- during related sample jobs yielded percentage recoveries of 153 ± 14%, 103 ± 4%, 106 ± 8%, and 111 ± 7%, respectively (Clauss et al. 1994; Ligotke et al.). No samples were reanalyzed to check repeatability. No sample leachates were spiked after initial analysis with quantities of NO_2^- to test analytical percentage recoveries.

2.4.3 Gravimetric Results. The mass concentration of material collected in the sorbent-trap trains, believed to be primarily water vapor, was 7.5 ± 0.9 mg/L. The result was based on an average mass gain of 22.7 mg from all five silica-gel sorbent traps.

3.0 Organic

3.1 SUMMA™ Canister Preparation

SUMMA™ canisters sent out to the field for sampling were new and clean, prehumidified with 100 μL of distilled water, and labeled with a field-sampling identification number.

3.2 Sample Analysis Method

The SUMMA™ canister samples were analyzed according to PNL Technical Procedure PNL-TVP-03, *Determination of TO-14 Volatile Organic Compounds in Hanford Waste Tank Headspace Samples Using SUMMA™ Passivated Canister Sampling and Gas Chromatographic-Mass Spectrometry Analysis*, which is a modified version of U. S. Environmental Protection Agency (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 and 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 SUMMA™ tank samples were 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 six data points ranging from 2 ppbv to 100 ppbv, using a standard gas mixture containing 40 volatile organic compounds listed in EPA compendium Method TO-14. A gas mixture containing bromochloromethane, 1,4-difluorobenzene, and chlorobenzene-d_5 was used as an internal standard (IS) for all blank, calibration standard, and sample analyses. Analyte response from sample components, ISs, and standards were obtained from the extracted ion plot from their selected mass ion. The calibration curve was generated by calculating the relative response ratios of the IS to calibration standard responses and plotting the ratios against the ratio of the calibration-standard concentration (in ppbv) to the IS concentration. A least-squares linear-regression routine was applied to the data set to generate the best-fit line for each compound. The equation for that line was then used to quantify the TO-14 compounds found in the tank samples.

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

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

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:

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

The calculated response factor was then multiplied by the TIC peak area to give an estimated concentration for that compound. For acetonitrile, the total peak area was multiplied by the response factor for chlorobenzene-d_5 to give an estimated concentration of 0.29 mg/m^3. The ISs 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 ppbv concentrations are calculated from mg/m^3 and the molecular weight of the analyte.

$$\mathrm{TIC\ in\ ppmv} = \frac{\mathrm{TIC\ (mg/m^3)\ \ x\ 22.4\ L/mole\ x\ 1000}}{\mathrm{TIC\ g\ mol\ wt}^{(a)}} \tag{3.3}$$

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-d_5. The IS concentrations were converted from ppbv to mg/m^3 at STP using a molecular weight of 129.39 (g/mol) for bromochloromethane, 114.09 for 1,4-difluorobenzene, and 117.6 for chlorobenzene-d_5.

(a) Nominal molecular weight.

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 sample collected from Tank C-105 were below the quantitation limit (2 ppb).

Table 3.2 lists the semiquantitative results for the TICs observed in the samples. Five compounds were observed above the instrument detection limit, a total average concentration 1.01 mg/m^3. The normal paraffin hydrocarbons (NPH), defined as n-alkanes from C_{11} to C_{15}, present were undecane, dodecane, and tridecane, which accounted for 77% of the TIC compounds. In addition, 1-butanol was detected. It should be noted that because the SUMMA™ canisters were not heated at the time of analysis, the NPH concentrations listed after the retention time of decane may not be a true accounting of all the NPH in the sample. Similarly, polar compounds, which may adhere to the inside surface of the canister, may also be under represented in this analysis.

4.0 Conclusions

The concentrations of selected inorganic and organic compounds were determined from samples of the headspace of Tank C-105. It is important to note that the inorganic samples were obtained and analyzed using procedures that were being developed, and that final procedures were not completed until later (Ligotke et al. 1994). Consequently, it is not known whether significant sampling or analytical errors occurred, and it is recommended that the headspace of Tank C-105 be sampled again using the improved methods should less qualified results be needed. The qualified results of inorganic samples were NH_3 (2.4 ± 0.3 ppmv), NO_2 ($\leq$0.1 ppmv), NO ($\leq$0.1 ppmv), and mass concentration (7.5 ± 0.9 mg/L). The mass concentration was expected to consist largely of water vapor. Listed uncertainties reflect repeatability; actual uncertainties were not determined.

No TO-14 compounds and only five TIC compounds were detected above instrumental detection limits, and these were in low concentrations because Tank C-105 is vented. Three NPH n-alkanes were dominant and accounted for 77% of all compounds observed. The organic 1-butonal is known to be a degradation product of tributyl phosphate.

5.0 References

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

Ligotke, M. W., K. H. Pool, and B. D. Lerner. 1994. *Vapor Space Characterization of Waste Tank 241-C-103: Inorganic Results from Sample Job 7B (5/12/94).* 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 for Samples from the Headspace of Tank C-105 from SUMMA™ Canister Samples Collected on 2/16/94

			S4005-04.B16[a] PNL 048[b] Concentration		S4005-05.B16[a] PNL 049[b] Concentration		S4005-06.B16[a] PNL 050[b] Concentration		Means and Standard Deviations	
TO-14 Analyte	CAS No.	Mol Wt	(mg/m^3)	(ppbv)	(mg/m^3)	(ppbv)	(mg/m^3)	(ppbv)	(mg/m^3)	St Dev
Dichlorodifluoromethane (FREON-12)	75-71-8	120	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
Methyl Chloride (Chloromethane)	74-87-3	50	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
1,2-Dichloro-1,1,2,2,-Tetrafluoroethane (FREON-114)	76-14-2	170	< 0.02	< 2	< 0.02	< 2	< 0.02	< 2	(c)	(c)
Chloroethene (Vinyl Chloride)	75-01-4	64	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
Methyl Bromide (Bromomethane)	74-83-9	94	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
Ethyl Chloride	75-00-3	62	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
Trichlorofluoromethane (FREON-11)	75-69-4	136	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
1,1-Dichloroethene (1,1-Dichloroethylene)	75-35-4	96	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
Dichloromethane (Methylene Chloride)	75-09-2	84	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
1,1,2-Trichloro-1,2,2-Trifluoroethane (FREON-113)	76-13-1	186	< 0.02	< 2	< 0.02	< 2	< 0.02	< 2	(c)	(c)
1,1-Dichloroethane	75-34-3	98	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
cis-1,2-Dichloroethene (cis-1,2-Dichloroethylene)	156-59-2	96	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
Trichloromethane (Chloroform)	67-66-3	118	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
cis 1,2-Dichloroethane	107-06-2	98	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
1,1,1-Trichloroethane	71-55-6	132	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
Benzene	71-43-2	78	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
Carbon Tetrachloride	56-23-5	152	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
1,2-Dichloropropane	78-87-5	112	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
Trichloroethylene	79-01-6	130	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
cis 1,3-Dichloropropene	61-01-5	110	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
trans 1,3-Dichloropropene	61-02-6	110	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
1,1,2-Trichloroethane	79-00-5	132	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
Methyl Benzene (Toluene)	108-88-3	92	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
1,2-Dibromoethane	106-93-4	186	< 0.02	< 2	< 0.02	< 2	< 0.02	< 2	(c)	(c)
Tetrachloroethene (Perchloroethylene)	127-18-4	164	< 0.02	< 2	< 0.02	< 2	< 0.02	< 2	(c)	(c)
Chlorobenzene	108-90-7	112	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
Ethylbenzene	100-41-4	106	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
m-Xylene (1,3-Dimethylbenzene)[d]	108-38-3	106	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
p-Xylene (1,4-Dimethylbenzene)[d]	106-42-3	106								
Styrene	100-42-5	104	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)

Table 3.1 (Contd)

			S4005-04.B16[a] PNL 048[b] Concentration		S4005-05.B16[a] PNL 049[b] Concentration		S4005-06.B16[a] PNL 050[b] Concentration		Means and Standard Deviations	
TO-14 Analyte	CAS No.	Mol Wt	(mg/m^3)	(ppbv)	(mg/m^3)	(ppbv)	(mg/m^3)	(ppbv)	(mg/m^3)	St Dev
1,1,2,2-Tetrachloroethane	79-34-5	166	< 0.02	< 2	< 0.02	< 2	< 0.02	< 2	(c)	(c)
o-Xylene (1,2-Dimethylbenzene)	95-47-6	106	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
1,3,5-Trimethylbenzene	108-67-8	120	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
1,2,4-Trimethylbenzene	95-63-6	120	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
Chloromethylbenzene, alpha (Benzyl Chloride)	100-44-7	126	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
m-Dichlorobenzene (1,3-Dichlorobenzene)	541-73-1	146	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
p-Dichlorobenzene (1,4-Dichlorobenzene)	106-46-7	146	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
o-Dichlorobenzene (1,2-Dichlorobenzene)	95-50-1	146	< 0.01	< 2	< 0.01	< 2	< 0.01	< 2	(c)	(c)
1,2,4-Trichlorobenzene	120-82-1	180	< 0.02	< 2	< 0.02	< 2	< 0.02	< 2	(c)	(c)
Hexachloro-1,3-Butadiene	87-68-3	258	< 0.02	< 2	< 0.02	< 2	< 0.02	< 2	(c)	(c)

(a) WHC sample identification number.
(b) PNL canister number.
(c) Average and standard deviation data are not meaningful for this analyte.
(d) m-Xylene and p-Xylene coelute; the reported concentration is the sum of these two compounds.

Table 3.2 Tentavtively Identified Compounds and Estimated Concentrations(a) in Headspace of Tank C-105 from SUMMA™ Canister Samples Collected on 2/16/94

Tentatively				S4005-04.B16(b) PNL 048(c)		S4005-05.B16(b) PNL 049(c)		S4006-06.B16(b) PNL 050(c)		Means and Standard Deviations			
Identified Compound(d)	CAS No.(d)	Mol. Wt.	Ret Time	(mg/m^3)	(ppbv)	(mg/m^3)	(ppbv)	(mg/m^3)	(ppbv)	(mg/m^3)	St Dev	(ppbv)	St Dev
Propene	115-07-1	42	3.87	0.05	28.43	0.05	29.3	0.05	28.46	0.05	0.00	28.45	0.49
1-Butanol	71-36-3	74	17.52	0.13	38.61	0.21	63.09	0.21	64.61	0.18	0.05	51.61	14.59
Undecane	1120-21-4	156	40.17	0.22	32.00	0.22	31.16	0.21	30.43	0.22	0.01	31.22	0.79
Dodecane	112-40-3	170	44.20	0.29	37.87	0.29	38.77	0.29	38.21	0.29	0.00	38.04	0.45
Tridecane	629-50-5	184	47.98	0.24	28.99	0.27	32.93	0.31	37.14	0.27	0.04	33.07	4.08

(a) Semi-quantitative estimate calculated using concentration of closest eluting internal standard.
(b) WHC sample identification number.
(c) PNL SUMMA™ canister number.
(d) Obtained by mass spectral interpretation amd comparison with the EPA/NIST/WILEY Library.

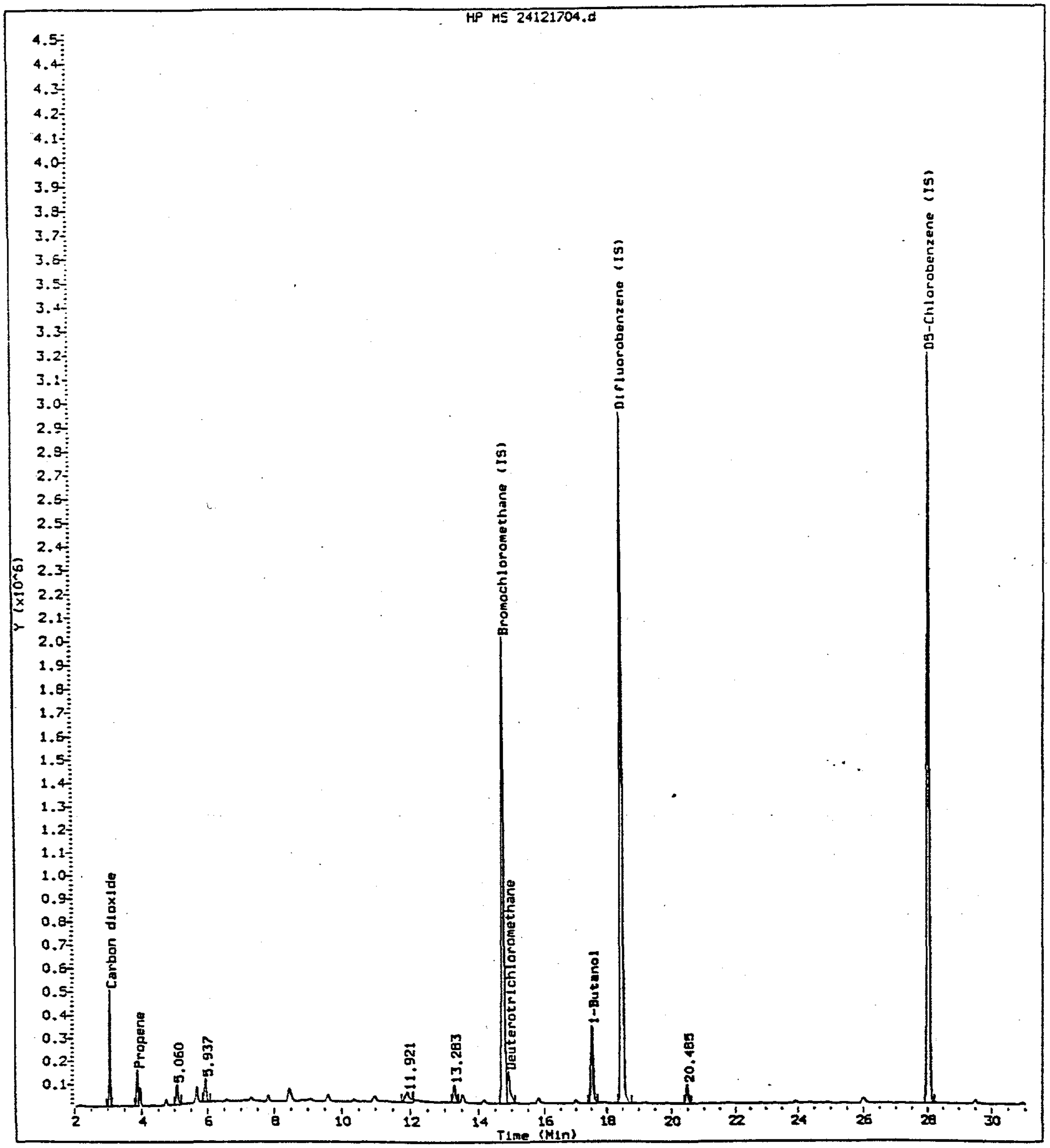

Figure 3.1a Total Ion Chromatogram (0 - 30 minutes) of Hanford Tank C-105 SUMMA™ Canister S4005 04.B16 Collected on 2/16/94

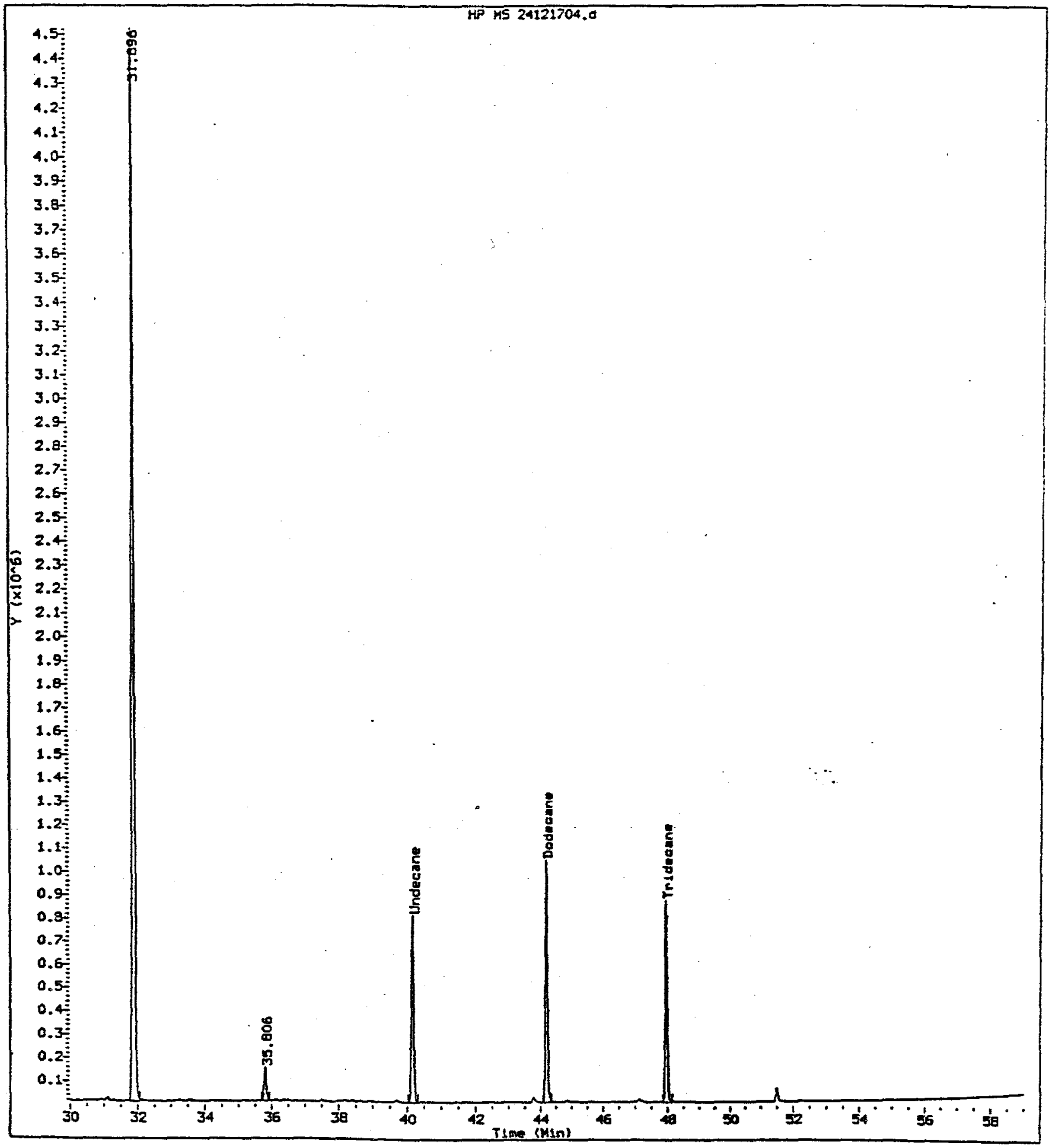

Figure 3.1b Total Ion Chromatogram (30 - 58 minutes) of Hanford Tank C-105 SUMMA™ Canister S4005 04.B16 Collected on 2/16/94

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