

TANK VAPOR CHARACTERIZATION PROJECT

Headspace Vapor Characterization of Hanford Waste Tank 241-S-101: Results from Samples Collected on 6/6/96

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Summary

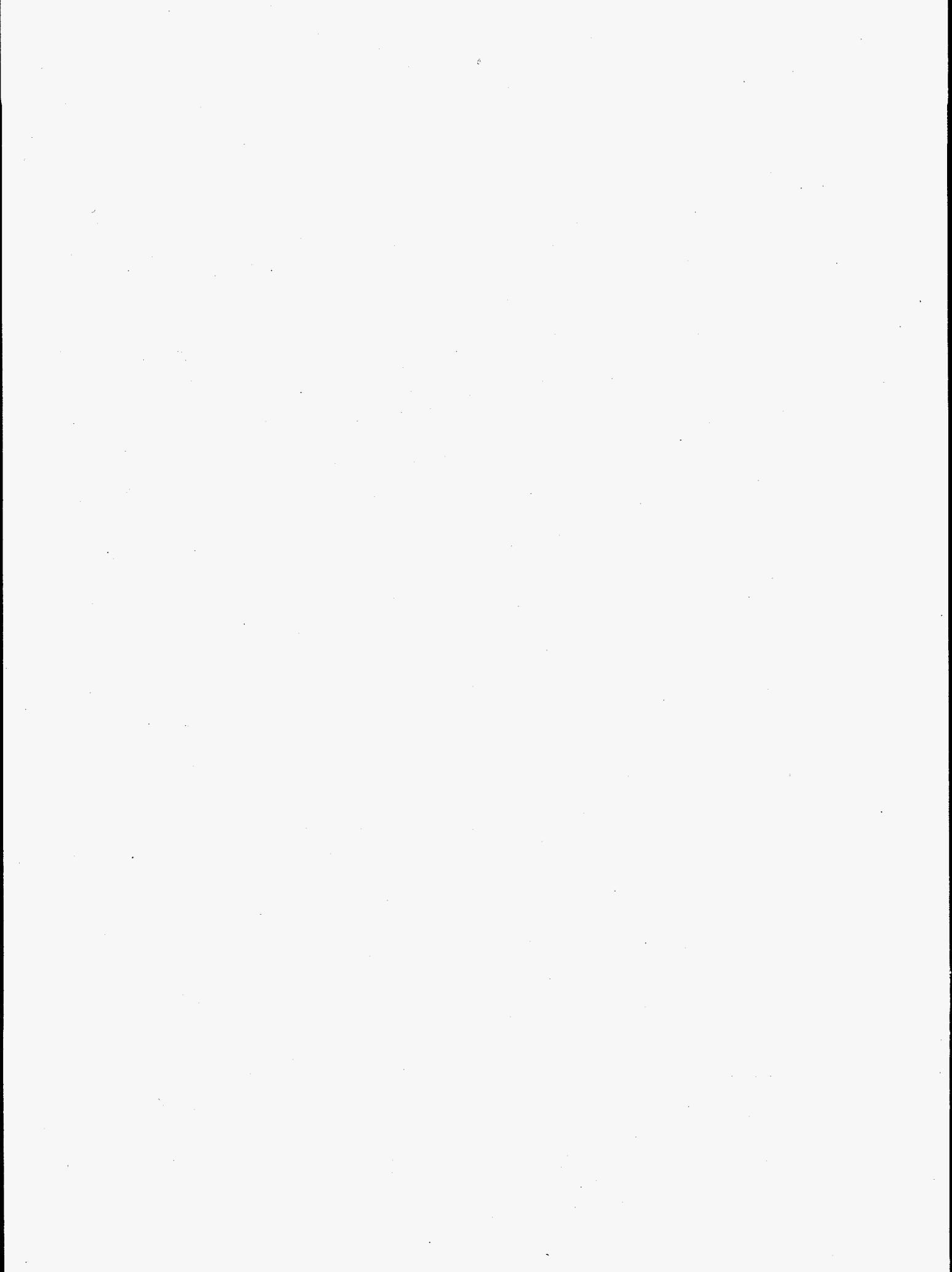
This report describes the analytical results of vapor samples taken from the headspace of the waste storage tank 241-S-101 (Tank S-101) at the Hanford Site in Washington State. The results described in this report were obtained to characterize the vapors present in the tank headspace and to support safety evaluations and tank farm operations. The results include air concentrations of selected inorganic and organic analytes and grouped compounds from samples obtained by Westinghouse Hanford Company (WHC) and provided for analysis to Pacific Northwest National Laboratory (PNNL). Analyses were performed by the Vapor Analytical Laboratory (VAL) at PNNL. Analyte concentrations were based on analytical results and, where appropriate, sample volumes provided by WHC. A summary of the inorganic analytes, permanent gases, and total non-methane organic compounds is listed in Table S.1. The three highest concentration analytes detected in SUMMA™ canister and triple sorbent trap samples are also listed in Table S.1. Detailed descriptions of the analytical results appear in the appendices.

Table S.1. Summary Results of Samples to Characterize the Headspace of Tank S-101 on 6/6/96

<u>Category</u>	<u>Sample Medium</u>	<u>Analyte</u>	<u>Vapor^(a) Concentration</u>	<u>Units</u>
Inorganic Analytes ^(b)	Sorbent Traps	NH ₃	773 ± 6	ppmv
		NO ₂	< 0.16	ppmv
		NO	< 0.16	ppmv
		H ₂ O	18.9 ± 1.4	mg/L
Permanent Gases	SUMMA™ Canister	H ₂	442	ppmv
		CH ₄	< 25	ppmv
		CO ₂	< 17	ppmv
		CO	< 17	ppmv
		N ₂ O	271	ppmv
Total Non-Methane Organic Compounds (TO-12)	SUMMA™ Canister	Non-Methane Organic Compounds	8.30	mg/m ³
Organics (TO-14)	SUMMA™ Canister	Methanol	5.450	ppmv
		1-Butanol	0.614	ppmv
		Ethanol	0.591	ppmv
Organics (PNL-TVP-10)	Sorbent Traps	Methanol	2.922	ppmv
		1-Butanol	0.509	ppmv
		Acetone	0.345	ppmv

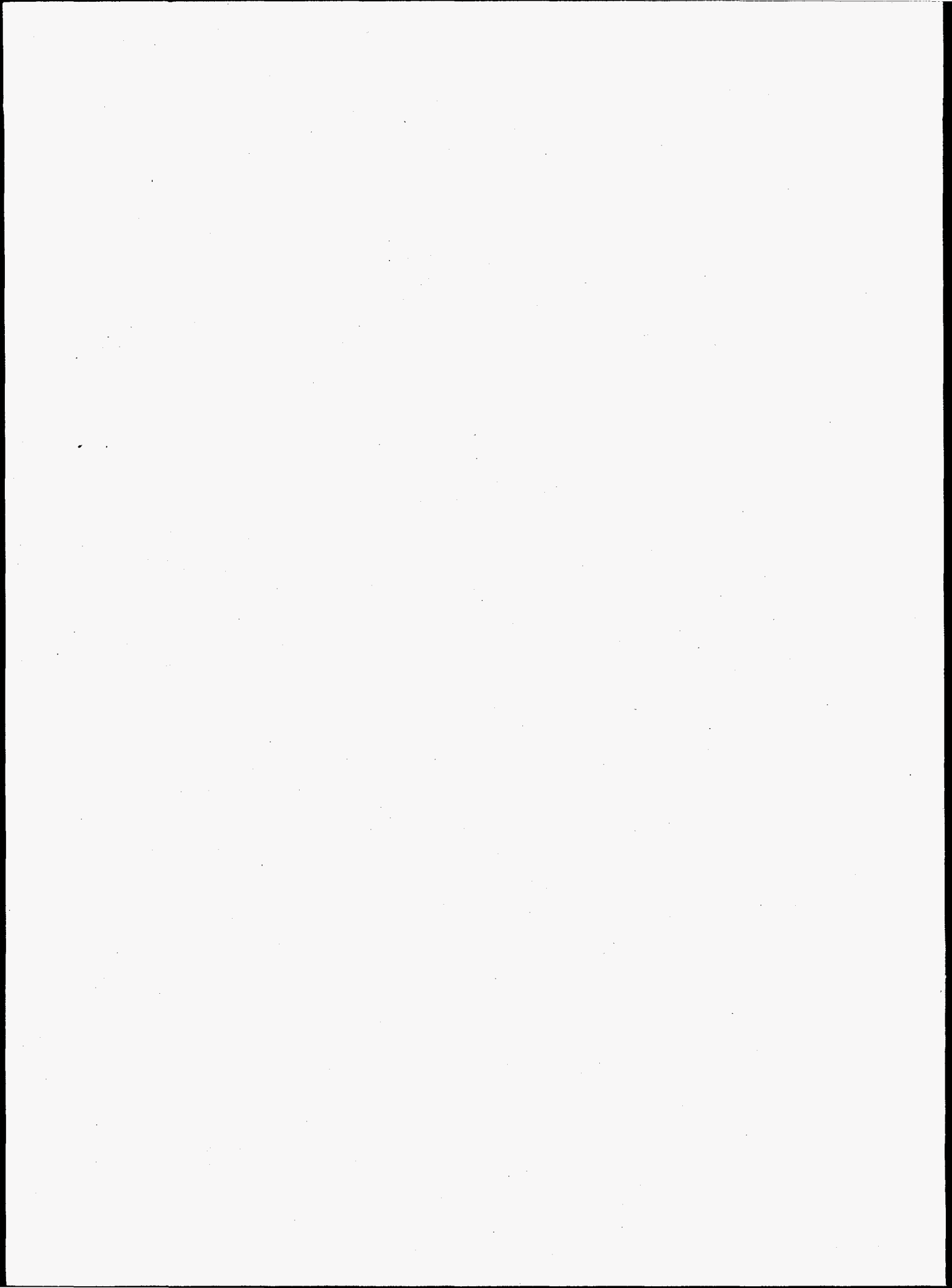
(a) Vapor concentrations were determined using sample-volume data provided by Westinghouse Hanford Company and are based on averaged data.

(b) Inorganic analyte concentrations are based on dry tank air at standard temperature and pressure (STP).



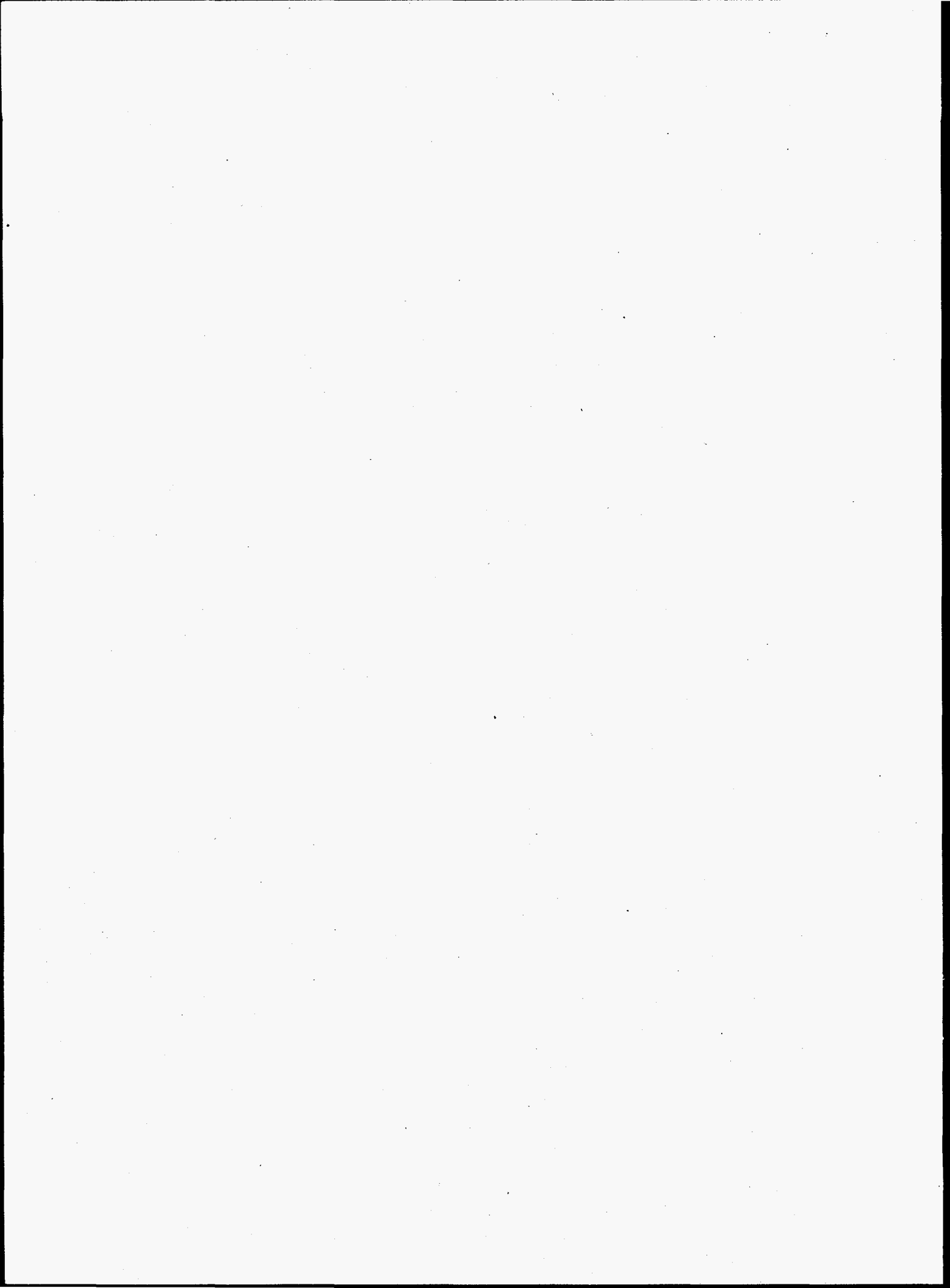
Acknowledgments

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Glossary

% D	% Difference
CAS	Chemical Abstracts Service
CCV	continuing calibration verification
COC	chain-of-custody
C _v	concentration by volume
DIW	deionized water
EPA	U.S. Environmental Protection Agency
GC/FID	gas chromatography/flame ionization detector
GC/MS	gas chromatograph/mass spectrometer
GC/TCD	gas chromatography/thermal conductivity detection
IC	ion chromatography
IL	impact level
IS	internal standard
ISVS	in situ vapor sampling system
MDL	method detection limit
NIST	National Institute for Standards and Technology
PNL	previous designation for Pacific Northwest Laboratory
PNNL	Pacific Northwest National Laboratory
ppbv	part per billion by volume
ppm	parts per million
ppmv	part per million by volume
QA	quality assurance
RPD	relative percent difference
RSD	relative standard deviation
SAP	sample and analysis plan
SCIC	suppressed-conductivity ion chromatography
SRM	standard reference material
STP	standard temperature and pressure
SUMMA™	stainless steel, passivated interior canister
TEA	triethanolamine
TIC	tentatively identified compound
TNMOC	total non-methane organic compounds
TST	triple sorbent trap
UHP	ultra high purity
VAL	Vapor Analytical Laboratory
WHC	Westinghouse Hanford Company



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1.0 Introduction

This report describes the results of vapor samples taken from the headspace of waste storage tank 241-S-101 (Tank S-101) at the Hanford Site in Washington State. Pacific Northwest National Laboratory (PNNL)^(a) contracted with Westinghouse Hanford Company (WHC) to provide sampling devices and analyze samples for inorganic and organic analytes collected from the tank headspace and ambient air near the tank. The analytical work was performed by the PNNL Vapor Analytical Laboratory (VAL) by the Tank Vapor Characterization Project. Work performed was based on a sample and analysis plan (SAP) prepared by WHC. The SAP provided job-specific instructions for samples, analyses, and reporting. The SAP for this sample job was "Vapor Sampling and Analysis Plan" (Homi 1995), and the sample job was designated S6058. Samples were collected by WHC on June 6, 1996 using the In Situ Vapor Sampling System (ISVS).

Sampling devices and controls provided for this job included six sorbent trains for selected inorganic analytes (four sample trains and two field blanks) and eight triple sorbent traps (TSTs) for semi-volatile organic analytes (four samples, two field blanks, and two trip blanks). Five SUMMA[™] canisters for permanent gases and volatile organic analytes (two samples and three ambient canisters) were also received. Three tank samples are usually collected; however, during the sampling of Tank S-101 only two tank samples were collected (see Appendix F page F.2). The samples and controls were provided to WHC on June 3, 1996. Exposed samples and controls were returned to PNNL on June 12, 1996. Samples and controls were handled, stored, and transported using chain-of-custody (COC) forms to ensure sample quality was maintained.

Samples and controls were handled and stored as per PNNL technical procedure. PNL-TVP-07^(b), and, upon return to PNNL, were logged into PNNL Laboratory Record Book 55408. Samples were stored at the VAL under conditions (e.g., ambient, refrigerated) required by technical procedures. Access to the samples was controlled and limited to PNNL staff trained in the application of specific technical procedures to handle samples for the tank vapor characterization project. Analyses were performed in the 300 Area at Hanford; specific analytical methods are described in the text. In summary, sorbent traps for inorganic analytes were either weighed (for water analysis) or weighed and desorbed with the appropriate aqueous solutions for analyzing inorganic analytes by either selective electrode or ion chromatography (IC).

Tank headspace samples were analyzed for

- *permanent gases* using gas chromatography/thermal conductivity detection (GC/TCD)
- *total non-methane organic compounds* using cryogenic preconcentration followed by gas chromatography/flame ionization detection (GC/FID)

^(a) Pacific Northwest National Laboratory is operated for the U. S. Department of Energy by Battelle under Contract DE-AC06-76RLO 1830. The previous name of the laboratory was Pacific Northwest Laboratory (PNL), which is used when previously published documents are cited.

^(b) PNL-TVP-07, Rev. 2, December 1995, *Sample Shipping and Receiving Procedure for PNL Waste Tank Samples*, PNL Technical Procedure, Tank Vapor Project, Pacific Northwest Laboratory, Richland, Washington.

- *volatile organic analytes* analyses using cryogenic preconcentration followed by gas chromatograph/mass spectrometer (GC/MS)
- *semi-volatile organic analytes* (TST samples) using thermal desorption followed by GC/MS.

This report provides summary and detailed analytical information related to the samples and controls. Section 2.0 provides a summary of analytical results. Section 3.0 provides conclusions. Descriptions of samples, analytical methods, quality assurance (QA) and quality control issues, and detailed sample results are provided for each category of samples and analyses in Appendices A, B, C, D, and E. Appendix F contains the completed COC forms.

2.0 Analytical Results

Samples obtained by WHC from the headspace of Tank S-101 on June 6, 1996 (Sample Job S6058) were analyzed in the PNNL Vapor Analytical Laboratory. Summarized results are described in this section; details of samples, analyses, and data tables are provided in the appendices.

2.1 Inorganic Analytes

The vapor concentrations of selected inorganic analytes (NH_3 , NO_2 , and NO) and vapor mass concentration (primarily H_2O) were determined. The average and one standard deviation of concentration results from inorganic sorbent sample trains used to sample headspace vapors were 773 ± 6 ppmv (NH_3), < 0.16 ppmv (NO_2), < 0.16 ppmv (NO), and 18.9 ± 1.4 mg/L (primarily H_2O). The vapor concentration results were based on four samples for each compound. All samples (100%) were successfully analyzed and used in the averages. Representative field blanks were also analyzed and used to correct data.

Results provided above are estimated to be accurate to within $\pm 10\%$ (assuming negligible error in the sample volume measurements) and are within the $\pm 30\%$ specified by the SAP. Measurement precision, as indicated by the relative standard deviation, was $< 8\%$ for the compounds found to be present at concentrations greater than the analytical method estimated quantitation limit (EQL), and within the 25% specified by the SAP. These uncertainties were confirmed by evaluation of spikes and continuing calibration standards (NH_3 and NO_2) and evaluation of the variability of field blanks (H_2O). All samples were analyzed within 14 days after being collected. No deviations from standard procedures were noted. Data and additional information on samples, analyses, and results are described in Appendix A. The COC form used to control samples, 100089, is included in Appendix F.

2.2 Permanent Gases

The complete results of the permanent gas analysis of Tank S-101 can be found in Appendix B. In summary, hydrogen at 442 ppmv and nitrous oxide at 271 ppmv were the only permanent gases detected in the tank headspace samples. Three tank samples are normally collected; however, during the sampling of Tank S-101 only two tank samples were collected.

2.3 Total Non-Methane Organic Compounds

The complete results of the TO-12 analysis of Tank S-101 can be found in Appendix C. In summary, the average concentration in two of tank headspace samples was 8.29 mg/m^3 . Three tank samples are normally collected; however, during the sampling of Tank S-101 only two tank samples were collected. The average value of 8.30 mg/m^3 compares to 14.6 mg/m^3 for the sum of all target compounds and tentatively identified compounds (TICs) identified in the analysis of the SUMMA™ canisters.

2.4 Organic Analytes by SUMMA™ Method

The complete results of the SUMMA™ analysis of Tank S-101 can be found in Appendix D. Three tank samples are normally collected; however, during the sampling of Tank S-101 only two tank samples were collected. In summary, 39 target analytes above the IDL and six TICs were detected in the tank headspace samples. Twenty-eight target analytes and three TICs were identified in the two tank headspace samples. Methanol at 7.80 mg/m³ and 1-butanol at 2.03 mg/m³ accounted for 69% of the target compounds and 67% of the total compounds identified in the analysis. The total concentration of the target analytes was 14.2 mg/m³. Butanal at 0.21 mg/m³ and 2-methyl-2-propanol at 0.14 mg/m³ were the two highest TICs found in two tank headspace samples. The total concentration of TICs identified was 0.45 mg/m³. The total concentration of all the compounds identified was 14.6 mg/m³. This compares to a total concentration of 8.30 mg/m³ identified in the TO-12 analysis of the two tank headspace samples.

SUMMA™ canister PNL 311 was analyzed in replicate for target analytes and TICs to determine analytical precision. Six of 27 target compounds and none of the three TICs had relative percent differences (RPDs) of less than 10%.

Forty-four target compounds were observed in one or both of the ambient air samples. All of the compounds were identified at trace levels. Trace levels of many of the target analytes may be false positives due to the fact that some of the compounds were found in the continuing calibration blank (CCB) above the EQL and are greater than 20 times the concentration found in the sample. These compounds are flagged with a "B" in the tables.

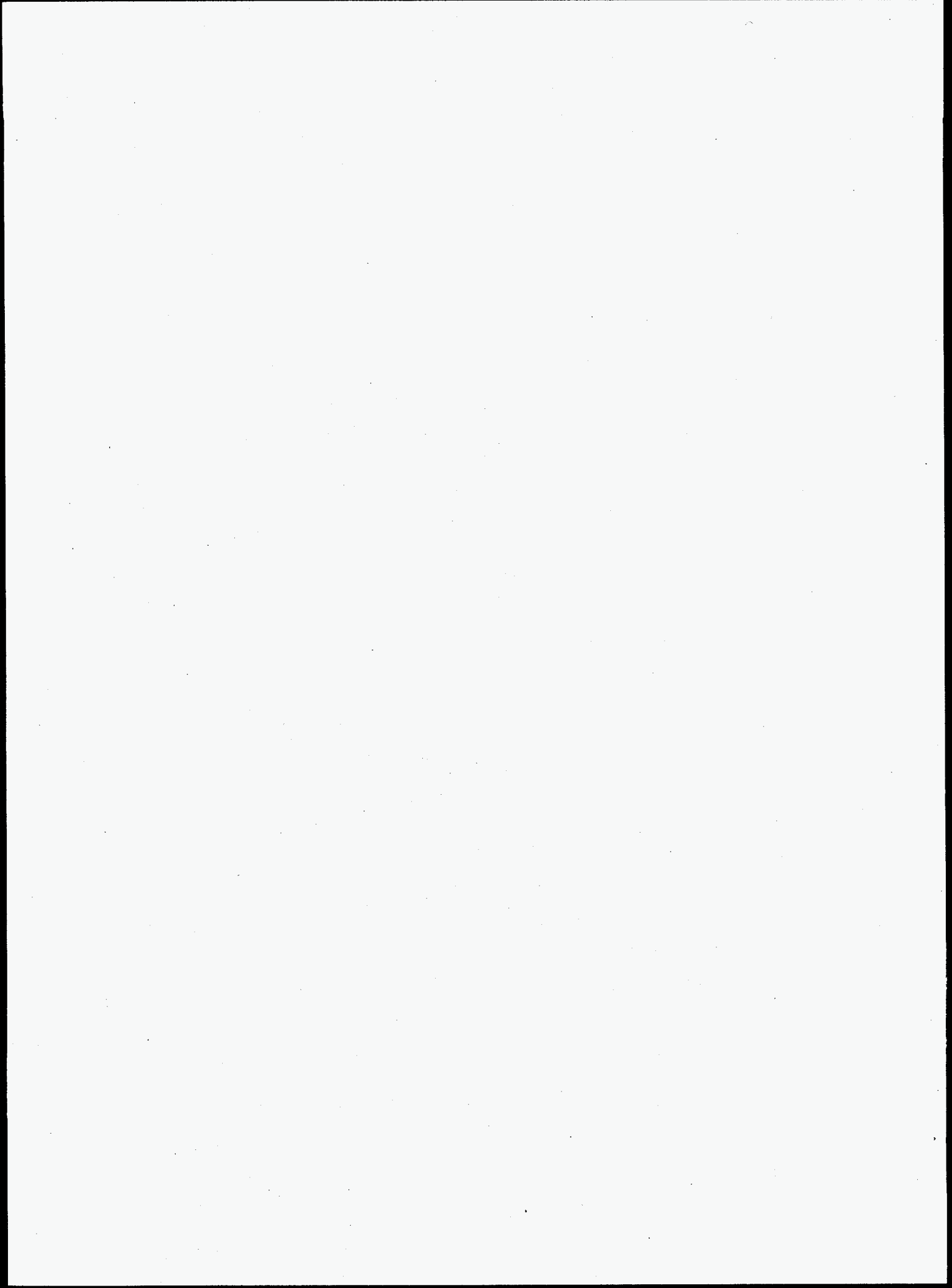
2.5 Organic Analytes by Triple Sorbent Trap Method

The complete results of the sorbent trap analysis of Tank S-101 can be found in Appendix E. In summary, 36 target analytes above the IDL and 13 TICs were detected in the tank headspace samples. Thirty-one of the target analytes and all 13 TICs were observed in two or more sorbent traps. Two of the TICs were not identified and were labeled as unknowns. Methanol at 4.18 mg/m³ and 1-butanol at 1.68 mg/m³ accounted for 62% of the target analytes and 44% of the total concentration identified by the analysis. The total concentration of the target analytes was 9.50 mg/m³ or 71% of the total concentration identified by the analyses. The predominant TICs observed in these samples were 1-fluoro-1,1-dichloroethane at 0.94 mg/m³ and 1-chloro-1,1-difluoroethane at 0.72 mg/m³. The total concentration of the TICs was 3.80 mg/m³ or 29% of the total concentration identified by analysis. The total concentration of all the compounds identified was 13.30 mg/m³.

Triple sorbent trap sample PNL 1024 was analyzed in replicate for target analytes and TICs to determine analytical precision. Twenty-four of 32 target compounds and 12 of 13 TICs had RPDs of less than 10%.

3.0 Conclusions

The concentrations of inorganic and organic analytes were determined from samples of the headspace of Tank S-101 on June 6, 1996 (Sample Job S6058). The vapor concentrations were based either on whole-volume samples (SUMMA™ canisters) or on sorbent traps exposed to sample flow. In the case of the canisters, the concentrations were based on analytical results and the tracking of dilution/concentration of sample volumes obtained directly from the canisters. In the case of the sorbent traps, concentrations were based on analytical results and sample volumes reported by WHC. Known sampling and analytical variances from established quality assurance requirements, where significant, were documented in this report, as required by the SAP (Homi 1995). WHC was immediately notified based on preliminary, uncorrected analytical results, when the ammonia concentration was determined to be above the notification level of 150 ppmv. Notification levels and notification procedures are described in the SAP (Homi 1995).



4.0 Reference and Further Reading

Reference

Homi, C.S. 1995. *Vapor Sampling and Analysis Plan*. WHC-SD-WM-TP-335, Rev. 2, Westinghouse Hanford Company, Richland, Washington.

Further Reading

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

Pacific Northwest Laboratory. *Quality Assurance Manual, Part 3: Procedures for Quality Assurance Program*. PNL-MA-70, Part 3, Pacific Northwest Laboratory, Richland, Washington.

Pacific Northwest National Laboratory. *Quality Assurance Plan for Activities Conducted by the Pacific Northwest National Laboratory Vapor Analytical Laboratory (VAL) and the Pacific Northwest National Laboratory Tank Vapor Characterization Project*. ETD-002, Rev. 0, Pacific Northwest National Laboratory, Richland, Washington.

U.S. Department of Energy. *Hanford Analytical Services Quality Assurance Plan (HASQAP)*. DOE/RL-94-55, Rev. 2, U. S. Department of Energy, Richland, Washington.

Westinghouse Hanford Company. *Quality Assurance Project Plan for Tank Vapor Characterization*. WHC-SD-WM-QAPP-013, Rev. 1, Westinghouse Hanford Company, Richland, Washington.

Appendix A

Tank Vapor Characterization:

Inorganic Analytes

Appendix A

Tank Vapor Characterization: Inorganic Analytes

Solid sorbent traps, prepared in multi-trap sampling trains, were supplied to Westinghouse Hanford Company (WHC) for sampling the tank headspace using the In Situ Vapor Sampling System (ISVS). Blanks, spiked blanks (when requested), and exposed samples were returned to Pacific Northwest National Laboratory (PNNL) 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_2O). Procedures were similar to those developed previously during sample jobs performed with the VSS connected to the headspace of Tank C-103 (Ligotke et al. 1994). During those sample jobs, control samples provided validation that the sorbent tubes effectively trapped NH_3 and mass. Samples were prepared, handled, and disassembled as described in Technical Procedure PNL-TVP-09^(a). Analytical accuracy was estimated based on procedures used. Sample preparation and analyses were performed following PNNL quality assurance (QA) impact level II requirements.

A.1 Sampling Methodology

Standard glass tubes containing sorbent materials to trap vapors of selected analytes of NH_3 , NO , NO_2 , and H_2O (supplied by SKC Inc., Eighty Four, Pennsylvania) were obtained, prepared, and submitted for vapor sampling. The sorbent traps were selected based on their use by the Occupational Safety and Health Administration 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, with 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 [$(\text{NH}_4)_2\text{SO}_4$]. The NO_2 traps contained a zeolite impregnated with triethanolamine (TEA), with 400 mg in the primary and 200 mg in the breakthrough sections. The NO_2 was absorbed and disproportionated to equi-molar quantities of nitrite ions (NO_2^-) and nitrate ions (NO_3^-). Glass tubes containing 800 mg of an oxidant such as chromate were used to convert NO to NO_2 . The converted NO was then collected as nitrite and nitrate in an NO_2 trap. The water traps contained 300 mg of silica gel in the primary and 150 mg in the breakthrough sections.

^(a) Pacific Northwest Laboratory. 12/95. *Sorbent Trap Preparation for Sampling and Analysis: Waste Tank Inorganic Vapor Samples*, PNL-TVP-09 (Rev. 2), PNL Technical Procedure, Pacific Northwest Laboratory, Richland, Washington.

Sorbent trains provided to trap inorganic compounds included all or some of the following: samples, spiked samples, spares, blanks, and spiked blanks. Sorbent trains were prepared from same-lot batches, with the oxidizer sections of the NO_x sorbent trains having been stored previously in a freezer. After sample preparation, sorbent trains were stored at ≤ 10°C 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.

The sorbent traps were prepared in multi-trap sorbent trains configured so sample flow passed in order through the traps, targeting specific analytes, and then through a desiccant trap. The specific order of traps within the various sorbent trains is described in Section A.4. The ends of the glass-tube traps were broken, and the traps were weighed and then connected to each other using uniform lengths of 3/8-in. perfluoroalkoxy-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 consist of a short section of tubing that has a 3/8-in. stainless steel Swagelok® nut, sealed using a Swagelok® cap. The trailing ends of the sorbent trains (the downstream end of the traps containing silica gel) 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. During vapor sampling, C-Flex® tubing was provided by WHC to connect the downstream ends of the sorbent trains to the sampling manifold exhaust connections.

A.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 moles. 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 by volume (C_v) of a 3.00-L sample containing 75.0 μg of NH₃ equals

$$C_v = \frac{75.0 \mu\text{g}}{17.0 \text{ g/mol}} \left[\frac{3.00 \text{ L}}{22.4 \text{ L/mol}} \right]^{-1} = 32.9 \text{ ppmv} \quad (\text{A.1})$$

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

A.2 Analytical Procedures

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

A.2.1 Ammonia Analysis. The sorbent material from the NH_3 -selective sorbent traps was placed into labeled 20-mL glass scintillation vials. Vials containing front-, or primary-, section sorbent material were treated with 10.0 mL of deionized water (DIW), and vials containing back-up-section sorbent material were treated with 5.0 mL of DIW. After extraction, the NH_3 sorbent traps were analyzed using the selective ion electrode procedure PNL-ALO-226 Rev. 0^(a). Briefly, this method includes 1) preparing a 1000- $\mu\text{g}/\text{mL}$ (ppm) NH_3 stock standard solution from dried reagent-grade NH_4Cl and DIW, 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 signal versus NH_3 concentration data obtained for the set of working standards, 4) performing a calibration-verification check, using a mid-range dilution of a certified National Institute for Standards and Technology (NIST)-traceable 0.1 M NH_4Cl standard from an independent source, after analyzing every five or six 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). Electromotive force (volts) signal measurements obtained for samples are compared to those for standards, either graphically or algebraically (using linear regression) to determine NH_3 concentration in the samples.

A.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^(b) 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 were 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 of 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

(a) Procedure entitled "Ammonia (Nitrogen) in Aqueous Samples," PNL-ALO-226, in the *Analytical Chemistry Laboratory (ACL) Procedure Compendium*, Vol. 3: Inorganic Instrumental Methods. Pacific Northwest Laboratory, Richland, Washington.

(b) Procedure entitled "Determination of Inorganic Anions by Ion Chromatography," PNL-ALO-212, in the *Analytical Chemistry Laboratory (ACL) Procedure Compendium*, Vol. 3: Inorganic Instrumental Methods. Pacific Northwest Laboratory, Richland, Washington.

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.

A.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 in accordance with procedure PNL-TVP-09. 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. Field blanks were used to correct results.

A.3 Quality Assurance/Quality Control

Analytical work was performed according to quality levels identified in the project QA plan and several PNNL documents including PNL-MA-70 (Part 3), PNL-ALO-212, PNL-ALO-226, and Quality Assurance Plan ETD-002. The samples were analyzed following PNNL Impact Level II. A summary of the analysis procedures and limits for the target inorganic compounds is provided in Table A.1. The table also shows generic expected notification ranges and describes related target analytical precision and accuracy levels for each analyte; the information in the table is based on the data quality objective assessment by Osborne et al. (1995). From the table, it can be seen that the EQL required to resolve the analyte at one-tenth of the recommended exposure limit for each of the target analytes is achieved using current procedures and with a vapor-sample volume of 3 L and a desorption-solution volume of 3 mL (10 mL for NH_3).

The accuracy of concentration measurements depends on potential errors associated with both sampling and analysis (see Section A.4). Sampling information, including sample volumes, was provided by WHC; sample-volume uncertainty was not provided. The uncertainty of analytical results, which depends on the method used, was estimated to be within allowable tolerances (Osborne et al. 1995; Table A.1). For NH_3 analyses, the accuracy of laboratory measurements by selective ion electrode was estimated to be $\pm 5\%$ relative, independent of concentration at $1 \mu\text{g/mL}$ or greater levels. The uncertainty includes preparation of standards, purity of the ammonium salt used to prepare standards, potential operator bias, ambient temperature variations, etc. Working standards are traceable to NIST standard reference material (SRM) by using an independent calibration verification standard certified to be NIST traceable. Nitrite analyses (for NO_2 and NO) are performed using certified but not NIST-traceable SRM; this is because NIST does not make a nitrite SRM. 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 $\pm 10\%$, and for samples derived from sampling for NO it is $\pm 5\%$ relative.

Table A.1. Analytical Procedures, Quantification Limits, and Notification Levels for Selected Inorganic Analytes^(a)

Analyte	Formula	Procedure	EQL ^(b) (μg)	EQL ^(b) (ppmv)	Notification Level ^(c) (ppmv)
Ammonia	NH ₃	PNL-ALO-226	1.0	0.71	≥ 150
Nitrogen Dioxide	NO ₂	PNL-ALO-212	0.3	0.15	≥ 10
Nitric oxide	NO	PNL-ALO-212	0.3	0.15	≥ 50
Mass (water) ^(d)	n/a	PNL-TVP-09	0.6 mg	0.3 mg/L	n/a

(a) Analytical precision and accuracy targets for results in the expected ranges equal $\pm 25\%$ and 70 to 130%, respectively (Osborne et al. 1995).

(b) The lowest calibration standard is defined as the EQL.

(c) As per Table 7-1 in Osborne et al. (1995). Notification levels require verbal and written reports to WHC on completion of preliminary analyses.

(d) The vapor-mass concentration, thought to be largely water vapor, is determined gravimetrically.

n/a = not applicable.

The accuracy of measurements of sample mass is typically ± 0.1 mg, or much less than 1% of the mass changes of most samples. The analytical accuracy of measurements of the change in mass of sorbent trains, based on the variability in mass change of field-blank sorbent trains, is determined for each sample job and is typically about ± 1 mg per five-trap sorbent train.

A.4 Inorganic Sample Results

Samples were obtained by WHC from the tank headspace of Tank S-101 on June 6, 1996 using the ISVS. The sample job designation number was S6058. Samples were prepared, submitted to WHC for the sample job, and then returned to PNNL and analyzed to provide information on the concentrations of NH₃, NO₂, NO, and mass (primarily H₂O). Samples were controlled using COC form 100089 (Appendix F). The inorganic samples and sample volume information were received from WHC on June 12, 1996. Analyses were completed on June 17, 1996 (gravimetric, 11 days elapsed), June 20, 1996 (ammonia, 14 days elapsed), and June 19, 1996 (nitrite, 13 days elapsed).

A list of samples, sampling information, sample volumes, and gravimetric results is shown in Table A.2. The types of sample trains used and the order of sorbent traps within each train are also shown in the table. For example, the sorbent train NH₃/NO_x/H₂O contained an NH₃ trap at the inlet end, a NO_x series in the middle (Section A.4.2), and a desiccant trap at the outlet end. Analytical mass and concentration results are shown in Table A.3. Sample volumes were provided by WHC; sample-volume uncertainty was not provided. Tank headspace concentration results (Table A.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. Percentage relative standard deviation (RSD) may be determined by dividing the standard deviation by the average result and multiplying by 100. Where analytical results from samples, corrected for blanks, were less than the EQL in Table A.1, the concentration results (Table A.3) are listed as "less-than" the EQL value. Results of control samples,

such as trip blanks, field blanks, and spiked blanks, are discussed in this section. Spiked blanks, when used, were transported to the field but not opened. Spiked samples, when used, were opened in the field and used to collect tank vapors. Sample results were not corrected for the percentage recoveries of spiked blanks.

A.4.1 Ammonia Results. The concentration of NH_3 was 773 ± 6 ppmv, based on all four samples. The blank-corrected NH_3 quantities in the sorbent traps ranged from 63.4 to 64.5 μmol in front sections; blank-corrected NH_3 was not found ($\leq 0.01 \mu\text{mol}$) in back sorbent sections. Blank corrections, 1.2 μmol in front and 0.06 μmol in back sections, were about 2% of collected quantities. The analysis of one sample was duplicated and yielded a repeatability of $\pm 0.3\%$. One blank sorbent trap was spiked with 17 μmol of NH_3 and yielded a percentage recovery of 103%. One sample leachate was spiked after initial analysis with roughly the quantity of ammonia in the sample and yielded a percentage recovery of 97%. The initial and continuing calibration verification standards, using NIST-traceable material, yielded percentage recoveries of 103% (ICV) and 106 and 100% (CCV) during the analytical session. A 5-point calibration was performed over an NH_3 range of 0.1 to 1000 $\mu\text{g/mL}$.

A.4.2 Nitrogen Oxides Results. The concentrations of NO_2 and NO were both < 0.16 ppmv based on all four samples. Blank-corrected NO_2^- quantities in the sorbent traps were all averaged $< 0.013 \mu\text{mol}$. Nitrite blank levels used to correct data were 0.0095 μmol in front (four of four blanks analyzed) and 0.0061 μmol in back (two of four blanks analyzed) sorbent sections. The analyses of two samples were duplicated and yielded repeatabilities of $\pm 0\%$ and $\pm 2.2\%$. Two sample leachates were spiked with 0.25 ppm NO_2^- and yielded percentage recoveries of 101 and 94%. A 4-point calibration was performed over a concentration range of 0 to 0.5 $\mu\text{g NO}_2^-$ per mL in the desorbing matrix. Although spiked blanks were not tested, blanks spiked with 0.0064, 0.047, 0.11, and 0.74 $\mu\text{mol NO}_2^-$ during previous sample jobs yielded percentage recoveries of 153 ± 14 , 103 ± 4 , 106 ± 8 , and $111 \pm 7\%$, respectively (Clauss et al. 1994; Ligothke et al. 1994).

A.4.3 Gravimetric Results. Gravimetric results yield water vapor concentrations. This is because the total mass concentration of other vapors in the headspaces of Hanford waste tanks, measured in $\mu\text{g/L}$, are typically two or three orders of magnitude less than the mg/L mass concentrations of the water vapor found in even relatively dry tanks. The water vapor mass concentration collected in the 5-trap sorbent trains was $18.9 \pm 1.4 \text{ mg/L}$, based on dry air sample volumes (0°C and 760 torr). The result was determined from an average mass gain of 39.8 mg from all four sample trains. The blank correction applied to the results was -4.7 mg per train, based on a mass gain of $4.7 \pm 0.5 \text{ mg}$ per two 5-trap field-blank sorbent trains. A sampling anomaly (see COC 100089) with one of the field blanks was noted and judged to have negligible impact on blank results and was therefore used in calculations. A control mass was measured and indicated a measurement accuracy of $\pm 0.1 \text{ mg}$. Although no spiked blanks were tested, the percentage recovery of mass from three blank H_2O traps spiked with 51 mg water was $103 \pm 2\%$ during a previous sample job (Clauss et al. 1994).

Corrected for a measured tank headspace temperature of 30.4°C and pressure of 753.6 torr, the actual water vapor mass concentration from the gravimetric results was $16.5 \pm 1.2 \text{ mg/L}$. Also based on analytical results, the partial pressure of water vapor was $17.3 \pm 1.3 \text{ torr}$, the relative humidity was $53 \pm 4\%$, and the dew point was $19.8 \pm 1.4^\circ\text{C}$.

Table A.2 List of PNNL Inorganic Samples, Controls, and Gravimetric Results
Obtained from the Headspace of Tank S-101 on 6/6/96

Sample Number	Sorbent Train Type	Sample Port and Volume Information ^(a)				Mass Gain (g)
		Sample Port	Flow Rate (mL/min)	Duration (min)	Volume (L)	
<u>Samples:</u>						
S6058-A07-S85	NH3/NOx/H2O	1	200.0	10.0	1.86	0.0436
S6058-A08-S86	NH3/NOx/H2O	2	200.0	10.0	1.86	0.0394
S6058-A09-S87	NH3/NOx/H2O	3	200.0	10.0	1.86	0.0379
S6058-A10-S88	NH3/H2O/H2O	4	200.0	10.0	1.86	0.0383
<u>Controls:</u>						
S6058-A15-S89	NH3/NOx/H2O Field Blank	n/a ^(b)	n/a	n/a	n/a	0.0042
S6058-A16-S90	NH3/NOx/H2O Field Blank	n/a	n/a	n/a	n/a	0.0053

(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.

Table A.3 Inorganic Vapor Sample Results Obtained from the Headspace of Tank S-101 on 6/6/96

Sample	Analytical Results (μmol)			Sample Volume (L)	Vapor ^(a) Concentration (ppmv)
	Front Section	Back Section	Total ^(b) Blank-Corrected		
<u>NH₃ Samples:</u>			<u>64.2</u>	<u>1.86</u>	<u>773 ± 6</u>
S6058-A07-S85	64.6	0.053	63.4	1.86	764
S6058-A08-S86	65.7	NA ^(c)	64.5	1.86	777
S6058-A09-S87	65.7	0.053	64.5	1.86	777
S6058-A10-S88	65.4	NA	64.2	1.86	773
<u>NO₂ Samples:</u>			<u><0.013</u>	<u>1.86</u>	<u><0.16</u>
S6058-A07-S85	0.0095	NA	<0.013	1.86	<0.16
S6058-A08-S86	0.0100	0.0063	<0.013	1.86	<0.16
S6058-A09-S87	0.0099	NA	<0.013	1.86	<0.16
S6058-A10-S88	0.0102	0.0059	<0.013	1.86	<0.16
<u>NO Samples:</u>			<u><0.013</u>	<u>1.86</u>	<u><0.16</u>
S6058-A07-S85	0.0101	0.0064	<0.013	1.86	<0.16
S6058-A08-S86	0.0113	NA	<0.013	1.86	<0.16
S6058-A09-S87	0.0110	0.0061	<0.013	1.86	<0.16
S6058-A10-S88	0.0113	NA	<0.013	1.86	<0.16
<u>Gravimetric Samples:</u>			<u>35.1 mg</u>	<u>1.86</u>	<u>18.9 ± 1.4 mg/L</u>
S6058-A07-S85	n/a ^(c)	n/a	38.9	1.86	20.9
S6058-A08-S86	n/a	n/a	34.7	1.86	18.7
S6058-A09-S87	n/a	n/a	33.2	1.86	17.8
S6058-A10-S88	n/a	n/a	33.6	1.86	18.1

- (a) Blank-corrected vapor concentrations were calculated using WHC-reported dry-air sample volumes (Table A.2). In the calculation for concentration, the nitrite values (listed) were doubled to account for unanalyzed nitrite. Sample results were not corrected for percentage recovery of spiked samples or spiked blanks. Underlined values represent the average of the set of samples. Concentration uncertainty equals ± 1 standard deviation (absolute) for each set of samples. Percentage RSD may be determined by dividing standard deviation by the average and multiplying the result by 100. The use of "<" is defined in Section A.4.
- (b) Total blank-corrected analyte masses (nitrite for NO₂ and NO) were determined, when significant, by subtracting the quantity of analyte found in blanks from that found in samples. The level of analytes found in blanks is described in the subsections of Section A.4.
- (c) NA = not analyzed; n/a = not applicable.

A.5 References

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

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

Osborne, J. W., J. L. Huckaby, E. R. Hewitt, C. M. Anderson, D. D. Mahlum, B. A. Pulsipher, and J. Y. Young. 1995. *Data Quality Objectives for Generic In-Tank Health and Safety Vapor Resolution*. WHC-SD-WM-DQO-002, Rev. 1, Westinghouse Hanford Company, Richland, Washington.

Appendix B

Tank Vapor Characterization:

Permanent Gases

Appendix B

Tank Vapor Characterization: Permanent Gases

B.1 Sampling Methodology

Before sending SUMMA™ canisters out to the field for sampling, the canisters are cleaned and verified contaminant-free according to Pacific Northwest National Laboratory (PNNL) Technical Procedure PNL-TVP-02^(a). The cleaning procedure uses an EnTech 3000 cleaning system that controls 1) filling the canisters with purified humid air and 2) evacuating, for several cycles with applied heat, before allowing the canister to evacuate overnight. The canister is filled a final time with purified humid air for analysis. If the canister is verified as clean by TO-12, the canister is evacuated to 5 mtorr, tagged, and stored for use in the field. Before sending the canisters out to the field for sampling, the canister vacuum is measured to determine if any leakage has occurred. If the vacuum has remained constant during storage, the canisters are prehumidified with 100 µL of distilled water and labeled with a field-sampling identification. Canisters stored more than 30 but less than 60 days are re-evacuated and rehumidified before use. If stored more than 60 days, the canisters are recleaned and validated before use.

B.2 Analytical Procedure

The SUMMA™ canister samples were analyzed for permanent gases according to PNNL Technical Procedure PNL-TVP-05^(b) with the exceptions listed in the following text and in the quality assurance/quality control section of this report. This method was developed in-house to analyze permanent gases, defined as hydrogen (H₂), carbon dioxide (CO₂), carbon monoxide (CO), methane (CH₄), and nitrous oxide (N₂O), by gas chromatograph/thermal conductivity detection (GC/TCD). Aliquots of sampled air are drawn directly from each canister into a 5-mL gas-tight syringe and injected into a Hewlett-Packard 5890 GC/TCD fitted with a loop injector valve and a column switching valve. An aliquot of 5 mL is used so that the 1.0-mL injection loop is completely purged with sample air, ensuring that no dilution of the sample takes place within the injection loop. One set of GC conditions is used to analyze for CO, CO₂, N₂O, and CH₄ using Helium (He) as the carrier gas. A second GC analysis is performed for H₂ (using nitrogen as the carrier gas) to enhance the signal sensitivity and lower the detection limit for this analyte. The permanent gases and associated EQLs are listed in Table B.1.

(a) Pacific Northwest Laboratory. 8/94. *Cleaning SUMMA™ Canisters and the Validation of the Cleaning Process*, PNL-TVP-02 (Rev. 0), PNL Technical Procedure, Pacific Northwest Laboratory, Richland, Washington.

(b) Pacific Northwest Laboratory. 5/96. *Analysis Method for the Determination of Permanent Gases in Hanford Waste Tank Vapor Samples Collected in SUMMA™ Passivated Stainless Steel Canisters*, PNL-TVP-05 (Rev. 2). PNL Technical Procedure, Pacific Northwest Laboratory, Richland, Washington.

Table B.1. Analytical Procedures and Detection Limits for Permanent Gases

<u>Analyte</u>	<u>Formula</u>	<u>Procedure</u>	<u>Estimated Quantitation Limit (ppmv)</u>
Carbon Dioxide	CO ₂	PNL-TVP-05	17
Carbon Monoxide	CO	PNL-TVP-05	17
Methane	CH ₄	PNL-TVP-05	25
Hydrogen	H ₂	PNL-TVP-05	17
Nitrous Oxide	N ₂ O	PNL-TVP-05	17

B.3 Quality Assurance/Quality Control

Standards for the permanent gas analysis were blended from commercially prepared and certified standards for each of the analytes reported in Table B.1. The instrument was calibrated for CH₄ over a range of 25 to 2100 parts per million by volume (ppmv) and for CO, CO₂, and N₂O over a range of 17 to 2100 ppmv using standards at five different concentrations and He as a carrier gas. A similar procedure was followed for H₂ with a range of 17 to 2120 ppmv, except the carrier gas was changed to N₂. An average response factor from the calculation was used for quantification of compound peak area.

Each analyte was quantitated by comparison of sample analyte peak area to the calibration plot generated for the compound. The estimated quantitation limit (EQL) for the method has been established as the low level calibration standard. Before and after each sample analysis set, a gas standard was run to evaluate system performance and to measure system accuracy. The calculated concentration of the individual gases in the standards fell within $\pm 25\%$ of the expected concentrations. One sample was run in duplicate to provide a measure of method precision. Results of the replicate analysis are presented in Table B.2. An N₂ reagent blank, an ambient-air sample collected ~ 10 m upwind of Tank S-101 and the ambient air collected through the In Situ Vapor Sampling System (ISVS) were used as method blanks and used to determine the potential for analyte interferences in the samples.

B.4 Permanent Gases Sample Results

Table B.2 lists results of the permanent gas analysis from samples collected from the headspace of Tank S-101, ambient air collected ~ 10 m upwind of the tank, and ambient air collected through the ISVS. Samples were analyzed on June 14 and 17, 1996. Hydrogen at an average concentration of 442 ppmv and nitrous oxide at an average concentration of 271 ppmv were the only permanent gases observed above the EQL in the tank headspace samples. A replicate analysis was performed on SUMMA™ PNL 381; however, only the results from the first analysis are included in the average concentration reported for the tank headspace samples. Three tank samples are normally collected; however, during the sampling of Tank S-101 only two tank samples were collected.

Table B.2

Permanent Gas Analysis Results for Samples Collected from the Headspace of Tank S-101
and for Ambient Air and Ambient Air Through the ISVS Collected near Tank S-101 in SUMMA (TM)
Canisters on 6/6/96

Permanent Gas Analyte	Ambient Air Upwind	Ambient Air Upwind	Ambient Air Through Bundle	Tank Samples			Average Concentration Tank Samples (ppmv)
	S6058-A01.308 ^(a) PNL 308 ^(b) Concentration (ppmv)	S6058-A02.309 ^(a) PNL 309 ^(b) Concentration (ppmv)	S6058-A04.310 ^(a) PNL 310 ^(b) Concentration (ppmv)	S6058-A05.311 ^(a) PNL 311 ^(b) Concentration (ppmv)	S6058-A06.312 ^(a) PNL312 ^(b) Concentration (ppmv)	S6058-A05.311 ^(a) PNL 311 ^{(b)(c)} Concentration (ppmv)	
Hydrogen	<17	<17	<17	439	444	432	442
Methane	<25	<25	<25	<25	<25	<25	<25
Carbon Dioxide	385	422	381	<17	<17	<17	<17
Carbon Monoxide	<17	<17	<17	<17	<17	<17	<17
Nitrous Oxide	<17	<17	<17	267	274	278	271

Footnotes

- (a) WHC sample identification number.
- (b) PNL canister number.
- (c) Replicate analysis for PNL 311; results are not included in the calculation of average concentrations.

B.3

Appendix C

Tank Vapor Characterization:

Total Non-Methane Organic Compounds

Appendix C

Tank Vapor Characterization: Total Non-Methane Organic Compounds

C.1 Sampling Methodology

Before sending SUMMA™ canisters out to the field for sampling, the canisters are cleaned and verified contaminant-free according to Pacific Northwest National Laboratory (PNNL) Technical Procedure PNL-TVP-02^(a). The cleaning procedure uses an EnTech 3000 cleaning system that controls 1) filling the canisters with purified humid air and 2) evacuating, for several cycles with applied heat, before allowing the canister to evacuate overnight. The canister is filled a final time with purified humid air for analysis. If the canister is verified as clean by TO-12, the canister is evacuated to 5 mtorr, tagged, and stored for use in the field. Before sending the canisters out to the field for sampling, the canister vacuum is measured to determine if any leakage has occurred. If the vacuum has remained constant during storage, the canisters are prehumidified with 100 µL of distilled water and labeled with a field-sampling identification. Canisters stored more than 30 but less than 60 days are re-evacuated and rehumidified before use. If stored more than 60 days, the canisters are recleaned and validated before use.

C.2 Analytical Procedure

The SUMMA™ canister samples were analyzed according to PNNL Technical Procedure PNL-TVP-08^(b), which is similar to U.S. Environmental Protection Agency (EPA) compendium Method TO-12. The method detection limits in the sub mg/m³ are required to determine total non-methane organic compounds (TNMOC) concentration in the tank samples.

The method uses an EnTech 7000 cryoconcentration system interfaced with a Hewlett-Packard 5890 gas chromatograph/flame ionization detector (GC/FID). The EnTech concentrator is used to pull a metered volume of 50 to 100 mL of sample air from the SUMMA™ canister mounted on an EnTech 7016CA 16-canister autosampler. The sample is cryogenically concentrated, and constituents are trapped in a stainless steel tube containing glass beads and Tenax. The glass bead/Tenax trap is heated to 180°C and purged with ultra high purity (UHP) helium (He). The purged TNMOCs are carried by a UHP He stream to the GC equipped with an FID where gross organic content is detected and measured.

The GC oven is programmed to run at a 150°C isothermal temperature. Chromatographic separation is not needed in this method since quantitation is from the entire FID response over the run time.

(a) Pacific Northwest Laboratory. 8/94. *Cleaning SUMMA™ Canisters and the Validation of the Cleaning Process*, PNL-TVP-02 (Rev. 0), PNL Technical Procedure, Pacific Northwest Laboratory, Richland, Washington.

(b) Pacific Northwest Laboratory. 12/95. *Determination of TO-12 Total Nonmethane Organic Compounds in Hanford Waste Tank Headspace Samples Using SUMMA™ Passivated Canister Sampling and Flame Ionization Detection*, PNL-TVP-08 (Rev. 1), PNL Technical Procedure, Pacific Northwest Laboratory, Richland, Washington.

Twenty-four hours before the analysis, the SUMMA™ canister samples are pressurized with purified air (supplied by Aadco Instruments, Inc., 1920 Sherwood St., Clearwater, Florida 34625). The starting pressure was first measured using a calibrated diaphragm gauge (Cole Parmer), then pressurized to a level exactly twice the original pressure. For example, if the canister had a starting pressure of 740 torr, it was pressurized to 1480 torr. The sample dilution was taken into account when calculating the analysis results.

C.3 Quality Assurance/Quality Control

This method requires user calibration (category 2 measuring and test equipment) of the analytical system in accordance with QA plan ETD-002.

The TNMOC is calibrated by using propane as the calibration standard. The instrument calibration mixture for the PNL-TVP-08 analysis consists of National Institute for Standards and Technology (NIST) 99.999% propane analyzed using an average response factor method for calibration.

A continuing calibration verification (CCV) standard of 100 ppmv propane is analyzed to confirm acceptability of instrument performance. The initial calibration is then used to quantify the samples.

Immediately before running the analysis sequence, a leak-check procedure, which includes evacuating the transfer lines and monitoring the pressure, must be performed on the sample manifold tower. The control limits on this test require that the change in pressure is < 1.5 psi, and the absolute pressure after evacuation is < 3 psi for each manifold position specified in the sequence table. If this criterion is not met, it must be corrected before the samples are analyzed.

Before the tank samples were analyzed, a diagnostic check was performed on the GC/FID instrument by running a system cleanliness procedure and an instrument continuing calibration as described in PNL-TVP-08. First, two blank volumes of Aadco purified air were analyzed to check the cleanliness of the system. This demonstrates through the analysis of a zero-air blank that the level of interference is acceptable in the analytical system. The system should be cleaned to 0.1 mg/m³ of TNMOCs. Second, an instrument continuing calibration is run using 100-mL UHP propane analyzed using the response factor as an external standard method followed by one blank volume of Aadco air.

C.3.1 Quantitation Results of Target Analytes. The mg/m³ was derived from the five-point multilevel calibration curve from the propane standard using the following equation:

$$\text{mg/m}^3 = \frac{(\text{ng TNMOC}) \times (\text{dilution factor})}{\text{mL sampled volume}} \quad (\text{C.1})$$

The ng/m³ concentrations are calculated from mg/m³ using the equation:

$$\text{ng/m}^3 \text{ TNMOC} = \frac{(\text{ng TNMOC})}{(\text{mL sampled})} \times \text{Dilution Factor} \times \frac{(\text{mg})}{(1 \times 10^6 \text{ mL})} \times \frac{(1 \times 10^6 \text{ mL})}{(\text{m}^3)} \quad (\text{C.2})$$

C.4 Total Non-Methane Organic Compounds Sample Results

Table C.1 lists results of the TO-12 gas analysis from samples collected from the headspace of Tank S-101, ambient air collected ~10 m upwind of the tank, and ambient air collected through the ISVS. Samples were analyzed on August 1, 1996. Concentrations in the ambient air samples ranged from 0.59 mg/m³ to 0.72 mg/m³. Concentrations in the ambient air sample through the ISVS sample bundle was 1.40 mg/m³ and was not used in the calculation of the average ambient air concentration. Concentrations in the two tank headspace samples ranged from 8.25 mg/m³ to 8.34 mg/m³ with an average concentration of 8.30 mg/m³. This compares to 14.6 mg/m³ for the sum of all target compounds and TICs identified in the analysis of the SUMMA™ canisters. Three tank samples are normally collected; however, during the sampling of Tank S-101 only two tank samples were collected.

Table C.1 TO-12 Results for Samples Collected Through the ISVS from the Headspace of Tank S-101 and from Ambient Air Near Tank S-101 in SUMMA™ Canisters on 6/6/96

	Ambient Air Upwind S6058-A01.308 ^(a) PNL 308 ^(b) Concentration (mg/m ³)	Ambient Air Upwind S6058-A02.309 ^(a) PNL 309 ^(b) Concentration (mg/m ³)	Ambient Air Through Bundle S6058-A04.310 ^(a) PNL 310 ^(b) Concentration (mg/m ³)	Tank Samples			Average Concentration Tank Samples (mg/m ³)
				S6058-A05.311 ^(a) PNL 311 ^(b) Concentration (mg/m ³)	S6058-A06.312 ^(a) PNL 312 ^(b) Concentration (mg/m ³)	S6058-A05.311 ^(a) PNL 311 ^{(b)(c)} Concentration (mg/m ³)	
TO-12	0.59 J	0.72 J	1.40	8.34	8.25	8.32	8.30

Data Qualifier Flags

J Flag denotes target compound detected above the IDL but below the EQL.

Footnotes

- (a) WHC sample identification number.
- (b) PNL canister number.
- (c) Replicate analysis for PNL 311; results are not included in the calculation of average concentrations.

C.4

Appendix D

Tank Vapor Characterization: Organic Analytes by SUMMATM Method

Appendix D

Tank Vapor Characterization: Organic Analytes by SUMMA™ Method

D.1 Sampling Methodology

Before sending SUMMA™ canisters out to the field for sampling, the canisters are cleaned and verified contaminant free according to Pacific Northwest Laboratory (PNNL) Technical Procedure PNL-TVP-02^(a). The cleaning procedure uses an EnTech 3000 cleaning system that controls 1) filling the canisters with purified humid air and 2) evacuating, for several cycles with applied heat, before allowing the canister to evacuate overnight. If the canister is verified as clean, free of TO-14 and unknown contaminants to a level of 5 parts per billion by volume (ppbv), the canister is evacuated to 5 mtorr, tagged, and stored for use in the field. Before sending the canisters out to the field for sampling, the canister vacuum is measured to determine if any leakage has occurred. If the vacuum has remained constant during storage, the canisters are prehumidified with 100 μ L of distilled water and labeled with a field-sampling identification. Cleaned canisters stored more than 30 but less than 60 days are re-evacuated and rehumidified before use. If stored more than 60 days, the canisters are recleaned and validated before use.

D.2 Analytical Procedure

The SUMMA™ canister sample was analyzed according to PNNL Technical Procedure PNL-TVP-03^(b), which is a modified version of EPA compendium Method TO-14. The method uses EnTech 7000 cryoconcentration systems interfaced with a 5972 Hewlett-Packard benchtop gas chromatograph/mass spectrometer (GC/MS). The EnTech concentrator is used to pull a metered volume of sample air from the SUMMA™ canister, cryogenically concentrate the air volume, then transfer the volume to the GC/MS for analysis. A 100-mL volume of sample is measured and analyzed from the tank headspace. The organic components in the sampled air are separated on an analytical column, J&W Scientific DB-1 phase, 60-m by 0.32-mm internal diameter with 3- μ m film thickness. The GC oven is programmed to run a temperature gradient beginning at 40°C, hold for 5 min, and ramp at 4°C per min to a final temperature of 260°C, with a 5-min hold. Twenty-four hours before the analysis, the SUMMA™ canister samples were pressurized with purified air (supplied by Aadco Instruments, Inc., 1920 Sherwood St., Clearwater, Florida 34625). The starting pressure was first measured using a calibrated diaphragm gauge (Cole Parmer), then pressurized to a level exactly twice the original pressure. For example, if the canister had a starting pressure of 740 torr, it was pressurized to 1480 torr. This dilution was an effort to improve the precision of the analysis. The sample dilution was taken into account when calculating the analysis results.

(a) Pacific Northwest Laboratory. 8/94. *Cleaning SUMMA™ Canisters and the Validation of the Cleaning Process*, PNL-TVP-02 (Rev. 0), PNL Technical Procedure, Richland, Washington.

(b) Pacific Northwest Laboratory. 8/96. *Determination of TO-14 Volatile Organic Compounds in Hanford Tank Headspace Samples Using SUMMA™ Passivated Canister Sampling and Gas Chromatographic-Mass Spectrometric Analysis*, PNL-TVP-03 (Rev. 2), PNL Technical Procedure, Richland, Washington.

The instrument calibration mixture for the PNL-TVP-03 analysis consists of 67 organic analytes. These 67 compounds that are directly quantified in this analysis make up the target analyte list (these 67 compounds will be referred to as target analytes). A summary of the target analytes is provided in Table D.1. The calibration mixture was prepared by blending a commercially prepared TO-14 calibration mixture with a mixture created using a Kin-Tek® permeation-tube standard

Table D.1 Target Organic Analytes

Dichlorodifluoromethane	p/m-Xylene
Chloromethane	1-Ethyl-2-methylbenzene
1,2-Dichloro-1,1,2,2-tetrafluoroethane	Styrene
Vinyl Chloride	1,1,2,2-Tetrachloroethane
Bromomethane	o-Xylene
Chloroethane	1,3,5-Trimethylbenzene
Trichlorofluoromethane	1,2,4-Trimethylbenzene
1,1-Dichloroethene	1,3-Dichlorobenzene
Methylene Chloride	1,4-Dichlorobenzene
1,1,2-Trichloro-1,2,2-trifluoroethane	1,2-Dichlorobenzene
1,1-Dichloroethane	1,2,4-Trichlorobenzene
cis-1,2-Dichloroethene	Hexachloro-1,3-butadiene
Chloroform	2-Butanone
1,2-Dichloroethane	Acetone
1,1,1-Trichloroethane	Acetonitrile
Benzene	Heptane
Carbon Tetrachloride	Tetrahydrofuran
1,2-Dichloropropane	Pyridine
Trichloroethene	Butanenitrile
cis-1,3-Dichloropropene	Cyclohexane
trans-1,3-Dichloropropene	Decane
1,1,2-Trichloroethane	Hexane
Toluene	4-Methyl-2-pentanone
1,2-Dibromoethane	Propanenitrile
Tetrachloroethylene	Cyclohexanone
Chlorobenzene	Propanol
Ethylbenzene	Nonane
Undecane	Dodecane
Tridecane	Tetradecane
Butane	Pentane
1-Butanol	Octane
Methanol ^(a)	Ethanol ^(a)
1,3-Butadiene	Pentanenitrile
Hexanenitrile	

(a) The low level standard is used as the EQL for these compounds

generation system. The operation of the permeation-tube system follows the method detailed in PNNL Technical Procedure PNL-TVP-06^(a). The standard calibration mix was analyzed using four aliquot sizes ranging from 30 mL to 200 mL, and a response factor for each compound was calculated. The GC/MS response for these compounds has been previously determined to be linearly related to concentration. Performance-based detection limits for the target analytes will be developed as a pool of calibration data becomes available. Currently, the nominal detection limit of 5 ppbv is used.

D.3 Quality Assurance/Quality Control

Before the tank sample was analyzed, a diagnostic check was performed on the GC/MS instrument by running an instrument "high-sensitivity 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 using a standard gas mixture containing 67 organic compounds. A gas mixture containing bromochloromethane, 1,4-difluorobenzene, chlorobenzene-d₅, and bromofluorobenzene was used as an internal standard (IS) for all blank, calibration standard, and sample analyses. Analyte responses from sample components, ISs, and standards were obtained from the extracted ion plot from their selected mass ion. The calibration 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. Once it is determined that the relative response is linear with increasing concentration, an average response factor is calculated for each target analyte and used to determine the concentration of target compounds in each sample. Method blanks are analyzed before and after calibration standards and tank headspace samples are analyzed.

D.3.1 Quantitation Results of Target Analytes. The quantitative-analysis results for the target analytes were calculated using the average response factors generated using the IS method described above and in PNL-TVP-03. The conversion from ppbv to mg/m³ assumes standard temperature and pressure (STP) conditions of 760 torr and 273K and was calculated directly from the following equation:

$$\text{mg/m}^3 = \frac{(\text{ppbv}/1000) \times \text{g mol wt of compound}}{22.4 \text{ L/mol}} \quad (\text{D.1})$$

D.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/National Institute for Standards and Technology (NIST) and WILEY electronic mass spectra libraries. Chromatographic peaks with an area count greater than, or equal to, one-tenth of the total area count of the nearest eluting IS are tentatively identified and quantitatively estimated. This is roughly equivalent to 10 ppbv, depending on the relative response factor of the individual TIC as compared with the nearest elution IS. The quality of the mass-spectral searches was then reviewed by the principal investigators before the identification was assigned to each chromatographic peak.

^(a) Pacific Northwest Laboratory. 11/94. *Preparation of TO-14 Volatile Organic Compounds Gas Standards*, PNL-TVP-06 (Rev. 0). PNL Technical Procedure, Richland, Washington.

The concentration of each TIC was estimated using a relative response factor calculated using the total peak area for the nearest eluting IS. The IS peak area was used to calculate a response factor using the IS concentration in mg/m³:

$$\text{Response Factor} = \frac{\text{IS conc. (mg/m}^3\text{)}}{\text{IS peak area}} \quad (\text{D.2})$$

The calculated response factor was then multiplied by the TIC peak area to give an estimated concentration for that compound.

The ppbv concentrations are calculated from mg/m³ and the molecular weight of the analyte.

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

All calculated sample concentrations were multiplied by a factor of 2 to account for the dilution step described in Section D.2.

D.4 Volatile Organic Sample Results

Five SUMMA™ canisters were returned to the laboratory on June 12 under WHC COC form 100087 (see Appendix F). Samples were analyzed on September 1 and 3, 1996. Three tank samples are normally collected; however, during the sampling of Tank S-101 only two tank samples were collected.

The results from the GC/MS analysis of the two tank headspace SUMMA™ samples are presented in Table D.2. The results of replicate analyses on a single SUMMA™ canister are presented in Table D.3. The results of the GC/MS analysis of the ambient air sample collected upwind of Tank S-101, through the ISVS near Tank S-101, and through the ISVS sample bundle are presented in Table D.4.

Table D.2 lists the quantitative results for compounds listed as target analytes and TICs. Target compounds not listed in Table D.2 were not detected in any of the tank headspace samples above the compound IDL. Thirty-nine target analytes above the IDL and six TICs were detected in the tank headspace samples. Twenty-eight target analytes and three TICs were identified in two tank headspace samples. Methanol at 7.80 mg/m³ and 1-butanol at 2.03 mg/m³ accounted for 69% of the target compounds and 67% of the total compounds identified in the analysis. The total concentration of the target analytes was 14.2 mg/m³. Butanal at 0.21 mg/m³ and 2-methyl-2-propanol at 0.14 mg/m³ were the two highest concentration TICs found in the two tank headspace samples. The total concentration of TICs identified was 0.45 mg/m³. The total concentration of all the compounds identified was 14.6 mg/m³. This compares to a total concentration of 8.30 mg/m³ identified in the TO-12 analysis of the two tank headspace samples.

SUMMA™ canister PNL 311 was analyzed in replicate for target analytes and TICs to determine analytical precision. Six of 27 target compounds and none of the three TICs had RPDs of less than 10%.

Forty-four target compounds were observed in one or both of the ambient air samples. All of the compounds were identified at trace levels. Trace levels of many of the target analytes may be false positives due to the fact that some of the compounds were found in the CCB above the EQL and are greater than 20 times the concentration found in the sample. These compounds are flagged with a "B" in the tables.

The following procedural changes and observations were noted during the analysis of Tank S-101:

Methanol and ethanol are not currently included in the method performance section of the procedure for System 1; however, both analytes were analyzed by this method. The low level standard is used as the EQL for these compounds. Sample results are flagged with a less-than symbol (<) when less than the EQL value.

Case Narrative for samples analyzed on September 3, 1996. This analytical sequence was run using 100 ml volumes to quantify target compounds in each tank sample and ISVS bundle sample.

Three target compounds (1,1,2,2-tetrachloroethane at 38.5%, tridecane at 34.0%, and tetradecane at 47.3%) surpassed the 30% relative standard deviation (% RSD) acceptance criteria for the initial calibration. None of these compounds were found in the tank samples at concentrations above the IDL, with the exception of tetradecane, which was found in tank sample S6058-A04.310 at a concentration between the IDL and the EQL.

Ten target compounds (bromomethane, ethanol, 1,1,2-trichloro-1,2,2-trifluoroethane, 1,1,1-trichloroethane, benzene, carbon tetrachloride, pyridine, 1,1,2,2-tetrachloroethane, 1,2,4-trichlorobenzene, and hexachloro-1,3-butadiene) were outside the 25% difference (% D) acceptance criteria for the continuing calibration verification (CCV) sample. However, the CCV passed the procedural criterion requiring +25% D passage for 85% of all target compounds. The compounds 1,1,1-trichloroethane, bromomethane, carbon tetrachloride, 1,1,2,2-tetrachloroethane, 1,2,4-trichlorobenzene, and hexachloro-1,3-butadiene were not found in the tank samples at concentrations above their IDLs, with the exceptions of 1,2,4-trichlorobenzene, which was found in tank sample S6058-A05.311 REP at a concentration between the IDL and the EQL, and bromomethane, which was found in tank sample S6058-A06.312 at a concentration between the IDL and the EQL. Pyridine was found in all tank samples at concentrations between the IDL and the EQL, but it was not found in tank sample S6058-A06.312. Ethanol, benzene, and 1,1,2-trichloro-1,2,2-trifluoroethane were found in all tank samples at concentrations between the EQL and the upper quantification limit, with the exception of tank sample S6058-A04.310, in which benzene was found at a concentration between the IDL and the EQL, and ethanol was found at a concentration below the IDL.

Target compounds methylene chloride, 1,1,2,2-tetrachloroethane, 1,2,4-trichlorobenzene, and butane were found in the continuing calibration blank (CCB) above their EQLs. Methylene chloride was found in initial calibration blank (ICB) above its EQL.

Case Narrative for samples analyzed on September 1, 1996. This analytical sequence was run using 100 ml volumes to quantify target compounds in each ambient air sample.

Three target compounds (1,1,2,2-tetrachloroethane at 38.5%, tridecane at 34.0%, and tetradecane at 47.3%) surpassed the 30% RSD acceptance criteria for the initial calibration. The compounds 1,1,2,2-tetrachloroethane, tridecane, and tetradecane were not found in the tank samples at concentrations above the IDL.

Eight target compounds (pyridine, 1,2,4-trimethylbenzene, undecane, 1,2,4-trichlorobenzene, dodecane, hexachloro-1,3-butadiene, tridecane, and tetradecane) were outside the 25% D acceptance criteria for the CCV sample. However, the CCV passed the procedural criterion requiring +25% D passage for 85% of all target compounds. Pyridine and 1,2,4-trimethylbenzene were found in both ambient air samples S6058-A01.308 and S6058-A02.309 at concentrations between the IDL and the EQL. Undecane and 1,2,4-trichlorobenzene were found in sample S6058-A01.308 at concentrations between the IDL and the EQL. Dodecane, hexachloro-1,3-butadiene, tridecane, and tetradecane were not found in the tank samples at concentrations above the IDL.

Target compound methylene chloride was found in the CCB above the EQL. This compound was found in the ICB above the EQL.

Table D.2. Positively Identified and Quantitated Target Analytes^(a) and Tentatively Identified Compounds and Estimated Concentrations^(b) for Samples from the Headspace in Tank S-101 in SUMMA canisters collected on 6/6/96

Target Analytes ^(a)	CAS	MW	Ret Time	S6058-A05.311 ^(c) ISVS			S6058-A06.312 ^(c) ISVS			Mean Values	
				(mg/m ³)	(ppbv)	Flag	(mg/m ³)	(ppbv)	Flag	(mg/m ³)	(ppbv)
Dichlorodifluoromethane	75-71-8	121	4.6	0.012	2.3	J	0.016	3.0	J	0.014	2.7
Chloromethane	74-87-3	50	5.0	0.017	7.6	J	0.025	11		0.021	9.3
Methanol	67-56-1	32	5.2	6.502	4546	E,Y	9.090	6355	E,Y	7.796	5450
Vinyl Chloride	75-01-4	63	5.5	0.002	0.57	U	0.006	2.0	J	e	e
Butane	106-97-8	58	5.9	0.150	58		0.185	71		0.167	65
Bromomethane	74-83-9	95	6.4	0.005	1.2	U	0.007	1.7	J	e	e
Ethanol	64-17-5	46	6.8	1.032	502	Y	1.398	681	Y	1.215	591
Acetonitrile	75-05-8	41	7.3	0.051	28		0.046	25		0.049	26
Acetone	67-64-1	58	7.9	1.053	406		1.034	399		1.044	403
Trichlorofluoromethane	75-69-4	137	8.3	0.281	46		0.304	50		0.293	48
Pentane	109-66-0	72	9.0	0.042	13		0.039	12		0.040	13
Methylene Chloride	75-09-2	85	9.7	0.030	8.0	B	0.030	7.8	B	0.030	7.9
1,1,2-trichloro-1,2,2-trifluoroethane	76-13-1	187	10.2	0.213	25		0.192	23		0.202	24
Propanol	71-23-8	60	10.9	0.116	43		0.116	43		0.116	43
Propanenitrile	107-12-0	55	10.9	0.012	4.7	J	0.014	5.7	J	0.013	5.2
2-Butanone	78-93-3	72	12.5	0.143	44		0.143	44		0.143	44
Hexane	110-54-3	86	13.8	0.032	8.4		0.034	9.0		0.033	8.7
Tetrahydrofuran	109-99-9	72	14.7	0.127	40		0.129	40		0.128	40
1,2-Dichloroethane	107-06-2	99	15.3	0.003	0.59	U	0.005	1.0	J	e	e
Butanenitrile	109-74-0	69	15.8	0.003	1.1	U	0.016	5.1	J	e	e
1-Butanol	71-36-3	74	16.3	2.212	668		1.849	559		2.030	614
Benzene	71-43-2	78	16.7	0.032	9.2		0.030	8.7		0.031	9.0
Cyclohexane	110-82-7	84	17.3	0.025	6.7	J	0.034	9.0	J	0.029	7.8
Heptane	142-82-5	100	19.3	0.020	4.6		0.021	4.7		0.021	4.6
4-Methyl-2-Pentanone	108-10-1	100	20.5	0.025	5.6	J	0.034	7.7		0.030	6.7
Pyridine	110-86-1	79	20.6	0.029	8.3	J	0.019	5.3	U	0.024	6.8
Toluene	108-88-3	92	22.6	0.671	163		0.575	140		0.623	151
Ethylbenzene	100-41-4	106	27.7	0.009	2.0	J	0.009	1.9	J	0.009	1.9
p/m-Xylene	106-42-3	106	28.1	0.020	4.1	J	0.019	4.0	J	0.019	4.0
o-Xylene	95-47-6	106	29.3	0.014	2.9	J	0.015	3.2	J	0.015	3.1
Nonane	111-84-2	128	29.8	0.014	2.4	J	0.010	1.8	J	0.012	2.1
1-Ethyl-2-Methyl-Benzene	611-14-3	120	32.9	0.002	0.34	U	0.007	1.2	J	e	e
1,3,5-Trimethylbenzene	108-67-8	120	32.9	0.002	0.34	U	0.006	1.2	J	e	e
1,2,4-Trimethylbenzene	95-63-6	120	34.2	0.003	0.48	U	0.007	1.2	B,J	e	e
Decane	124-18-5	142	34.4	0.017	2.8	J	0.022	3.5	J	0.020	3.1
1,3-Dichlorobenzene	541-73-1	147	34.7	0.002	0.27	U	0.008	1.2	J	e	e
1,4-Dichlorobenzene	106-46-7	147	34.9	0.002	0.27	U	0.007	1.1	J	e	e
1,2-Dichlorobenzene	95-50-1	147	36.1	0.002	0.27	U	0.009	1.3	J	e	e
Undecane	1120-21-4	156	38.8	0.003	0.37	U	0.013	1.8	J	e	e

Tentatively Identified Compounds^(b)

Propane	74-98-6	44	4.5	0.159	81	N	nd	nd		e	e
Methyl nitrite	624-91-9	61	4.8	nd	nd		0.143	53	N	e	e
Cyclopropane	75-19-4	42	5.0	nd	nd		0.129	69	N	e	e
2-Propanol, 2-methyl-	75-65-0	74	9.5	0.150	45	N	0.130	39	N	0.140	42
Butanal	123-72-8	72	12.3	0.222	69	N	0.194	60	N	0.208	65
1,3-Diazine	289-95-2	80	19.8	0.105	29	N	0.104	29	N	0.104	29

Data Quality Flags

B Compound found in associated laboratory blank.

E Target compound exceeds upper quantification limit (UQL).

J Target compound detected above the IDL but below the EQL.

N Denotes tentatively identified compound

U Target compound not detected at or above the IDL.

Y Initial calibration and CCV was performed; however, the analyte was not part of the current operating procedure.

Footnotes

(a) Detected target analytes.

(b) Semi-quantitative estimate calculated using concentration of closest eluting IS.

(c) WHC sample identification number.

(d) Replicates of this sample are found in Table D.3.

(e) Mean and/or standard deviation are not meaningful for this analyte.

nd Not detected

Table D.3. Positively Identified and Quantitated Target Analytes^(a) and Tentatively Identified Compounds and Estimated Concentrations^(b) of Replicate Analysis on a Single SUMMATM Canister Sample from the Headspace of Tank S-101 on 6/6/96

Target Analytes ^(a)	CAS	MW	Ret Time	S6058-A05.311 ^(c) ISVS						Relative Percent Difference ^(d)
				(mg/m ³)	(ppbv)	Flag	(mg/m ³)	(ppbv)	Flag	%
Dichlorodifluoromethane	75-71-8	121	4.6	0.012	2.3	J	0.017	3.1	J	29
Chloromethane	74-87-3	50	5.0	0.017	7.6	J	0.026	11		41
Methanol	67-56-1	32	5.2	6.502	4546	E,Y	9.637	6737	E,Y	39
Butane	106-97-8	58	5.9	0.150	58		0.221	85		38
Ethanol	64-17-5	46	6.8	1.032	502	Y	1.485	723	Y	36
Acetonitrile	75-05-8	41	7.3	0.051	28		0.071	39		34
Acetone	67-64-1	58	7.9	1.053	406		1.362	525		26
Trichlorofluoromethane	75-69-4	137	8.3	0.281	46		0.395	64		34
Pentane	109-66-0	72	9.0	0.042	13		0.058	18		34
Methylene Chloride	75-09-2	85	9.7	0.030	8.0		0.031	8.2		3
1,1,2-trichloro-2,2,2-trifluoroethane	76-13-1	187	10.2	0.213	25		0.247	30		15
Propanol	71-23-8	60	10.9	0.116	43		0.151	56		26
Propanenitrile	107-12-0	55	10.9	0.012	4.7	J	0.018	7.5	J	46
2-Butanone	78-93-3	72	12.5	0.143	44		0.185	57		26
Hexane	110-54-3	86	13.8	0.032	8.4		0.044	12		31
Tetrahydrofuran	109-99-9	72	14.7	0.127	40		0.170	53		29
1-Butanol	71-36-3	74	16.3	2.212	668		2.401	726		8
Benzene	71-43-2	78	16.7	0.032	9.2		0.038	11		17
Cyclohexane	110-82-7	84	17.3	0.025	6.7	J	0.028	7.6	J	13
Heptane	142-82-5	100	19.3	0.020	4.6		0.026	5.8		24
4-Methyl-2-Pentanone	108-10-1	100	20.5	0.025	5.6	J	0.033	7.3	J	27
Pyridine	110-86-1	79	20.6	0.029	8.3	J	0.023	6.5	J	24
Toluene	108-88-3	92	22.6	0.671	163		0.627	152		7
Chlorobenzene	108-90-7	113	26.8	0.003	0.52	U	0.006	1.3	J	
Hexanenitrile	628-73-9	97	27.0	0.005	1.2	U	0.015	3.5	J	
Ethylbenzene	100-41-4	106	27.7	0.009	2.0	J	0.010	2.1	J	8
p/m-Xylene	106-42-3	106	28.1	0.020	4.1	J	0.021	4.4	J	7
o-Xylene	95-47-6	106	29.3	0.014	2.9	J	0.003	0.59	U	
Nonane	111-84-2	128	29.8	0.014	2.4	J	0.013	2.2	J	8
1,2,4-Trimethylbenzene	95-63-6	120	34.2	0.003	0.48	U	0.006	1.2	J	
Decane	124-18-5	142	34.4	0.017	2.8	J	0.021	3.3	J	19
1,2,4-Trichlorobenzene	120-82-1	181	42.3	0.003	0.35	U	0.009	1.0	B,J	

Tentatively Identified Compounds^(b)

Propane	74-98-6	44	4.5	0.159	81	N	0.114	58	N	33
Methyl nitrite	624-91-9	61	4.8	nd	nd		0.260	96	N	
Cyclopropane	75-19-4	42	5.0	nd	nd		0.150	80	N	
2-Propanol, 2-methyl-	75-65-0	74	9.5	0.150	45	N	0.173	52	N	14
Butanal	123-72-8	72	12.3	0.222	69	N	0.264	82	N	17
Pyrazine	290-37-9	80	19.8	nd	nd		0.133	37	N	
1,3-Diazine	289-95-2	80	19.8	0.105	29	N	nd	nd		

Data Quality Flags

- B Compound found in associated laboratory blank.
- E Target compound exceeds upper quantification limit (UQL).
- J Target compound detected above the IDL but below the EQL.
- N Denotes tentatively identified compound
- U Target compound not detected at or above the IDL.
- Y Initial calibration and CCV was performed; however, the analyte was not part of the current operating procedure.

Footnotes

- (a) Detected target analytes.
- (b) Semi-quantitative estimate calculated using concentration of closest eluting IS.
- (c) WHC sample identification number.
- (d) Relative percent differences (RPDs) based on mg/m³ values.
- nd Not detected

Table D.4. Positively Identified and Quantitated Target Analytes^(a) and Tentatively Identified Compounds and Estimated Concentrations^(b) in Ambient Air and Ambient Air Through the ISVS Collected Near Tank S-101 in SUMMATM Canisters on 6/6/96

Target Analytes ^(a)	CAS	MW	Ret Time	S6058-A02.309 ^(c)			S6058-A04.310 ^(c)			S6058-A01.308 ^(c)		
				Ambient Air			ISVS Bundle Air			Upwind Ambient Air		
				(mg/m ³)	(ppbv)	Flag	(mg/m ³)	(ppbv)	Flag	(mg/m ³)	(ppbv)	Flag
Dichlorodifluoromethane	75-71-8	121	4.6	0.005	0.94	J	0.017	3.2	J	0.003	0.61	J
Chloromethane	74-87-3	50	5.0	0.004	1.6	J	0.008	3.4	J	0.002	1.0	J
Methanol	67-56-1	32	5.2	0.065	45	Y	0.171	120	Y	0.080	56	Y
Butane	106-97-8	58	5.9	0.005	1.7	J	0.007	2.8	J	0.002	0.92	U
Ethanol	64-17-5	46	6.8	0.024	12	Y	0.011	5.4	Y	0.023	11	Y
Acetonitrile	75-05-8	41	7.3	0.006	3.0	J	0.007	3.9	J	0.004	2.3	J
Acetone	67-64-1	58	7.9	0.035	14	J	0.059	23		0.035	14	J
Pentane	109-66-0	72	9.0	0.002	0.62	J	0.004	1.2	U	0.001	0.36	J
1,1-Dichloroethene	75-35-4	97	9.5	0.004	0.88	U	0.004	0.88	U	0.002	0.48	J
Methylene Chloride	75-09-2	85	9.7	0.019	5.0	B,J	0.030	7.8	B	0.019	5.0	B,J
1,1,2-trichloro-2,2,2-trifluoroethane	76-13-1	187	10.2	0.004	0.48	U	1.025	123		0.004	0.48	U
Propanol	71-23-8	60	10.9	0.009	3.5	J	0.024	9.0	J	0.014	5.2	J
Propanenitrile	107-12-0	55	10.9	0.006	2.5	J	0.009	3.6	J	0.006	2.6	J
1,1-Dichloroethane	75-34-3	99	11.8	0.003	0.61	J	0.002	0.45	U	0.002	0.45	U
2-Butanone	78-93-3	72	12.5	0.025	7.7	J	0.029	8.9		0.027	8.4	J
Hexane	110-54-3	86	13.8	0.004	0.96	J	0.004	1.1	J	0.004	0.90	J
Chloroform	67-66-3	119	13.9	0.005	0.89	J	0.003	0.49	U	0.004	0.69	J
Tetrahydrofuran	109-99-9	72	14.7	0.002	0.50	U	0.002	0.50	U	0.002	0.76	J
Butanenitrile	109-74-0	69	15.8	0.003	1.1	U	0.013	4.2	J	0.003	1.1	U
1,1,1-Trichloroethane	71-55-6	133	15.8	0.005	0.84	J	0.003	0.54	U	0.004	0.61	J
1-Butanol	71-36-3	74	16.3	0.007	2.1	J	0.029	8.6	J	0.014	4.3	J
Benzene	71-43-2	78	16.7	0.003	0.79	J	0.005	1.5	J	0.003	0.86	J
Carbon Tetrachloride	56-23-5	154	17.0	0.003	0.50	U	0.003	0.50	U	0.004	0.53	J
1,2-Dichloropropane	78-87-5	113	18.3	0.003	0.67	J	0.003	0.59	U	0.003	0.59	U
Trichloroethene	79-01-6	131	18.8	0.004	0.69	J	0.002	0.41	U	0.004	0.70	J
4-Methyl-2-Pentanone	108-10-1	100	20.5	0.003	0.76	U	0.016	3.5	J	0.010	2.2	J
Pyridine	110-86-1	79	20.6	0.006	1.6	J	0.037	11	J	0.014	4.0	J
Pentanenitrile	110-59-8	83	21.6	0.004	1.1	U	0.011	3.1	J	0.006	1.6	J
Toluene	108-88-3	92	22.6	0.003	0.60	J	0.005	1.2	J	0.003	0.73	J
Chlorobenzene	108-90-7	113	26.8	0.003	0.55	J	0.008	1.6	J	0.004	0.77	J
Hexanenitrile	628-73-9	97	27.0	0.005	1.1	J	0.021	4.8	J	0.005	1.2	U
Ethylbenzene	100-41-4	106	27.7	0.002	0.37	J	0.006	1.2	J	0.002	0.46	J

D.9

Table D.4. Positively Identified and Quantitated Target Analytes^(a) and Tentatively Identified Compounds and Estimated Concentrations^(b) in Ambient Air and Ambient Air Through the ISVS Collected Near Tank S-101 in SUMMATM Canisters on 6/6/96

Target Analytes ^(a)	CAS	MW	Ret Time	S6058-A02.309 ^(c)			S6058-A04.310 ^(c)			S6058-A01.308 ^(c)		
				Ambient Air			ISVS Bundle Air			Upwind Ambient Air		
				(mg/m ³)	(ppbv)	Flag	(mg/m ³)	(ppbv)	Flag	(mg/m ³)	(ppbv)	Flag
p/m-Xylene	106-42-3	106	28.1	0.003	0.62	J	0.013	2.7	U	0.004	0.93	J
Cyclohexanone	108-94-1	98	28.5	0.006	1.3	U	0.006	1.3	U	0.004	0.84	J
Styrene	100-42-5	104	29.0	0.002	0.47	U	0.010	2.0	J	0.004	0.82	J
o-Xylene	95-47-6	106	29.3	0.003	0.59	U	0.008	1.6	J	0.003	0.59	U
Nonane	111-84-2	128	29.8	0.003	0.59	J	0.008	1.5	J	0.004	0.63	J
1-Ethyl-2-Methyl-Benzene	611-14-3	120	32.9	0.002	0.34	U	0.007	1.3	J	0.003	0.56	J
1,3,5-Trimethylbenzene	108-67-8	120	32.9	0.002	0.34	U	0.008	1.5	J	0.003	0.55	J
1,2,4-Trimethylbenzene	95-63-6	120	34.2	0.002	0.34	J	0.008	1.5	B,J	0.003	0.53	J
Decane	124-18-5	142	34.4	0.005	0.80	J	0.020	3.2	J	0.008	1.2	J
1,3-Dichlorobenzene	541-73-1	147	34.7	0.002	0.27	U	0.012	1.8	J	0.004	0.65	J
1,4-Dichlorobenzene	106-46-7	147	34.9	0.002	0.27	U	0.012	1.8	J	0.005	0.69	J
1,2-Dichlorobenzene	95-50-1	147	36.1	0.002	0.27	U	0.013	2.0	J	0.005	0.78	J
Undecane	1120-21-4	156	38.8	0.003	0.37	U	0.020	2.9	J	0.003	0.48	J
1,2,4-Trichlorobenzene	120-82-1	181	42.3	0.003	0.35	U	0.003	0.35	U	0.005	0.66	J
Tetradecane	629-59-4	198	50.0	0.004	0.47	U	0.021	2.4	J	0.004	0.47	U
1,3-Butadiene	106-99-0	54	5.8	0.002	0.95	J	0.008	3.4	U	0.008	3.4	U

Tentatively

Identified Compounds^(b)

Acetaldehyde	75-07-0	44	5.2	nd	nd		0.155	79	N	nd	nd	
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Data Quality Flags

B Compound found in associated laboratory blank.

J Target compound detected above the IDL but below the EQL.

N Denotes tentatively identified compound

U Target compound not detected at or above the IDL.

Y Initial calibration and CCV was performed; however, the analyte was not part of the current operating procedure.

Footnotes

(a) Detected target analytes.

(b) Semi-quantitative estimate calculated using concentration of closest eluting IS.

(c) WHC sample identification number.

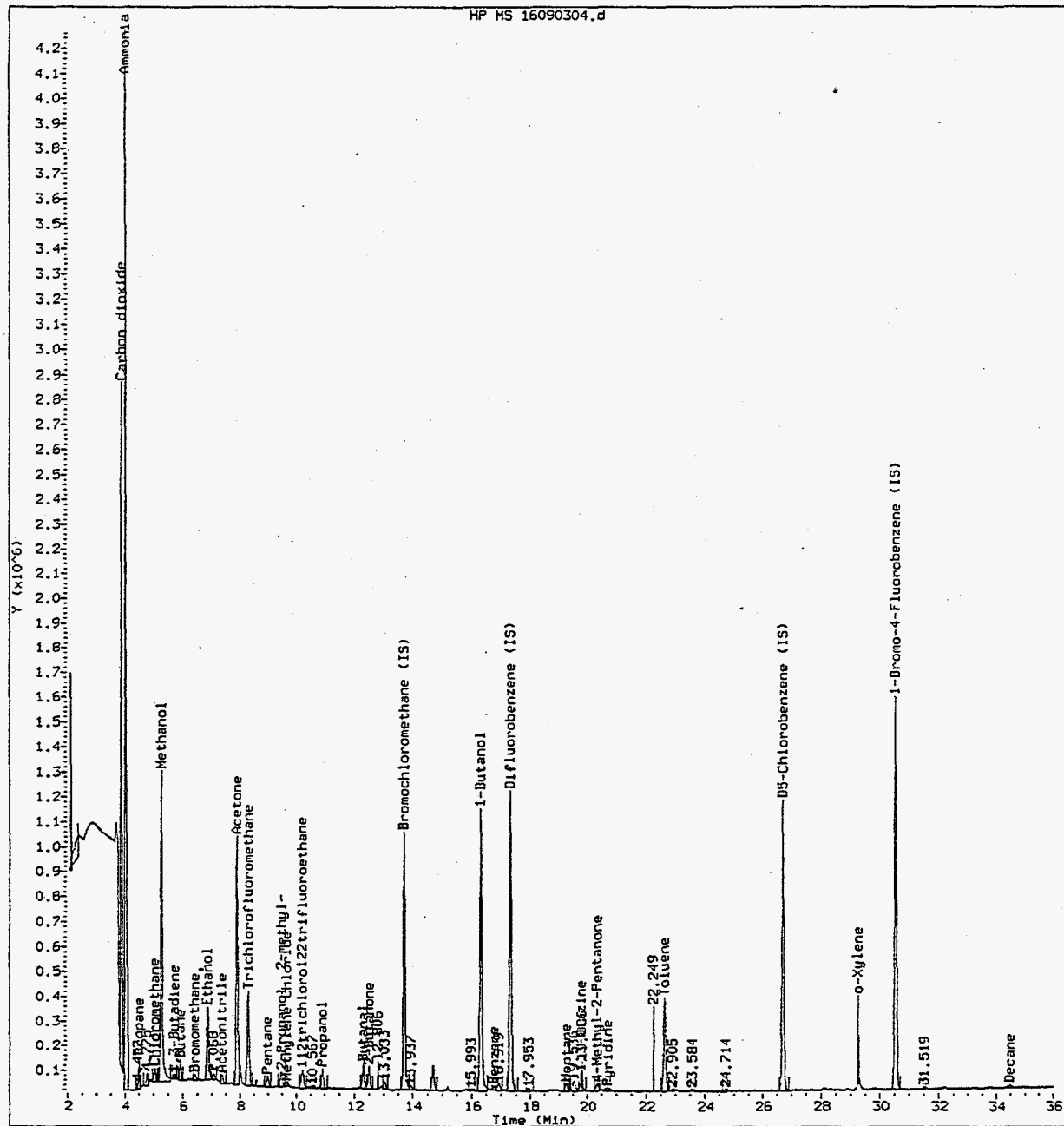


Figure D.1a Total Ion Chromatogram (2 - 36 min) for Hanford Waste Tank S-101
SUMMA™ Canister Sample S6058-A05-311 Collected on 6/6/96

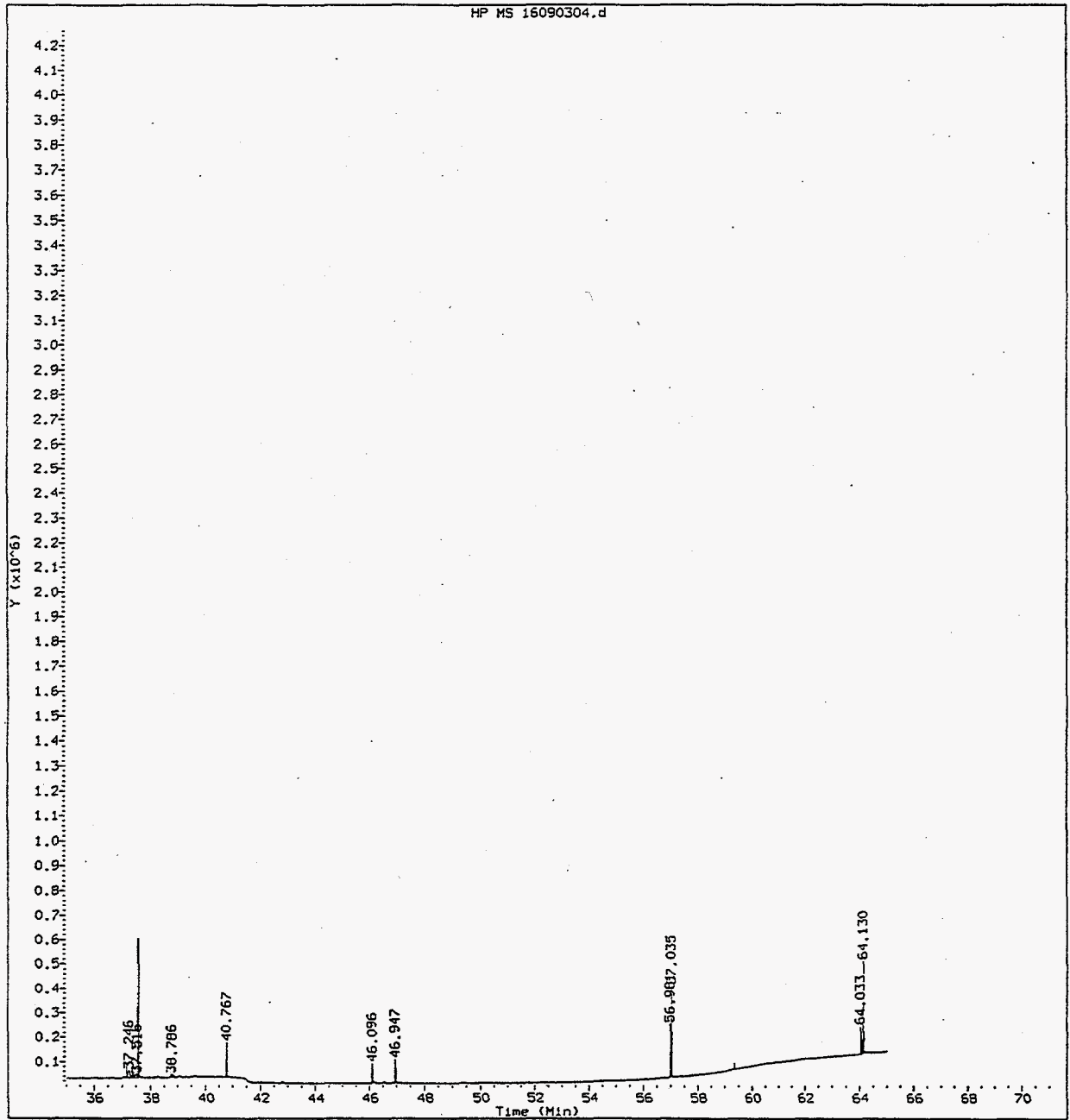


Figure D.1b Total Ion Chromatogram (36 - 70 min) for Hanford Waste Tank S-101
SUMMA™ Canister Sample S6058-A05-311 Collected on 6/6/96

Appendix E

Tank Vapor Characterization: Organic Analytes by Triple Sorbent Trap Method

Appendix E

Tank Vapor Characterization: Organic Analytes by Triple Sorbent Trap Method

E.1 Sampling Methodology

Samples are collected on Supelco 300 graphite based triple sorbent traps (TST). Before field deployment, each trap is heated to 380°C under inert gas flow for a minimum of 60 min. Tubes are prepared in batches with each tank sampling job constituting one batch. One tube is selected from each batch and run immediately to verify cleanliness. All remaining tubes in the batch receive equal amounts of 3 surrogate compounds (hexafluorobenzene, toluene-d8, and bromobenzene-d5). One per batch tube is run immediately to verify successful addition of surrogate spikes to that batch. Tubes are then placed in individually labeled plastic shipping tubes (Supelco TD³), which are sealed with gasketed end caps, thus providing a rugged, headspace-free shipping and storage medium. As a precautionary measure, sample tubes are kept in refrigerated storage before and after sampling.

E.2 Analytical Procedure

The Supelco 300 tubes were analyzed according to Pacific Northwest National Laboratory (PNNL) Technical Procedure PNL-TVP-10^(a), with the exceptions noted in Section E.4. The method employs Supelco Carbotrap™ 300 traps for sample collection and preconcentration. The traps are ground-glass tubes (11.5 cm long X 6 mm OD, 4 mm ID) containing a series of sorbents arranged in order of increasing retentivity. Each trap contains 300 mg of Carbotrap™ C, 200 mg of Carbotrap™ B, and 125 mg of Carbosieve™ S-III. The first 2 sorbents are deactivated graphite with limited sorption power for less volatile compounds. The final trapping stage, the Carbosieve™ S-III, is a graphitized molecular sieve used to retain the most volatile components, including some permanent gases such as Freon-12. Following sample collection and addition of internal standard (IS), the traps are transferred to a Dynatherm ACEM 900 thermal desorber unit for analysis. The trap on the ACEM 900 is then desorbed by ballistic heating to 350°C with the sample then transferred to a smaller focusing trap. A 10:1 split is used during the transfer with 10% of the sample analyzed and the rest retained for reanalysis. The split sample collected on a second identical Carbotrap™ 300 trap is used for repeat analysis on at least one sample per batch. Since the IS also follows the same path, quantitation may be performed directly on the repeat run without changing the calibration. Following desorption from the Carbotrap™ 300 trap, the analyte is transferred to a long, thin focusing trap filled with the same type of trapping materials as the Carbotrap™ 300 traps and in approximately the same ratios. The purpose of the focusing trap is to provide an interface to a capillary gas chromatography (GC) column, which may be thermally desorbed at a helium (He) flow rate compatible with the column and mass spectrometry (MS) interface (1.2 mL/min). The focusing trap is

^(a) Pacific Northwest Laboratory. 2/96. *Determination of Volatile Organic Compounds in Hanford Waste Tank Headspace Samples Using Triple Sorbent Trap Sampling and Gas Chromatograph-Mass Spectrometer Analysis*, PNL-TVP-10 (Rev. 2), PNL Technical Procedure, Richland, Washington.

ballistically heated to thermally desorb components onto a capillary GC column. The column is subsequently temperature programmed to separate the method analytes, which are then detected by MS.

The instrument calibration mixture for the TST analysis consists of 66 compounds. These 66 compounds that are directly quantified in this analysis make up the target analyte list (these 66 compounds will be referred to as target analytes). A summary of the target analytes is provided in Table E.1. The calibration mixture is prepared in common with the mixture used for the SUMMA™ analysis (see Section D.2). The standard calibration mix was analyzed using 4 aliquot sizes ranging from 100 mL to 1200 mL, and a response factor for each compound was calculated. Volumes of

Table E.1 Target Organic Analytes

<i>Dichlorodifluoromethane</i>	p/m-Xylene
<i>Chloromethane</i>	Styrene
<i>1,2-Dichloro-1,1,2,2-tetrafluoroethane</i>	1,1,2,2-Tetrachloroethane
<i>Vinyl Chloride</i>	o-Xylene
<i>Chloroethane</i>	1,3,5-Trimethylbenzene
<i>Trichlorofluoromethane</i>	1,2,4-Trimethylbenzene
1,1-Dichloroethene	1,3-Dichlorobenzene
Methylene Chloride	1,4-Dichlorobenzene
1,1,2-Trichloro-1,2,2-trifluoroethane	1,2-Dichlorobenzene
1,1-Dichloroethane	1,2,4-Trichlorobenzene
cis-1,2-Dichloroethene	Hexachloro-1,3-butadiene
Chloroform	2-Butanone
1,2-Dichloroethane	Chlorobenzene
1,1,1-Trichloroethane	<i>Acetonitrile</i>
Benzene	Heptane
Carbon Tetrachloride	Tetrahydrofuran
1,2-Dichloropropane	Pyridine
Trichloroethene	Butanenitrile
cis-1,3-Dichloropropene	Cyclohexane
trans-1,3-Dichloropropene	Decane
1,1,2-Trichloroethane	Hexane
Toluene	4-Methyl-2-pentanone
1,2-Dibromoethane	Propanenitrile
Tetrachloroethylene	Cyclohexanone
Ethylbenzene	Propanol
Butane	<i>Acetone</i>
Pentane	Undecane
Dodecane	Tridecane
1-Butanol	Pentanenitrile
Octane	Hexanenitrile
Tetradecane	Nonane
1-Ethyl-2-methylbenzene	Methanol ^(a)
Ethanol ^(a)	1,3-Butadiene

(a) The low level standard is used as the EQL for these compounds.

Note: Compounds shown in italics have an exceptionally high volatility. They are routinely included in the standard and are quantified, but have a restricted linear dynamic range because of the potential for trap breakthrough.

standard added to the traps are measured by pressure difference on a SUMMA™ canister of known volume. The GC/MS response for these compounds has been previously determined to be linearly related to concentration. Instrument detection limits and EQLs for the target analytes have been developed.

E.3 Quality Assurance/Quality Control

Before the tank sample was analyzed, a diagnostic check was performed on the GC/MS instrument by running a full auto tune, as described in PNL-TVP-10. Upon satisfactory completion of the instrument diagnostic check, a blank tube was analyzed to check the cleanliness of the system. The instrument was then calibrated using a 300-mL volume of standard gas mixture containing 66 compounds shown in Table E.1. A gas mixture containing difluorobenzene, chlorobenzene-d₅, and 1,4-bromofluorobenzene was used as an IS for all calibration standard and sample analyses. Analyte responses from sample components, ISs, and standards were obtained from the extracted ion plot from their selected mass ion. A continuing calibration 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. Once it is determined that the relative response is linear with increasing concentration, an average response factor is calculated for each target analyte and used to determine the concentration of target compounds in each sample.

E.3.1 Quantitation Results of Target Analytes. The quantitative-analysis results for the target analytes were calculated directly from the calibration curve generated using the IS method described above and in PNL-TVP-10. The conversion from ppbv to mg/m³ assumes standard temperature and pressure (STP) conditions of 760 torr and 273K and was calculated directly from the following equation:

$$\text{mg/m}^3 = \frac{(\text{ppbv}/1000) \times \text{g mol wt of compound}}{22.4 \text{ L/mol}} \quad (\text{E.1})$$

E.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 U.S. Environmental Protection Agency (EPA)/National Institute for Standards and Technology (NIST) and WILEY Libraries, which are a part of the Hewlett-Packard 5971/5972 instrument operating system. Chromatographic peaks with an area count greater than, or equal to, one-tenth of the total area count of the nearest eluting IS are tentatively identified and quantitatively estimated. The quality of the mass-spectral searches was then reviewed by the principal investigators before the identification was assigned to each chromatographic peak.

The concentration of each TIC was estimated using a relative response factor calculated using the total peak area for the nearest eluting IS. The IS peak area was used to calculate a response factor using the IS concentration in mg/m³:

$$\text{Response Factor} = \frac{\text{IS conc. (mg/m}^3\text{)}}{\text{IS peak area}} \quad (\text{E.2})$$

The calculated response factor was then multiplied by the TIC peak area to give an estimated concentration for that compound.

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

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

E.4 Organic Sample Results

Eight triple sorbent traps consisting of four samples, two field blanks and two trip blanks were returned to the laboratory on June 12, 1996 under WHC COC form 100088. Samples were analyzed on August 21 and 22, 1996.

The results from the GC/MS analysis of the tank headspace TST samples are presented in Table E.2. The results of replicate analyses on a single TST are presented in Table E.3.

Table E.2 lists the quantitative results for compounds listed as target analytes and TICs. Target compounds not listed in Table E.2 were not detected in any of the tank headspace samples above the compound IDL. Thirty-six target analytes above the IDL and 13 TICs were detected in the tank headspace samples. Thirty-one of the target analytes and all 13 TICs were observed in two or more sorbent traps. Two of the TICs were not identified and were labelled as unknowns. Methanol at 4.18 mg/m^3 and 1-butanol at 1.68 mg/m^3 accounted for 62% of the target analytes and 44% of the total concentration identified by the analysis. The total concentration of the target analytes was 9.50 mg/m^3 or 71% of the total concentration identified by the analyses. The predominant TICs observed in these samples were 1-fluoro-1,1-dichloroethane at 0.94 mg/m^3 and 1-chloro-1,1-difluoroethane at 0.72 mg/m^3 . The total concentration of the TICs was 3.80 mg/m^3 or 29% of the total concentration identified by analysis. The total concentration of all the compounds identified was 13.30 mg/m^3 .

Triple sorbent trap sample PNL 1024 was analyzed in replicate for target analytes and TICs to determine analytical precision. Twenty-four of 32 target compounds and 12 of 13 TICs had RPDs of less than 10%.

The following procedural changes and observations were noted during the analysis of Tank S-101:

Methanol and ethanol are not currently included in procedure PNL-TVP-10; however, both compounds were analyzed per this method. The low level standard is used as the EQL for these compounds. Sample results are flagged with a less-than symbol (<) when less than the EQL value.

Tributyl phosphate is included in the target list based on a calibration performed on January 5 and 9, 1996. The TBP was introduced onto a series of double sorbent traps as a methanolic solution standard rather than a vapor standard. This served to determine the retention time

and verify the mass spectral characteristics of the compound. However, verification of the calibration acceptability was not performed because the compound is not present in the CCV. At present, it is not possible to prepare a gas standard from this material. The calibration information on TBP demonstrated that detectability at 0.8 ppbv (based on 200 mL sample) was possible. Tributyl phosphate was not detected in the tank samples.

Very narrow air spikes (mass 32) occasionally are present in chromatograms from this period. This problem has been traced to high frequency air bursts from the surface of MS vacuum system o-rings. Attempts at permanently eliminating this problem have been unsuccessful to date, and the matter has been referred to Hewlett Packard for further investigation. It has no known impact on data quality but the spikes do appear as features on the total ion chromatogram.

Field blanks, one trip blank, and all samples contained minor amounts of 1-chloro-1,1-difluoroethane. This compound has appeared persistently in most samples sent to the field in the past including blanks. It is believed to be a fugitive refrigerant. This material is never present in tubes archived for a similar amount of time in the 326 Vapor Lab or 329 Building temporary storage. The origin of the material is unclear, but since it has shown up in trip blanks as well as field blanks, the most likely candidate is one of the refrigerators used for interim storage.

Case narrative for Tank S-101 tank samples analyzed on August 21, 1996. Samples included in this batch consisted of the two field blanks and two trip blanks.

The CCV showed acceptable performance as specified in the procedure for all target compounds with the exception of 1,2-dichloro-1,1,2,2-tetrafluoroethane (40%), methanol (52%), 1,3-butadiene (48%), butane (36%), ethanol (29%), and tetradecane (51%). Samples contained only low levels (below EQL) of tetradecane. The CCB contained trace amounts (below EQL) of methylene chloride, benzene, and tetradecane. It was otherwise clean of all target and TIC compounds.

No target compounds were observed in either field or trip blanks at levels in excess of the EQL. Trace amounts (below EQL) of acetone, trichlorofluoromethane, methylene chloride, toluene, hexane, ethyl benzene, xylenes, decane, undecane, and tetradecane were observed in at least one of the field blanks. The trip blanks showed only very trace quantities of trichlorofluoromethane, methylene chloride, toluene and tetradecane. Environmental contamination problems apparently associated in past work with field bundle preparation were very minimal in this sampling job.

Case narrative for samples analyzed on August 22, 1996. Samples included in this batch consisted of the three tanks samples and one repeat analysis of a tank sample.

The CCV was within nominal limits for all compounds except methanol (45%) and 1,3-butadiene (34%). Samples contained significant quantities of methanol but no 1,3-butadiene. Accuracy limitations on the methanol calibration should be noted. The CCB was clean except for minor traces of methylene chloride, toluene, and ethyl benzene at levels below the EQL.

A relatively limited list of TICs was observed including acetaldehyde, 2-methyl-1-propene, 2,2-dimethyl-propane, isopropyl alcohol, N-nitrosodimethylamine, pyrazine, and 2,4 dimethyl heptane. One unusual compound, 1-fluoro-1,1-dichloroethane, appeared in all three samples at widely varying levels with the second sample having very high levels of that compound. The second sample also contained minor amounts of several chlorinated hydrocarbon target compounds not observed in the other two samples. All of the samples and field blanks contained a pair of siloxane compounds typically found in silicone rubbers. These materials are sometimes also seen in the system blanks, apparently as degradation products from the column lining, but that has not been observed for some time. It is likely that these compounds are a form of environmental blank associated with the use of C-Flex tubing, a form of silicone rubber in the ISVS bundle.

Sample volumes for all ISVS tank samples have been corrected to STP from the 21°C calibration used on the sampling cart flowmeters. The correction was included in the reported data to provide seamless compatibility with past VSS data that were collected using a 0°C calibration.

According to field sampling notes on the COC form, the TST sample S6058-A12.1023 sample line was disconnected at the 5/16 inch Tygon connection. It was unknown if the Tygon tubing came off before or after the tank gas was drawn through; therefore, the volume is considered suspect. This sample was not analyzed due to the sampling discrepancy. Additionally, it was noted that TST field blank sample S6058-A18.1027 was disconnected and not reconnected before being lowered into the tank. This field blank was analyzed and a discussion is provided on the results.

Table E.2. Positively Identified and Quantitated Target Analytes^(a) and Tentatively Identified Compounds and Estimated Concentrations^(b)
for Triple Sorbent Traps Collected from the Headspace of Tank S-101 on 6/6/96

Target Analytes ^(a)	CAS	MW	Ret Time	S6058-A11.1022 ^(c) ISVS			S6058-A13.1024 ^(c,d) ISVS			S6058-A14.1025 ^(c) ISVS			Mean and Standard Deviation			
				(mg/m ³)	(ppbv)	Flag	(mg/m ³)	(ppbv)	Flag	(mg/m ³)	(ppbv)	Flag	(mg/m ³)	St. Dev.	(ppbv)	St. Dev.
Dichlorodifluoromethane	75-71-8	121	7.8	0.004	0.81	U	0.022	4.2	J	0.030	5.5	J	0.026	e	4.8	e
Methanol	67-56-1	32	10.1	3.134	2191	Y	5.672	3965	E,Y	3.735	2611	E,Y	4.180	1.326	2922	927
Butane	106-97-8	58	10.7	0.090	35		0.089	34		0.078	30		0.086	0.007	33	2.7
Ethanol	64-17-5	46	12.5	0.314	153	Y	0.804	391	Y	0.336	163	Y	0.484	0.277	235	135
Acetonitrile	75-05-8	41	13.0	0.088	48		0.152	83		0.101	55		0.114	0.034	62	19
Acetone	67-64-1	58	13.6	0.846	326		1.013	391		0.827	319		0.895	0.103	345	40
Trichlorofluoromethane	75-69-4	137	14.1	0.190	31		0.776	127		0.193	32		0.386	0.337	63	55
Pentane	109-66-0	72	14.9	0.043	13		0.041	13		0.037	12		0.040	0.003	13	0.92
1,1-Dichloroethene	75-35-4	97	15.5	0.002	0.49	U	0.090	21		0.002	0.49	U	e	e	e	e
Methylene Chloride	75-09-2	85	15.7	0.042	11	J	1.051	277		0.061	16	J	0.384	0.577	101	152
112trichloro122trifluoroethane	76-13-1	187	16.3	0.005	0.64	J	0.031	3.7	J	0.005	0.55	J	0.014	0.015	1.6	1.8
Propanenitrile	107-12-0	55	17.0	0.012	5.1	J	0.015	6.1	J	0.013	5.2	J	0.013	0.001	5.5	0.57
Propanol	71-23-8	60	17.0	0.113	42		0.136	51		0.099	37		0.116	0.019	43	7.1
2-Butanone	78-93-3	72	18.6	0.147	46		0.191	59		0.141	44		0.160	0.027	50	8.5
Hexane	110-54-3	86	19.8	0.032	8.2		0.038	9.7		0.032	8.3		0.034	0.003	8.8	0.85
Tetrahydrofuran	109-99-9	72	20.7	0.153	47		0.158	49		0.153	48		0.155	0.003	48	0.94
Butanenitrile	109-74-0	69	21.8	0.020	6.6		0.024	7.9		0.016	5.1		0.020	0.004	6.6	1.4
1,1,1-Trichloroethane	71-55-6	133	21.9	0.003	0.46	U	0.014	2.4	J	0.003	0.46	U	e	e	e	e
1-Butanol	71-36-3	74	22.3	1.652	500		1.724	522		1.663	503		1.680	0.039	509	12
Benzene	71-43-2	78	22.7	0.021	6.2		0.025	7.0		0.021	6.0		0.022	0.002	6.4	0.57
Trichloroethene	79-01-6	131	24.7	0.004	0.63	U	0.025	4.3	J	0.004	0.63	U	e	e	e	e
Heptane	142-82-5	100	25.1	0.023	5.1		0.035	7.7		0.024	5.3		0.027	0.007	6.0	1.4
4-Methyl-2-Pentanone	108-10-1	100	26.3	0.033	7.5		0.033	7.4		0.031	7.0		0.033	0.001	7.3	0.23
Pyridine	110-86-1	79	26.5	0.064	18	J	0.052	15	J	0.046	13	J	0.054	0.009	15	2.6
Toluene	108-88-3	92	28.4	0.430	104		0.535	130		0.408	99		0.458	0.068	111	17
Octane	111-65-9	114	30.4	0.008	1.6	J	0.010	1.9	J	0.008	1.5	J	0.008	0.001	1.7	0.19
Tetrachloroethylene	127-18-4	166	31.0	0.003	0.35	U	0.003	0.36	U	0.003	0.46	J	e	e	e	e
Hexanenitrile	628-73-9	97	32.7	0.005	1.2	J	0.004	0.97	J	0.005	1.1	J	0.005	0.000	1.1	0.093
Ethylbenzene	100-41-4	106	33.4	0.008	1.7	J	0.011	2.2	J	0.008	1.8	J	0.009	0.001	1.9	0.29
p/m-Xylene	106-42-3	106	33.8	0.026	5.6	J	0.035	7.3		0.028	6.0	J	0.030	0.004	6.3	0.90
o-Xylene	95-47-6	106	35.0	0.012	2.5	J	0.016	3.3	J	0.013	2.7	J	0.013	0.002	2.8	0.39
1,2,4-Trimethylbenzene	95-63-6	120	39.9	0.003	0.60	J	0.004	0.68	J	0.003	0.48	U	0.003	e	0.64	e
Decane	124-18-5	142	40.1	0.014	2.2	J	0.019	2.9	J	0.018	2.8	J	0.017	0.003	2.6	0.41
Undecane	1120-21-4	156	44.4	0.013	1.9	J	0.018	2.5	J	0.018	2.6	J	0.016	0.003	2.3	0.38

E-7

Table E.2. Positively Identified and Quantitated Target Analytes^(a) and Tentatively Identified Compounds and Estimated Concentrations^(b) for Triple Sorbent Traps Collected from the Headspace of Tank S-101 on 6/6/96

Target Analytes ^(a)	CAS	MW	Ret Time	S6058-A11.1022 ^(c) ISVS			S6058-A13.1024 ^{(c)(d)} ISVS			S6058-A14.1025 ^(c) ISVS			Mean and Standard Deviation			
				(mg/m ³)	(ppbv)	Flag	(mg/m ³)	(ppbv)	Flag	(mg/m ³)	(ppbv)	Flag	(mg/m ³)	St. Dev. (ppbv)	St. Dev.	
Tridecane	629-50-5	184	52.2	0.055	6.7	U	0.057	7.0	U	0.110	13	J	e	e	e	e
Tetradecane	629-59-4	198	55.7	0.021	2.4	J	0.020	2.2	J	0.025	2.8	J	0.022	0.003	2.5	0.29
Tentatively Identified Compounds^(b)																
Ethane, 1-chloro-1,1-difluoro-	75-68-3	100	8.8	0.060	13	N	1.997	447	N	0.101	23	N	0.719	1.107	161	248
Acetaldehyde	75-07-0	44	9.5	0.035	18	N	0.058	30	N	0.072	37	N	0.055	0.019	28	9.7
1-Propene, 2-methyl-	115-11-7	56	10.4	0.044	18	N	0.080	32	N	0.065	26	N	0.063	0.018	25	7.0
Propane, 2,2-dimethyl-	463-82-1	72	11.2	0.019	5.9	N	0.022	6.9	N	0.023	7.2	N	0.021	0.002	6.7	0.66
Isopropyl Alcohol	67-63-0	60	14.2	0.103	39	N	0.212	79	N	0.116	43	N	0.144	0.060	54	22
1-Fluoro-1,1-dichloro-ethane	0-00-0	116	14.4	0.019	3.7	N	2.744	530	N	0.049	9.5	N	0.937	1.564	181	302
N-Nitrosodimethylamine	62-75-9	74	25.4	0.094	28	N	0.104	32	N	0.103	31	N	0.101	0.006	30	1.7
Pyrazine	290-37-9	80	25.7	0.160	45	N	0.173	48	N	0.170	48	N	0.168	0.007	47	1.8
Cyclotrisiloxane, hexamethyl-	541-05-9	222	31.1	0.203	20	N	0.224	23	N	0.277	28	N	0.235	0.038	24	3.9
Heptane, 2,4-dimethyl-	2213-23-2	128	31.7	0.112	20	N	0.141	25	N	0.145	25	N	0.132	0.018	23	3.2
Cyclotetrasiloxane, octamethyl-	556-67-2	296	39.4	0.482	36	N	0.557	42	N	0.797	60	N	0.612	0.164	46	12
Unknown C10 Alkane		142	42.9	0.335	53	N	0.429	68	N	0.454	72	N	0.406	0.063	64	10
Unknown C10 Alkane		142	43.1	nd	nd		0.189	30	N	0.221	35	N	0.205	e	33	e

Data Quality Flags

E Target compound exceeds upper quantification limit (UQL).

J Target compound detected above the IDL but below the EQL.

N Denotes tentatively identified compound

U Target compound not detected at or above the IDL.

Y Initial calibration was performed; however, a CCV was not performed. Concentration is considered an estimate.

Footnotes

(a) Detected target analytes.

(b) Semi-quantitative estimate calculated using concentration of closest eluting IS.

(c) WHC sample identification number.

(d) Replicates of this sample are found in Table D.3.

(e) Mean and/or standard deviation are not meaningful for this analyte.

nd Not detected

Table E.3. Positively Identified and Quantitated Target Analytes^(a) and Tentatively Identified Compounds and Estimated Concentrations^(b) of Replicate Analysis of a Single Triple Sorbent Trap Collected from the Headspace of Tank S-101 on 6/6/96

Target Analytes ^(a)	CAS	MW	Ret Time	S6058-A13.1024 ^(c) ISVS						Relative Perce
				(mg/m ³)	(ppbv)	Flag	(mg/m ³)	(ppbv)	Flag	Difference ^(d)
									%	
Dichlorodifluoromethane	75-71-8	121	7.8	0.022	4.2	J	0.005	0.84	U	
Methanol	67-56-1	32	10.1	5.672	3965	E,Y	6.781	4741	E,Y	18
Butane	106-97-8	58	10.7	0.089	34		0.123	47		32
Ethanol	64-17-5	46	12.5	0.804	391	Y	1.077	523	Y	29
Acetonitrile	75-05-8	41	13.0	0.152	83		0.157	86		3
Acetone	67-64-1	58	13.6	1.013	391		0.919	355		10
Trichlorofluoromethane	75-69-4	137	14.1	0.776	127		0.768	125		1
Pentane	109-66-0	72	14.9	0.041	13		0.040	12		1
1,1-Dichloroethene	75-35-4	97	15.5	0.090	21		0.085	20		5
Methylene Chloride	75-09-2	85	15.7	1.051	277		1.025	270		2
112trichloro122trifluoroethane	76-13-1	187	16.3	0.031	3.7	J	0.030	3.6	J	3
Propanenitrile	107-12-0	55	17.0	0.015	6.1	J	0.015	5.9	J	3
Propanol	71-23-8	60	17.0	0.136	51		0.127	47		7
2-Butanone	78-93-3	72	18.6	0.191	59		0.180	56		6
Hexane	110-54-3	86	19.8	0.038	9.7		0.037	9.6		2
Tetrahydrofuran	109-99-9	72	20.7	0.158	49		0.155	48		2
Butanenitrile	109-74-0	69	21.8	0.024	7.9		0.034	11		34
1,1,1-Trichloroethane	71-55-6	133	21.9	0.014	2.4	J	0.013	2.2	J	9
1-Butanol	71-36-3	74	22.3	1.724	522		1.490	451		15
Benzene	71-43-2	78	22.7	0.025	7.0		0.025	7.1		0
Trichloroethene	79-01-6	131	24.7	0.025	4.3	J	0.025	4.3	J	2
Heptane	142-82-5	100	25.1	0.035	7.7		0.033	7.5		3
4-Methyl-2-Pentanone	108-10-1	100	26.3	0.033	7.4		0.030	6.7		9
Pyridine	110-86-1	79	26.5	0.052	15	J	0.048	14	J	7
Toluene	108-88-3	92	28.4	0.535	130		0.537	131		0
Octane	111-65-9	114	30.4	0.010	1.9	J	0.009	1.7	J	10
Hexanenitrile	628-73-9	97	32.7	0.004	0.97	J	0.003	0.70	U	
Ethylbenzene	100-41-4	106	33.4	0.011	2.2	J	0.011	2.2	J	0
p/m-Xylene	106-42-3	106	33.8	0.035	7.3		0.033	7.0		4
o-Xylene	95-47-6	106	35.0	0.016	3.3	J	0.015	3.2	J	3
1,2,4-Trimethylbenzene	95-63-6	120	39.9	0.004	0.68	J	0.004	0.66	J	6
Decane	124-18-5	142	40.1	0.019	2.9	J	0.018	2.9	J	3
Undecane	1120-21-4	156	44.4	0.018	2.5	J	0.015	2.1	J	19
Tetradecane	629-59-4	198	55.7	0.020	2.2	J	0.021	2.3	J	4
Tentatively Identified Compounds^(b)										
Ethane, 1-chloro-1,1-difluoro-	75-68-3	100	8.8	1.997	447	N	1.929	432	N	3
Acetaldehyde	75-07-0	44	9.5	0.058	30	N	0.050	26	N	15
1-Propene, 2-methyl-	115-11-7	56	10.4	0.080	32	N	0.073	29	N	8
Propane, 2,2-dimethyl-	463-82-1	72	11.2	0.022	6.9	N	0.023	7.1	N	3
Isopropyl Alcohol	67-63-0	60	14.2	0.212	79	N	0.213	80	N	0
1-Fluoro-1,1-dichloro-ethane	0-00-0	116	14.4	2.744	530	N	2.810	543	N	2
N-Nitrosodimethylamine	62-75-9	74	25.4	0.104	32	N	0.104	31	N	0
Pyrazine	290-37-9	80	25.7	0.173	48	N	0.168	47	N	3
Cyclotrisiloxane, hexamethyl-	541-05-9	222	31.1	0.224	23	N	0.217	22	N	3

Table E.3. Positively Identified and Quantitated Target Analytes^(a) and Tentatively Identified Compounds and Estimated Concentrations^(b) of Replicate Analysis of a Single Triple Sorbent Trap Collected from the Headspace of Tank S-101 on 6/6/96

Tentatively Identified Compounds ^(b)	CAS	MW	Ret Time	S6058-A13.1024 ^(c) ISVS						Relative Percent Difference ^(d)
				(mg/m ³)	(ppbv)	Flag	(mg/m ³)	(ppbv)	Flag	%
Heptane, 2,4-dimethyl-	2213-23-2	128	31.7	0.141	25	N	0.141	25	N	0
Cyclotetrasiloxane, octamethyl-	556-67-2	296	39.4	0.557	42	N	0.542	41	N	3
Unknown C10 Alkane		142	42.9	0.429	68	N	0.431	68	N	0
Unknown C10 Alkane		142	43.1	0.189	30	N	0.205	32	N	8

Data Quality Flags

E Target compound exceeds upper quantification limit (UQL).

J Target compound detected above the IDL but below the EQL.

N Denotes tentatively identified compound

U Target compound not detected at or above the IDL.

Y Initial calibration was performed; however, a CCV was not performed. Concentration is considered an estimate.

Footnotes

(a) Detected target analytes.

(b) Semi-quantitative estimate calculated using concentration of closest eluting IS.

(c) WHC sample identification number.

(d) Relative percent differences (RPDs) based on mg/m³ values.

nd Not detected

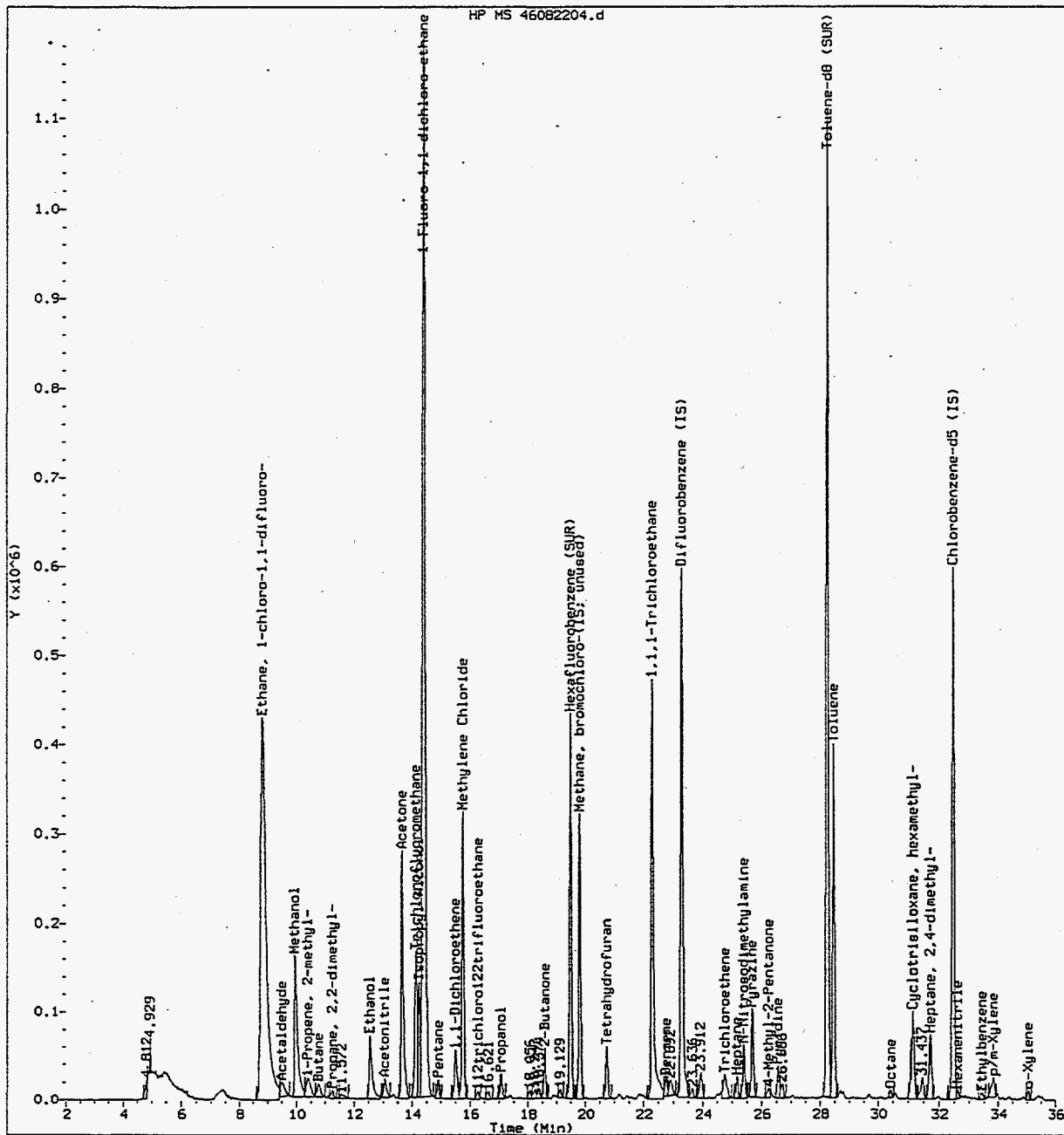


Figure E.1a Total Ion Chromatogram (2 - 36 min) for Hanford Waste Tank S-101 Triple Sorbent Trap Sample S6058-A13-1024 Collected on 6/6/96

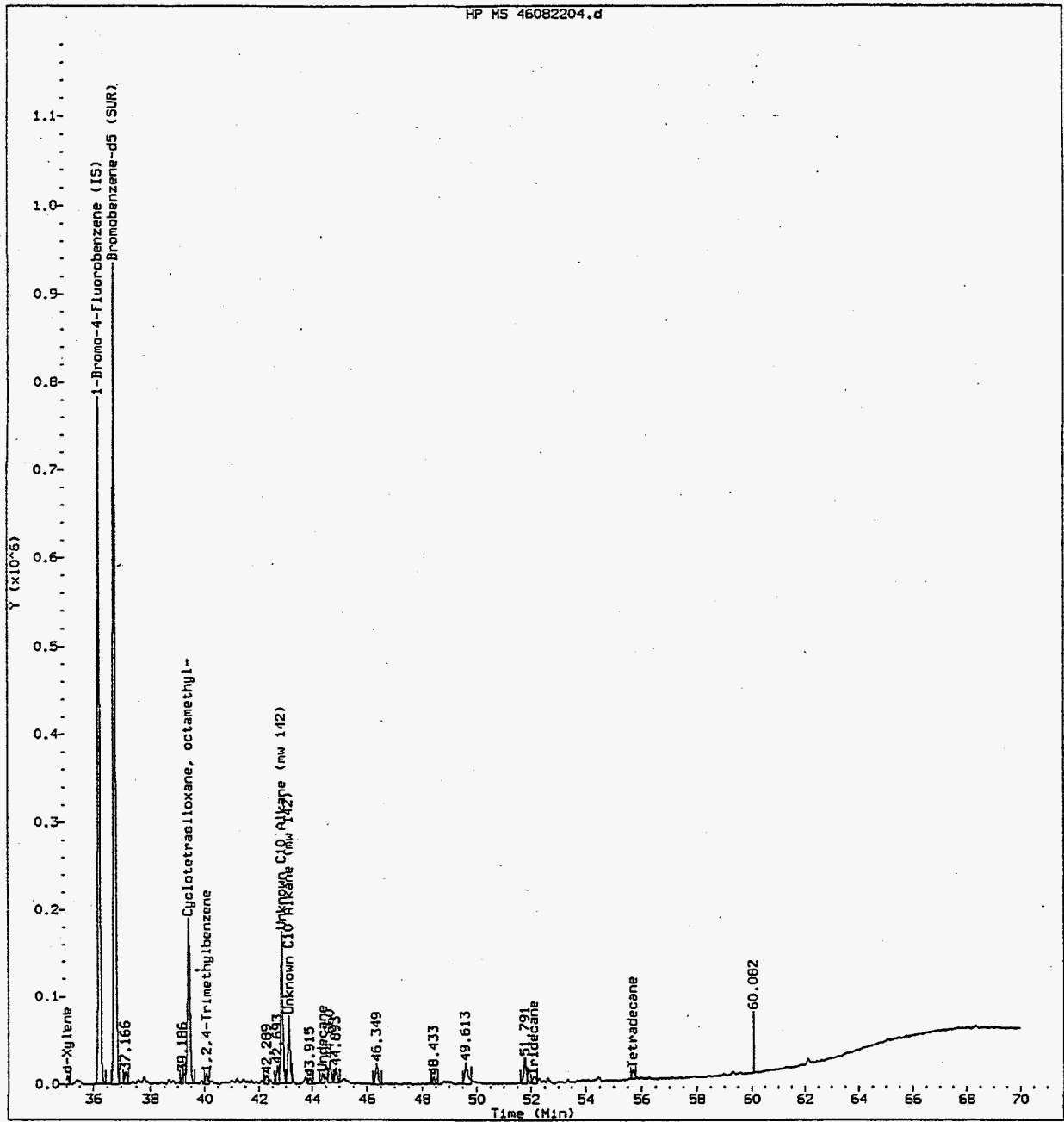


Figure E.1b Total Ion Chromatogram (36 - 70 min) for Hanford Waste Tank S-101 Triple Sorbent Trap Sample S6058-A13-1024 Collected on 6/6/96

Appendix F

Tank Vapor Characterization:

Chain of Custody Sample Control Forms

Custody Form Initiator J. A. Edwards - PNNL Telephone (509) 373-0141
Page 85-3009 / FAX 376-2329

Company Contact R. D. Mahon - WHC Telephone (509) 373-7437
Page 85-9656 / FAX 373-3793

Project Designation/Sampling Locations 200 West Tank Farm Collection date 06 - 06 - 96
241-S-101 Tank Vapor Sample SAF S6058 Preparation date 05 - 30 - 96
(ISVS Cart)

Ice Chest No. Field Logbook No. WHC-N-647-8

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

Method of Shipment Government Truck

Shipped to PNNL

Possible Sample Hazards/Remarks Unknown at time of sampling

Sample Identification

S6058 - A07 . S85- Collect NH₃/NO_x/H₂O Sorbent Trap
S6058 - A08 . S86- Collect NH₃/NO_x/H₂O Sorbent Trap
S6058 - A09 . S87, Collect NH₃/NO_x/H₂O Sorbent Trap
S6058 - A10 . S88 Collect NH₃/NO_x/H₂O Sorbent Trap

S6058 - A15 . S89 Open, close and store NH₃/NO_x/H₂O field blank #1
S6058 - A16 . S90 Open, close and store NH₃/NO_x/H₂O field blank #2

[] Field Transfer of Custody		[X] Chain of Possession		(Sign and Print Names)		
Relinquished By	Date	Time	Received By	Date	Time	
G W Dennis <i>G.W. Dennis</i>	05-31-96	1100	J A Edwards <i>J A Edwards</i>	05-31-96	1100	
J A Edwards <i>J A Edwards</i>	6-3-96	1255	C M McClellan <i>C M McClellan</i>	6-07-96	1255	
C M McClellan <i>C M McClellan</i>	6-12-96	1146	GS CAPRIO <i>GS CAPRIO</i>	6-12-96	1146	
GS CAPRIO <i>GS CAPRIO</i>	6-12-96	1230	J A EDWARDS <i>J A EDWARDS</i>	6-12-96	1230	
J A EDWARDS <i>J A EDWARDS</i>	6-13-96	1335	G.W. Dennis <i>G.W. Dennis</i>	6-13-96	1335	
G.W. Dennis <i>G.W. Dennis</i>	6-18-96	1215	K.H. Pool <i>K.H. Pool</i>	6-18-96	1215	

Final Sample Disposition

Comments:

- PNNL (only) Checklist
- ◇ Media labeled and checked? Y N
 - ◇ Letter of instruction? Y N
 - ◇ Media in good condition? Y N
 - ◇ COC info/signatures complete? Y N
 - ◇ Rad release stickers on samples? Y N
 - ◇ Activity report from 222S? Y N
 - ◇ RSR/release? (a ≤100/B ≤400 pCi/g) Y N
 - ◇ COC copy for LRB, RIDS filed? Y N

Comments:

S6058-A16, S90 → NH₃ Field Blank was disconnected at 5/16" TYGON to Silica Gel. Because this was a field blank it was not reconnected before being lowered into the tank.
6/12/96 JAC

POC POC

Custody Form Initiator J. A. Edwards - PNNL

Telephone (509) 373-0141
Page 85-3009 / FAX 376-2329

Company Contact R. D. Mahon - WHC

Telephone (509) 373-2891
Page 85-3656 / FAX 373-3793

Project Designation/Sampling Locations 200 West Tank Farm
241-S-101 Tank Vapor Sample SAF S6058
(ISVS Cart)

Collection date 06 - 06 - 96
Preparation date 05 - 30 - 96

Ice Chest No.

Field Logbook No. WHC-147-8

Bill of Lading/Airbill No. N/A

Offsite Property No. N/A

Method of Shipment Government Truck

Shipped to PNNL

Possible Sample Hazards/Remarks Unknown at time of sampling

Sample Identification

S6058 - A01 . 308 Collect Ambient Air Sample SUMMA #1
S6058 - A02 . 309 Collect Ambient Air Sample SUMMA #2 (through tube bundle)

S6058 - A04 . 310 Collect SUMMA #3
S6058 - A05 . 311 Collect SUMMA #4
S6058 - A06 . 312 Collect SUMMA #5

[] Field Transfer of Custody		[X] Chain of Possession		(Sign and Print Names)	
Relinquished By	Date	Time	Received By	Date	Time
J A Edwards <i>J Edwards</i>	06-03-96	1255	CSM McCall <i>CSM McCall</i>	06-03-96	1255
<i>CSM McCall</i>	6-12-96	1146	GS Caprio <i>GS Caprio</i>	6-12-96	1146
GS Caprio <i>GS Caprio</i>	6-12-96	1230	J A Edwards <i>J A Edwards</i>	6-12-96	1230

Final Sample Disposition

Comments:

- PNNL (only) Checklist
- ◇ Media labeled and checked? Y/N
 - ◇ Letter of instruction? Y/N
 - ◇ Media in good condition? Y/N
 - ◇ COC info/signatures complete? Y/N
 - ◇ Rad release stickers on samples? Y/N
 - ◇ Activity report from 222S? Y/N
 - ◇ RSR/release? (a ≤100/B ≤400 pCi/g) Y/N
 - ◇ COC copy for LRB, RIDS filed? Y/N

POC *[Signature]*

POC *[Signature]*

Comments:

S6058-A02.309 Summa line was not connected to ISVS when this sample was collected. This sample collected air drawn in through the Summa port on the cart

S6058-A04.310 Tank Gas Summa was used for ambient air through the Summa line to make up for Summa 309 mistake
(Revised 05/30/96 PNNL)

JLX 6/12/96

(WHC-SD-WM-TP-335, REV. 2, Table 2b)

Custody Form Initiator J. A. Edwards - PNL

Telephone (509) 373-0141
Page 85-3009 / P8-08 / FAX 376-0418

Company Contact R. D. Mahon - WHC

Telephone (509) 373-7437
Page 85-9656 / S3-27 / FAX 373-7076

Project Designation/Sampling Locations 200 West Tank Farm
241-S-101 Tank Vapor Sample SAF S6058
(ISVS Cart)

Collection date 06-06-96
Preparation date 06-03-96

Ice Chest No.

Field Logbook No. WHC-N-647-8

Ertco Hi/Lo thermometer No. PNL-T-006

Bill of Lading/Airbill No. N/A

Offsite Property No. N/A

Method of Shipment Government Truck

Shipped to WHC-

Possible Sample Hazards/Remarks Unknown at time of sampling

Sample Identification

S6058 - A11 . 1022 .	PNL Triple Sorbent Trap (TST) Sample # 1
S6058 - A12 . 1023 .	PNL TST Sample # 2
S6058 - A13 . 1024 .	PNL TST Sample # 3
S6058 - A14 . 1025 .	PNL TST Sample # 4
S6058 - A17 . 1026 .	Open, close & store TST Field Blank # 1
S6058 - A18 . 1027 .	Open, close & store TST Field Blank # 2
S6058 - A19 . 1029 .	Store TST Trip Blank #1
S6058 - A20 . 1030 .	Store TST Trip Blank #2

[] Field Transfer of Custody		[X] Chain of Possession		(Sign and Print Names)		
Relinquished By	Date	Time	Received By	Date	Time	
JL Julia	06-04-96	1230	JA Edwards	06-04-96	1230	
JA Edwards	06-04-96	1255	CS McCellan	06-03-96	1255	
CS McCellan	06-12-96	1146	GS Caprio	06-12-96	1146	
GS Caprio	06-12-96	1230	JA Edwards	06-12-96	1230	
JA Edwards	06-17-96	1012	JL Julia	06-17-96	1012	

Final Sample Disposition

Comments:

PNL (only) Checklist		Pick-up / Delivery	
Media labeled and checked?	<input checked="" type="checkbox"/> Y <input type="checkbox"/> N	<input checked="" type="checkbox"/> Y <input type="checkbox"/> N	
Letter of instruction?	<input checked="" type="checkbox"/> Y <input type="checkbox"/> N	<input checked="" type="checkbox"/> Y <input type="checkbox"/> N	
Media in good condition?	<input checked="" type="checkbox"/> Y <input type="checkbox"/> N	<input checked="" type="checkbox"/> Y <input type="checkbox"/> N	
COC info/signatures complete?	<input checked="" type="checkbox"/> Y <input type="checkbox"/> N	<input checked="" type="checkbox"/> Y <input type="checkbox"/> N	
Sorbents shipped on ice? (<5°C)	<input checked="" type="checkbox"/> Y <input type="checkbox"/> N	<input checked="" type="checkbox"/> Y <input type="checkbox"/> N	
Hi/Lo thermometer - <u>Keep upright!</u>	<input checked="" type="checkbox"/> Y <input type="checkbox"/> N	<input checked="" type="checkbox"/> Y <input type="checkbox"/> N	
Hi/Lo thermometer	<input type="checkbox"/> Y <input type="checkbox"/> N	<input checked="" type="checkbox"/> Y <input type="checkbox"/> N	
Rad release stickers on samples?	<input type="checkbox"/> Y <input type="checkbox"/> N	<input checked="" type="checkbox"/> Y <input type="checkbox"/> N	
Activity report from 222S?	<input type="checkbox"/> Y <input type="checkbox"/> N	<input checked="" type="checkbox"/> Y <input type="checkbox"/> N	
COC copy for LRB, RIDS filed?	<input type="checkbox"/> Y <input type="checkbox"/> N	<input checked="" type="checkbox"/> Y <input type="checkbox"/> N	

Comments:

S6058-A12.1023 → TST sample line was disconnected at 5/16" tygon connection to silica gel. It is unknown if the tygon came off before or after tank gas was drawn through it. Volume is suspect.

1. Cooler Temperature Status
 | Hi -20°C / Lo -20°C (pick up at PNL to WHC) |
 | Hi ___°C / Lo ___°C (delivery at WHC from PNL) |
 | Hi 10°C / Lo 10°C (at return to PNL from WHC) |
 | Hi +13°C / Lo -21°C (at delivery from WHC to PNL) |

S6058-A18.1027 → TST Field blank was disconnected at 5/16" TYGON to silica gel. (Revised 06/21/95 PNL) Because this was a field blank, it was not reconnected before being lowered into tank.

POC (Signature)

6/12/96 JJK

Distribution List

PNNL-11258

PNNL

Karl Pool	P8-08
Berta Thomas	P8-08
John Evans	K6-96
Khris Olsen	K6-96
Kurt Silvers	K9-08
Jon Fruchter	K6-96
Jim Huckaby	K6-80
Brenda Thornton	K6-80
Darlene Varley	K1-06
Katherine Savard	K9-04
Kris Walters	K6-80 (5 copies)

Lockheed

Larry Pennington	S7-21
Luther Buckley	R2-12

DOE-RL

Carol Babel	S7-54
Jim Thompson	S7-54