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TANK VAPOR CHARACTERIZATION PROJECT

Headspace Vapor Characterization of Hanford Waste Tank 241-S-103: Results from Samples Collected on 6/12/96

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DISCLAIMER

Summary

This report describes the analytical results of vapor samples taken from the headspace of the waste storage tank 241-S-103 (Tank S-103) 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-103 on 6/12/96

Category	Sample Medium	Analyte	Vapor[(a)] Concentration	Units
Inorganic Analytes[(b)]	Sorbent Traps	NH_3	150 ± 4	ppmv
		NO_2	< 0.16	ppmv
		NO	< 0.16	ppmv
		H_2O	11.2 ± 0.2	mg/L
Permanent Gases	SUMMA™ Canister	H_2	79	ppmv
		CH_4	<50	ppmv
		CO_2	<34	ppmv
		CO	<34	ppmv
		N_2O	136	ppmv
Total Non-Methane Organic Compounds (TO-12)	SUMMA™ Canister	Non-Methane Organic Compounds	1.25	mg/m^3
Volatile Organics (TO-14)	SUMMA™ Canister	Methanol	2.112	ppmv
		Ethanol	0.574	ppmv
		Acetone	0.114	ppmv
Semi-Volatile Organics (PNL-TVP-10)	Sorbent Traps	Methanol	0.807	ppmv
		Toluene	0.282	ppmv
		3-Methyl-Hexane	0.163 N	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).

N Tentatively identified compound.

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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-103 (Tank S-103) 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 S6060. Samples were collected by WHC on June 12, 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), five SUMMA™ canisters for permanent gases and volatile organic analytes (three samples and two ambient canisters), and eight triple sorbent traps (TSTs) for semi-volatile organic analytes (four samples, two field blanks, and two trip blanks). The samples and controls were provided to WHC on June 10, 1996. Exposed samples and controls were returned to PNNL on June 18, 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)
- *volatile organic analytes* analyses using cryogenic preconcentration followed by gas chromatograph/mass spectrometer (GC/MS)

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[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.

- *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 S-103 on June 12, 1996 (Sample Job S6060) 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 150 ± 4 ppmv (NH_3), < 0.16 ppmv (NO_2), < 0.16 ppmv (NO), and 11.2 ± 0.2 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 ± 10% (assuming negligible error in the sample volume measurements) and are within the ± 30% specified by the SAP. Measurement precision, as indicated by the relative standard deviation, was 5% 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 chain-of-custody form used to control samples, 100092, is included in Appendix F.

2.2 Permanent Gases

The complete results of the permanent gas analysis of Tank S-103 can be found in Appendix B. In summary, hydrogen at 79 ppmv and nitrous oxide at 136 ppmv were the only permanent gases observed in the tank headspace samples.

2.3 Total Non-Methane Organic Compounds

The complete results of the TO-12 analysis of Tank S-103 can be found in Appendix C. In summary, the average concentration in the three tank headspace was 1.25 mg/m^3. This compares to 6.92 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-103 can be found in Appendix D. In summary, 64 target analytes and 30 TICs were detected in the tank headspace samples. Sixty-three target analytes and 15 TICs were identified in two or more tank headspace samples. Twelve TICs were not identified and were labelled as unknowns. Methanol at 3.02 mg/m^3 and ethanol at 1.18 mg/m^3 accounted for 61% of the compounds identified in the analysis. The total concentration of the target analytes was 6.57 mg/m^3. Methyl cyclohexane (0.06 mg/m^3) and pyrazine (0.04 mg/m^3), the two highest concentration TICs, accounted for 30% of the TICs and 1.5% of the total compounds identified in the analysis. The total concentration of the TICs was 0.35 mg/m^3. The total concentration of all the compounds identified was 6.92 mg/m^3. This compares to a total concentration of 1.25 mg/m^3 identified in the TO-12 analysis of the three tank headspace samples.

SUMMA™ canister PNL 082 was analyzed in replicate for target analytes and TICs to determine analytical precision. Twenty-four of 63 target compounds and one of 11 TICs had RPDs of less than 10%.

Sixty-three target compounds and 18 TICS were observed in one or both of the ambient air samples. Many of the compounds were identified at trace levels (below EQL). Several noted exceptions included: methanol, acetone, propanol, 2-butanone, butanenitrile, 1-butanol, cyclohexane, butane, pentanenitrile, 1,1,2-trichloro-1,2,2-trifluoromethane, 4-methyl-2-pentanone, and cyclohexanone. 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-103 can be found in Appendix E. In summary, 39 target analytes above the IDL and 28 TICs were detected in the tank headspace samples. Thirty-six of the target analytes and 13 TICs were observed in two or more sorbent traps. Methanol at 1.15 mg/m^3 and toluene at 1.16 mg/m^3 accounted for 44% of the target analytes and 28% of the total concentration identified by the analyses. The total concentration of the target analytes was 5.20 mg/m^3 or 64% of the total concentration identified by the analyses. The predominant TICs observed in these samples were 3-methyl hexane at 0.73 mg/m^3 and 2-methyl hexane at 0.42 mg/m^3. The total concentration of the TICs was 2.96 mg/m^3 or 36% of the total concentration identified by the analysis. The total concentration of all the compounds identified was 8.16 mg/m^3.

Triple sorbent trap sample PNL 987 was analyzed in replicate for target analytes and TICs to determine analytical precision. Twenty-seven of 36 target compounds and 13 of 14 TICs had RPDs of less than 10%.

Review of the TST data found the field blanks badly contaminated with a group of compounds characteristic of the 3M adhesive tape used on previous ISVS jobs. The special handling associated with preventing radiological contamination of the sample bundle from the riser appears to have severely exacerbated the tape problem which had not in any case been completely eliminated. Because of the tape problem, TST tank results from this sampling activity should be generally considered as suspect.

3.0 Conclusions

The concentrations of inorganic and organic analytes were determined from samples of the headspace of Tank S-103 on April 12, 1996 (Sample Job S6060). 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 $[(NH_4)_2SO_4]$. 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 NH_3 equals

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

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-μg/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

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[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 ± 5% relative, independent of concentration at 1 μg/mL or greater levels. The uncertainty includes preparation of standards, purity of the ammonium salt used to prepare standards, potential operator bias, ambient temperature variations, etc. 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 ± 10%, and for samples derived from sampling for NO it is ± 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	0.16	≥ 10
Nitric oxide	NO	PNL-ALO-212	0.3	0.16	≥ 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 ± 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-103 on June 12, 1996 using the ISVS. The sample job designation number was S6060. Samples were prepared, submitted to WHC for the sample job, and then returned to PNNL and analyzed to provide information on the concentrations of NH_3, NO_2, NO, and mass (primarily H_2O). Samples were controlled using COC form 100092 (Appendix F). The inorganic samples and sample volume information were received from WHC on June 18, 1996. Analyses were completed on June 20, 1996 (gravimetric, 8 days elapsed), June 25, 1996 (ammonia, 13 days elapsed), and June 25, 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 $NH_3/NO_x/H_2O$ contained an NH_3 trap at the inlet end, an 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 150 ± 4 ppmv, based on all four samples. The blank-corrected NH_3 quantities in the sorbent traps ranged from 12.2 to 12.7 μmol in front sections; blank-corrected NH_3 was not found ($\leq$ 0.01 μmol) in back sorbent sections. Blank corrections, 0.37 μmol in front and 0.07 μmol in back sections, were about 3% of collected quantities. The analysis of one sample was duplicated and yielded a repeatability of ±3.5%. One blank sorbent trap was spiked with 17 μmol of NH_3 and yielded a percentage recovery of 104%. One sample leachate was spiked after initial analysis with roughly the quantity of ammonia in the sample and yielded a percentage recovery of 94%. The initial calibration verification (ICV) and continuing calibration verification (CCV) standards, using NIST-traceable material, yielded percentage recoveries of 98% (ICV) and 96, 100 and 100% (CCV) during the analytical session. A 5-point calibration was performed over an NH_3 range of 0.1 to 1000 μg/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 < 0.013 μmol. Nitrite blank levels used to correct data were 0.0070 μmol in front (four of four blanks analyzed) and 0.0041 μmol in back (two of four blanks analyzed) sorbent sections. The analyses of two samples were duplicated and yielded repeatabilities of ± 0% and ± 1.0%. Two sample leachates were spiked with 0.25 ppm NO_2^- and yielded percentage recoveries of 101 and 108%. A 4-point calibration was performed over a concentration range of 0 to 0.5 μg 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 μmol NO_2^- during previous sample jobs yielded percentage recoveries of 153 ± 14, 103 ± 4, 106 ± 8, and 111 ± 7%, respectively (Clauss et al. 1994; Ligotke 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 μg/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 11.2 ± 0.2 mg/L, based on dry air sample volumes (0°C and 760 torr). The result was determined from an average mass gain of 22.3 mg from all four sample trains. The blank correction applied to the results was - 1.35 mg per train, based on a mass gain of 1.35 ± 0.8 mg per two 5-trap field-blank sorbent trains. A control mass was measured and indicated a measurement accuracy of ± 0.1 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 ± 2% during a previous sample job (Clauss et al. 1994).

Corrected for a measured tank headspace temperature of 22.6°C and pressure of 743.7 torr, the actual water vapor mass concentration from the gravimetric results was 10.0 ± 0.2 mg/L. Also based on analytical results, the partial pressure of water vapor was 10.2 ± 0.2 torr, the relative humidity was 50 ± 1%, and the dew point was 11.5 ± 0.2°C.

Table A.2 List of PNNL Inorganic Samples, Controls, and Gravimetric Results Obtained from the Headspace of Tank S-103 on 6/12/96

		Sample Port and Volume Information[a]				
Sample Number	Sorbent Train Type	Sample Port	Flow Rate (mL/min)	Duration (min)	Volume (L)	Mass Gain (g)
Samples:						
S6060-A07-S91	NH3/NOx/H2O	1	200.0	10.0	1.86	0.0221
S6060-A08-S92	NH3/NOx/H2O	2	200.0	10.0	1.86	0.0217
S6060-A09-S93	NH3/NOx/H2O	3	200.0	10.0	1.86	0.0227
S6060-A10-S94	NH3/H2O/H2O	4	200.0	10.0	1.86	0.0225
Controls:						
S6060-A15-S95	NH3/NOx/H2O Field Blank	n/a[b]	n/a	n/a	n/a	0.0008
S6060-A16-S96	NH3/NOx/H2O Field Blank	n/a	n/a	n/a	n/a	0.0019

(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-103 on 6/12/96

	Analytical Results (µmol)			Sample	Vapor[a]
Sample	Front Section	Back Section	Total[b] Blank-Corrected	Volume (L)	Concentration (ppmv)
NH_3 Samples:			12.5	1.86	150 ± 4
S6060-A07-S91	12.6	0.058	12.2	1.86	147
S6060-A08-S92	13.1	NA[c]	12.7	1.86	153
S6060-A09-S93	13.1	0.076	12.7	1.86	153
S6060-A10-S94	12.6	NA	12.2	1.86	147
NO_2 Samples:			<0.013	1.86	<0.16
S6060-A07-S91	0.0101	NA	<0.013	1.86	<0.16
S6060-A08-S92	0.0101	0.0059	<0.013	1.86	<0.16
S6060-A09-S93	0.0069	NA	<0.013	1.86	<0.16
S6060-A10-S94	0.0069	0.0041	<0.013	1.86	<0.16
NO Samples:			<0.013	1.86	<0.16
S6060-A07-S91	0.0111	0.0055	<0.013	1.86	<0.16
S6060-A08-S92	0.0113	NA	<0.013	1.86	<0.16
S6060-A09-S93	0.0074	0.0042	<0.013	1.86	<0.16
S6060-A10-S94	0.0066	NA	<0.013	1.86	<0.16
Gravimetric Samples:			20.9 mg	1.86	11.2 ± 0.2 mg/L
S6060-A07-S91	n/a[c]	n/a	20.8	1.86	11.2
S6060-A08-S92	n/a	n/a	20.4	1.86	10.9
S6060-A09-S93	n/a	n/a	21.4	1.86	11.5
S6060-A10-S94	n/a	n/a	21.2	1.86	11.4

(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 NO_2 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. Ligotke, B. D. McVeety, K. H. Pool, R. B. Lucke, J. S. Fruchter, and S. C. Goheen. 1994. *Vapor Space Characterization of Waste Tank 241-BY-104: Results from Samples Collected on 6/24/94.* PNL-10208. Pacific Northwest National Laboratory, Richland, Washington.

Ligotke, M. W., K. H. Pool, and B. D. Lerner. 1994. *Vapor Space Characterization of Waste Tank 241-C-103: Inorganic Results from Sample Job 7B (5/12/94 - 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 (H_2), carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), and nitrous oxide (N_2O), 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, CO_2, N_2O, and CH_4 using Helium (He) as the carrier gas. A second GC analysis is performed for H_2 (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.

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

Analyte	Formula	Procedure	Estimated Quantitation Limit (ppmv)
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_2O	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 CH_4 over a range of 25 to 2100 parts per million by volume (ppmv) and for CO, CO_2, and N_2O 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 H_2 with a range of 17 to 2120 ppmv, except the carrier gas was changed to N_2. 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 ± 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 N_2 reagent blank, an ambient-air sample collected ~10 m upwind of Tank S-103 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-103, ambient air collected ~10 m upwind of the tank, and ambient air collected through the ISVS. Samples were analyzed on June 25 and July 3, 1996. Hydrogen and nitrous oxide were observed in the tank headspace at an average value of 79 ppmv and 136 ppmv, respectively. A replicate analysis was performed on SUMMA™ PNL 082; however, only the results from the first analysis are included in the average concentration reported for the tank headspace samples.

The original permanent gas analyses were performed on Tank S-103 canisters prior to the 2X dilution using clean air. The continuing calibration blank for hydrogen for the original analyses (56062501.b) was above the low level standard concentration used in the initial calibration. In addition, the carbon dioxide concentration data derived from the original analyses were erratic. A leaking gas tight syringe was the suspected cause. Because of these analytical problems, the diluted canisters were reanalyzed for all fixed gases (hydrogen, carbon dioxide, nitrous oxide, methane, and carbon monoxide). The dilution required reporting detection limits at two times the low level standard concentration (34 ppmv for hydrogen, carbon dioxide, nitrous oxide, and carbon monoxide and 50 ppmv for methane). The QC samples (blanks and continuing calibration checks) for all analyses were within acceptance criteria.

Table B.2 Permanent Gas Analysis Results for Samples Collected from the Headspace of Tank S-103 and for Ambient Air and Ambient Air Through the ISVS Collected near Tank S-103 in SUMMA (TM) Canisters on 6/12/96

			Tank Samples				
Permanent Gas Analyte	Ambient Air Upwind S6060-A01.001[a] PNL 001[b] Concentration (ppmv)	Ambient Air Through Bundle S6060-A02.010[a] PNL 010[b] Concentration (ppmv)	S6060-A04.080[a] PNL 080[b] Concentration (ppmv)	S6060-A05.082[a] PNL 082[b] Concentration (ppmv)	S6060-A06.083[a] PNL083 [b] Concentration (ppmv)	S6060-A05.082[a] PNL 082 [b][c] Concentration (ppmv)	Average Concentration Tank Samples (ppmv)
Hydrogen	<34	<34	81	78	79	78	79
Methane	<50	<50	<50	<50	<50	<50	<50
Carbon Dioxide	360	360	<34	<34	<34	<34	<34
Carbon Monoxide	<34	<34	<34	<34	<34	<34	<34
Nitrous Oxide	<34	<34	134	135	139	137	136

Footnotes

(a) WHC sample identification number.

(b) PNL canister number.

(c) Replicate analysis for PNL 082; results are not included in the calculation of average concentrations.

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/m^3 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.

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[a] Pacific Northwest Laboratory. 8/94. *Cleaning SUMMA™ Canisters and the Validation of the Cleaning Process*, PNL-TVP-02 (Rev. 0), PNL Technical Procedure, 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/m^3 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/m^3 was derived from the five-point multilevel calibration curve from the propane standard using the following equation:

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

The ng/m^3 concentrations are calculated from mg/m^3 using the equation:

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

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-103, ambient air collected ~10 m upwind of the tank, and ambient air collected through the ISVS. Samples were analyzed on August 12, 1996. Concentrations in the ambient air samples ranged from estimates of 0.34 mg/m^3 to 0.54 mg/m^3. Concentrations in the three tank headspace samples ranged from 1.23 mg/m^3 to 1.27 mg/m^3 with an average concentration of 1.25 mg/m^3. This compares to 6.92 mg/m^3 for the sum of all compounds identified in the target and TIC analysis of the SUMMA™ canisters.

Table C.1. TO-12 Results for Samples Collected Through the ISVS from the Headspace of Tank S-103 and from Ambient Air Near Tank S-103 in SUMMA$^{(TM)}$ Canisters on 6/12/96.

	Ambient Air Upwind	Ambient Air Through Bundle	Tank Samples				
	S6060-A01.001[a] PNL 001[b] Concentration (mg/m^3)	S6060-A02.010[a] PNL 010[b] Concentration (mg/m^3)	S6060-A04.080[a] PNL 080[b] Concentration (mg/m^3)	S6060-A05.082[a] PNL 082[b] Concentration (mg/m^3)	S6060-A06.083[a] PNL 083 [b] Concentration (mg/m^3)	S6060-A05.082(a) PNL 082(b) [c] Concentration (mg/m^3)	Average Concentration Tank Samples (mg/m^3)
TO-12	0.34 J	0.54 J	1.27	1.23	1.23	1.23	1.25

Data Qualifier Flags

J Target compound detected above Instrument Detection Limit (IDL), but below Estimated Quantitation Limit (EQL).

Footnotes

(a) WHC sample identification number.

(b) PNL canister number.

(c) Replicate analysis for PNL 082; results are not included in the calculation of average concentrations.

Appendix D

Tank Vapor Characterization:

Organic Analytes by SUMMA™ 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 μL 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-μm 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.

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

[b] Pacific Northwest Laboratory. 8/96. *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 66 organic analytes. 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 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
Chloromethane
1,2-Dichloro-1,1,2,2-tetrafluoroethane
Vinyl Chloride
Bromomethane
Chloroethane
Trichlorofluoromethane
1,1-Dichloroethene
Methylene Chloride
1,1,2-Trichloro-1,2,2-trifluoroethane
1,1-Dichloroethane
cis-1,2-Dichloroethene
Chloroform
1,2-Dichloroethane
1,1,1-Trichloroethane
Benzene
Carbon Tetrachloride
1,2-Dichloropropane
Trichloroethene
cis-1,3-Dichloropropene
trans-1,3-Dichloropropene
1,1,2-Trichloroethane
Toluene
1,2-Dibromoethane
Tetrachloroethylene
Chlorobenzene
Ethylbenzene
Undecane
Tridecane
Butane
1-Butanol
1-Hexanenitrile
Methanol(a)

p/m-Xylene
1-Pentanenitrile
Styrene
1,1,2,2-Tetrachloroethane
o-Xylene
1,3,5-Trimethylbenzene
1,2,4-Trimethylbenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
1,2-Dichlorobenzene
1,2,4-Trichlorobenzene
Hexachloro-1,3-butadiene
2-Butanone
Acetone
Acetonitrile
Heptane
Tetrahydrofuran
Pyridine
Butanenitrile
Cyclohexane
Decane
Hexane
4-Methyl-2-pentanone
Propanenitrile
Cyclohexanone
Propanol
Nonane
Dodecane
Tetradecane
Pentane
Octane
1-Ethyl-2-methylbenzene
Ethanol(a)

(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. Instrument detection limits and EQLs for the target analytes have been determined. 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.

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 66 organic compounds. A gas mixture containing bromochloromethane, 1,4-difluorobenzene, chlorobenzene-d_5, 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/m^3 assumes standard temperature and pressure (STP) conditions of 760 torr and 273K and was calculated directly from the following equation:

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

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

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[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.

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.

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/m^3:

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

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/m^3 and the molecular weight of the analyte.

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

D.4 Organic Sample Results

Five SUMMA™ canisters were returned to the laboratory on June 18, 1996 under WHC COC form 100090 (see Appendix F). Samples were analyzed on July 10, 1996.

The results from the GC/MS analysis of the 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-103 and through the ISVS near Tank S-103 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 samples above the compound IDL. Sixty-four target analytes above the IDL and 30 TICs were detected in the tank headspace samples. Sixty-three target analytes and 17 TICs were identified in two or more tank headspace samples. Twelve TICs were not identified and were labeled as unknowns. Methanol at 3.02 mg/m^3 and ethanol at 1.18 mg/m^3 accounted for 61% of the compounds identified in the analysis. The total concentration of the target analytes was 6.57 mg/m^3. Methyl cyclohexane (0.06 mg/m^3) and pyrazine (0.04 mg/m^3), the two highest concentration TICs, accounted for 30% of the TICs and 1.5% of the total compounds identified in the analysis. The total concentration of the TICs was 0.35 mg/m^3. The total concentration of all the compounds identified was 6.92 mg/m^3. This compares to a total concentration of 1.25 mg/m^3 identified in the TO-12 analysis of the three tank headspace samples.

SUMMA™ canister PNL 082 was analyzed in replicate for target analytes and TICs to determine analytical precision. Twenty-four of 64 target compounds and one of 11 TICs had RPDs of less than 10%.

Sixty-three target compounds and 18 TICS were observed in one or both of the ambient air samples. Many of the compounds were identified at trace levels. Several noted exceptions included: methanol, acetone, propanol, 2-butanone, butanenitrile, 1-butanol, cyclohexane, butane, pentanenitrile, 1,1,2-trichloro-1,2,2-trifluoromethane, 4-methyl-2-pentanone, and cyclohexanone. 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-103:

> 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.
>
> This analytical sequence was run using 100 mL volumes to quantify target compounds in each tank sample.
>
> Three target compounds (pyridine at 79.3%, tridecane at 38.7%, and tetradecane at 51.5%) surpassed the 30% relative standard deviation (%RSD) acceptance criteria for the initial calibration. Pyridine was found in all the tank samples in concentrations between the IDL and the EQL. Pyridine was also found in the continuing calibration blank in concentrations between the IDL and the EQL; therefore, one can assume that this substance presents in the tank samples due to crossover contamination of the device. Tridecane and tetradecane were not found in the tank sample at concentrations above the IDL.
>
> Seven target compounds (pyridine, butanenitrile, 1,2,4-trichlorobenzene, dodecane, hexachloro-1,3-butadiene, tridecane, and tetradecane) 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. Tetradecane and tridecane were not found in tank samples in concentrations above the IDL. Butanenitrile was found in tank samples S6060-A02.010, S6060-A04.080, and S6060-A04.082 in concentrations between the EQL and the upper quantitation limit (UQL). These concentrations may be under estimated. Also, butanenitrile was found in the other tank samples at concentrations between the IDL and the EQL. The compounds 1,2,4-trichlorobenzene and hexachloro-1,3-butadiene were found in all the samples in concentrations between the IDL and the EQL. Dodecane was found in samples S6060-A01.001, S6060-A02.010, S6060-A04.080, and S6060-A05.082 REP in concentrations between the IDL and the EQL. Dodecane was also found in the other tank samples at concentrations below the IDL. Pyridine was found in all of the tank samples.
>
> Twenty-six target compounds were found din the CCB above the EQL, but the concentrations of all of them were less than 4 ppbv and slightly exceeded the EQL. The compound 1,2,4-trichlorobenzene was detected in the initial calibration blank above the EQL. This compound was also found in the CCB above the EQL, but was not found in the tank samples above the EQL.

The internal standard quantification area percent recoveries for all of the tank samples were within the acceptance criterion (50% to 200%) allowed by procedure PNL-TVP-03, except the second internal standard for tank sample S6060-A04.082 (44.98%).

Table D.2. Positively Identified and Quantitated Target Analytes and Tentatively Identifed Compounds and Estimated Concentrations for Samples from the Headspace in Tank S-103 in SUMMA canisters collected on 6/12/96

			Ret	S6060-A04.080(c) ISVS			S6060-A05.082(c)(d) ISVS			S6060-A06.083(c) ISVS			Mean and Standard Deviation			
Target Analytes(a)	CAS	MW	Time	(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	4.6	0.030	5.5	B	0.031	5.7	B	0.031	5.8	B	0.030	0.001	5.6	0.17
Chloromethane	74-87-3	50	4.9	0.014	6.2	J	0.017	7.7	J	0.015	6.7	J	0.015	0.002	6.8	0.75
12dichloro1122-tetrafluoroethane	76-14-2	171	5.2	0.027	3.5	J	0.034	4.4	J	0.028	3.6	J	0.029	0.004	3.9	0.48
Methanol	67-56-1	32	5.2	2.446	1710	Y	3.835	2681	Y	2.783	1946	Y	3.021	0.724	2112	506
Vinyl Chloride	75-01-4	63	5.4	0.014	5.2	J	0.019	6.8		0.014	5.1	J	0.016	0.003	5.7	0.98
Butane	106-97-8	58	5.9	0.042	16		0.049	19		0.044	17		0.045	0.004	17	1.4
Bromomethane	74-83-9	95	6.3	0.019	4.4	J	0.021	4.9	J	0.020	4.8	J	0.020	0.001	4.7	0.25
Chloroethane	75-00-3	65	6.7	0.016	5.6	J	0.019	6.7	J	0.023	8.1	J	0.020	0.004	6.8	1.3
Ethanol	64-17-5	46	6.8	0.907	442	Y	1.272	619	Y	1.357	660	Y	1.178	0.239	574	116
Acetonitrile	75-05-8	41	7.3	0.047	26		0.044	24		0.047	25		0.046	0.002	25	1.1
Acetone	67-64-1	58	7.8	0.283	109		0.298	115		0.307	118		0.296	0.012	114	4.5
Trichlorofluoromethane	75-69-4	137	8.3	0.081	13		0.096	16		0.090	15		0.089	0.007	14	1.2
Pentane	109-66-0	72	8.9	0.022	6.7	J	0.029	9.0	J	0.030	9.4	J	0.027	0.005	8.4	1.4
1,1-Dichloroethene	75-35-4	97	9.5	0.013	3.1	J	0.016	3.7	J	0.016	3.6	J	0.015	0.001	3.5	0.32
Methylene Chloride	75-09-2	85	9.7	0.032	8.4	B	0.034	9.0	B	0.034	9.0	B	0.033	0.001	8.8	0.30
112trichloro122trifluoroethane	76-13-1	187	10.2	0.047	5.6		0.052	6.2		0.047	5.6		0.049	0.003	5.8	0.33
Propanol	71-23-8	60	10.9	0.079	29	B	0.078	29	B	0.079	29	B	0.079	0.001	29	0.33
Propanenitrile	107-12-0	55	10.9	0.036	15	J	0.026	11	J	0.033	13	J	0.032	0.005	13	2.1
1,1-Dichloroethane	75-34-3	99	11.8	0.023	5.2	B	0.026	5.9	B	0.027	6.0	B	0.025	0.002	5.7	0.44
2-Butanone	78-93-3	72	12.5	0.078	24	B	0.066	21	B	0.074	23	B	0.073	0.006	23	1.8
cis-1,2-Dichloroethene	156-59-2	97	13.4	0.018	4.2	J	0.021	4.8	J	0.020	4.5	J	0.019	0.001	4.5	0.30
Hexane	110-54-3	86	13.7	0.036	9.3	B	0.037	9.6	B	0.034	8.8	B	0.036	0.002	9.2	0.39
Chloroform	67-66-3	119	13.9	0.026	4.8	J	0.028	5.2		0.029	5.4		0.027	0.002	5.2	0.29
Tetrahydrofuran	109-99-9	72	14.7	0.033	10	B	0.033	10	B	0.033	10	B	0.033	0.000	10	0.0058
1,2-Dichloroethane	107-06-2	99	15.3	0.019	4.2	J	0.021	4.8	J	0.020	4.5	J	0.020	0.001	4.5	0.30
Butanenitrile	109-74-0	69	15.8	0.043	14		0.035	11		0.030	9.7	J	0.036	0.007	12	2.1
1,1,1-Trichloroethane	71-55-6	133	15.8	0.033	5.5	B	0.035	5.9	B	0.034	5.7	B	0.034	0.001	5.7	0.23
1-Butanol	71-36-3	74	16.3	0.205	62	B	0.238	72	B	0.211	64	B	0.218	0.018	66	5.4
Benzene	71-43-2	78	16.7	0.022	6.2	B	0.024	6.9	B	0.023	6.5	B	0.023	0.001	6.5	0.35
Carbon Tetrachloride	56-23-5	154	17.0	0.029	4.3	J,B	0.031	4.5	J,B	0.028	4.1	J,B	0.029	0.001	4.3	0.17
Cyclohexane	110-82-7	84	17.3	0.118	31		0.121	32		0.124	33		0.121	0.003	32	0.82
1,2-Dichloropropane	78-87-5	113	18.3	0.026	5.1	J	0.028	5.5	J	0.033	6.5		0.029	0.004	5.7	0.74
Trichloroethene	79-01-6	131	18.8	0.029	4.9	B	0.027	4.6	B	0.028	4.8	B	0.028	0.001	4.8	0.13
Heptane	142-82-5	100	19.3	0.032	7.1	B	0.029	6.4	B	0.030	6.8	B	0.030	0.002	6.8	0.37
4-Methyl-2-Pentanone	108-10-1	100	20.5	0.056	12	B	0.048	11	B	0.047	10	B	0.050	0.005	11	1.1
cis-1,3-Dichloropropene	10061-01-5	111	20.5	0.022	4.4	J	0.018	3.6	J	0.020	4.1	J	0.020	0.002	4.0	0.44
Pyridine	110-86-1	79	20.6	0.071	20	J	0.054	15	J	0.051	14	J	0.058	0.011	17	3.1
trans-1,3-Dichloropropene	10061-02-6	111	21.5	0.028	5.7		0.020	4.0		0.020	4.0		0.023	0.005	4.6	1.0

Table D.2. Positively Identified and Quantitated Target Analytes and Tentatively Identifed Compounds and Estimated Concentrations for Samples from the Headspace in Tank S-103 in SUMMA canisters collected on 6/12/96

Target Analytes[a]	CAS	MW	Ret Time	S6060-A04.080[c] ISVS (mg/m^3)	(ppbv)	Flag	S6060-A05.082[c][d] ISVS (mg/m^3)	(ppbv)	Flag	S6060-A06.083[c] ISVS (mg/m^3)	(ppbv)	Flag	Mean and Standard Deviation (mg/m^3)	St. Dev.	(ppbv)	St. Dev.
Pentanenitrile	110-59-8	83	21.6	0.049	13	B	0.034	9.0	J,B	0.039	10	J,B	0.041	0.008	11	2.2
1,1,2-Trichloroethane	79-00-5	133	22.0	0.038	6.3	B	0.029	4.9	B	0.030	5.0	B	0.032	0.005	5.4	0.80
Toluene	108-88-3	92	22.6	0.029	6.9		0.038	9.2		0.040	9.7		0.035	0.006	8.6	1.5
1,2-Dibromoethane	106-93-4	188	24.2	0.024	2.9	J	0.026	3.1	J	0.027	3.2	J	0.026	0.002	3.1	0.20
Octane	111-65-9	114	24.7	0.014	2.8	J	0.018	3.4	J	0.016	3.2	J	0.016	0.002	3.1	0.31
Tetrachloroethylene	127-18-4	166	25.2	0.037	5.0	J	0.048	6.4		0.050	6.7		0.045	0.007	6.1	0.92
Chlorobenzene	108-90-7	113	26.8	0.016	3.2	J	0.017	3.3	J	0.017	3.3	J	0.016	0.000	3.3	0.078
Hexanenitrile	628-73-9	97	27.1	0.030	6.9	J	0.032	7.3	J	0.029	6.7	J	0.030	0.001	7.0	0.30
Ethylbenzene	100-41-4	106	27.7	0.016	3.4	J	0.018	3.8	J	0.017	3.6	J	0.017	0.001	3.6	0.18
p/m-Xylene	106-42-3	106	27.7	0.082	17	J	0.086	18	J	0.085	18	J	0.084	0.002	18	0.47
Cyclohexanone	108-94-1	98	28.5	0.019	4.4	J	0.025	5.7	J	0.022	5.1	J	0.022	0.003	5.0	0.67
Styrene	100-42-5	104	29.0	0.013	2.9	J	0.012	2.5	J	0.012	2.6	J	0.012	0.001	2.7	0.19
1,1,2,2-Tetrachloroethane	79-34-5	168	29.3	0.027	3.6	J	0.025	3.4	J	0.027	3.6	J	0.027	0.001	3.5	0.13
o-Xylene	95-47-6	106	29.3	0.017	3.5	J	0.015	3.2	J	0.016	3.4	J	0.016	0.001	3.4	0.16
Nonane	111-84-2	128	29.8	0.015	2.6	J,B	0.012	2.2	J,B	0.015	2.6	J,B	0.014	0.001	2.5	0.26
1-Ethyl-2-Methyl-Benzene	611-14-3	120	33.0	0.018	3.3	J,B	0.015	2.8	J,B	0.016	3.0	J,B	0.016	0.001	3.0	0.26
1,3,5-Trimethylbenzene	108-67-8	120	33.0	0.015	2.8	J	0.013	2.5	J	0.015	2.8	J	0.014	0.001	2.7	0.19
1,2,4-Trimethylbenzene	95-63-6	120	34.2	0.016	2.9	J	0.013	2.4	J	0.015	2.8	J	0.014	0.002	2.7	0.30
Decane	124-18-5	142	34.5	0.029	4.6	J,B	0.028	4.3	J,B	0.030	4.7	J,B	0.029	0.001	4.5	0.17
1,3-Dichlorobenzene	541-73-1	147	34.7	0.016	2.4	J,B	0.014	2.1	J,B	0.015	2.3	J,B	0.015	0.001	2.3	0.17
1,4-Dichlorobenzene	106-46-7	147	34.7	0.016	2.4	J,B	0.014	2.1	J,B	0.015	2.3	J,B	0.015	0.001	2.2	0.17
1,2-Dichlorobenzene	95-50-1	147	36.1	0.016	2.5	J,B	0.014	2.2	J,B	0.015	2.3	J,B	0.015	0.001	2.3	0.15
Undecane	1120-21-4	156	38.8	0.013	1.9	J	0.013	1.8	J	0.015	2.2	J	0.014	0.001	1.9	0.21
1,2,4-Trichlorobenzene	120-82-1	181	42.3	0.009	1.1	J,B	0.010	1.2	J,B	0.010	1.3	J,B	0.010	0.001	1.2	0.085
Dodecane	112-40-3	170	42.8	0.013	1.7	J	0.010	1.3	U	0.010	1.3	U	e	e	e	e
Hexachloro-1,3-butadiene	87-68-3	261	44.1	0.023	1.9	J,B	0.021	1.8	J,B	0.020	1.7	J,B	0.021	0.001	1.8	0.10
Tentatively Identified Compounds[b]																
Cyclopropane	75-19-4	42	4.4	nd	nd		nd	nd		0.016	8.4	N	e	e	e	e
Propene	115-07-1	42	4.4	0.018	9.7	N	0.015	8.0	N	0.044	22	N	0.026	0.016	13	7.8
Propane	74-98-6	44	4.4	nd	nd		0.044	22	N	nd	nd		e	e	e	e
Unknown Alkane			4.5	0.040	f		nd	nd		nd	nd		e	e	e	e
Unknown			4.9	0.009	f		0.023	f		nd	nd		0.016	e	e	e
Cyclopropane	75-19-4	42	5.0	0.028	15	N	0.048	26	N	nd	nd		0.038	e	20	e
Unknown			6.2	0.010	f		0.010	f		0.024	f		0.015	0.008	e	e
Unknown			9.1	0.004	f		nd	nd		0.008	f		0.006	e	e	e
2-Propanol, 2-methyl-	75-65-0	74	9.4	nd	nd		nd	nd		0.016	4.7	N	e	e	e	e

Table D.2. Positively Identified and Quantitated Target Analytes and Tentatively Identifed Compounds and Estimated Concentrations for Samples from the Headspace in Tank S-103 in SUMMA canisters collected on 6/12/96

Tentatively			Ret	S6060-A04.080[c] ISVS			S6060-A05.082[c][d] ISVS			S6060-A06.083[c] ISVS			Mean and Standard Deviation			
Identified Compounds[b]	CAS	MW	Time	(mg/m^3)	(ppbv)	Flag	(mg/m^3)	(ppbv)	Flag	(mg/m^3)	(ppbv)	Flag	(mg/m^3)	St. Dev.	(ppbv)	St. Dev.
Unknown Alcohol			9.4	0.050	f		nd	nd		nd	nd		e	e	e	e
1-Propene, 3-chloro-	107-05-1	76	9.9	0.009	2.7	N	0.012	3.7	N	0.016	4.8	N	0.013	0.003	3.7	1.0
Silanol, trimethyl-	1066-40-6	90	11.6	0.023	5.6	N	nd	nd		nd	nd		e	e	e	e
Butanal	123-72-8	72	12.3	0.042	13	N	0.042	13	N	nd	nd		0.042	e	13	e
2-Butanol, (.+/-.)-	15892-23-6	74	13.0	nd	nd		nd	nd		0.022	6.6	N	e	e	e	e
2-Butanol	78-92-2	74	13.0	0.023	6.9	N	nd	nd		nd	nd		e	e	e	e
Unknown			16.9	0.022	f		0.019	f		0.011	f		0.017	0.005	e	e
N-Nitrosodimethylamine	62-75-9	74	19.6	0.010	3.1	N	0.007	2.2	N	0.007	2.2	N	0.008	0.002	2.5	0.52
1,3-Diazine	289-95-2	80	19.8	0.014	4.0	N	nd	nd		nd	nd		e	e	e	e
Pyrazine	290-37-9	80	19.8	nd	nd		0.046	13	N	0.040	11	N	0.043	e	12	e
Unknown			20.3	0.011	f		0.015	f		0.014	f		0.013	0.002	e	e
Cyclohexane, methyl-	108-87-2	98	20.8	0.058	13	N	0.047	11	N	0.080	18	N	0.062	0.017	14	3.8
2-Hexanone	591-78-6	100	23.0	0.003	0.77	N	0.004	0.82	N	0.004	0.81	N	0.004	0.000	0.80	0.026
Hexanal	66-25-1	100	23.6	0.026	5.7	N	0.021	4.8	N	0.022	5.0	N	0.023	0.002	5.1	0.50
Cyclotrisiloxane, hexamethyl-	541-05-9	222	25.5	nd	nd		nd	nd		0.084	8.4	N	e	e	e	e
Unknown			28.9	0.002	f		nd	nd		nd	nd		e	e	e	e
Unknown			33.8	0.002	f		nd	nd		nd	nd		e	e	e	e
Unknown Alkane			37.2	0.016	f		0.021	f		0.007	f		0.015	0.007	e	e
Unknown Alkane			37.5	0.003	f		0.007	f		0.008	f		0.006	0.003	e	e
Unknown Alkane			46.2	nd	nd		0.012	f		0.005	f		0.009	e	e	e

Data Quality Flags

B	Target compound detected in associated laboratory blank and sample
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.

(f) No molecular weight available for calculation.

nd Not detected

Table D.3. Positively Identified and Quantitated Target Analytes[a] and Tentatively Identifed Compounds and Estimated Concentrations[b] of Replicate Analysis of a single SUMMA™ Cannister Collected from the Headspace of Tank S-103 on 6/12/96

				S6060-A05.082[c] ISVS						Relative Percent Difference[d]
Target Analytes[a]	CAS	MW	Ret Time	(mg/m^3)	(ppbv)	Flag	(mg/m^3)	(ppbv)	Flag	%
Dichlorodifluoromethane	75-71-8	121	4.6	0.031	5.7	B	0.028	5.2	B	8
Chloromethane	74-87-3	50	4.9	0.017	7.7	J	0.015	6.7	J	14
12dichloro1122-tetrafluoroethane	76-14-2	171	5.2	0.034	4.4	J	0.032	4.2	J	4
Methanol	67-56-1	32	5.2	3.835	2681		2.852	1994		29
Vinyl Chloride	75-01-4	63	5.4	0.019	6.8		0.016	5.8		16
Butane	106-97-8	58	5.9	0.049	19		0.047	18		5
Bromomethane	74-83-9	95	6.3	0.021	4.9	J	0.021	4.9	J	0
Chloroethane	75-00-3	65	6.7	0.019	6.7	J	0.027	9.3	J	32
Ethanol	64-17-5	46	6.8	1.272	619		1.188	579		7
Acetonitrile	75-05-8	41	7.3	0.044	24		0.036	20	J	19
Acetone	67-64-1	58	7.8	0.298	115		0.226	87		27
Trichlorofluoromethane	75-69-4	137	8.3	0.096	16		0.086	14		11
Pentane	109-66-0	72	8.9	0.029	9.0	J	0.029	9.0	J	0
1,1-Dichloroethene	75-35-4	97	9.5	0.016	3.7	J	0.015	3.3	J	9
Methylene Chloride	75-09-2	85	9.7	0.034	9.0	B	0.031	8.2	B	9
112trichloro122trifluoroethane	76-13-1	187	10.2	0.052	6.2		0.043	5.2		18
Propanol	71-23-8	60	10.9	0.078	29	B	0.062	23	B	22
Propanenitrile	107-12-0	55	10.9	0.026	11	J	0.024	9.7	J	9
1,1-Dichloroethane	75-34-3	99	11.8	0.026	5.9	B	0.021	4.8	B	22
2-Butanone	78-93-3	72	12.5	0.066	21	B	0.052	16	B	25
cis-1,2-Dichloroethene	156-59-2	97	13.4	0.021	4.8	J	0.017	4.0	J	18
Hexane	110-54-3	86	13.7	0.037	9.6	B	0.032	8.4	B	13
Chloroform	67-66-3	119	13.9	0.028	5.2		0.025	4.7	J	11
Tetrahydrofuran	109-99-9	72	14.7	0.033	10	B	0.024	7.5	B	30
1,2-Dichloroethane	107-06-2	99	15.3	0.021	4.8	J	0.017	3.8	J	24
Butanenitrile	109-74-0	69	15.8	0.035	11		0.023	7.4	J	43
1,1,1-Trichloroethane	71-55-6	133	15.8	0.035	5.9	B	0.025	4.2	J,B	35
1-Butanol	71-36-3	74	16.3	0.238	72	B	0.127	38	B	61
Benzene	71-43-2	78	16.7	0.024	6.9	B	0.019	5.6	B	21
Carbon Tetrachloride	56-23-5	154	17.0	0.031	4.5	J,B	0.024	3.5	J,B	24
Cyclohexane	110-82-7	84	17.3	0.121	32		0.110	29		10
1,2-Dichloropropane	78-87-5	113	18.3	0.028	5.5	J	0.024	4.8	J	13
Trichloroethene	79-01-6	131	18.8	0.027	4.6	B	0.025	4.3	B	6
Heptane	142-82-5	100	19.3	0.029	6.4	B	0.029	6.5	B	2
4-Methyl-2-Pentanone	108-10-1	100	20.5	0.048	11	B	0.025	5.6	J,B	63
cis-1,3-Dichloropropene	10061-01-5	111	20.5	0.018	3.6	J	0.017	3.4	J	4
Pyridine	110-86-1	79	20.6	0.054	15	J	0.032	8.9	J	52
trans-1,3-Dichloropropene	10061-02-6	111	21.5	0.020	4.0		0.013	2.7	J	39
Pentanenitrile	110-59-8	83	21.6	0.034	9.0	J,B	0.021	5.6	J,B	48
1,1,2-Trichloroethane	79-00-5	133	22.0	0.029	4.9	B	0.023	3.9	J,B	23
Toluene	108-88-3	92	22.6	0.038	9.2		0.047	11		21
1,2-Dibromoethane	106-93-4	188	24.2	0.026	3.1	J	0.025	2.9	J	6
Octane	111-65-9	114	24.7	0.018	3.4	J	0.018	3.5	J	3
Tetrachloroethylene	127-18-4	166	25.2	0.048	6.4		0.057	7.7		18
Chlorobenzene	108-90-7	113	26.8	0.017	3.3	J	0.015	3.1	J	8
Hexanenitrile	628-73-9	97	27.1	0.032	7.3	J	0.022	5.0	J	37
Ethylbenzene	100-41-4	106	27.7	0.018	3.8	J	0.015	3.1	J	19
p/m-Xylene	106-42-3	106	27.7	0.086	18	J	0.070	15	J	21
Cyclohexanone	108-94-1	98	28.5	0.025	5.7	J	0.013	3.0	J	63
Styrene	100-42-5	104	29.0	0.012	2.5	J	0.012	2.7	J	6
1,1,2,2-Tetrachloroethane	79-34-5	168	29.3	0.025	3.4	J	0.024	3.2	J	6
o-Xylene	95-47-6	106	29.3	0.015	3.2	J	0.017	3.5	J	10
Nonane	111-84-2	128	29.8	0.012	2.2	J,B	0.016	2.8	J,B	24
1-Ethyl-2-Methyl-Benzene	611-14-3	120	33.0	0.015	2.8	J,B	0.013	2.5	J,B	12

Table D.3. Positively Identified and Quantitated Target Analytes[a] and Tentatively Identifed Compounds and Estimated Concentrations[b] of Replicate Analysis of a single SUMMA™ Cannister Collected from the Headspace of Tank S-103 on 6/12/96

			Ret	S6060-A05.082[c] ISVS						Relative Percent Difference[d]
Target Analytes[a]	CAS	MW	Time	(mg/m^3)	(ppbv)	Flag	(mg/m^3)	(ppbv)	Flag	%
1,3,5-Trimethylbenzene	108-67-8	120	33.0	0.013	2.5	J,B	0.013	2.5	J,B	0
1,2,4-Trimethylbenzene	95-63-6	120	34.2	0.013	2.4	J	0.013	2.5	J	5
Decane	124-18-5	142	34.5	0.028	4.3	J,B	0.028	4.4	J,B	0
1,3-Dichlorobenzene	541-73-1	147	34.7	0.014	2.1	J,B	0.013	2.0	J,B	4
1,4-Dichlorobenzene	106-46-7	147	34.7	0.014	2.1	J,B	0.014	2.1	J,B	1
1,2-Dichlorobenzene	95-50-1	147	36.1	0.014	2.2	J,B	0.014	2.2	J,B	1
Undecane	1120-21-4	156	38.8	0.013	1.8	J	0.011	1.6	J	10
1,2,4-Trichlorobenzene	120-82-1	181	42.3	0.010	1.2	J,B	0.008	1.0	J,B	18
Dodecane	112-40-3	170	42.8	0.010	1.3	U	0.013	1.7	J	
Hexachloro-1,3-butadiene	87-68-3	261	44.1	0.021	1.8	J,B	0.019	1.7	J,B	6
Tentatively Identified Compounds[b]										
Cyclopropane	75-19-4	42	4.4	nd	nd		0.015	7.9	N	
Propene	115-07-1	42	4.4	0.015	8.0	N	0.043	22	N	97
Propane	74-98-6	44	4.4	0.044	22	N	nd	nd		
Unknown			4.7	nd	nd		0.005	e		
Unknown			4.9	0.023	e		nd	nd		
Cyclopropane	75-19-4	42	5.0	0.048	26	N	nd	nd		
Unknown			6.2	0.010	e		0.015	e		36
Unknown			9.1	nd	nd		0.002	e		
1-Propene, 3-chloro-	107-05-1	76	9.9	0.012	3.7	N	0.022	6.4	N	55
Butanal	123-72-8	72	12.3	0.042	13	N	0.029	9.1	N	36
2-Butanol, (.+/-.)-	15892-23-6	74	13.0	nd	nd		0.014	4.2	N	
2-Pentanone	107-87-9	86	16.0	nd	nd		0.003	0.89	N	
Unknown			16.9	0.019	e		nd	nd		
Propane, 1,2-dichloro-	78-87-5	112	18.3	nd	nd		0.019	3.8	N	
N-Nitrosodimethylamine	62-75-9	74	19.6	0.007	2.2	N	0.002	0.48	N	126
Pyrazine	290-37-9	80	19.8	0.046	13	N	0.023	6.5	N	66
Unknown			20.3	0.015	e		0.007	e		73
Cyclohexane, methyl-	108-87-2	98	20.8	0.047	11	N	0.074	17	N	44
2-Hexanone	591-78-6	100	23.0	0.004	0.82	N	nd	nd		
Hexanal	66-25-1	100	23.6	0.021	4.8	N	nd	nd		
Unknown Alkane			37.2	0.021	e		0.013	e		51
Unknown Alkane			37.5	0.007	e		0.007	e		1
Unknown Alkane			46.2	0.012	e		0.015	e		18

Data Quality Flags

B Target compound detected in associated laboratory blank and sample

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) TO-14 plus 26 additional 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.

(e) No molecular weight available for calculation

nd Not detected

Table D.4. Positively Identified and Quantitated Target Analytes(a) and Tentatively Identifed Compounds and Estimated Concentrations(b) in Ambient Air and Ambient Air Through the ISVS Collected Near Tank S-103 in SUMMA™ Canisters Collected on 6/12/96

				S6060-A01.001(c)			S6060-A02.010(c)		
			Ret	ISVS Upwind Ambient			ISVS Amb Thru Bundle		
Target Analytes(a)	CAS	MW	Time	(mg/m^3)	(ppbv)	Flag	(mg/m^3)	(ppbv)	Flag
Dichlorodifluoromethane	75-71-8	121	4.6	0.016	3.0	J,B	0.037	6.9	B
Chloromethane	74-87-3	50	4.9	0.006	2.8	J	0.015	6.5	J
12dichloro1122-tetrafluoroethane	76-14-2	171	5.2	0.013	1.7	U	0.038	5.0	J
Methanol	67-56-1	32	5.2	< 0.110	< 77	Y	0.127	89	Y
Vinyl Chloride	75-01-4	63	5.4	0.007	2.4	J	0.016	5.8	
Butane	106-97-8	58	5.9	0.010	3.9	J	0.027	11	
Bromomethane	74-83-9	95	6.3	0.008	1.9	J	0.024	5.7	J
Chloroethane	75-00-3	65	6.7	0.005	1.9	U	0.019	6.6	J
Acetonitrile	75-05-8	41	7.3	0.008	4.2	J	0.012	6.8	J
Acetone	67-64-1	58	7.8	0.036	14		0.076	29	
Trichlorofluoromethane	75-69-4	137	8.3	0.010	1.6	J	0.030	5.0	J
Pentane	109-66-0	72	8.9	0.006	2.0	J	0.027	8.3	J
1,1-Dichloroethene	75-35-4	97	9.5	0.006	1.3	J	0.018	4.2	J
Methylene Chloride	75-09-2	85	9.7	0.021	5.6	B	0.035	9.3	B
112trichloro122trifluoroethane	76-13-1	187	10.2	0.012	1.4	J	0.090	11	
Propanol	71-23-8	60	10.9	0.023	8.4	J,B	0.042	16	B
Propanenitrile	107-12-0	55	10.9	0.016	6.7	J	0.023	9.3	J
1,1-Dichloroethane	75-34-3	99	11.8	0.011	2.5	J,B	0.025	5.8	B
2-Butanone	78-93-3	72	12.5	0.020	6.4	J,B	0.033	10	B
cis-1,2-Dichloroethene	156-59-2	97	13.4	0.010	2.3	J	0.016	3.8	J
Hexane	110-54-3	86	13.7	0.015	3.9	J,B	0.033	8.4	B
Chloroform	67-66-3	119	13.9	0.015	2.9	J	0.027	5.0	
Tetrahydrofuran	109-99-9	72	14.7	0.012	3.7	J,B	0.020	6.3	B
1,2-Dichloroethane	107-06-2	99	15.3	0.012	2.6	J	0.017	3.8	J
Butanenitrile	109-74-0	69	15.8	0.015	4.9	J	0.044	14	
1,1,1-Trichloroethane	71-55-6	133	15.8	0.016	2.7	J,B	0.039	6.6	B
1-Butanol	71-36-3	74	16.3	0.035	11	B	0.079	24	B
Benzene	71-43-2	78	16.7	0.009	2.7	J,B	0.019	5.5	B
Carbon Tetrachloride	56-23-5	154	17.0	0.016	2.3	J,B	0.035	5.1	B
Cyclohexane	110-82-7	84	17.3	0.093	25		0.115	30	
1,2-Dichloropropane	78-87-5	113	18.3	0.019	3.8	J	0.003	0.59	U
Trichloroethene	79-01-6	131	18.8	0.018	3.0	J,B	0.027	4.5	B
Heptane	142-82-5	100	19.3	0.017	3.8	J,B	0.023	5.1	B
4-Methyl-2-Pentanone	108-10-1	100	20.5	0.030	6.8	J,B	0.073	16	B
cis-1,3-Dichloropropene	10061-01-5	111	20.5	0.016	3.1	J	0.017	3.4	J
Pyridine	110-86-1	79	20.6	0.042	12	J	0.130	37	J
trans-1,3-Dichloropropene	10061-02-6	111	21.5	0.015	3.0	J	0.023	4.7	
Pentanenitrile	110-59-8	83	21.6	0.022	5.9	J,B	0.053	14	B
1,1,2-Trichloroethane	79-00-5	133	22.0	0.022	3.7	J	0.030	5.0	
Toluene	108-88-3	92	22.6	0.014	3.5	J,B	0.016	3.9	J,B
1,2-Dibromoethane	106-93-4	188	24.2	0.021	2.5	J	0.028	3.3	J
Octane	111-65-9	114	24.7	0.014	2.8	J	0.016	3.1	J
Tetrachloroethylene	127-18-4	166	25.2	0.020	2.7	J	0.021	2.9	J
Chlorobenzene	108-90-7	113	26.8	0.013	2.6	J	0.017	3.3	J
Hexanenitrile	628-73-9	97	27.1	0.024	5.5	J	0.051	12	J
Ethylbenzene	100-41-4	106	27.7	0.011	2.4	J	0.017	3.6	J
p/m-Xylene	106-42-3	106	27.7	0.055	12	J	0.093	20	J
Cyclohexanone	108-94-1	98	28.5	0.016	3.7	J	0.064	15	
Styrene	100-42-5	104	29.0	0.011	2.3	J	0.012	2.6	J
1,1,2,2-Tetrachloroethane	79-34-5	168	29.3	0.021	2.8	J	0.029	3.9	J

Table D.4. Positively Identified and Quantitated Target Analytes[a] and Tentatively Identifed Compounds and Estimated Concentrations[b] in Ambient Air and Ambient Air Through the ISVS Collected Near Tank S-103 in SUMMA™ Canisters Collected on 6/12/96

				S6060-A01.001[c]			S6060-A02.010[c]		
				ISVS Upwind Ambient			ISVS Amb Thru Bundle		
Target Analytes[a]	CAS	MW	Ret Time	(mg/m^3)	(ppbv)	Flag	(mg/m^3)	(ppbv)	Flag
o-Xylene	95-47-6	106	29.3	0.012	2.5	J	0.014	2.9	J
Nonane	111-84-2	128	29.8	0.012	2.1	J,B	0.014	2.5	J,B
1-Ethyl-2-Methyl-Benzene	611-14-3	120	33.0	0.012	2.3	J,B	0.017	3.2	J,B
1,3,5-Trimethylbenzene	108-67-8	120	33.0	0.012	2.2	J,B	0.016	2.9	J,B
1,2,4-Trimethylbenzene	95-63-6	120	34.2	0.012	2.2	J	0.016	3.1	J
Decane	124-18-5	142	34.5	0.021	3.4	J,B	0.028	4.4	J,B
1,3-Dichlorobenzene	541-73-1	147	34.7	0.013	2.0	J,B	0.017	2.6	J,B
1,4-Dichlorobenzene	106-46-7	147	34.7	0.014	2.1	J,B	0.016	2.4	J,B
1,2-Dichlorobenzene	95-50-1	147	36.1	0.015	2.2	J,B	0.019	2.8	B
Undecane	1120-21-4	156	38.8	0.008	1.2	J	0.015	2.1	J
1,2,4-Trichlorobenzene	120-82-1	181	42.3	0.008	1.0	J,B	0.014	1.7	J,B
Dodecane	112-40-3	170	42.8	0.011	1.4	J	0.013	1.7	J
Hexachloro-1,3-butadiene	87-68-3	261	44.1	0.021	1.8	J,B	0.026	2.2	J,B
Tentatively Identified Compounds[b]									
Cyclopropane	75-19-4	42	4.4	0.010	5.1	N	nd	nd	
Propene	115-07-1	42	4.4	nd	nd		0.016	8.4	N
Unknown			4.4	0.009	d		nd	nd	
Acetaldehyde	75-07-0	44	5.2	0.022	11	N	nd	nd	
1-Propene, 3-chloro-	107-05-1	76	9.9	nd	nd		0.015	4.5	N
Unknown			10.4	0.017	d		nd	nd	
Silanol, trimethyl-	1066-40-6	90	11.6	nd	nd		0.068	17	N
Butanal	123-72-8	72	12.3	0.007	2.2	N	0.008	2.4	N
2-Hexanone	591-78-6	100	23.0	0.003	0.55	N	nd	nd	
Unknown			23.0	nd	nd		0.005	d	
Hexanal	66-25-1	100	23.6	0.015	3.3	N	0.082	18	N
Cyclotrisiloxane, hexamethyl-	541-05-9	222	25.5	0.012	1.2	N	0.013	1.3	N
Heptanal	111-71-7	114	28.9	nd	nd		0.004	0.77	N
Unknown			33.8	nd	nd		0.004	d	
Unknown Alkane			37.2	nd	nd		0.023	d	
Unknown Alkane			37.5	nd	nd		0.006	d	
Unknown			42.8	nd	nd		0.022	d	
Unknown Alkane			46.2	nd	nd		0.027	d	

Data Quality Flags

B Target compound detected in associated laboratory blank and sample

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) TO-14 plus 26 additional target analytes.

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

(c) WHC sample identification number.

(d) No molecular weight available for calculation.

nd Not detected

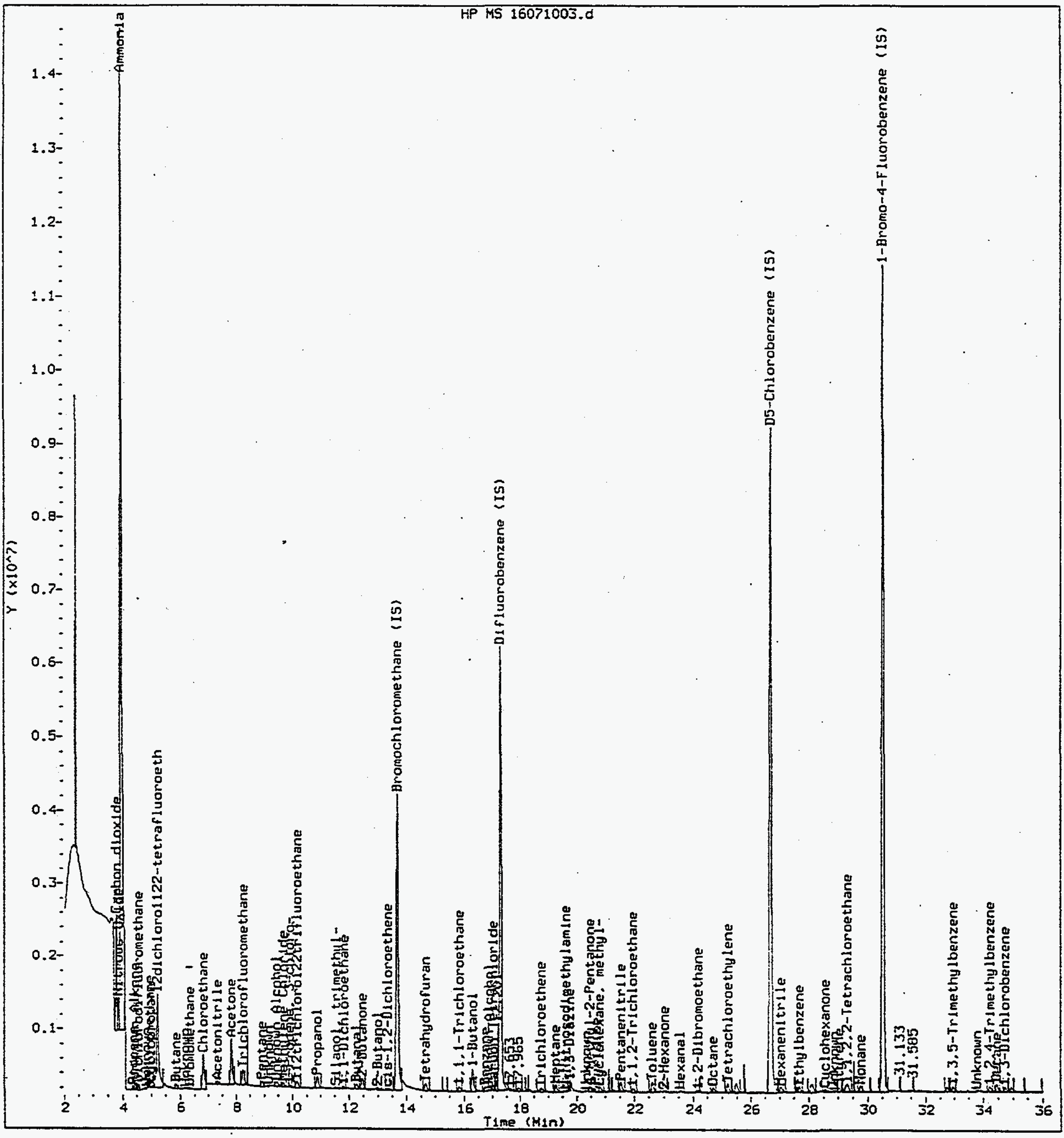

Figure D.1a Total Ion Chromatogram (2 - 36 min) for Hanford Waste Tank S-103 SUMMA™ Canister Sample S6060-A04-080 Collected on 6/12/96

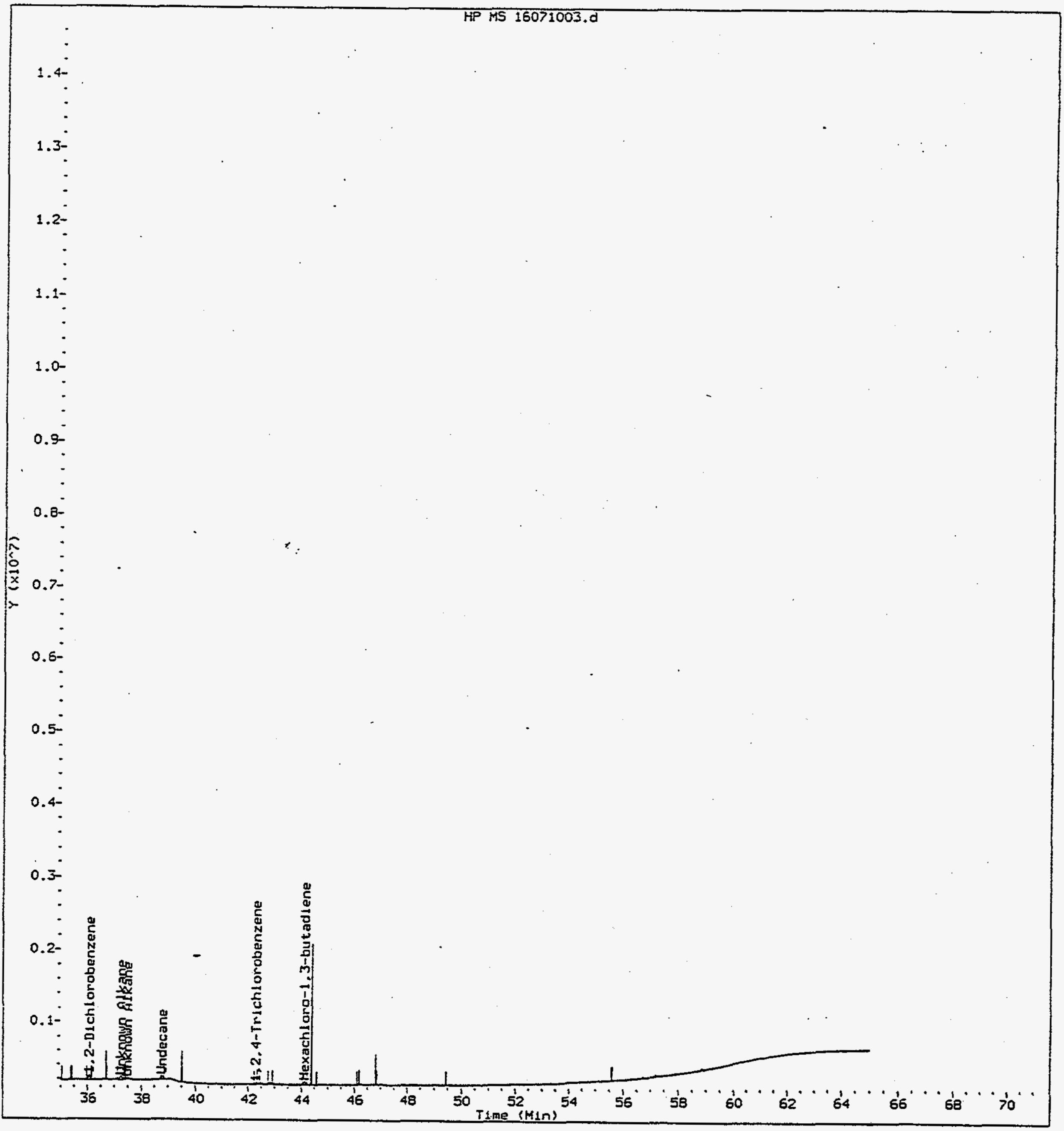

Figure D.1b Total Ion Chromatogram (36 - 70 min) for Hanford Waste Tank S-103 SUMMA™ Canister Sample S6060-A04-080 Collected on 6/12/96

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 TD^3), 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 graphetized 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

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[(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 65 compounds. These 65 compounds that are directly quantified in this analysis make up the target analyte list (these 65 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

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

(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 65 compounds shown in Table E.1. A gas mixture containing difluorobenzene, chlorobenzene-d_5, 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/m^3 assumes standard temperature and pressure (STP) conditions of 760 torr and 273K and was calculated directly from the following equation:

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

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/m^3:

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

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.

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

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 18, 1996 under WHC COC form 100091. Samples were analyzed on June 28 and July 1, 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 D.2 were not detected in any of the tank samples above the compound IDL. A total of 39 target analytes above the IDL and 28 TICs were detected in the tank headspace samples. Thirty-six of the target analytes and 13 TICs were observed in two or more sorbent traps. Methanol at 1.15 mg/m^3 and toluene at 1.16 mg/m^3 accounted for 44% of the target analytes and 28% of the total concentration identified by the analyses. The total concentration of the target analytes was 5.20 mg/m^3 or 64% of the total concentration identified by the analyses. The predominant TICs observed in these samples were 3-methyl hexane at 0.73 mg/m^3 and 2-methyl hexane at 0.42 mg/m^3. The total concentration of the TICs was 2.96 mg/m^3 or 36% of the total concentration identified by the analysis. The total concentration of all the compounds identified was 8.16 mg/m^3.

Triple sorbent trap sample PNL 987 was analyzed in replicate for target analytes and TICs to determine analytical precision. Twenty-seven of 36 target compounds and 13 of 14 TICs had RPDs of less than 10%.

The following procedural changes and observations were noted during the analysis of Tank S-103:

> 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 problems 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.

At the completion of sampling, a large amount of contamination came out of the riser, requiring special handling techniques. The field blanks were badly contaminated with a group of compounds characteristic of the 3M adhesive tape used on previous ISVS jobs. The special handling associated with the riser contamination appears to have severely exacerbated the tape problem, which had not in any case been completely eliminated. The field blank contained numerous target compounds at levels in excess of the EQL including acetone, 2-butanone, hexane, 1-butanol, cyclohexane, heptane, 4-methyl-2-pentanone, toluene, ethylbenzene, and p/m xylene. A number of compounds were detected in at least one of the blanks at trace levels (below EQL). Numerous TICs typical of adhesive tape emanations were also observed, including methyl cyclohexane, which provides a characteristic signature for the 3M tape. Two other compounds that showed up in both field blanks as well as the tank samples were isopropanol and 1-fluoro-1,1-dichloroethane. The origin of these compounds is unclear. They may be associated in some way with the decontamination operation. In addition, Field blanks, trip blanks, and 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 such as the 222S lab. Because of the tape problem, TST tank results from this sampling activity should be generally considered as suspect.

The tank samples contained numerous target compounds at levels in excess of the EQL. Compounds that were not observed in the field blanks at levels in excess of the EQL included methanol, ethanol, acetonitrile, trichlorofluoromethane, benzene, 1,1,2 trichloroethane, styrene, and decane. A number of compounds were detected in at least one of the samples at trace levels (below EQL). Many of the target compounds observed (acetone, 2-butanone, hexane, 1-butanol, cyclohexane, heptane, 4-methyl-2-pentanone, toluene, ethylbenzene, p/m xylene, and o-xylene) and numerous TICs including methylcyclohexane are generally ascribable to contamination during sampling and subsequent handling associated with the use of 3M adhesive tape as described previously.

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.

The TST samples were analyzed in two batches. The analytical sequence runs (batches) were as follows:

Batch 6/28/96 (file identifier 46062801.d) - S6060-A17.991, S6060-A18.992, S6060-A19.993, S6060-A20.994;

Batch 7/1/96 (file identifier 46070101.d) - S6060-A11.986, S6060-A12.987, S6060-A12.987REP, S6060-A13.988.

The following discussion provides details regarding QC criterion failures for each batch.

Batch 6/28/96:

Samples included in this batch consisted of the two field blanks and two trip blanks. The first CCV run was within nominal limits as specified in the procedure for all target compounds, with the exception of ethanol (22.5%) and tridecane (37.5%). The computer shut down just before elution of the tetradecane peak and data were not available for that compound. A second CCV was run to verify the response to tetradecane. The second CCV was generally less satisfactory, and for the purpose of calculation, the first CCV was used. This is considered to be the best approach because the second CCV did not produce a good quality tetradecane response as is almost always the case for daily calibration samples, and the field and trip blanks did not show the presence of significant quantities of tetradecane. Due to the absence of tetradecane CCV data, tetradecane was quantified using the average relative response factor value from the initial calibration. The continuing calibration blank (CCB) contained trace amounts (below EQL) of methylene chloride and tetradecane. The CCB was otherwise clean.

Batch 7/1/96:

Samples included in this batch consisted of the three tanks samples and one repeat analysis of a tank sample. The first CCV run was outside nominal limits as specified in the procedure for all target compounds, and a second CCV was run. The second CCV was within nominal limits for all compounds with the exception of 1-butanol (31.1%), trichloroethene (27.6%), cis-1,3-dichloropropene (25.5%), 1,2-dibromoethane (30.8%), cyclohexanone (41.7%), and 1,1,2,2 tetrachloroethane (44.9%). The CCB contained trace amounts (below EQL) of methylene chloride, toluene, and tetradecane. The CCB was otherwise clean.

Table E.2. Positively Identified and Quantitated Target Analytes[a] and Tentatively Identifed Compounds and Estimated Concentrations[b] for Triple Sorbent Traps Collected from the Headspace of Tank S-103 on 6/12/96

			Ret	S6060-A11.986[c] ISVS			S6060-A12.987[c][d] ISVS			S6060-A13.988[c] ISVS			**Mean and Standard Deviation**			
Target Analytes[a]	CAS	MW	Time	(mg/m^3)	(ppbv)	Flag	(mg/m^3)	(ppbv)	Flag	(mg/m^3)	(ppbv)	Flag	(mg/m^3)	St. Dev.	(ppbv)	St. Dev.
Methanol	67-56-1	32	10.1	1.430	1000	Y	0.888	621	Y	1.143	799	Y	1.154	0.271	807	190
Butane	106-97-8	58	10.8	0.022	8.6	J	0.018	6.9	J	0.018	6.9	J	0.019	0.002	7.4	0.97
Ethanol	64-17-5	46	12.6	0.293	143	Y	<0.275	< 133	Y	0.353	171	Y	0.323	e	157	e
Acetonitrile	75-05-8	41	13.1	0.048	26		0.033	18	J	0.044	24		0.042	0.007	23	4.0
Acetone	67-64-1	58	13.7	0.319	123		0.270	104		0.283	109		0.291	0.025	112	9.6
Trichlorofluoromethane	75-69-4	137	14.2	0.055	9.0		0.057	9.2		0.060	9.7		0.057	0.002	9.3	0.37
Pentane	109-66-0	72	15.0	0.006	2.0	J	0.007	2.2	J	0.005	1.5	J	0.006	0.001	1.9	0.36
1,1-Dichloroethene	75-35-4	97	15.6	0.007	1.7	J	0.002	0.49	U	0.002	0.52	U	e	e	e	e
Methylene Chloride	75-09-2	85	15.8	0.087	23	J	0.052	14	J	0.070	19	J	0.070	0.018	18	4.6
112trichloro122trifluoroethane	76-13-1	187	16.3	0.006	0.69	J	0.014	1.7	J	0.007	0.81	J	0.009	0.004	1.1	0.53
Propanol	71-23-8	60	17.1	0.055	21	J	0.044	16	J	0.047	17	J	0.049	0.006	18	2.2
2-Butanone	78-93-3	72	18.6	0.054	17		0.052	16		0.050	16		0.052	0.002	16	0.62
Hexane	110-54-3	86	19.9	0.073	19		0.071	19		0.072	19		0.072	0.001	19	0.24
Tetrahydrofuran	109-99-9	72	20.8	0.008	2.6	J	0.011	3.4	J	0.008	2.5	J	0.009	0.002	2.8	0.48
Benzene	71-43-2	78	22.8	0.015	4.3		0.013	3.6	J	0.014	4.0	J	0.014	0.001	4.0	0.37
1,1,1-Trichloroethane	71-55-6	133	22.0	0.014	2.3	J	0.016	2.7	J	0.025	4.2	J	0.018	0.006	3.1	1.0
1-Butanol	71-36-3	74	22.3	0.305	92		0.290	88		0.245	74		0.280	0.031	85	9.3
Cyclohexane	110-82-7	84	23.4	0.115	31		0.112	30		0.108	29		0.112	0.004	30	0.96
Trichloroethene	79-01-6	131	24.8	0.004	0.73	J	0.004	0.64	U	0.004	0.68	U	e	e	e	e
Heptane	142-82-5	100	25.2	0.740	165		0.655	146		0.660	148		0.685	0.047	153	11
4-Methyl-2-Pentanone	108-10-1	100	26.4	0.034	7.7		0.030	6.7		0.013	2.9	J	0.026	0.011	5.7	2.5
Pyridine	110-86-1	79	26.6	0.069	19	J	0.053	15	J	0.053	15	J	0.058	0.009	17	2.5
Pentanenitrile	110-59-8	83	27.4	0.002	0.60	J	0.002	0.57	J	0.002	0.53	J	0.002	0.000	0.57	0.035
1,1,2-Trichloroethane	79-00-5	133	27.9	0.033	5.5		0.002	0.27	U	0.002	0.29	U	e	e	e	e
Toluene	108-88-3	92	28.5	1.175	286		1.078	262		1.225	298		1.159	0.075	282	18
Tetrachloroethylene	127-18-4	166	31.1	0.025	3.4	J	0.027	3.6		0.020	2.6	J	0.024	0.004	3.2	0.53
Hexanenitrile	628-73-9	97	32.8	0.007	1.7	J	0.005	1.0	J	0.651	150		0.221	0.372	51	86
Ethylbenzene	100-41-4	106	33.5	0.049	10		0.043	9.1		0.036	7.5		0.043	0.007	9.0	1.4
p/m-Xylene	106-42-3	106	33.9	0.172	36		0.154	33		0.136	29		0.154	0.018	32	3.7

Table E.2. Positively Identified and Quantitated Target Analytes(a) and Tentatively Identifed Compounds and Estimated Concentrations(b) for Triple Sorbent Traps Collected from the Headspace of Tank S-103 on 6/12/96

				S6060-A11.986(c) ISVS			S6060-A12.987(c)(d) ISVS			S6060-A13.988(c) ISVS			Mean and Standard Deviation			
Target Analytes(a)	CAS	MW	Ret Time	(mg/m^3)	(ppbv)	Flag	(mg/m^3)	(ppbv)	Flag	(mg/m^3)	(ppbv)	Flag	(mg/m^3)	St. Dev.	(ppbv)	St. Dev.
Styrene	100-42-5	104	34.8	0.035	7.6		0.031	6.7		0.036	7.7		0.034	0.002	7.3	0.54
o-Xylene	95-47-6	106	35.1	0.052	11		0.047	9.9		0.033	7.0		0.044	0.010	9.3	2.1
Nonane	111-84-2	128	35.5	0.010	1.8	J	0.009	1.5	J	0.007	1.2	J	0.009	0.002	1.5	0.27
1-Ethyl-2-methyl benzene	611-14-3	120	38.5	0.008	1.5	J	0.007	1.3	J	0.007	1.3	J	0.007	0.001	1.4	0.11
1,3,5-Trimethylbenzene	108-67-8	120	38.7	0.007	1.2	J	0.007	1.3	J	0.007	1.4	J	0.007	0.000	1.3	0.080
1,2,4-Trimethylbenzene	95-63-6	120	40.0	0.026	4.9		0.023	4.2	J	0.024	4.4	J	0.024	0.002	4.5	0.34
Decane	124-18-5	142	40.2	0.043	6.8		0.029	4.6	J	0.027	4.2	J	0.033	0.009	5.2	1.4
Undecane	1120-21-4	156	44.5	0.020	2.9	J	0.015	2.2	J	0.011	1.6	J	0.016	0.005	2.2	0.68
Tridecane	629-50-5	184	52.3	0.087	11	J	0.076	9.2	J	0.060	7.3	U	0.082	e	9.9	e
Tetradecane	629-59-4	198	55.8	0.041	4.6	J	0.030	3.4	J	0.050	5.7	J	0.040	0.010	4.5	1.1
Tentatively Identified Compounds(b)																
Ethane, 1-chloro-1,1-difluoro-	75-68-3	100	8.8	0.374	84	N	0.071	16	N	0.055	15	N	0.166	0.180	38	39
Acetaldehyde	75-07-0	44	9.5	nd	nd		0.026	13	N	0.037	19	N	0.032	e	16	e
1-Propene, 2-methyl-	115-11-7	56	10.4	nd	nd		0.097	39	N	nd	nd		e	e	e	e
Isopropyl Alcohol	67-63-0	60	14.3	0.031	12	N	0.034	13	N	0.026	9.7	N	0.030	0.004	11	1.5
1-Fluoro-1,1-dichloro-ethane	0-00-0	116	14.4	0.333	64	N	0.346	67	N	0.479	92	N	0.386	0.081	74	16
2-Propanol, 2-methyl-	75-65-0	74	15.6	nd	nd		0.044	13	N	0.027	8.0	N	0.035	e	11	e
Cyclopentane, methyl-	96-37-7	84	21.5	nd	nd		0.064	17	N	nd	nd		e	e	e	e
Pentane, 3,3-dimethyl-	562-49-2	100	23.0	nd	nd		0.110	25	N	0.115	26	N	0.112	e	25	e
Hexane, 2-methyl-	591-76-4	100	23.5	0.476	107	N	0.428	96	N	0.352	79	N	0.418	0.063	94	14
Pentane, 2,3-dimethyl-	565-59-3	100	23.7	0.240	54	N	0.283	63	N	0.268	60	N	0.263	0.022	59	4.9
Hexane, 3-methyl-	589-34-4	100	24.0	0.766	172	N	0.748	168	N	0.665	149	N	0.726	0.054	163	12
4-Ethyl-1-hexene	0-00-0	112	24.6	nd	nd		0.205	41	N	nd	nd		e	e	e	e
1-Octene, 3-ethyl-	74630-08-3	140	24.6	0.191	31	N	nd	nd		nd	nd		e	e	e	e
4-Ethyl-1-hexene	0-00-0	112	24.6	nd	nd		nd	nd		0.205	41	N	e	e	e	e
Cyclopentane, 1,2-dimethyl-	2452-99-5	98	24.8	nd	nd		0.338	77	N	nd	nd		e	e	e	e
1-Hexene, 4-methyl-	3769-23-1	98	24.8	nd	nd		nd	nd		0.440	101	N	e	e	e	e

Table E.2. Positively Identified and Quantitated Target Analytes[a] and Tentatively Identifed Compounds and Estimated Concentrations[b] for Triple Sorbent Traps Collected from the Headspace of Tank S-103 on 6/12/96

Tentatively Identified Compounds[b]	CAS	MW	Ret Time	S6060-A11.986[c] ISVS			S6060-A12.987[c][d] ISVS			S6060-A13.988[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.
Cyclohexane, methyl-	108-87-2	98	26.8	1.221	279	N	nd	nd		nd	nd		e	e	e	e
Hexane, 2,4-dimethyl-	589-43-5	114	27.1	0.154	30	N	0.169	33	N	0.176	35	N	0.167	0.011	33	2.2
Cyclopentane, 1,2,4-trimethyl-	2815-58-9	112	27.7	0.169	34	N	0.188	38	N	0.194	39	N	0.184	0.013	37	2.5
Heptane, 2-methyl-	592-27-8	114	28.8	0.140	27	N	0.130	26	N	0.124	24	N	0.131	0.008	26	1.5
Cyclotrisiloxane, hexamethyl-	541-05-9	222	31.2	0.283	29	N	nd	nd		nd	nd		e	e	e	e
Hexane, 2,3,5-trimethyl-	1069-53-0	128	31.6	0.115	20	N	nd	nd		nd	nd		e	e	e	e
Heptane, 2,4-dimethyl-	2213-23-2	128	31.8	0.418	73	N	0.371	65	N	0.140	24	N	0.309	0.149	54	26
Cyclotetrasiloxane, octamethyl-	556-67-2	296	39.5	0.812	61	N	nd	nd		nd	nd		e	e	e	e
Unknown C12 Alkane		170	43.0	0.625	82	N	0.524	69		0.152	19		0.434	0.249	57	34
Unknown C12 Alkane		170	43.2	0.304	40	N	0.288	38		0.129	17		0.240	0.097	32	13

Data Quality Flags

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.

(f) No molecular weight available for calculation.

nd Not detected

Table E.3. Positively Identified and Quantitated Target Analytes[a] and Tentatively Identifed Compounds and Estimated Concentrations[b] of Replicate Analysis of a Single Triple Sorbent Trap Collected from the Headspace of Tank S-103 on 6/12/96

			Ret	S6060-A12.987[c] ISVS						Relative Percent Difference[d]
Target Analytes[a]	CAS	MW	Time	(mg/m^3)	(ppbv)	Flag	(mg/m^3)	(ppbv)	Flag	%
Methanol	67-56-1	32	10.1	0.888	621	Y	0.916	640	Y	3
Butane	106-97-8	58	10.8	0.018	6.9	J	0.019	7.1	J	4
Ethanol	64-17-5	46	12.6	< 0.275	< 133	Y	< 0.275	< 133	Y	
Acetonitrile	75-05-8	41	13.1	0.033	18	J	0.036	20		8
Acetone	67-64-1	58	13.7	0.270	104		0.256	99		5
Trichlorofluoromethane	75-69-4	137	14.2	0.057	9.2		0.056	9.1		1
Pentane	109-66-0	72	15.0	0.007	2.2	J	0.007	2.1	J	4
Methylene Chloride	75-09-2	85	15.8	0.052	14	J	0.060	16	J	14
112trichloro122trifluoroethane	76-13-1	187	16.3	0.014	1.7	J	0.012	1.5	J	12
Propanol	71-23-8	60	17.1	0.044	16	J	0.041	15	J	8
2-Butanone	78-93-3	72	18.6	0.052	16		0.047	15		10
Hexane	110-54-3	86	19.9	0.071	19		0.071	19		0
Tetrahydrofuran	109-99-9	72	20.8	0.011	3.4	J	0.009	2.8	J	17
Benzene	71-43-2	78	22.8	0.013	3.6	J	0.013	3.8	J	5
1,1,1-Trichloroethane	71-55-6	133	22.0	0.016	2.7	J	0.016	2.7	J	1
1-Butanol	71-36-3	74	22.3	0.290	88		0.276	83		5
Cyclohexane	110-82-7	84	23.4	0.112	30		0.109	29		3
Heptane	142-82-5	100	25.2	0.655	146		0.654	146		0
4-Methyl-2-Pentanone	108-10-1	100	26.4	0.030	6.7		0.020	4.5	J	40
Pyridine	110-86-1	79	26.6	0.053	15	J	0.053	15	J	1
Pentanenitrile	110-59-8	83	27.4	0.002	0.57	J	0.037	9.9		178
Toluene	108-88-3	92	28.5	1.078	262		1.081	263		0
Tetrachloroethylene	127-18-4	166	31.1	0.027	3.6		0.026	3.5		3
Hexanenitrile	628-73-9	97	32.8	0.005	1.0	J	0.005	1.1	J	6
Ethylbenzene	100-41-4	106	33.5	0.043	9.1		0.042	8.8		4
p/m-Xylene	106-42-3	106	33.9	0.154	33		0.154	33		0
Styrene	100-42-5	104	34.8	0.031	6.7		0.031	6.6		1
o-Xylene	95-47-6	106	35.1	0.047	9.9		0.046	9.8		1
Nonane	111-84-2	128	35.5	0.009	1.5	J	0.008	1.5	J	6
1-Ethyl-2-methyl benzene	611-14-3	120	38.5	0.007	1.3	J	0.006	1.2	J	9
1,3,5-Trimethylbenzene	108-67-8	120	38.7	0.007	1.3	J	0.007	1.2	J	4
1,2,4-Trimethylbenzene	95-63-6	120	40.0	0.023	4.2	J	0.022	4.2	J	1
Decane	124-18-5	142	40.2	0.029	4.6	J	0.028	4.5	J	3
Undecane	1120-21-4	156	44.5	0.015	2.2	J	0.013	1.9	J	15
Tridecane	629-50-5	184	52.3	0.076	9.2	J	0.066	8.0	J	14
Tetradecane	629-59-4	198	55.8	0.030	3.4	J	0.031	3.5	J	3
Tentatively Identified Compounds[b]										
Ethane, 1-chloro-1,1-difluoro-	75-68-3	100	8.8	0.071	16	N	0.061	17	N	14
Acetaldehyde	75-07-0	44	9.5	0.026	13	N	0.025	13	N	2
1-Propene, 2-methyl-	115-11-7	56	10.4	0.097	39	N	nd	nd		
Isopropyl Alcohol	67-63-0	60	14.3	0.034	13	N	0.034	13	N	1
1-Fluoro-1,1-dichloro-ethane	0-00-0	116	14.4	0.346	67	N	0.340	66	N	2
2-Propanol, 2-methyl-	75-65-0	74	15.6	0.044	13	N	0.043	13	N	3
Pentane, 3-methyl-	96-14-0	86	19.1	nd	nd		0.062	16	N	
Cyclopentane, methyl-	96-37-7	84	21.5	0.064	17	N	nd	nd		
Pentane, 3,3-dimethyl-	562-49-2	100	23.0	0.110	25	N	0.107	24	N	3
Hexane, 2-methyl-	591-76-4	100	23.5	0.428	96	N	0.433	97	N	1
Pentane, 2,3-dimethyl-	565-59-3	100	23.7	0.283	63	N	0.279	62	N	1
Hexane, 3-methyl-	589-34-4	100	24.0	0.748	168	N	0.733	164	N	2
4-Ethyl-1-hexene	0-00-0	112	24.6	0.205	41	N	nd	nd		

Table E.3. Positively Identified and Quantitated Target Analytes[a] and Tentatively Identifed Compounds and Estimated Concentrations[b] of Replicate Analysis of a Single Triple Sorbent Trap Collected from the Headspace of Tank S-103 on 6/12/96

Tentatively			Ret	S6060-A12.987[c] ISVS						Relative Percent Difference[d]
Identified Compounds[b]	CAS	MW	Time	(mg/m^3)	(ppbv)	Flag	(mg/m^3)	(ppbv)	Flag	%
Hexane, 2,3-dimethyl-	584-94-1	114	24.6	nd	nd		0.209	41	N	
Cyclopentane, 1,2-dimethyl-, cis-	1192-18-3	98	24.7	nd	nd		0.096	22	N	
Cyclopentane, 1,2-dimethyl-	2452-99-5	98	24.8	0.338	77	N	0.338	77	N	0
Cyclohexane, methyl-	108-87-2	98	26.8	nd	nd		1.325	303	N	
Hexane, 2,4-dimethyl-	589-43-5	114	27.1	0.169	33	N	0.169	33	N	0
Cyclopentane, ethyl-	1640-89-7	98	27.3	nd	nd		0.105	24	N	
Cyclopentane, 1,2,4-trimethyl-	2815-58-9	112	27.7	0.188	38	N	nd	nd		
Heptane, 2-methyl-	592-27-8	114	28.8	0.130	26	N	0.129	25	N	1
Heptane, 2,4-dimethyl-	2213-23-2	128	31.8	0.371	65	N	0.369	64	N	1
Unknown C12 Alkane		170	43.0	0.524	69	N	0.508	67	N	3
Unknown C12 Alkane		170	43.2	0.288	38	N	0.243	32	N	17

Data Quality Flags

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

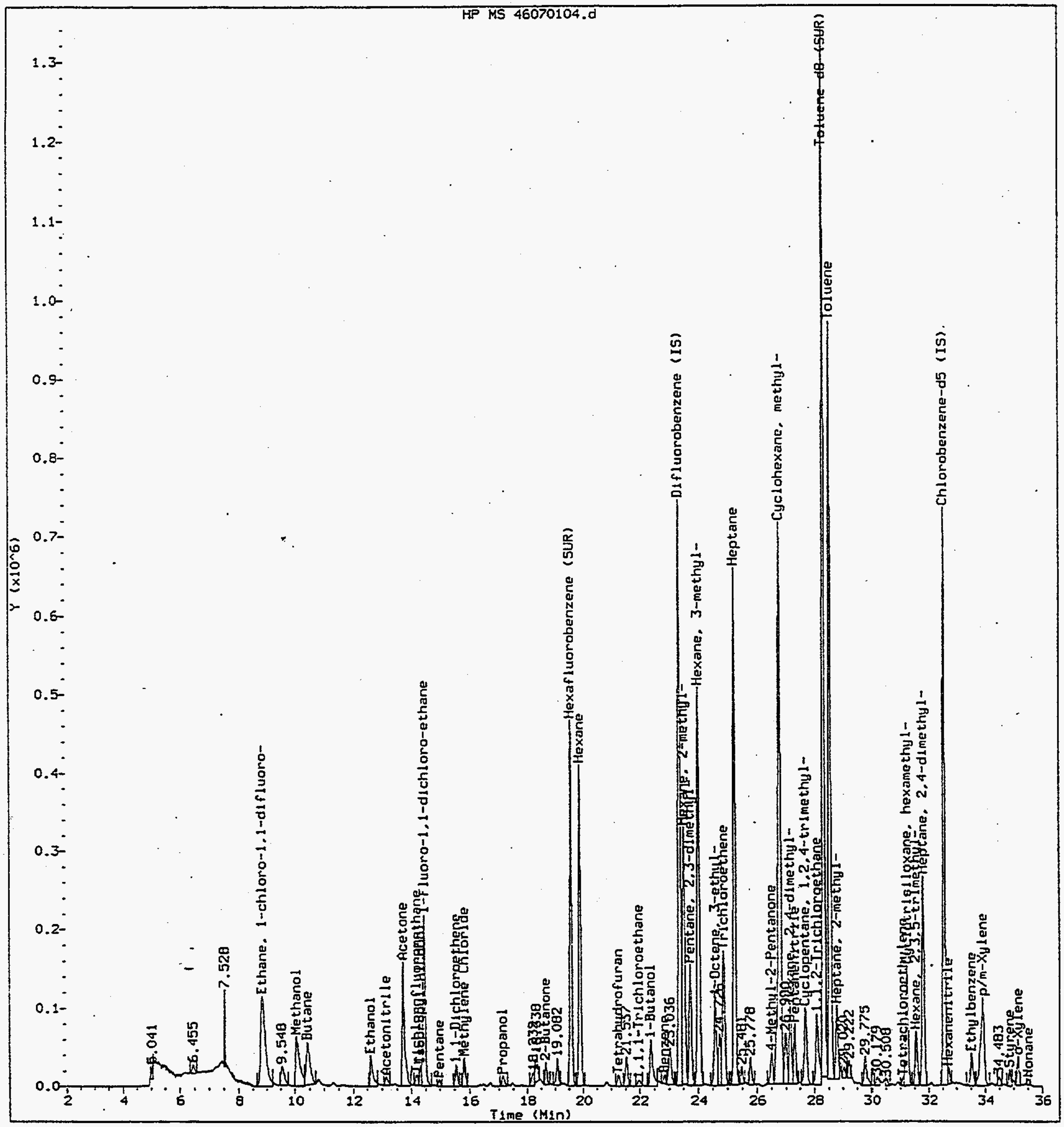

Figure E.1a Total Ion Chromatogram (2 - 36 min) for Hanford Waste Tank S-103 Triple Sorbent Trap Sample S6060-A11-986 Collected on 6/12/96

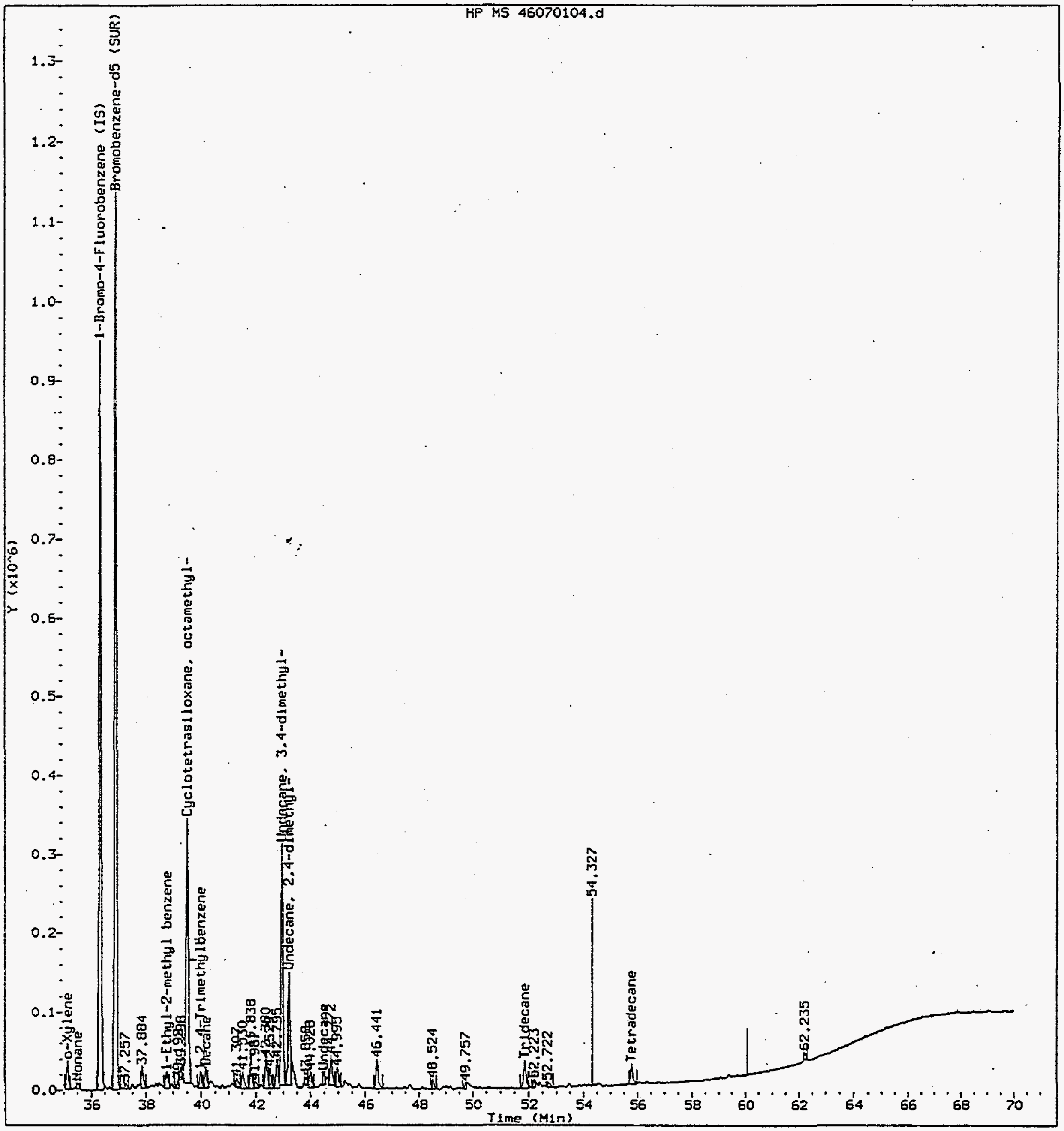

Figure E.1b Total Ion Chromatogram (36 - 70 min) for Hanford Waste Tank S-103 Triple Sorbent Trap Sample S6060-A11-986 Collected on 6/12/96

Appendix F

Tank Vapor Characterization:
Chain of Custody Sample Control Forms

Battelle Pacific National Northwest Lab	CHAIN OF CUSTODY	WHC 100092

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
241-S-103 Tank Vapor Sample SAF S6060
(ISVS Cart)
Collection date 06 - 12 - 96
Preparation date 06 - 07 - 96

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

S6060 - A07 . S91	Collect $NH_3/NO_x/H_2O$ Sorbent Trap
S6060 - A08 . S92	Collect $NH_3/NO_x/H_2O$ Sorbent Trap
S6060 - A09 . S93	Collect $NH_3/NO_x/H_2O$ Sorbent Trap
S6060 - A10 . S94	Collect $NH_3/NO_x/H_2O$ Sorbent Trap
S6060 - A15 . S95	Open, close and store $NH_3/NO_x/H_2O$ field blank #1
S6060 - A16 . S96	Open, close and store $NH_3/NO_x/H_2O$ field blank #2

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

Relinquished By	Date	Time	Received By	Date	Time
G W Dennis	06 - 10 -96	1130	J A Edwards JA Edwards	06 - 10 -96	1130
J A Edwards JA Edwards	06 - 10 -96	1430	RM ARNOLD RM Arnold	06 - 10 -96	1430
RM Arnold RM Arnold	06-11-96	1230	RD Mahon RD Mahon	06-11-96	1230
RD Mahon RD Mahon	06-18-96	0811	GS CAPRIO	06-18-96	0811
GS CAPRIO	06-18-96	1043	JA EDWARDS JA Edwards	06-18-96	1043
JA EDWARDS JA Edwards	6-20-96	1145	G.W. Dennis	6-20-96	1145
G.W. Dennis	6-20-96	1530	S.O. Slate S.O. Slate	6-20-96	1530

Final Sample Disposition

Comments:

PNNL (only) Checklist	Pick-up	/ Delivery	Comments:
◊ Media labeled and checked?	[✓ Y]/N		
◊ Letter of instruction?	[✓ Y]/N		
◊ Media in good condition?	[✓ Y]/N	/ [✓ Y]/N	
◊ COC info/signatures complete?	[✓ Y]/N	/ [✓ Y]/N	
◊ Rad release stickers on samples?		/ [✓ Y]/N	
◊ Activity report from 222S?		/ [✓ Y]/N	
◊ RSR/release? (a ≤100/ß ≤400 pCi/g)		/ [✓ Y]/N	
◊ COC copy for LRB, RIDS filed?		/ [✓ Y]/N	

POC ______ POC ______

(WHC-SD-WM-TP-335, REV. 2, Table 2b)
A-6000-407 (12/92) WEF061

1 of 1

(Revised 05/30/96 PNNL)

Battelle Pacific National Northwest Lab	CHAIN OF CUSTODY	WHC 100090

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-103 Tank Vapor Sample SAF S6060
(ISVS Cart)
Collection date 06 - 12 - 96
Preparation date 06 - 10 - 96

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

S6060 - A01 . 001	Collect Ambient Air Sample SUMMA #1
S6060 - A02 . 010	Collect Ambient Air Sample SUMMA #2 (through tube bundle)
S6060 - A04 . 080	Collect SUMMA #3
S6060 - A05 . 082	Collect SUMMA #4
S6060 - A06 . 083	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	06- 10 -96	1430	RM Arnold	06- 10 -96	1430
RM Arnold	06-11-96	1230	RD Mahon	06-11-96	1230
RD Mahon	06-18-96	0811	GS CAPRIO	06-18-96	0811
GS CAPRIO	06-18-96	1053	J A EDWARDS	06-18-96	1053

Final Sample Disposition

Comments:

PNNL (only) Checklist	Pick-up	/ Delivery	Comments:
◊ Media labeled and checked?	[✓ Y]/N		
◊ Letter of instruction?	[✓ Y]/N		
◊ Media in good condition?	[✓ Y]/N	/ [✓ Y]/N	
◊ COC info/signatures complete?	[✓ Y]/N	/ [✓ Y]/N	
◊ Rad release stickers on samples?		/ [✓ Y]/N	
◊ Activity report from 222S?		/ [✓ Y]/N	
◊ RSR/release? (a ≤100/ß ≤400 pCi/g)		/ [✓ Y]/N	
◊ COC copy for LRB, RIDS filed?		/ [✓ Y]/N	

POC POC

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

(Revised 05/30/96 PNNL)

A-6000-407 (12/92) WEF061

1 of 1

Battelle Pacific Northwest Laboratory | **CHAIN OF CUSTODY** | **WHC 100091**

Custody Form Initiator	J. A. Edwards - PNL	Telephone Page	(509) 373-0141 85-3009 / P8-08 / FAX 376-0418
Company Contact	R. D. Mahon - WHC	Telephone Page	(509) 373-7437 85-9656 / S3-27 / FAX 373-7076
Project Designation/Sampling Locations 241-S-103 Tank	200 West Tank Farm Vapor Sample SAF S6060 (ISVS Cart)	Collection date Preparation date	06 - 12 - 96 06- 07 - 96
Ice Chest No.		Field Logbook No.	WHC-N 647-8
Ertco Hi/Lo thermometer No.	PNL-T-003		
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

S6060 - A11 . 986	PNL Triple Sorbent Trap (TST) Sample # 1
S6060 - A12 . 987	PNL TST Sample # 2
S6060 - A13 . 988	PNL TST Sample # 3
S6060 - A14 . 989	PNL TST Sample # 4
S6060 - A17 . 991	Open, close & store TST Field Blank # 1
S6060 - A18 . 992	Open, close & store TST Field Blank #2
S6060 - A19 . 993	Store TST Trip Blank #1
S6060 - A20 . 994	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 Julya J L Julya	06-07-96	1425	JA Edwards JA Edwards	06-07-96	1425
JA Edwards JA Edwards	06-10-96	1430	RM ARNOLD Rm Arnold	06-10-96	1430
RM Arnold Rm Arnold	06-11-96	1230	RD Mahon RD Mahon	06-11-96	1230
RD Mahon RD Mahon	06-18-96	0811	GS CAPRIO	06-18-96	0811
GS CAPRIO	06-18-96	1046	JA EDWARDS JA Edwards	06-18-96	1046
JA EDWARDS JA Edwards	6-19-96	0850	JL Julya	6-19-96	0850

Final Sample Disposition

Comments:

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

Comments:

Cooler Temperature Status
Hi -15 °C / Lo -15 °C (pick up at PNL to WHC)
Hi ____°C / Lo ____°C (delivery at WHC from PNL)
Hi -15 °C / Lo ____°C (at return to PNL from WHC)
Hi -15 °C / Lo +5 °C (at delivery from WHC to PNL)

(Revised 06/21/95 PNL)

Distribution List

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