

TANK VAPOR CHARACTERIZATION PROJECT

Headspace Vapor Characterization of Hanford Waste Tank 241-S-106: Results from Samples Collected on 6/13/96

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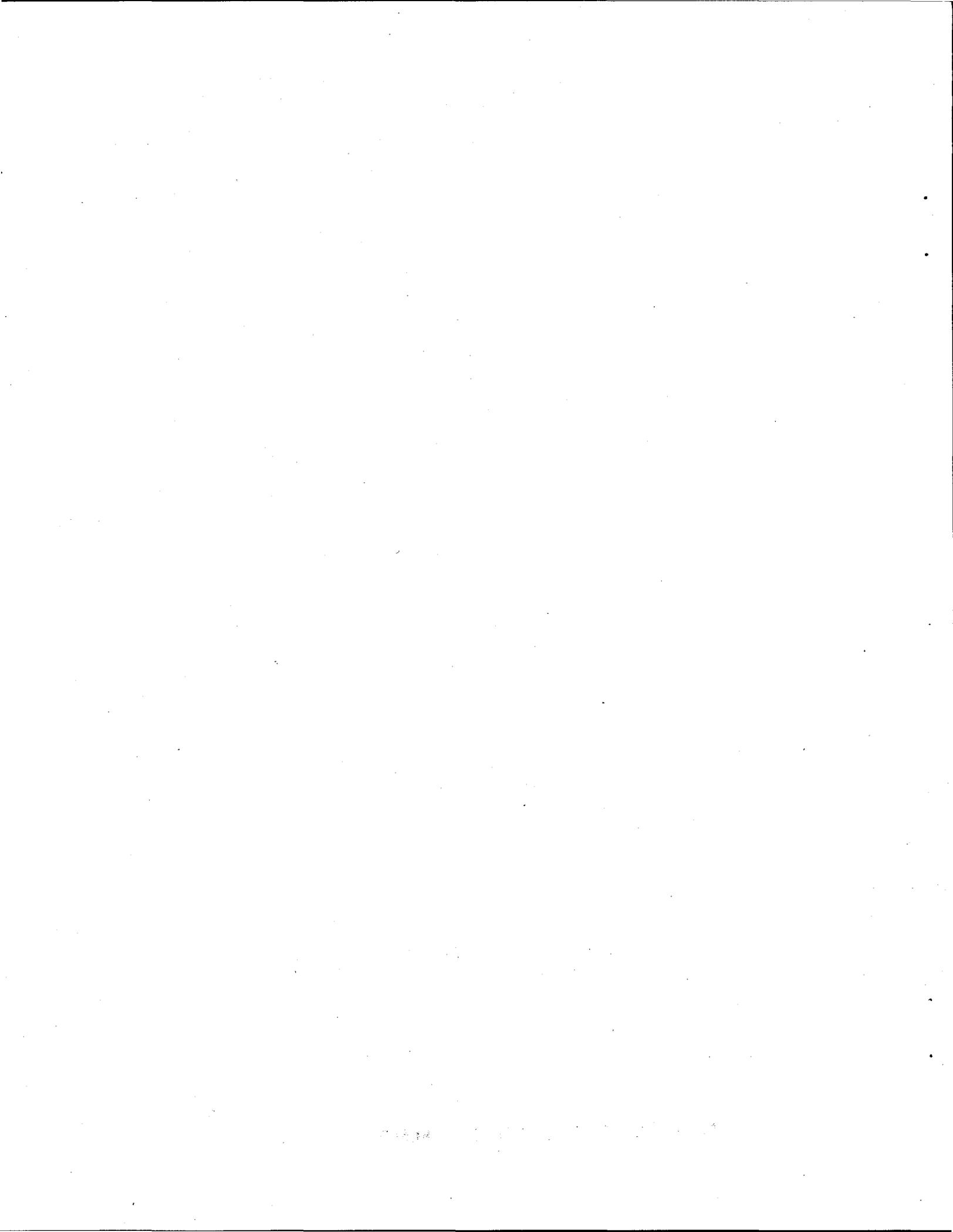
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Summary

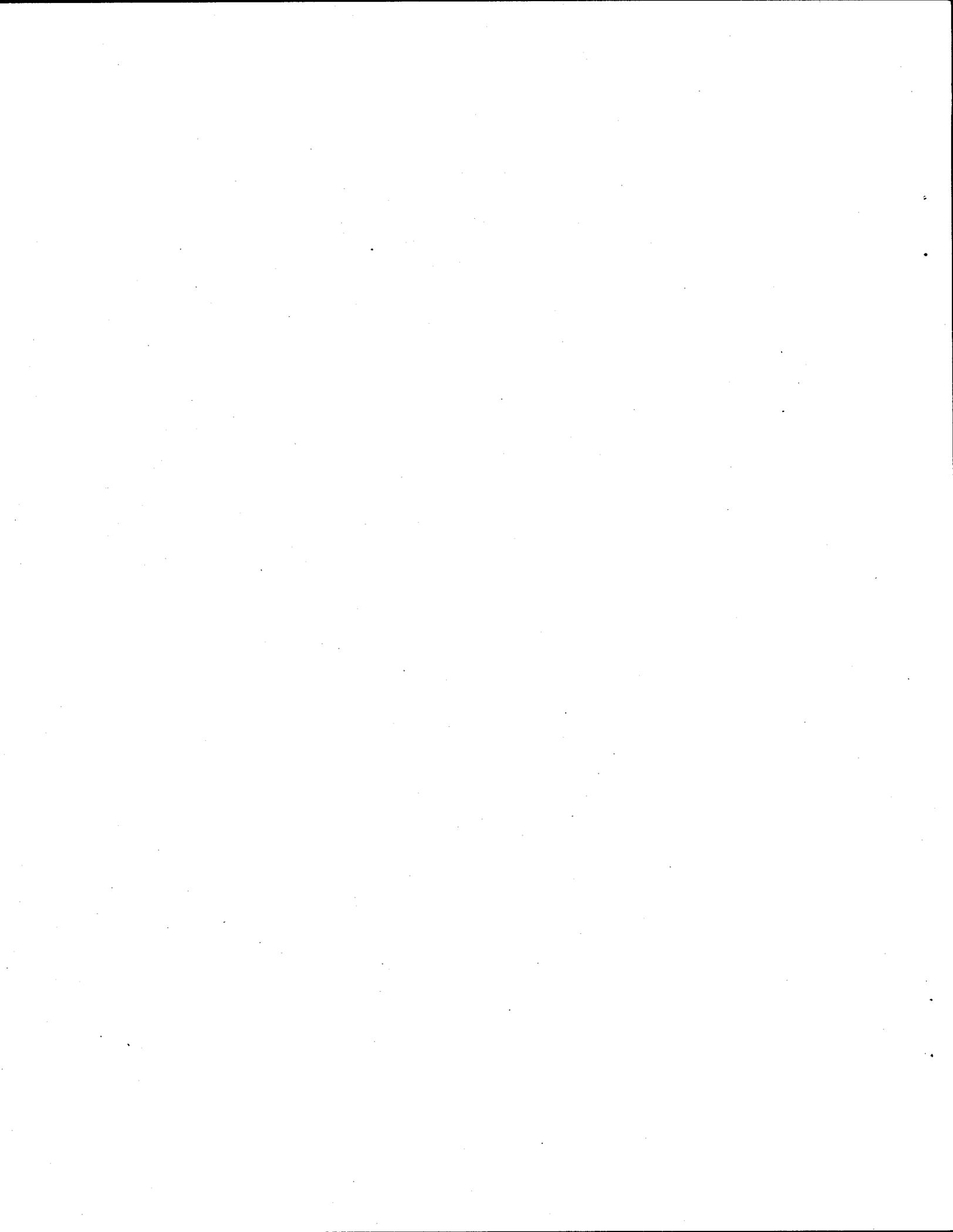
This report describes the analytical results of vapor samples taken from the headspace of the waste storage tank 241-S-106 (Tank S-106) at the Hanford Site in Washington State. The results described in this report were obtained to characterize the vapors present in the tank headspace and to support safety 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-106 on 6/13/96

<u>Category</u>	<u>Sample Medium</u>	<u>Analyte</u>	<u>Vapor^(a) Concentration</u>	<u>Units</u>
Inorganic Analytes ^(b)	Sorbent Traps	NH ₃	36.5 ± 3.4	ppmv
		NO ₂	< 0.16	ppmv
		NO	< 0.16	ppmv
		H ₂ O	8.9 ± 0.3	mg/L
Permanent Gases	SUMMA™ Canister	H ₂	< 17	ppmv
		CH ₄	< 25	ppmv
		CO ₂	< 17	ppmv
		CO	< 17	ppmv
		N ₂ O	< 17	ppmv
Total Non-Methane Organic Compounds (TO-12)	SUMMA™ Canister	Non-Methane Organic Compounds	1.82	mg/m ³
Organics (TO-14)	SUMMA™ Canister	Methanol	2.652	ppmv
		Ethanol	1.378	ppmv
		Acetone	0.221	ppmv
Organics (PNL-TVP-10)	Sorbent Traps	Methanol	0.747	ppmv
		Ethanol	0.604	ppmv
		Methylcyclohexane	0.314	ppmv

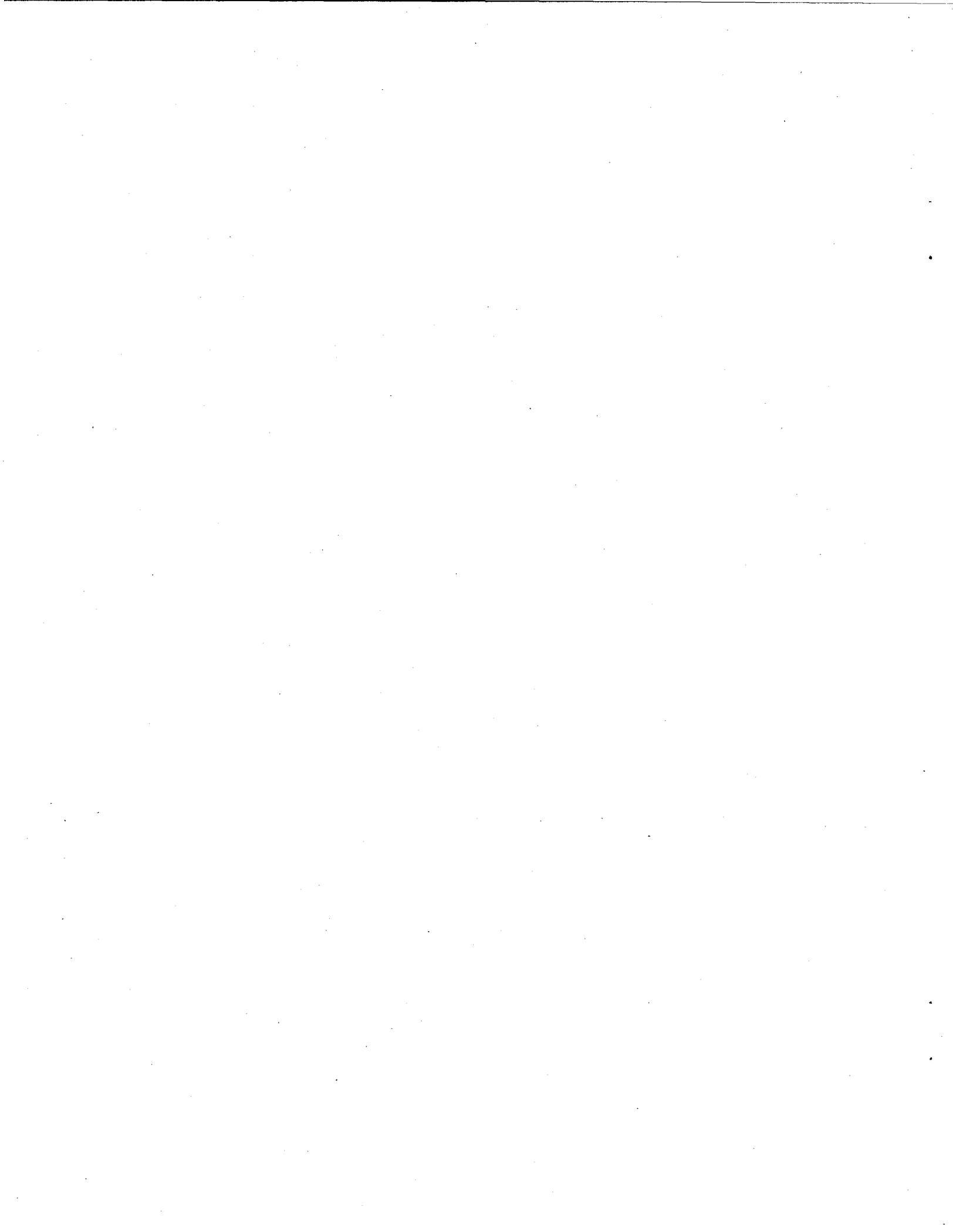
(a) Vapor concentrations were determined using sample-volume data provided by Westinghouse Hanford Company and are based on averaged data.

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



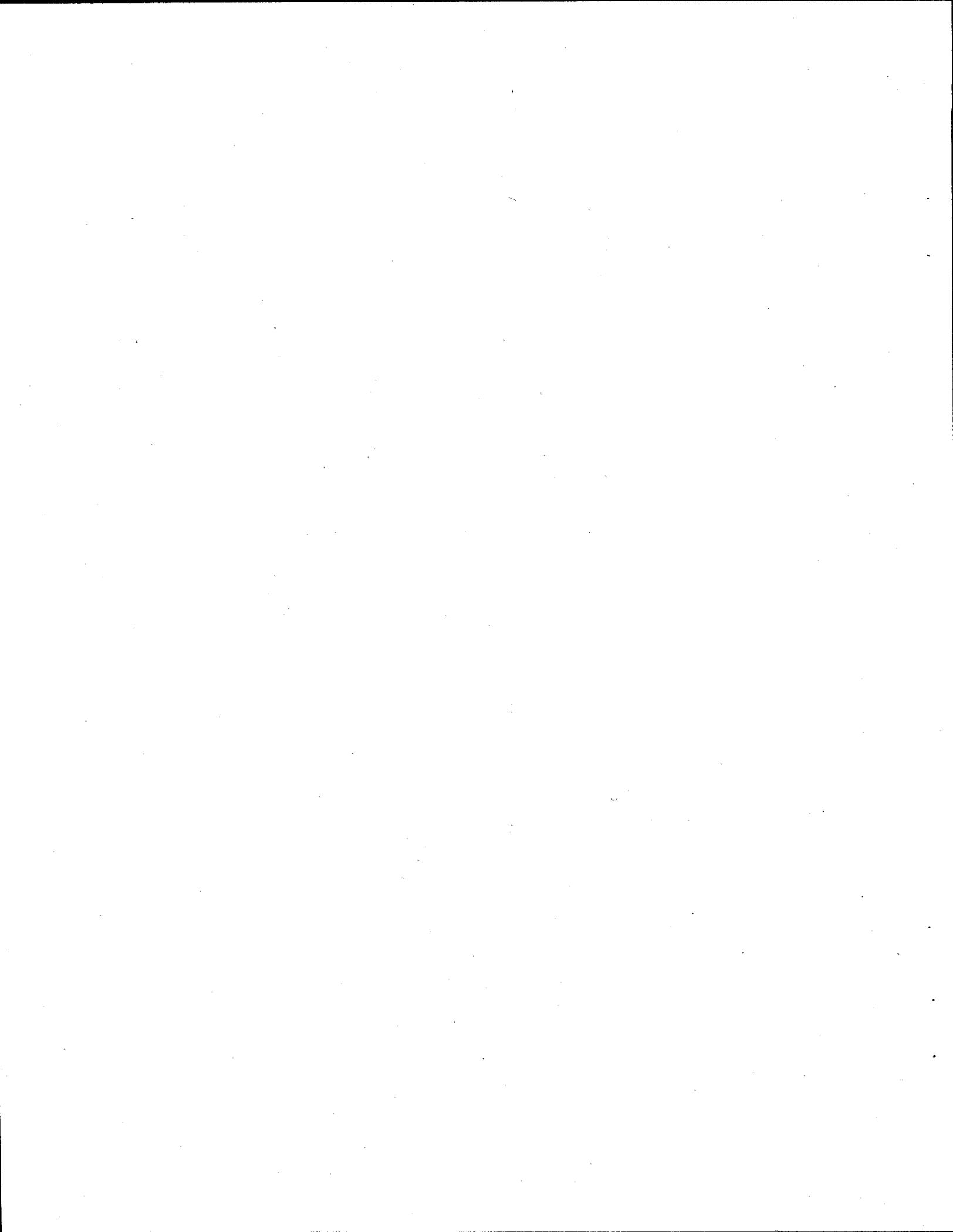
Acknowledgments

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Glossary

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



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1.0 Introduction

This report describes the results of vapor samples taken from the headspace of waste storage tank 241-S-106 (Tank S-106) 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 S6061. Samples were collected by WHC on June 13, 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)
- *organic analytes* analyses using cryogenic preconcentration followed by gas chromatograph/mass spectrometer (GC/MS)

(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.

- *organic analytes* (TST samples) using thermal desorption followed by GC/MS.

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

2.0 Analytical Results

Samples obtained by WHC from the headspace of Tank S-106 on June 13, 1996 (Sample Job S6061) 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 36.5 ± 3.4 pmv (NH_3), < 0.16 ppmv (NO_2), < 0.16 ppmv (NO), and 8.9 ± 0.3 mg/L (primarily H_2O). The vapor concentration results were based on four samples for each compound. All samples (100%) were successfully analyzed and used in the averages. Representative field blanks were also analyzed and used to correct data.

Results provided above are estimated to be accurate to within $\pm 10\%$ (assuming negligible error in the sample volume measurements) and are within the $\pm 30\%$ specified by the SAP. Measurement precision, as indicated by the relative standard deviation, was $< 10\%$ 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 12 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, 100095, is included in Appendix F.

2.2 Permanent Gases

The complete results of the permanent gas analysis for Tank S-106 can be found in Appendix B. In summary, no permanent gases were detected in the tank headspace samples above the EQL.

2.3 Total Non-Methane Organic Compounds

The complete results of the TO-12 analysis for Tank S-106 can be found in Appendix C. In summary, the average concentration in the three tank headspace samples was 1.82 mg/m³. This compares to 8.78 mg/m³, 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-106 can be found in Appendix D. In summary, 54 target analytes above the IDL and seven TICs were detected in the tank headspace samples. Forty-nine target analytes and five TICs were identified in two or more tank headspace samples. Two of the TICs were not identified and were labelled as unknowns. Methanol at 3.79 mg/m³ and ethanol at 2.83 mg/m³ accounted for 77% of the target compounds and 75% of the total compounds identified in the analysis. The total concentration of the target analytes was 8.65 mg/m³. An unknown (0.05 mg/m³) and propane (0.03 mg/m³) were the two highest concentration TICs identified in two or more of the tank headspace samples. The total concentration of TICs identified was 0.13 mg/m³. The total concentration of all the compounds identified was 8.78 mg/m³. This compares to a total concentration of 1.82 mg/m³ identified in the TO-12 analysis of the three tank headspace samples.

SUMMA™ canister PNL 108 was analyzed in replicate for target analytes and TICs to determine analytical precision. Twenty-four of 43 target compounds and one of three TICs had RPDs of less than 10%.

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

2.5 Organic Analytes by Triple Sorbent Trap Method

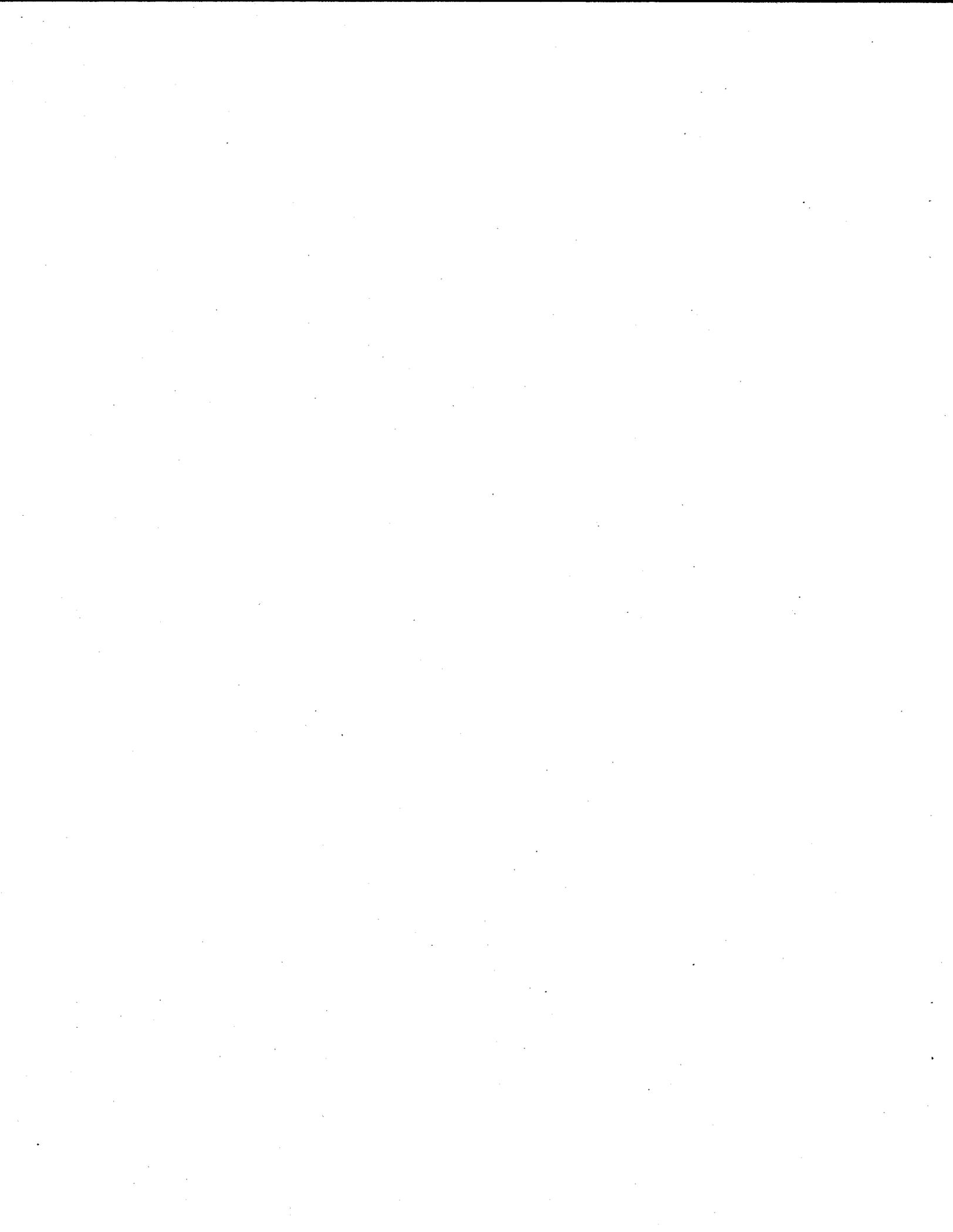
The complete results of the sorbent trap analysis of Tank S-106 can be found in Appendix E. In summary, 36 target analytes above the IDL and 27 TICs were detected in the tank headspace samples. All 36 of the target analytes and 26 TICs were observed in two or more sorbent traps. Ethanol at 1.24 mg/m³ and methanol at 1.07 mg/m³ accounted for 40% of the target analytes and 16% of the total concentration identified by the analysis. The total concentration of the target analytes was 5.71 mg/m³ or 40% of the total concentration identified by the analyses. The predominant TICs observed in these samples were methylcyclohexane at 1.37 mg/m³ and octamethylcyclotetrasiloxane at 1.00 mg/m³. The total concentration of the TICs was 8.69 mg/m³ or 60% of the total concentration identified by analysis. The total concentration of all the compounds identified was 14.41 mg/m³.

Triple sorbent trap sample PNL 1002 was analyzed in replicate for target analytes and TICs to determine analytical precision. Twelve of 35 target compounds and 10 of 27 TICs had RPDs of less than 10%.

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 concerns associated with preventing contamination of the bundle from the riser appears to have severely exacerbated the tape problem which had not been completely eliminated. Because of the tape problem, 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-106 on June 13, 1996 (Sample Job S6061). 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). No immediate notifications were provided because analytical results indicated no specific analytes exceeded the notification levels; 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. 2A, Westinghouse Hanford Company, Richland, Washington.

Further Reading

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

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

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

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

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

Appendix A

Tank Vapor Characterization:

Inorganic Analytes

Appendix A

Tank Vapor Characterization: Inorganic Analytes

Solid sorbent traps, prepared in multi-trap sampling trains, were supplied to Westinghouse Hanford Company (WHC) for sampling the tank headspace using the In Situ Vapor Sampling System (ISVS). Blanks, spiked blanks (when requested), and exposed samples were returned to Pacific Northwest National Laboratory (PNNL) for analysis. Analyses were performed to provide information on the tank headspace concentration of the following analytes: ammonia (NH_3), nitrogen dioxide (NO_2), nitric oxide (NO), and water (H_2O). Procedures were similar to those developed previously during sample jobs performed with the VSS connected to the headspace of Tank C-103 (Ligotke et al. 1994). During those sample jobs, control samples provided validation that the sorbent tubes effectively trapped NH_3 and mass. Samples were prepared, handled, and disassembled as described in Technical Procedure PNL-TVP-09^(a). Analytical accuracy was estimated based on procedures used. Sample preparation and analyses were performed following PNNL quality assurance (QA) impact level II requirements.

A.1 Sampling Methodology

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

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

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

Sorbent trains provided to trap inorganic compounds included all or some of the following: samples, spiked samples, spares, blanks, and spiked blanks. Sorbent trains were prepared from same-lot batches, with the oxidizer sections of the NO_x sorbent trains having been stored previously in a freezer. After sample preparation, sorbent trains were stored at ≤ 10°C because of handling recommendations for the oxidizer tubes attached to some samples. After receipt of exposed and radiologically cleared samples from WHC and disassembly of the sorbent trains, samples were provided to the analytical laboratory at ambient temperature.

The sorbent traps were prepared in multi-trap sorbent trains configured so sample flow passed in order through the traps, targeting specific analytes, and then through a desiccant trap. The specific order of traps within the various sorbent trains is described in Section A.4. The ends of the glass-tube traps were broken, and the traps were weighed and then connected to each other using uniform lengths of 3/8-in. perfluoroalkoxy-grade Teflon® tubing. The tubing was heated in hot air and forced over the open ends of the traps to form a tight seal. The inlets of the sorbent trains each consist of a short section of tubing that has a 3/8-in. stainless steel Swagelok® nut, sealed using a Swagelok® cap. The trailing ends of the sorbent trains (the downstream end of the traps containing silica gel) were each sealed with red plastic end caps provided by the manufacturer. The sorbent-tube trains remained sealed other than during the actual sampling periods. During vapor sampling, C-Flex® tubing was provided by WHC to connect the downstream ends of the sorbent trains to the sampling manifold exhaust connections.

A.1.1 Concentration Calculations. The concentrations of target compounds in the tank headspace were determined from sample results, assuming effective sample transport to the sorbent traps. Concentration, in parts per million by volume (ppmv), was determined by dividing the mass of the compound, in μmol, by the volume of the dried tank air sampled in moles. The micromolar sample mass was determined by dividing the compound mass, in μg, by the molecular weight of the compound, in g/mol. The molar sample volume was determined, excluding water vapor, by dividing the standard sample volume (at 0°C and 760 torr), in L, by 22.4 L/mol. For example, the concentration by volume (C_v) of a 3.00-L sample containing 75.0 μg of NH₃ equals

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

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

A.2 Analytical Procedures

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

A.2.1 Ammonia Analysis. The sorbent material from the NH_3 -selective sorbent traps was placed into labeled 20-mL glass scintillation vials. Vials containing front-, or primary-, section sorbent material were treated with 10.0 mL of deionized water (DIW), and vials containing back-up-section sorbent material were treated with 5.0 mL of DIW. After extraction, the NH_3 sorbent traps were analyzed using the selective ion electrode procedure PNL-ALO-226 Rev 0^(a). Briefly, this method includes 1) preparing a 1000- $\mu\text{g}/\text{mL}$ (ppm) NH_3 stock standard solution from dried reagent-grade NH_4Cl and DIW, 2) preparing 0.1-, 0.5-, 1.0-, 10-, and 100-ppm NH_3 working calibration standards by serial dilution of the freshly made stock standard, 3) generating an initial calibration curve from the measured electromotive force signal versus NH_3 concentration data obtained for the set of working standards, 4) performing a calibration-verification check, using a mid-range dilution of a certified National Institute for Standards and Technology (NIST)-traceable 0.1 M NH_4Cl standard from an independent source, after analyzing every five or six samples, 5) continuing this sequence until all samples of the batch have been measured, including duplicates and spiked samples, and 6) remeasuring the complete set of calibration standards (at the end of the session). Electromotive force (volts) signal measurements obtained for samples are compared to those for standards, either graphically or algebraically (using linear regression) to determine NH_3 concentration in the samples.

A.2.2 Nitrite Analysis. The sorbent traps for NO_2 and NO were desorbed in an aqueous TEA and n-butanol solution and analyzed by suppressed-conductivity ion chromatography (SCIC) for nitrite according to PNL-ALO-212, Rev. 1^(b) modified to obviate interferences by concentrations of non-target analytes. Specifically, the modifications used were 1) eluent 1.44 mM Na_2CO_3 + 1.8 mM NaHCO_3 at 2.0 mL/min, 2) one guard column (AG4A) and two separator columns (AS4A) in series instead of just one separator column, and 3) all standards, samples, and blanks were injected into the IC sample loop through 0.45- μm syringe filters.

For the analysis, the sorbent materials were placed into labeled 20-mL glass scintillation vials. To each vial, 3.0 mL of desorbing solution (15 g TEA + 1 mL n-butanol in 1.0 L of DIW) was added. Primary sorbent-tube sample materials and back-up (breakthrough) sorbent-trap materials were analyzed separately using identical procedures. Each analytical session was conducted as follows. Working nitrite standards (0, 0.1, 0.25, and 0.5 ppm) were prepared by diluting a stock nitrite standard with desorbing solution. An initial calibration curve was prepared from the instrument response (chromatographic peak height) versus nitrite standard concentration data for the set of working standards. A calibration verification check using one of the midrange standards was

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

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

performed after the analysis of every six samples. If the instrument response indicated that sample nitrite concentration was outside the calibration range (> 0.5 ppm nitrite), the sample was diluted with desorbing solution and reanalyzed. After all samples of a batch were analyzed, the complete set of calibration standards was remeasured to verify consistent instrument response, and the analytical session was terminated.

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

A.2.3 Mass (Water) Analysis. Sorbent traps used to make each sample train were weighed using a semi-micro mass balance, after labeling and breaking the glass tube ends, without plastic end caps in accordance with procedure PNL-TVP-09. After receipt of exposed samples, the sorbent traps were again weighed to determine the change in mass. Records of the measurements were documented on sample-preparation data sheets. The mass concentration, generally roughly equal to the concentration of water, was determined by dividing the combined change in mass from all traps in a sorbent train by the actual volume of gas sampled. Field blanks were used to correct results.

A.3 Quality Assurance/Quality Control

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

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

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

Analyte	Formula	Procedure	EQL ^(b) (μg)	EQL ^(b) (ppmv)	Notification Level ^(c) (ppmv)
Ammonia	NH ₃	PNL-ALO-226	1.0	0.71	≥ 150
Nitrogen Dioxide	NO ₂	PNL-ALO-212	0.3	0.16	≥ 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 $\pm 25\%$ and 70 to 130%, respectively (Osborne et al. 1995).
- (b) The lowest calibration standard is defined as the EQL.
- (c) As per Table 7-1 in Osborne et al. (1995). Notification levels require verbal and written reports to WHC on completion of preliminary analyses.
- (d) The vapor-mass concentration, thought to be largely water vapor, is determined gravimetrically.
n/a = not applicable.

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

A.4 Inorganic Sample Results

Samples were obtained by WHC from the headspace of Tank S-106 on June 13, 1996 using the ISVS. The sample job designation number was S6061. Samples were prepared, submitted to WHC for the sample job, and then returned to PNNL and analyzed to provide information on the concentrations of NH₃, NO₂, NO, and mass (primarily H₂O). Samples were controlled using COC form 100095 (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, 7 days elapsed), June 25, 1996 (ammonia, 12 days elapsed), and June 24, 1996 (nitrite, 11 days elapsed).

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

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

A.4.1 Ammonia Results. The concentration of NH_3 was 36.5 ± 3.4 ppmv, based on all four samples. The blank-corrected NH_3 quantities in the sorbent traps ranged from 2.67 to 3.27 μmol in front sections; blank-corrected NH_3 was not found ($\leq 0.01 \mu\text{mol}$) in back sorbent sections. Blank corrections, 0.16 μmol in front and 0.07 μmol in back sections, were about 5% of collected quantities. The analysis of one sample was duplicated and yielded a repeatability of $\pm 1.6\%$. 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 93%. The initial and continuing calibration verification 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 $\mu\text{g/mL}$.

A.4.2 Nitrogen Oxides Results. The concentrations of NO_2 and NO were both < 0.16 ppmv based on all four samples. Blank-corrected NO_2^- quantities in the sorbent traps were all $< 0.013 \mu\text{mol}$. Nitrite blank levels used to correct data were 0.0072 μmol in front (four of four blanks analyzed) and 0.0037 μmol in back (two of four blanks analyzed) sorbent sections. The analyses of two samples were duplicated and yielded repeatabilities of $\pm 3.1\%$ and $\pm 0.0\%$. Two sample leachates were spiked with 0.25 and 0.125 ppm NO_2^- and yielded percentage recoveries of 96 and 98% respectively. A 4-point calibration was performed over a concentration range of 0 to 0.5 $\mu\text{g NO}_2^-$ per mL in the desorbing matrix. Although spiked blanks were not tested, blanks spiked with 0.0064, 0.047, 0.11, and 0.74 $\mu\text{mol NO}_2^-$ during previous sample jobs yielded percentage recoveries of 153 ± 14 , 103 ± 4 , 106 ± 8 , and $111 \pm 7\%$, respectively (Clauss et al. 1994; Ligothke et al. 1994).

A.4.3 Gravimetric Results. Gravimetric results yield water vapor concentrations. This is because the total mass concentration of other vapors in the headspaces of Hanford waste tanks, measured in $\mu\text{g/L}$, are typically two or three orders of magnitude less than the mg/L mass concentrations of the water vapor found in even relatively dry tanks. The water vapor mass concentration collected in the 5-trap sorbent trains was $8.9 \pm 0.3 \text{ mg/L}$, based on dry air sample volumes (0°C and 760 torr). The result was determined from an average mass gain of 18.5 mg from all four sample trains. The blank correction applied to the results was - 2.4 mg per train, based on a mass gain of 2.4 ± 0.6 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 $103 \pm 2\%$ during a previous sample job (Clauss et al. 1994).

Corrected for a measured tank headspace temperature of 19.1°C and pressure of 739.9 torr, the actual water vapor mass concentration from the gravimetric results was $8.0 \pm 0.3 \text{ mg/L}$. Also based on analytical results, the partial pressure of water vapor was 8.1 ± 0.3 torr, the relative humidity was $49 \pm 2\%$, and the dew point was $8.1 \pm 0.3^\circ\text{C}$.

Table A.2 List of PNNL Inorganic Samples, Controls, and Gravimetric Results
Obtained from the Headspace of Tank S-106 on 6/13/96

Sample Number	Sorbent Train Type	Sample Port and Volume Information ^(a)				
		Sample Port	Flow Rate (mL/min)	Duration (min)	Volume (L)	Mass Gain (g)
<u>Samples:</u>						
S6061-A07-S97	NH3/NOx/H2O	1	200.0	10.0	1.86	0.0182
S6061-A08-S98	NH3/NOx/H2O	2	200.0	10.0	1.86	0.0195
S6061-A09-S99	NH3/NOx/H2O	3	200.0	10.0	1.86	0.0188
S6061-A10-01R	NH3/H2O/H2O	4	200.0	10.0	1.86	0.0194
<u>Controls:</u>						
S6061-A15-02R	NH3/NOx/H2O Field Blank	n/a ^(b)	n/a	n/a	n/a	0.0028
S6061-A16-03R	NH3/NOx/H2O Field Blank	n/a	n/a	n/a	n/a	0.0020

(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-106 on 6/13/96

Sample	Analytical Results (μmol)			Sample Volume (L)	Vapor ^(a) Concentration (ppmv)
	Front Section	Back Section	Total ^(b) Blank-Corrected		
<u>NH₃ Samples:</u>			<u>3.03</u>	<u>1.86</u>	<u>36.5 ± 3.4</u>
S6061-A07-S97	3.10	0.061	2.94	1.86	35.4
S6061-A07-S98	3.39	NA ^(c)	3.23	1.86	38.9
S6061-A07-S99	3.43	0.055	3.27	1.86	39.4
S6061-A07-01R	2.83	NA	2.67	1.86	32.2
<u>NO₂ Samples:</u>			<u><0.013</u>	<u>1.86</u>	<u><0.16</u>
S6061-A07-S97	0.0074	NA	<0.013	1.86	<0.16
S6061-A07-S98	0.0067	0.0038	<0.013	1.86	<0.16
S6061-A07-S99	0.0069	NA	<0.013	1.86	<0.16
S6061-A07-01R	0.0063	0.0036	<0.013	1.86	<0.16
<u>NO Samples:</u>			<u><0.013</u>	<u>1.86</u>	<u><0.16</u>
S6061-A07-S97	0.0086	0.0037	<0.013	1.86	<0.16
S6061-A07-S98	0.0086	NA	<0.013	1.86	<0.16
S6061-A07-S99	0.0094	0.0036	<0.013	1.86	<0.16
S6061-A07-01R	0.0094	NA	<0.013	1.86	<0.16
<u>Gravimetric Samples:</u>			<u>16.6 mg</u>	<u>1.86</u>	<u>8.9 ± 0.3 mg/L</u>
S6061-A07-S97	n/a ^(c)	n/a	15.8	1.86	8.5
S6061-A07-S98	n/a	n/a	17.1	1.86	9.2
S6061-A07-S99	n/a	n/a	16.4	1.86	8.8
S6061-A07-01R	n/a	n/a	17.0	1.86	9.1

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

A.5 References

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

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

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

Appendix B

Tank Vapor Characterization:

Permanent Gases

Appendix B

Tank Vapor Characterization: Permanent Gases

B.1 Sampling Methodology

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

B.2 Analytical Procedure

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

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

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

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

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

B.3 Quality Assurance/Quality Control

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

Each analyte was quantitated by comparison of sample analyte peak area to the calibration plot generated for the compound. The estimated quantitation limit (EQL) for the method has been established as the low level calibration standard. Before and after each sample analysis set, a gas standard was run to evaluate system performance and to measure system accuracy. The calculated concentration of the individual gases in the standards fell within $\pm 25\%$ of the expected concentrations. One sample was run in duplicate to provide a measure of method precision. Results of the replicate analysis are presented in Table B.2. An N₂ reagent blank, an ambient-air sample collected ~10 m upwind of Tank S-106 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-106, ambient air collected ~10 m upwind of the tank, and ambient air collected through the ISVS. Samples were analyzed on June 21 and 24, 1996. No permanent gases above the EQL were observed in the tank headspace samples. A replicate analysis was performed on SUMMA™ canister PNL 108; however, only the results from the first analysis are included in the average concentration reported for the tank headspace samples.

Table B.2 Permanent Gas Analysis Results for Samples Collected from the Headspace of Tank S-106 and for Ambient Air and Ambient Air Through the ISVS Collected Near Tank S-106 in SUMMA (TM) Canisters on 6/13/96

Permanent Gas Analyte	Ambient Air Upwind		Ambient Air Through Bundle		Tank Samples				Average Concentration Tank Samples (ppmv)			
	S6061-A01.086 ^(a) PNL 086 ^(b) Concentration (ppmv)	<17 <25 365 <17 <17	S6061-A02.089 ^(a) PNL 089 ^(b) Concentration (ppmv)	<17 <25 366 <17 <17	S6061-A04.097 ^(a) PNL 097 ^(b) Concentration (ppmv)	<17 <25 <17 <17 <17	S6061-A05.108 ^(a) PNL 108 ^(b) Concentration (ppmv)	<17 <25 <17 <17 <17		S6061-A06.120 ^(a) PNL120 ^(b) Concentration (ppmv)	<17 <25 <17 <17 <17	S6061-A05.108 ^(a) PNL 108 ^{(b)(c)} Concentration (ppmv)
Hydrogen												
Methane												
Carbon Dioxide												
Carbon Monoxide												
Nitrous Oxide												

Footnotes

- (a) WHC sample identification number.
- (b) PNL canister number.
- (c) Replicate analysis for PNL 108; 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/m³ are required to determine total non-methane organic compounds (TNMOC) concentration in the tank samples.

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

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

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

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

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

C.3 Quality Assurance/Quality Control

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

The TNMOC is calibrated by using propane as the calibration standard and using that response factor as an external standard method. The instrument calibration mixture for the PNL-TVP-08 analysis consists of National Institute for Standards and Technology (NIST) 99.999% propane analyzed using a five-point, multi-level, linear regression curve.

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

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

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

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

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

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

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

C.4 Total Non-Methane Organic Compounds Sample Results

Table C.1 lists results of the TO-12 gas analysis from samples collected from the headspace of Tank S-106, ambient air collected ~10 m upwind of the tank, and ambient air collected through the ISVS. Samples were analyzed on August 13, 1996. Concentrations in the ambient air samples ranged from 0.39 mg/m³ to 0.70 mg/m³. Concentrations in the three tank headspace samples ranged from 1.76 mg/m³ to 1.91 mg/m³ with an average concentration of 1.82 mg/m³. This compares to 8.78 mg/m³ for the sum of all target compounds and TICs identified in the analysis of the SUMMA™ canisters. A replicate analysis was performed on SUMMA™ canister PNL 108; however, only the results from the first analysis are included in the average concentration reported for the tank headspace samples.

Table C.1. TO-12 Results for Samples Collected Through the ISVS from the Headspace of Tank S-106 and from Ambient Air Near Tank S-106 in SUMMA (TM) Canisters on 6/13/96.

TO-12	Ambient Air		Tank Samples				Average Concentration Tank Samples (mg/m ³)
	Upwind	Ambient Air Through Bundle	S6061-A04.097 ^(a)	S6061-A05.108 ^(a)	S6061-A06.120 ^(a)	S6061-A05.108 ^(a)	
	PNL 086 ^(b)	S6061-A02.089 ^(a)	PNL 097 ^(b)	PNL 108 ^(b)	PNL 120 ^(b)	PNL 108 ^(b)	
	Concentration (mg/m ³)						
	0.39 J	0.70 J	1.91	1.78	1.76	1.79	1.82

Data Qualifier Flags

J Result above the IDL but below the EQL.

Footnotes

(a) WHC sample identification number.

(b) PNL canister number.

(c) Replicate analysis for PNL 108; 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 μ L of distilled water and labeled with a field-sampling identification. Cleaned canisters stored more than 30 but less than 60 days are re-evacuated and rehumidified before use. If stored more than 60 days, the canisters are recleaned and validated before use.

D.2 Analytical Procedure

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

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

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

The instrument calibration mixture for the PNL-TVP-03 analysis consists of 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	p/m-Xylene
Chloromethane	Pentanenitrile
1,2-Dichloro-1,1,2,2-tetrafluoroethane	Styrene
Vinyl Chloride	1,1,2,2-Tetrachloroethane
Bromomethane	o-Xylene
Chloroethane	1,3,5-Trimethylbenzene
Trichlorofluoromethane	1,2,4-Trimethylbenzene
1,1-Dichloroethene	1,3-Dichlorobenzene
Methylene Chloride	1,4-Dichlorobenzene
1,1,2-Trichloro-1,2,2-trifluoroethane	1,2-Dichlorobenzene
1,1-Dichloroethane	1,2,4-Trichlorobenzene
cis-1,2-Dichloroethene	Hexachloro-1,3-butadiene
Chloroform	2-Butanone
1,2-Dichloroethane	Acetone
1,1,1-Trichloroethane	Acetonitrile
Benzene	Heptane
Carbon Tetrachloride	Tetrahydrofuran
1,2-Dichloropropane	Pyridine
Trichloroethene	Butanenitrile
cis-1,3-Dichloropropene	Cyclohexane
trans-1,3-Dichloropropene	Decane
1,1,2-Trichloroethane	Hexane
Toluene	4-Methyl-2-pentanone
1,2-Dibromoethane	Propanenitrile
Tetrachloroethylene	Cyclohexanone
Chlorobenzene	Propanol
Ethylbenzene	Nonane
Undecane	Dodecane
Tridecane	Tetradecane
Butane	Pentane
1-Butanol	Octane
Hexanenitrile	1-Ethyl-2-methylbenzene
Methanol ^(a)	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-d₅, and bromofluorobenzene was used as an internal standard (IS) for all blank, calibration standard, and sample analyses. Analyte responses from sample components, ISs, and standards were obtained from the extracted ion plot from their selected mass ion. The calibration was generated by calculating the relative response ratios of the IS to calibration standard responses and plotting the ratios against the ratio of the calibration-standard concentration (in ppbv) to the IS concentration. Once it is determined that the relative response is linear with increasing concentration, an average response factor is calculated for each target analyte and used to determine the concentration of target compounds in each sample. Method blanks are analyzed before and after calibration standards and tank headspace samples are analyzed.

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

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

D.3.2 Identification and Quantitation of Tentatively Identified Compounds. The tentatively identified compounds (TICs) are determined by mass-spectral interpretation and comparison of the spectra with the EPA/National Institute for Standards and Technology (NIST) and WILEY electronic mass spectra libraries. Chromatographic peaks with an area count greater than, or equal to, one-tenth of the total area count of the nearest eluting IS are tentatively identified and quantitatively estimated. This is roughly equivalent to 10 ppbv, depending on the relative response

^(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/m³:

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

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

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

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

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

D.4 Organic Sample Results

Five SUMMA™ canisters were returned to the laboratory on June 18, 1996 under WHC COC form 100093 (see Appendix F). Samples were analyzed on July 9, 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-106 and through the ISVS near Tank S-106 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 above the compound IDL in any of the tank headspace samples. Fifty-four target analytes above the IDL and seven TICs were detected in the tank headspace samples. Forty-nine target analytes and five TICs were identified in two or more tank headspace samples. Two of the TICs were not identified and were labelled as unknowns. Methanol at 3.79 mg/m³ and ethanol at 2.83 mg/m³ accounted for 77% of the target compounds and 75% of the total compounds identified in the analysis. The total concentration of the target analytes was 8.65 mg/m³. An unknown (0.05 mg/m³) and propane (0.03 mg/m³) were the two highest concentration TICs identified in two or more of the tank headspace samples. The total concentration of TICs identified was 0.13 mg/m³. The total concentration of all of the compounds identified was 8.78 mg/m³. This compares to a total concentration of 1.82 mg/m³ identified in the TO-12 analysis of the three tank headspace samples.

SUMMA™ canister PNL 108 was analyzed in replicate for target analytes and TICs to determine analytical precision. Twenty-four of 43 target compounds and one of three TICs had RPDs of less than 10%.

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

The following procedural changes and observations were noted during the analysis of Tank S-106:

This analytical sequence was run using 100 ml volumes to quantify target compounds in each tank and ambient air 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. Tridecane was found in tank sample S6061-A05.108 at a concentration between the IDL and the EQL. Pyridine was found in the tank samples at concentrations between the IDL and the EQL. Tetradecane was not found in the tank samples at concentrations above the IDL.

Four target compounds (tetrahydrofuran, pyridine, nonane, and decane) were outside the 25% difference (% D) acceptance criteria for the CCV sample; however, the CCV passed the procedural criterion requiring +25% D passage for 85% of all target compounds. Decane was found in all of the samples at concentrations between the EQL and the upper quantitation limit (UQL), with the exception of tank sample S6061-A01.086 which was at a concentration between the IDL and the EQL. Tetrahydrofuran and nonane were found in all tank samples at concentrations below the IDL, with the exceptions of S6061-A04.097, in which nonane was found at a concentration between the EQL and the UQL, and S6061-A05.108, in which nonane was found at a concentration between the IDL and the EQL. Tetrahydrofuran was found in tank samples S6061-A04.097 and S6061-A05.108 at concentrations between the EQL and the UQL, and in tank sample S6061-A01.86 at a concentration between the IDL and the EQL. Pyridine was found in tank samples at concentrations between the IDL and the EQL.

Thirteen target compounds (dichlorofluoromethane, methylene chloride, tetrahydrofuran, 1-butanol, heptane, 4-methyl-2-pentanone, 1,1,2-trichloroethane, 1-ethyl-2-methylbenzene, 1,3,5-trimethylbenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, decane, and 1,2-dichlorobenzene) were found in the continuing calibration blank (CCB) above their EQLs. The compound 1,2,4-trichlorobenzene was found in initial calibration blank above the EQL.

Table D.2. Positively Identified and Quantitated Target Analytes^(a) and Tentatively Identified Compounds and Estimated Concentrations^(b) for Samples from the Headspace in Tank S-106 in SUMMA Canisters Collected on 6/13/96

Target Analytes ^(a)	CAS	MW	Ret Time	S6061-A04.097 ^(c) ISVS		S6061-A05.108 ^(c) ISVS		S6061-A06.120 ^(c) ISVS		Mean and Standard Deviation			
				(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)	(mg/m ³)	St. Dev.	(ppbv)	St. Dev.
Dichlorodifluoromethane	75-71-8	121	4.6	0.031	5.7	0.029	5.5	0.036	6.6	0.032	0.003	5.9	0.58
Chloromethane	74-87-3	50	5.0	0.014	6.2	0.013	5.8	0.015	6.5	0.014	0.001	6.2	0.38
1,2-dichloro-1,1,2,2-tetrafluoroethane	76-14-2	171	5.2	0.026	3.3	0.026	3.4	0.027	3.5	0.026	0.001	3.4	0.090
Methanol	67-56-1	32	5.3	4.360	3048	2.904	2030	4.118	2879	3.794	0.780	2652	545
Bromomethane	74-83-9	95	6.4	0.017	4.1	0.018	4.1	0.018	4.3	0.018	0.000	4.2	0.11
Ethanol	64-17-5	46	6.9	3.242	1578	2.241	1091	3.006	1463	2.830	0.523	1378	255
Acetonitrile	75-05-8	41	7.4	0.025	13	0.022	12	0.022	12	0.023	0.001	13	0.70
Acetone	67-64-1	58	7.9	0.529	204	0.510	197	0.682	263	0.573	0.094	221	36
Trichlorofluoromethane	75-69-4	137	8.3	0.040	6.5	0.046	7.5	0.051	8.3	0.046	0.006	7.4	0.90
Pentane	109-66-0	72	9.0	0.004	1.2	0.004	1.2	0.030	9.3	e	e	e	e
1,1-Dichloroethene	75-35-4	97	9.5	0.014	3.3	0.015	3.5	0.016	3.7	0.015	0.001	3.5	0.20
Methylene Chloride	75-09-2	85	9.7	0.028	7.4	0.030	7.8	0.032	8.3	0.030	0.002	7.9	0.44
1,1,2-trichloro-1,1,2,2-tetrafluoroethane	76-13-1	187	10.2	0.037	4.4	0.042	5.1	0.045	5.4	0.041	0.004	4.9	0.49
Propanol	71-23-8	60	10.9	0.056	21	0.052	20	0.073	27	0.061	0.011	23	4.1
Propanenitrile	107-12-0	55	11.0	0.004	1.6	0.028	12	0.004	1.6	e	e	e	e
1,1-Dichloroethane	75-34-3	99	11.9	0.018	4.2	0.018	4.1	0.022	4.9	0.019	0.002	4.4	0.47
cis-1,2-Dichloroethene	156-59-2	97	13.4	0.014	3.2	0.013	3.0	0.003	0.79	0.014	e	3.1	e
Hexane	110-54-3	86	13.8	0.022	5.7	0.026	6.8	0.030	7.7	0.026	0.004	6.8	0.98
Chloroform	67-66-3	119	14.0	0.020	3.7	0.020	3.8	0.023	4.2	0.021	0.001	3.9	0.27
Tetrahydrofuran	109-99-9	72	14.7	0.046	14	0.047	15	0.002	0.50	0.047	e	14	e
1,1,1-Trichloroethane	71-55-6	133	15.9	0.021	3.5	0.024	3.9	0.028	4.7	0.024	0.004	4.0	0.59
1-Butanol	71-36-3	74	16.4	0.218	66	0.208	63	0.333	101	0.253	0.070	76	21
Benzene	71-43-2	78	16.8	0.012	3.4	0.013	3.6	0.016	4.5	0.013	0.002	3.8	0.60
Carbon Tetrachloride	56-23-5	154	17.1	0.020	2.9	0.023	3.3	0.027	3.9	0.023	0.004	3.4	0.51
Trichloroethene	79-01-6	131	18.8	0.021	3.6	0.023	3.8	0.024	4.1	0.023	0.002	3.9	0.27
Heptane	142-82-5	100	19.3	0.018	4.0	0.021	4.7	0.021	4.7	0.020	0.002	4.5	0.44
4-Methyl-2-Pentanone	108-10-1	100	20.5	0.042	9.4	0.036	8.0	0.049	11	0.042	0.007	9.5	1.5
cis-1,3-Dichloropropene	10061-01-5	111	20.5	0.016	3.2	0.017	3.4	0.016	3.3	0.016	0.000	3.3	0.087
Pyridine	110-86-1	79	20.7	0.057	16	0.044	12	0.061	17	0.054	0.009	15	2.5
Pentanenitrile	110-59-8	83	21.6	0.035	9.4	0.027	7.2	0.035	9.4	0.032	0.005	8.7	1.3
1,1,2-Trichloroethane	79-00-5	133	22.0	0.023	3.9	0.026	4.3	0.025	4.2	0.025	0.001	4.1	0.22
Toluene	108-88-3	92	22.7	0.025	6.1	0.032	7.7	0.027	6.6	0.028	0.003	6.8	0.83
1,2-Dibromoethane	106-93-4	188	24.2	0.026	3.1	0.031	3.7	0.031	3.7	0.029	0.003	3.5	0.36
Octane	111-65-9	114	24.7	0.015	2.9	0.002	0.47	0.002	0.47	e	e	e	e
Tetrachloroethylene	127-18-4	166	25.3	0.026	3.6	0.031	4.2	0.031	4.1	0.029	0.003	4.0	0.34
Chlorobenzene	108-90-7	113	26.9	0.017	3.3	0.019	3.9	0.019	3.7	0.018	0.001	3.6	0.28
Hexanenitrile	628-73-9	97	27.1	0.037	8.6	0.032	7.4	0.042	9.8	0.037	0.005	8.6	1.2
Ethylbenzene	100-41-4	106	27.7	0.016	3.4	0.018	3.9	0.017	3.6	0.017	0.001	3.6	0.24
p/m-Xylene	106-42-3	106	27.7	0.030	6.3	0.033	7.0	0.032	6.7	0.031	0.002	6.6	0.36
Cyclohexanone	108-94-1	98	28.6	0.027	6.2	0.006	1.3	0.006	1.3	e	e	e	e

Table D.2. Positively Identified and Quantitated Target Analytes^(a) and Tentatively Identified Compounds and Estimated Concentrations^(b) for Samples from the Headspace in Tank S-106 in SUMMA Canisters Collected on 6/13/96

Target Analytes ^(a)	CAS	MW	Ret Time	S6061-A04.097 ^(c) ISVS		S6061-A05.108 ^{(c)(d)} ISVS		S6061-A06.120 ^(c) ISVS		Mean and Standard Deviation						
				(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)	St. Dev.	St. Dev.			
Styrene	100-42-5	104	29.1	0.015	3.2	J	0.016	3.5	J	0.013	2.8	J	0.015	0.002	3.1	0.33
1,1,2,2-Tetrachloroethane	79-34-5	168	29.3	0.037	4.9	J	0.037	4.9	J	0.036	4.8	J	0.037	0.000	4.9	0.057
o-Xylene	95-47-6	106	29.4	0.017	3.7	J	0.019	4.1	J	0.016	3.4	J	0.018	0.002	3.7	0.34
Nonane	111-84-2	128	29.8	0.019	3.3	J	0.018	3.1	J	0.002	0.31	U	0.018	e	3.2	e
1-Ethyl-2-Methyl-Benzene	611-14-3	120	33.0	0.020	3.7	B	0.020	3.8	B	0.018	3.3	B,J	0.019	0.001	3.6	0.23
1,3,5-Trimethylbenzene	108-67-8	120	33.0	0.020	3.7	B	0.020	3.8	B	0.018	3.3	B,J	0.019	0.001	3.6	0.23
1,2,4-Trimethylbenzene	95-63-6	120	34.3	0.021	3.9	J	0.020	3.8	J	0.018	3.4	J	0.020	0.002	3.7	0.28
Decane	124-18-5	142	34.5	0.044	6.9	B	0.041	6.4	B	0.038	6.0	B	0.041	0.003	6.4	0.49
1,3-Dichlorobenzene	541-73-1	147	34.8	0.022	3.4	B	0.022	3.4	B	0.021	3.2	B	0.022	0.001	3.3	0.11
1,4-Dichlorobenzene	106-46-7	147	34.8	0.022	3.4	B	0.022	3.4	B	0.021	3.2	B	0.022	0.001	3.3	0.095
1,2-Dichlorobenzene	95-50-1	147	36.1	0.024	3.7	B	0.023	3.6	B	0.023	3.5	B	0.023	0.001	3.6	0.095
Undecane	1120-21-4	156	38.8	0.024	3.5	J	0.018	2.6	J	0.003	0.37	U	0.021	e	3.1	e
Hexachloro-1,3-butadiene	87-68-3	261	44.2	0.032	2.8	J	0.031	2.7	J	0.034	3.0	J	0.033	0.002	2.8	0.14
Tridecane	629-50-5	184	46.6	0.006	0.73	U	0.037	4.5	J	0.006	0.73	U	e	e	e	e
Tentatively Identified Compounds^(b)																
Propene	115-07-1	42	4.4	0.015	7.8	N	0.008	4.3	N	0.012	6.5	N	0.012	0.003	6.2	1.8
Propane	74-98-6	44	4.5	0.027	14	N	0.023	12	N	0.030	15	N	0.027	0.004	14	1.9
Methyl nitrite	624-91-9	61	4.7	0.018	6.7	N	0.020	7.2	N	0.022	8.0	N	0.020	0.002	7.3	0.66
Butanal	123-72-8	72	12.3	0.264	82	N	nd	nd	nd	nd	nd	nd	e	e	e	e
2-Hexanone	591-78-6	100	23.1	0.007	1.5	N	nd	nd	nd	nd	nd	nd	e	e	e	e
Unknown Alkane			37.3	0.048	f		0.049	f		0.038	f		0.045	0.006	e	e
Unknown Alkane			37.5	0.023	f		nd	nd		0.025	f		0.024	e	e	e

Data Quality Flags

- B Compound found in associated laboratory blank.
- J Target compound detected above the IDL but below the EQL.
- N 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 Identified Compounds and Estimated Concentrations^(b) of Replicate Analysis of a Single SUMMATM Canister Collected from the Headspace of Tank S-106 on 6/13/96

Tentatively Identified Compounds ^(b)	CAS	MW	Ret Time	S6061- A05.108 ^(c) ISVS						Relative Percent Difference ^(d)
				(mg/m ³)	(ppbv)	Flag	(mg/m ³)	(ppbv)	Flag	%
Dichlorodifluoromethane	75-71-8	121	4.6	0.029	5.5	B	0.031	5.8	B	6
Chloromethane	74-87-3	50	5.0	0.013	5.8	J	0.013	5.7	J	2
1,1,1,2,2-tetrafluoroethane	76-14-2	171	5.2	0.026	3.4	J	0.025	3.2	J	7
Methanol	67-56-1	32	5.3	2.904	2030	Y	3.152	2203	Y	8
Bromomethane	74-83-9	95	6.4	0.018	4.1	J	0.017	4.0	J	4
Ethanol	64-17-5	46	6.9	2.241	1091	Y	2.315	1127	Y	3
Acetonitrile	75-05-8	41	7.4	0.022	12	J	0.004	2.2	U	
Acetone	67-64-1	58	7.9	0.510	197		0.498	192		2
Trichlorofluoromethane	75-69-4	137	8.3	0.046	7.5	J	0.044	7.2	J	4
1,1-Dichloroethene	75-35-4	97	9.5	0.015	3.5	J	0.018	4.2	J	17
Methylene Chloride	75-09-2	85	9.7	0.030	7.8	B	0.030	7.9	B	0
1,1,2-trichloro-2,2-trifluoroethane	76-13-1	187	10.2	0.042	5.1		0.040	4.8		5
Propanol	71-23-8	60	10.9	0.052	20		0.056	21		7
Propanenitrile	107-12-0	55	11.0	0.028	12	J	0.004	1.6	U	
1,1-Dichloroethane	75-34-3	99	11.9	0.018	4.1	J	0.019	4.3	J	4
cis-1,2-Dichloroethene	156-59-2	97	13.4	0.013	3.0	J	0.015	3.3	J	11
Hexane	110-54-3	86	13.8	0.026	6.8	J	0.026	6.7	J	2
Chloroform	67-66-3	119	14.0	0.020	3.8	J	0.020	3.8	J	2
Tetrahydrofuran	109-99-9	72	14.7	0.047	15	B	0.002	0.50	U	
1,1,1-Trichloroethane	71-55-6	133	15.9	0.024	3.9	J	0.023	3.8	J	4
1-Butanol	71-36-3	74	16.4	0.208	63		0.217	66		4
Benzene	71-43-2	78	16.8	0.013	3.6	J	0.013	3.7	J	3
Carbon Tetrachloride	56-23-5	154	17.1	0.023	3.3	J	0.023	3.4	J	3
Trichloroethene	79-01-6	131	18.8	0.023	3.8	J	0.022	3.7	J	3
Heptane	142-82-5	100	19.3	0.021	4.7	B	0.019	4.4	B	9
4-Methyl-2-Pentanone	108-10-1	100	20.5	0.036	8.0	B	0.030	6.7	B,J	17
cis-1,3-Dichloropropene	10061-01-5	111	20.5	0.017	3.4	J	0.002	0.48	U	
Pyridine	110-86-1	79	20.7	0.044	12	J	0.041	12	J	7
Pentanenitrile	110-59-8	83	21.6	0.027	7.2	J	0.004	1.1	U	
1,1,2-Trichloroethane	79-00-5	133	22.0	0.026	4.3	B,J	0.016	2.7	B,J	47
Toluene	108-88-3	92	22.7	0.032	7.7		0.034	8.3		8
1,2-Dibromoethane	106-93-4	188	24.2	0.031	3.7	J	0.026	3.1	J	19
Octane	111-65-9	114	24.7	0.002	0.47	U	0.014	2.8	J	
Tetrachloroethylene	127-18-4	166	25.3	0.031	4.2	J	0.030	4.1	J	2
Chlorobenzene	108-90-7	113	26.9	0.019	3.9	J	0.015	3.1	J	23
Hexanenitrile	628-73-9	97	27.1	0.032	7.4	J	0.039	9.0	J	19
Ethylbenzene	100-41-4	106	27.7	0.018	3.9	J	0.015	3.1	J	21
p/m-Xylene	106-42-3	106	27.7	0.033	7.0	J	0.027	5.7	J	21
Styrene	100-42-5	104	29.1	0.016	3.5	J	0.012	2.5	J	32
1,1,2,2-Tetrachloroethane	79-34-5	168	29.3	0.037	4.9	J	0.031	4.2	J	15
o-Xylene	95-47-6	106	29.4	0.019	4.1	J	0.015	3.1	J	27
Nonane	111-84-2	128	29.8	0.018	3.1	J	0.002	0.31	U	
1-Ethyl-2-Methyl-Benzene	611-14-3	120	33.0	0.020	3.8	B	0.017	3.2	B,J	18
1,3,5-Trimethylbenzene	108-67-8	120	33.0	0.020	3.8	B	0.017	3.2	B,J	18
1,2,4-Trimethylbenzene	95-63-6	120	34.3	0.020	3.8	J	0.018	3.3	J	15
Decane	124-18-5	142	34.5	0.041	6.4	B	0.036	5.7	B	12
1,3-Dichlorobenzene	541-73-1	147	34.8	0.022	3.4	B	0.019	2.9	B	18
1,4-Dichlorobenzene	106-46-7	147	34.8	0.022	3.4	B	0.019	2.9	B	17
1,2-Dichlorobenzene	95-50-1	147	36.1	0.023	3.6	B	0.021	3.2	B	12
Undecane	1120-21-4	156	38.8	0.018	2.6	J	0.003	0.37	U	
Hexachloro-1,3-butadiene	87-68-3	261	44.2	0.031	2.7	J	0.031	2.6	J	2
Tridecane	629-50-5	184	46.6	0.037	4.5	J	0.006	0.73	U	
Propene	115-07-1	42	4.4	0.008	4.3	N	0.012	6.6	N	43
Propane	74-98-6	44	4.5	0.023	12	N	0.038	19	N	48

Table D.3. Positively Identified and Quantitated Target Analytes^(a) and Tentatively Identified Compounds and Estimated Concentrations^(b) of Replicate Analysis of a Single SUMMA™ Canister Collected from the Headspace of Tank S-106 on 6/13/96

Tentatively Identified Compounds ^(b)	CAS	MW	Ret Time	S6061- A05.108 ^(c) ISVS					Relative Percent Difference ^(d)
				(mg/m ³)	(ppbv)	Flag	(mg/m ³)	(ppbv)	Flag
Methyl nitrite	624-91-9	61	4.7	0.020	7.2	N	nd	nd	
Pyrazine	290-37-9	80	19.8	nd	nd		0.004	0.99	N
Unknown Alkane			37.3	0.049	e		0.047	e	3
Unknown Alkane			39.3	nd	nd		0.006	e	

Data Quality Flags

B Compound found in associated laboratory blank.

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

N 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.

(e) No molecular weight available for calculation.

nd Not detected

Table D.4. Positively Identified and Quantitated Target Analytes^(a) and Tentatively Identified Compounds and Estimated Concentrations^(b) in Ambient Air and Ambient Air Through the ISVS Collected Near Tank S-106 in SUMMATM Canisters Collected on 6/13/96

Target Analytes ^(a)	CAS	MW	Ret Time	S6061- A02.089 ^(c) ISVS			S6061- A01.086 ^(c) ISVS		
				Ambient Air Through Bundle			Upwind Ambient Air		
				(mg/m ³)	(ppbv)	Flag	(mg/m ³)	(ppbv)	Flag
Dichlorodifluoromethane	75-71-8	121	4.6	0.0297	5.5	B	0.0091	1.7	B,J
Chloromethane	74-87-3	50	5.0	0.0122	5.4	J	0.0024	1.1	U
1,1,1,2-tetrachloroethane	76-14-2	171	5.2	0.0344	4.5	J	0.013	1.7	U
Bromomethane	74-83-9	95	6.4	0.0165	3.9	J	0.0052	1.2	U
Acetone	67-64-1	58	7.9	0.0399	15.4		0.0036	1.4	U
Trichlorofluoromethane	75-69-4	137	8.3	0.0261	4.3	J	0.0052	0.85	J
1,1-Dichloroethene	75-35-4	97	9.5	0.0167	3.9	J	0.0038	0.88	U
Methylene Chloride	75-09-2	85	9.7	0.0312	8.2	B	0.0161	4.3	B,J
1,1,1,2-tetrachloroethane	76-13-1	187	10.2	0.0718	8.6		0.004	0.48	U
Propanol	71-23-8	60	10.9	0.0195	7.3	J	0.0028	1.0	U
1,1-Dichloroethane	75-34-3	99	11.9	0.0206	4.7		0.002	0.45	U
2-Butanone	78-93-3	72	12.5	0.0028	0.87	U	0.0175	5.4	J
cis-1,2-Dichloroethene	156-59-2	97	13.4	0.0148	3.4	J	0.0034	0.79	U
Hexane	110-54-3	86	13.8	0.0258	6.7	J	0.0084	2.2	J
Chloroform	67-66-3	119	14.0	0.0234	4.4	J	0.0104	2.0	J
Tetrahydrofuran	109-99-9	72	14.7	0.0016	0.50	U	0.011	3.4	B,J
1,1,1-Trichloroethane	71-55-6	133	15.9	0.0259	4.3	J	0.0101	1.7	J
1-Butanol	71-36-3	74	16.4	0.027	8.2	B,J	0.019	5.7	B,J
Benzene	71-43-2	78	16.8	0.0138	4.0	J	0.0068	1.9	J
Carbon Tetrachloride	56-23-5	154	17.1	0.0247	3.6	J	0.0104	1.5	J
Trichloroethene	79-01-6	131	18.8	0.0231	3.9	J	0.0121	2.1	J
Heptane	142-82-5	100	19.3	0.0203	4.6	B	0.011	2.5	B,J
4-Methyl-2-Pentanone	108-10-1	100	20.5	0.0336	7.5	B,J	0.0197	4.4	B,J
cis-1,3-Dichloropropene	10061-01-5	111	20.5	0.0129	2.6	J	0.0024	0.48	U
Pyridine	110-86-1	79	20.7	0.0489	14	J	0.0449	13	J
Pentanenitrile	110-59-8	83	21.6	0.0252	6.8	J	0.0164	4.4	J
1,1,2-Trichloroethane	79-00-5	133	22.0	0.0194	3.3	B,J	0.0143	2.4	B,J
Toluene	108-88-3	92	22.7	0.0235	5.7		0.0111	2.7	J
1,2-Dibromoethane	106-93-4	188	24.2	0.0052	0.62	U	0.0167	2.0	J
Octane	111-65-9	114	24.7	0.0155	3.0	J	0.0102	2.0	J
Tetrachloroethylene	127-18-4	166	25.3	0.0285	3.9	J	0.0158	2.1	J
Chlorobenzene	108-90-7	113	26.9	0.017	3.4	J	0.0115	2.3	J
Hexanenitrile	628-73-9	97	27.1	0.0372	8.6	J	0.0118	2.7	J
Ethylbenzene	100-41-4	106	27.7	0.0166	3.5	J	0.010	2.1	J
p/m-Xylene	106-42-3	106	27.7	0.0299	6.3	J	0.0451	9.5	J
Cyclohexanone	108-94-1	98	28.6	0.0261	6.0	J	0.0058	1.3	U
Styrene	100-42-5	104	29.1	0.0129	2.8	J	0.0094	2.0	J
1,1,2,2-Tetrachloroethane	79-34-5	168	29.3	0.0318	4.2	J	0.0206	2.8	J
o-Xylene	95-47-6	106	29.4	0.0149	3.2	J	0.0105	2.2	J
1-Ethyl-2-Methyl-Benzene	611-14-3	120	33.0	0.0174	3.2	B,J	0.0115	2.2	B,J
1,3,5-Trimethylbenzene	108-67-8	120	33.0	0.0174	3.2	B,J	0.0109	2.0	B,J
1,2,4-Trimethylbenzene	95-63-6	120	34.3	0.0179	3.3	J	0.0103	1.9	J
Decane	124-18-5	142	34.5	0.0347	5.5	B	0.0181	2.9	B,J
1,3-Dichlorobenzene	541-73-1	147	34.8	0.0194	3.0	B	0.0126	1.9	B,J
1,4-Dichlorobenzene	106-46-7	147	34.8	0.0194	3.0	B	0.0125	1.9	B,J
1,2-Dichlorobenzene	95-50-1	147	36.1	0.021	3.2	B	0.0137	2.1	B,J
Undecane	1120-21-4	156	38.8	0.0179	2.6	J	0.0026	0.37	U
Hexachloro-1,3-butadiene	87-68-3	261	44.2	0.0307	2.6	J	0.0046	0.40	U

Table D.4. Positively Identified and Quantitated Target Analytes^(a) and Tentatively Identified Compounds and Estimated Concentrations^(b) in Ambient Air and Ambient Air Through the ISVS Collected Near Tank S-106 in SUMMATM Canisters Collected on 6/13/96.

Tentatively Identified Compounds ^(b)	CAS	MW	Ret Time	S6061- A02.089 ^(c) ISVS			S6061- A01.086 ^(c) ISVS		
				Ambient Air Through Bundle		Flag	Upwind Ambient Air		Flag
				(mg/m ³)	(ppbv)			(mg/m ³)	
Carbonyl sulfide	463-58-1	60	4.5	nd	nd		0.011	4.3	N
Acetaldehyde	75-07-0	44	5.2	nd	nd		0.101	51	N
Cyclopropane	75-01-4	62	5.5	0.010	5.3	N	nd	nd	
Butanal	123-72-8	72	12.3	nd	nd		0.009	2.9	N
Cyclotrisiloxane, hexamethyl-	541-05-9	222	25.5	nd	nd		0.038	3.8	N
Unknown Alkane			37.5	0.065	d		nd	nd	
Unknown Alkane			37.6	0.034	d		nd	nd	
Unknown Alkane			40.3	0.016	d		nd	nd	

Data Quality Flags

B Compound found in associated laboratory blank.

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

N Tentatively identified compound.

U Target compound not detected at or above the IDL.

Footnotes

(a) Detected 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

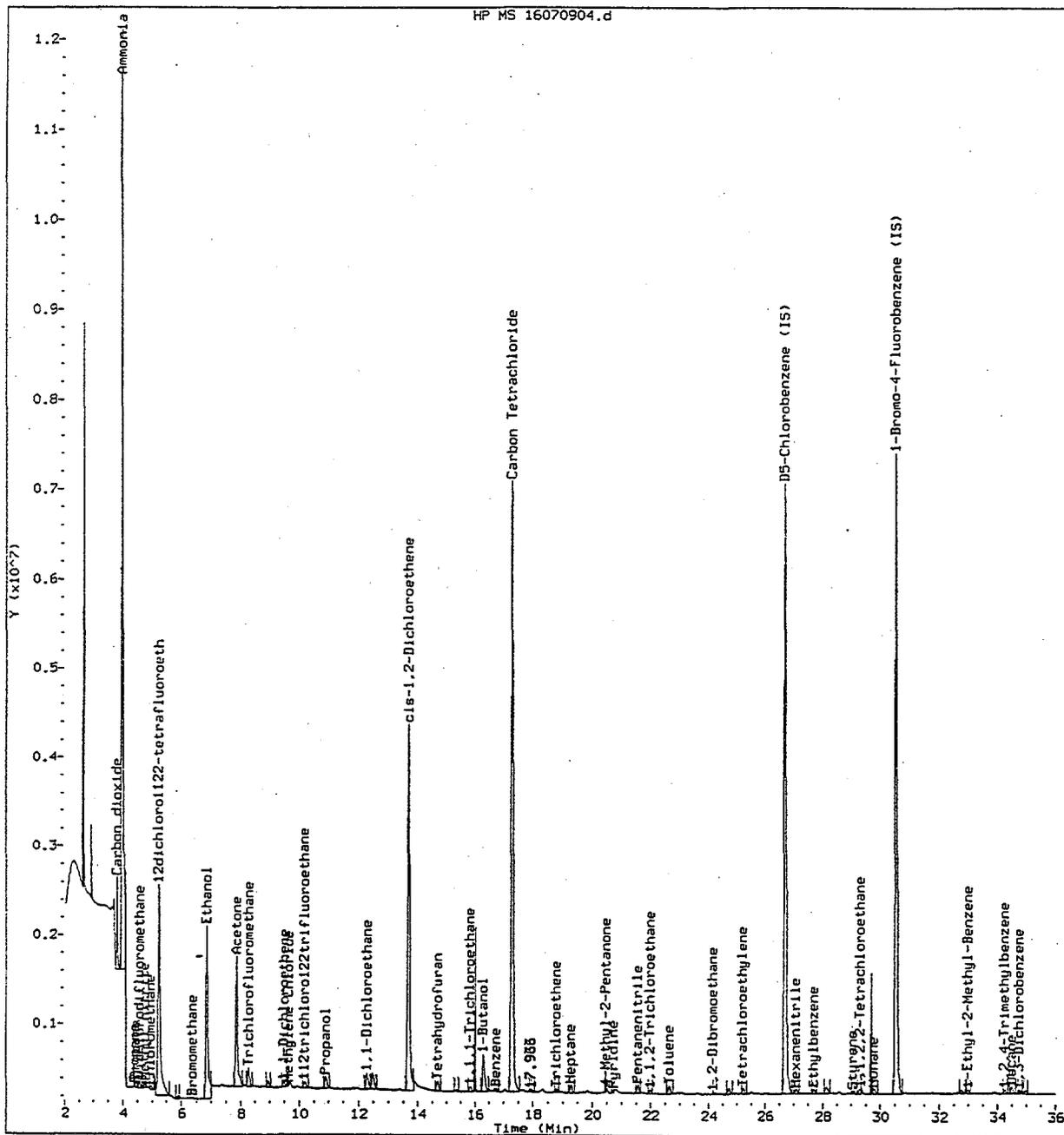


Figure D.1a Total Ion Chromatogram (2 - 36 min) for Hanford Waste Tank S-106
SUMMA™ Canister Sample S6061-A05-108 Collected on 6/13/96

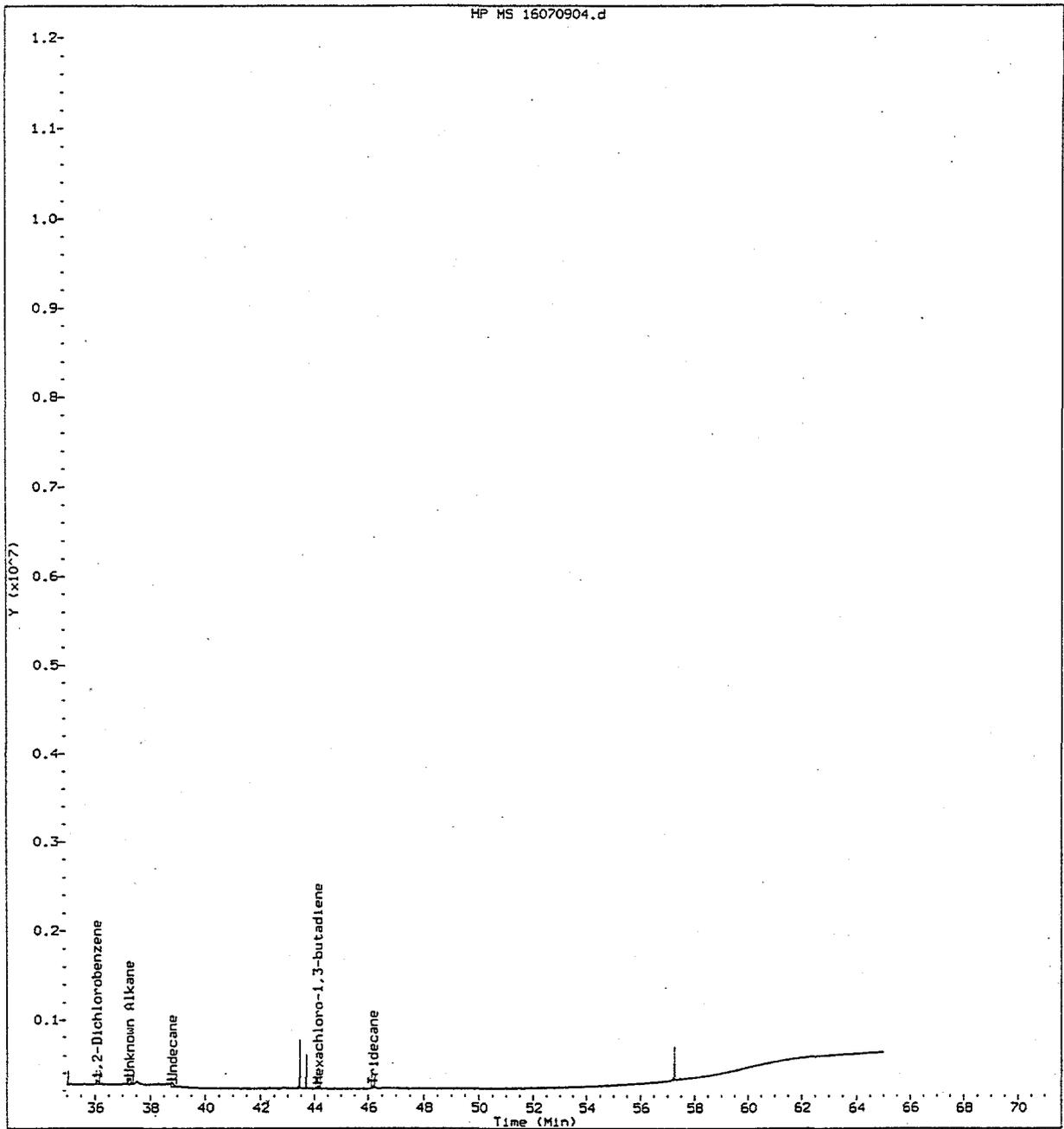


Figure D.1b Total Ion Chromatogram (36 - 70 min) for Hanford Waste Tank S-106
SUMMA™ Canister Sample S6061-A05-108 Collected on 6/13/96

Appendix E

Tank Vapor Characterization: Organic Analytes by Triple Sorbent Trap Method

Appendix E

Tank Vapor Characterization: Organic Analytes by Triple Sorbent Trap Method

E.1 Sampling Methodology

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

E.2 Analytical Procedure

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

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

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

The instrument calibration mixture for the TST analysis consists of 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

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

(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. Methanol and ethanol are not currently included in the method; 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.

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-d₅, and 1,4-bromofluorobenzene was used as an IS for all calibration standard and sample analyses. Analyte responses from sample components, ISs, and standards were obtained from the extracted ion plot from their selected mass ion. A continuing calibration was generated by calculating the relative response ratios of the IS to calibration standard responses and plotting the ratios against the ratio of the calibration-standard concentration (in ppbv) to the IS concentration. Once it is determined that the relative response is linear with increasing concentration, an average response factor is calculated for each target analyte and used to determine the concentration of target compounds in each sample.

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

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

E.3.2 Identification and Quantitation of Tentatively Identified Compounds. The tentatively identified compounds (TICs) are determined by mass-spectral interpretation and comparison of the spectra with the U.S. Environmental Protection Agency (EPA)/National Institute for Standards and Technology (NIST) and WILEY Libraries, which are a part of the Hewlett-Packard 5971/5972 instrument operating system. Chromatographic peaks with an area count greater than, or equal to, one-tenth of the total area count of the nearest eluting IS are tentatively identified and quantitatively estimated. The quality of the mass-spectral searches was then reviewed by the principal investigators before the identification was assigned to each chromatographic peak.

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

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

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

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

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

E.4 Semi-Volatile 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 100094. Samples were analyzed on July 11, 1996 for the field and trip blanks and on July 12, 1996 for tank samples.

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

Table E.2 lists the quantitative results for compounds listed as target analytes and TICs. Target compounds not listed in Table E.2 were not detected in any of the tank headspace samples above the compound IDL. Thirty-six target analytes above the IDL and 27 TICs were detected in the tank headspace samples. All 36 of the target analytes and 26 TICs were observed in two or more sorbent traps. Ethanol at 1.24 mg/m³ and methanol at 1.07 mg/m³ accounted for 40% of the target analytes and 16% of the total concentration identified by the analysis. The total concentration of the target analytes was 5.71 mg/m³ or 40% of the total concentration identified by the analyses. The predominant TICs observed in these samples were methylcyclohexane at 1.37 mg/m³ and octamethyl-cyclotetrasiloxane at 1.00 mg/m³. The total concentration of the TICs was 8.69 mg/m³ or 60% of the total concentration identified by the analysis. The total concentration of all the compounds identified was 14.41 mg/m³.

Triple sorbent trap sample PNL 1002 was analyzed in replicate for target analytes and TICs to determine analytical precision. Twelve of 35 target compounds and 10 of 27 TICs had RPDs of less than 10%.

The following procedural changes and observations were noted during the analysis of Tank S-106:

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.

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, which were collected using a 0°C calibration.

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. Two compounds that appeared 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. 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. The special handling associated with the riser contamination appears to have severely exacerbated the tape problem that had not been completely eliminated. Because of the tape problem, tank results from this sampling activity should be generally considered as suspect.

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.

Batch 7/11/96:

Samples included in this batch consisted of the two field blanks and two trip blanks.

The first CCV run showed unacceptable performance and a second CCV was run. The second CCV was within nominal limits as specified in the procedure for all target compounds except chloromethane (28.4%), ethanol (39.8%), decane (30.7%), and tetradecane (36.7%). Internal standard (IS) responses were more erratic than normally acceptable with the CCV,

showing an unusually high response. Because the IS responses for the CCV were higher than normal, all subsequent IS responses showed a low percent relative response. Variations in IS response with this method are associated with minor differences in tube packing density, which can result in a decrease in split ratio and an increased sensitivity. In this method, performance studies including detection limits were run at the highest split ratio (i.e., lowest sensitivity) with data quality not impacted provided the IS responses for individual samples are not anomalously low in absolute, as opposed to relative, intensity. In this run, the internal standard responses for several samples were slightly below the nominal minimums (relative to CCV) specified in the procedure. Since the absolute responses for these blank samples were within normal tolerances, the required detectability should be readily obtained. Rerun of the samples was not possible. The CCB contained trace amounts (below the EQL) of methylene chloride, 1-butanol, benzene, and tetradecane. The CCB was otherwise clean.

The field and trip blanks contained numerous target compounds at levels in excess of the EQL including acetone, trichlorofluoromethane, 2-butanone, hexane, 1-butanol, cyclohexane, heptane, toluene, ethylbenzene, p/m xylene, styrene, and o-xylene. A number of compounds were detected in at least one of the blanks at trace levels (below the EQL). The target compounds observed are generally ascribable to contamination during sampling and subsequent handling associated with the use of 3M adhesive tape. Numerous TICs typical of adhesive tape emanations were also observed including methyl cyclohexane, which provides a characteristic signature for the 3M tape.

Batch 7/12/96:

Samples included in this batch consisted of the three tank samples and one repeat analysis of a tank sample.

The CCV was within nominal limits for all compounds except ethanol (51.2%), nonane (25.4%), and decane (34.45%). The CCB contained trace amounts (below the EQL) of methylene chloride and tetradecane. The CCB was otherwise clean.

The 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, 4-methyl-2-pentanone, and decane. A number of other target compounds were detected in at least one of the samples at trace levels (below the EQL). Many of the target compounds observed (acetone, 2-butanone, hexane, 1-butanol, cyclohexane, heptane, toluene, ethylbenzene, p/m xylene, styrene, and o-xylene) are generally ascribable to contamination during sampling and subsequent handling associated with the use of 3M adhesive tape. Methanol and ethanol were also present in the field blanks at trace levels that probably represent a passive sampling contribution since those compounds are not typically associated with adhesive tape.

Table E.2. Positively Identified and Quantitated Target Analytes^(a) and Tentatively Identified Compounds and Estimated Concentrations^(b) for Triple Sorbent Traps Collected from the Headspace of Tank S-106 on 6/13/96

Target Analytes ^(a)	CAS	MW	Ret Time (min)	S6061-A11.1001 ^(c) ISVS		S6061-A12.1002 ^{(c)(d)} ISVS		S6061-A13.1003 ^(c) ISVS		Mean and Standard Deviation						
				(mg/m ³)	Flag	(mg/m ³)	Flag	(mg/m ³)	Flag	(mg/m ³)	St. Dev.	(ppbv)	St. Dev.			
Methanol	67-56-1	32	10.0	1.316	920	Y	1.119	782	Y	0.772	540	Y	1.069	0.275	747	193
Ethanol	64-17-5	46	12.6	1.403	682	Y	1.303	633	Y	1.018	495	Y	1.241	0.200	604	97
Acetonitrile	75-05-8	41	13.0	0.022	12	J	0.020	11	J	0.015	8.1	J	0.019	0.004	10	2.0
Acetone	67-64-1	58	13.7	0.566	218	J	0.401	155	J	0.366	141	J	0.444	0.107	171	41
Trichlorofluoromethane	75-69-4	137	14.2	0.022	3.6	J	0.024	3.8	J	0.023	3.8	J	0.023	0.001	3.8	0.12
Pentane	109-66-0	72	15.0	0.009	2.8	J	0.008	2.4	J	0.004	1.3	J	0.007	0.002	2.2	0.77
Methylene Chloride	75-09-2	85	15.8	0.061	16	J	0.062	16	J	0.039	10	J	0.054	0.013	14	3.5
1,1,1-Trichloroethane	76-13-1	187	16.3	0.011	1.3	J	0.004	0.46	J	0.003	0.40	J	0.006	0.004	0.72	0.50
Propanol	71-23-8	60	17.1	0.044	16	J	0.036	13	J	0.027	10	J	0.036	0.009	13	3.2
2-Butanone	78-93-3	72	18.6	0.057	18	J	0.059	18	J	0.046	14	J	0.054	0.007	17	2.1
Hexane	110-54-3	86	19.9	0.051	13	J	0.069	18	J	0.035	9.1	J	0.052	0.017	13	4.4
Tetrahydrofuran	109-99-9	72	20.8	0.018	5.6	J	0.019	5.9	J	0.017	5.4	J	0.018	0.001	5.6	0.24
Benzene	71-43-2	78	22.8	0.007	2.1	J	0.009	2.7	J	0.006	1.6	J	0.007	0.002	2.1	0.52
1,1,1-Trichloroethane	71-55-6	133	22.0	0.016	2.6	J	0.028	4.6	J	0.018	3.0	J	0.020	0.006	3.4	1.1
1-Butanol	71-36-3	74	22.3	0.216	65	J	0.291	88	J	0.211	64	J	0.239	0.045	72	14
Cyclohexane	110-82-7	84	23.4	0.053	14	J	0.322	86	J	0.053	14	J	0.143	0.155	38	41
Heptane	142-82-5	100	25.2	0.551	123	J	0.784	175	J	0.441	99	J	0.592	0.175	132	39
4-Methyl-2-Pentanone	108-10-1	100	26.4	0.022	4.9	J	0.041	9.2	J	0.005	1.1	J	0.023	0.018	5.1	4.1
Pyridine	110-86-1	79	26.6	0.041	12	J	0.054	15	J	0.056	16	J	0.050	0.008	14	2.2
Toluene	108-88-3	92	28.5	0.976	237	J	1.373	334	J	0.931	226	J	1.093	0.243	266	59
Octane	111-65-9	114	30.5	0.008	1.7	J	0.010	2.1	J	0.003	0.56	U	0.009	e	1.9	e
Tetrachloroethylene	127-18-4	166	31.1	0.003	0.36	U	0.012	1.6	J	0.003	0.42	J	0.007	e	1.0	e
Ethylbenzene	100-41-4	106	33.5	0.038	8.0	J	0.051	11	J	0.034	7.2	J	0.041	0.009	8.6	1.8
p/m-Xylene	106-42-3	106	33.9	0.141	30	J	0.186	39	J	0.133	28	J	0.153	0.029	32	6.1
Styrene	100-42-5	104	34.8	0.028	6.0	J	0.039	8.4	J	0.026	5.7	J	0.031	0.007	6.7	1.5
o-Xylene	95-47-6	106	35.1	0.047	10	J	0.055	12	J	0.037	7.8	J	0.046	0.009	9.7	1.9
Nonane	111-84-2	128	35.5	0.009	1.6	J	0.011	2.0	J	0.007	1.2	J	0.009	0.002	1.6	0.40
1-Ethyl-2-methyl benzene	611-14-3	120	38.5	0.006	1.2	J	0.008	1.5	J	0.005	0.97	J	0.007	0.002	1.2	0.28
1,3,5-Trimethylbenzene	108-67-8	120	38.7	0.007	1.3	J	0.009	1.7	J	0.006	1.1	J	0.007	0.002	1.3	0.29
1,2,4-Trimethylbenzene	95-63-6	120	40.0	0.022	4.1	J	0.028	5.2	J	0.018	3.3	J	0.023	0.005	4.2	0.97
Decane	124-18-5	142	40.1	0.038	5.9	J	0.035	5.6	J	0.025	4.0	J	0.033	0.007	5.2	1.0
1,3-Dichlorobenzene	541-73-1	147	40.5	0.004	0.55	J	0.005	0.73	J	0.003	0.50	J	0.004	0.001	0.59	0.12
1,4-Dichlorobenzene	106-46-7	147	40.7	0.004	0.55	J	0.005	0.72	J	0.003	0.49	J	0.004	0.001	0.59	0.12
Undecane	1120-21-4	156	44.5	0.016	2.4	J	0.019	2.7	J	0.015	2.1	J	0.017	0.002	2.4	0.29
Tridecane	629-50-5	184	52.2	0.067	8.2	J	0.097	12	J	0.067	8.2	J	0.077	0.017	9.4	2.1
Tetradecane	629-59-4	198	55.8	0.075	8.5	J	0.063	7.1	J	0.033	3.8	J	0.057	0.021	6.4	2.4

Table E.2. Positively Identified and Quantitated Target Analytes^(a) and Tentatively Identified Compounds and Estimated Concentrations^(b) for Triple Sorbent Traps Collected from the Headspace of Tank S-106 on 6/13/96

Tentatively Identified Compounds ^(b)	CAS	MW	Ret Time	S6061-A11.1001 ^(c) ISVS		S6061-A12.1002 ^{(c)(d)} ISVS		S6061-A13.1003 ^(c) ISVS		Mean and Standard Deviation						
				(mg/m ³)	(ppbv)	Flag	(mg/m ³)	(ppbv)	Flag	(mg/m ³)	(ppbv)	St. Dev.	(ppbv)	St. Dev.		
Formaldehyde	50-00-0	30	6.5	0.088	66	N	0.023	17	N	0.010	7.8	N	0.040	0.042	30	31
Ethane, 1-chloro-1,1-difluoro-	75-68-3	100	8.8	0.189	42	N	0.066	15	N	0.016	3.6	N	0.091	0.089	20	20
Acetaldehyde	75-07-0	44	9.5	0.255	130	N	0.142	72	N	0.153	78	N	0.183	0.063	93	32
1-Propene, 2-methyl-	115-11-7	56	10.4	0.386	154	N	0.186	74	N	0.151	60	N	0.241	0.127	96	51
Isopropyl Alcohol	67-63-0	60	14.3	0.673	251	N	0.094	35	N	0.186	69	N	0.317	0.311	118	116
1-Fluoro-1,1-dichloro-ethane	0-00-0	116	14.4	0.295	57	N	0.443	86	N	0.283	55	N	0.340	0.089	66	17
2-Propanol, 2-methyl-	75-65-0	74	15.5	0.192	58	N	0.072	22	N	0.089	27	N	0.118	0.065	36	20
Pentane, 2,3-dimethyl-	562-49-2	100	23.0	0.093	21	N	0.129	29	N	0.088	20	N	0.103	0.022	23	4.9
Hexane, 2-methyl-	591-76-4	100	23.5	0.435	97	N	0.462	103	N	0.286	64	N	0.394	0.094	88	21
Pentane, 2,3-dimethyl-	565-59-3	100	23.7	0.239	54	N	0.284	64	N	0.265	59	N	0.263	0.022	59	5.0
Hexane, 3-methyl-	589-34-4	100	24.0	0.703	157	N	0.833	186	N	0.552	124	N	0.696	0.140	156	31
Hexane, 2,3-dimethyl-	584-94-1	114	24.6	0.183	36	N	0.234	46	N	0.195	38	N	0.204	0.027	40	5.2
Cyclopentane, 1,3-dimethyl-, cis-	2532-58-3	98	24.7	0.076	17	N	0.113	26	N	0.085	19	N	0.091	0.020	21	4.5
Cyclopentane, 1,2-dimethyl-	2452-99-5	98	24.8	0.365	83	N	0.429	98	N	0.370	85	N	0.388	0.036	89	8.1
Cyclohexane, methyl-	108-87-2	98	26.8	1.247	285	N	1.449	331	N	1.421	325	N	1.372	0.110	314	25
Hexane, 2,5-dimethyl-	592-13-2	114	27.0	0.119	23	N	0.130	26	N	0.086	17	N	0.112	0.023	22	4.5
Hexane, 2,4-dimethyl-	589-43-5	114	27.1	0.192	38	N	0.228	45	N	0.161	32	N	0.194	0.034	38	6.6
Cyclopentane, 1,2,4-trimethyl-	2815-58-9	112	27.6	0.195	39	N	0.247	49	N	0.197	39	N	0.213	0.029	42	6.0
Cyclopentane, 1,2,3-trimethyl-	2815-57-8	112	28.1	0.221	44	N	0.291	58	N	0.219	44	N	0.244	0.041	49	8.2
Heptane, 2-methyl-	592-27-8	114	28.7	0.163	32	N	0.190	37	N	0.098	19	N	0.150	0.048	30	9.4
Cyclohexane, 1,3-dimethyl-, cis-	638-04-0	112	29.7	nd	nd		0.115	23	N	nd	nd		e	e	e	e
Cyclotrisiloxane, hexamethyl-	541-05-9	222	31.2	0.305	31	N	0.489	49	N	0.372	38	N	0.389	0.093	39	9.4
Hexane, 2,3,5-trimethyl-	1069-53-0	128	31.5	0.126	22	N	0.154	27	N	0.110	19	N	0.130	0.022	23	3.9
Heptane, 2,4-dimethyl-	2213-23-2	128	31.8	0.445	78	N	0.528	92	N	0.335	59	N	0.436	0.097	76	17
Cyclotetrasiloxane, octamethyl-	556-67-2	296	39.5	0.769	58	N	1.312	99	N	0.908	69	N	0.996	0.282	75	21
1-Undecene, 4-methyl-	74630-39-0	168	42.9	0.584	78	N	0.723	96	N	0.523	70	N	0.610	0.103	81	14
Unknown C12 Alkane			43.2	0.366	f		0.358	f		nd	nd		0.362	e	e	e

Data Quality Flags

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

N Tentatively identified compound.

U 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 Identified Compounds and Estimated Concentrations^(b) of Replicate Analysis of a Single Triple Sorbent Trap Collected from the Headspace of Tank S-106 on 6/13/96

Target Analytes ^(a)	CAS	MW	Ret Time	S6061-A12.1002 ^(c) ISVS						Relative Percent Difference ^(d)
				(mg/m ³)	(ppbv)	Flag	(mg/m ³)	(ppbv)	Flag	%
Methanol	67-56-1	32	10.0	1.119	782	Y	0.669	467	Y	50
Ethanol	64-17-5	46	12.6	1.303	633	Y	0.815	396	Y	46
Acetonitrile	75-05-8	41	13.0	0.020	11	J	0.013	7.1	J	43
Acetone	67-64-1	58	13.7	0.401	155		0.314	121		24
Trichlorofluoromethane	75-69-4	137	14.2	0.024	3.8	J	0.023	3.7	J	4
Pentane	109-66-0	72	15.0	0.008	2.4	J	0.003	1.1	J	79
Methylene Chloride	75-09-2	85	15.8	0.062	16	J	0.070	18	J	12
1,1,1-trichloro-2,2,2-trifluoroethane	76-13-1	187	16.3	0.004	0.46	J	0.003	0.39	U	
Propanol	71-23-8	60	17.1	0.036	13	J	0.020	7.5	J	55
2-Butanone	78-93-3	72	18.6	0.059	18		0.045	14		25
Hexane	110-54-3	86	19.9	0.069	18		0.051	13		30
Tetrahydrofuran	109-99-9	72	20.8	0.019	5.9	J	0.015	4.7	J	22
Benzene	71-43-2	78	22.8	0.009	2.7	J	0.010	2.9	J	8
1,1,1-Trichloroethane	71-55-6	133	22.0	0.028	4.6	J	0.028	4.6	J	0
1-Butanol	71-36-3	74	22.3	0.291	88		0.213	65		31
Cyclohexane	110-82-7	84	23.4	0.322	86		0.053	14		144
Heptane	142-82-5	100	25.2	0.784	175		0.679	152		14
4-Methyl-2-Pentanone	108-10-1	100	26.4	0.041	9.2		0.011	2.4	J	119
Pyridine	110-86-1	79	26.6	0.054	15	J	0.038	11	J	34
Toluene	108-88-3	92	28.5	1.373	334		1.353	329		1
Octane	111-65-9	114	30.5	0.010	2.1	J	0.008	1.6	J	22
Tetrachloroethylene	127-18-4	166	31.1	0.012	1.6	J	0.005	0.62	J	87
Ethylbenzene	100-41-4	106	33.5	0.051	11		0.047	10		7
p/m-Xylene	106-42-3	106	33.9	0.186	39		0.184	39		1
Styrene	100-42-5	104	34.8	0.039	8.4		0.035	7.6		10
o-Xylene	95-47-6	106	35.1	0.055	12		0.053	11		4
Nonane	111-84-2	128	35.5	0.011	2.0	J	0.009	1.6	J	19
1-Ethyl-2-methyl benzene	611-14-3	120	38.5	0.008	1.5	J	0.008	1.5	J	4
1,3,5-Trimethylbenzene	108-67-8	120	38.7	0.009	1.7	J	0.008	1.5	J	8
1,2,4-Trimethylbenzene	95-63-6	120	40.0	0.028	5.2		0.026	4.8	J	9
Decane	124-18-5	142	40.1	0.035	5.6		0.029	4.6	J	19
1,3-Dichlorobenzene	541-73-1	147	40.5	0.005	0.73	J	0.004	0.66	J	11
1,4-Dichlorobenzene	106-46-7	147	40.7	0.005	0.72	J	0.004	0.65	J	9
Undecane	1120-21-4	156	44.5	0.019	2.7	J	0.016	2.3	J	13
Tridecane	629-50-5	184	52.2	0.097	12	J	0.088	11	J	9
Tetradecane	629-59-4	198	55.8	0.063	7.1	J	0.048	5.4	J	27
Tentatively Identified Compounds^(b)										
Formaldehyde	50-00-0	30	6.5	0.023	17	N	0.045	34	N	67
Ethane, 1-chloro-1,1-difluoro-	75-68-3	100	8.8	0.066	15	N	0.047	11	N	33
Acetaldehyde	75-07-0	44	9.5	0.142	72	N	0.062	32	N	78
1-Propene, 2-methyl-	115-11-7	56	10.4	0.186	74	N	0.148	59	N	23
Isopropyl Alcohol	67-63-0	60	14.3	0.094	35	N	0.060	22	N	44
1-Fluoro-1,1-dichloro-ethane	0-00-0	116	14.4	0.443	86	N	0.458	88	N	3
2-Propanol, 2-methyl-	75-65-0	74	15.5	0.072	22	N	0.057	17	N	23
Pentane, 3,3-dimethyl-	562-49-2	100	23.0	0.129	29	N	0.117	26	N	10
Hexane, 2-methyl-	591-76-4	100	23.5	0.462	103	N	0.397	89	N	15
Pentane, 2,3-dimethyl-	565-59-3	100	23.7	0.284	64	N	0.250	56	N	13
Hexane, 3-methyl-	589-34-4	100	24.0	0.833	186	N	0.724	162	N	14
Hexane, 2,3-dimethyl-	584-94-1	114	24.6	0.234	46	N	0.202	40	N	14
Cyclopentane, 1,3-dimethyl-, cis-	2532-58-3	98	24.7	0.113	26	N	0.093	21	N	19
Cyclopentane, 1,2-dimethyl-	2452-99-5	98	24.8	0.429	98	N	0.384	88	N	11

Table E.3. Positively Identified and Quantitated Target Analytes^(a) and Tentatively Identified Compounds and Estimated Concentrations^(b) of Replicate Analysis of a Single Triple Sorbent Trap Collected from the Headspace of Tank S-106 on 6/13/96

Tentatively Identified Compounds ^(b)	CAS	MW	Ret Time	S6061-A12.1002 ^(c) ISVS						Relative Percent Difference ^(d)
				(mg/m ³)	(ppbv)	Flag	(mg/m ³)	(ppbv)	Flag	%
Cyclohexane, methyl-	108-87-2	98	26.8	1.449	331	N	1.346	308	N	7
Hexane, 2,5-dimethyl-	592-13-2	114	27.0	0.130	26	N	0.117	23	N	10
Hexane, 2,4-dimethyl-	589-43-5	114	27.1	0.228	45	N	0.206	41	N	10
Cyclopentane, 1,2,4-trimethyl-	2815-58-9	112	27.6	0.247	49	N	0.222	44	N	11
Cyclopentane, 1,2,3-trimethyl-	2815-57-8	112	28.1	0.291	58	N	0.279	56	N	4
Heptane, 2-methyl-	592-27-8	114	28.7	0.190	37	N	0.167	33	N	13
Cyclohexane, 1,3-dimethyl-, cis-	638-04-0	112	29.7	0.115	23	N	0.110	22	N	5
Cyclotrisiloxane, hexamethyl-	541-05-9	222	31.2	0.489	49	N	0.507	51	N	4
Hexane, 2,3,5-trimethyl-	1069-53-0	128	31.5	0.154	27	N	0.142	25	N	8
Heptane, 2,4-dimethyl-	2213-23-2	128	31.8	0.528	92	N	0.495	87	N	6
Cyclotetrasiloxane, octamethyl-	556-67-2	296	39.5	1.312	99	N	1.284	97	N	2
1-Undecene, 4-methyl-	74630-39-0	168	42.9	0.723	96	N	0.665	89	N	8
Unknown C12 Alkane			43.2	0.358	f		0.338	f		6

Data Quality Flags

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

N Tentatively identified compound.

U 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.

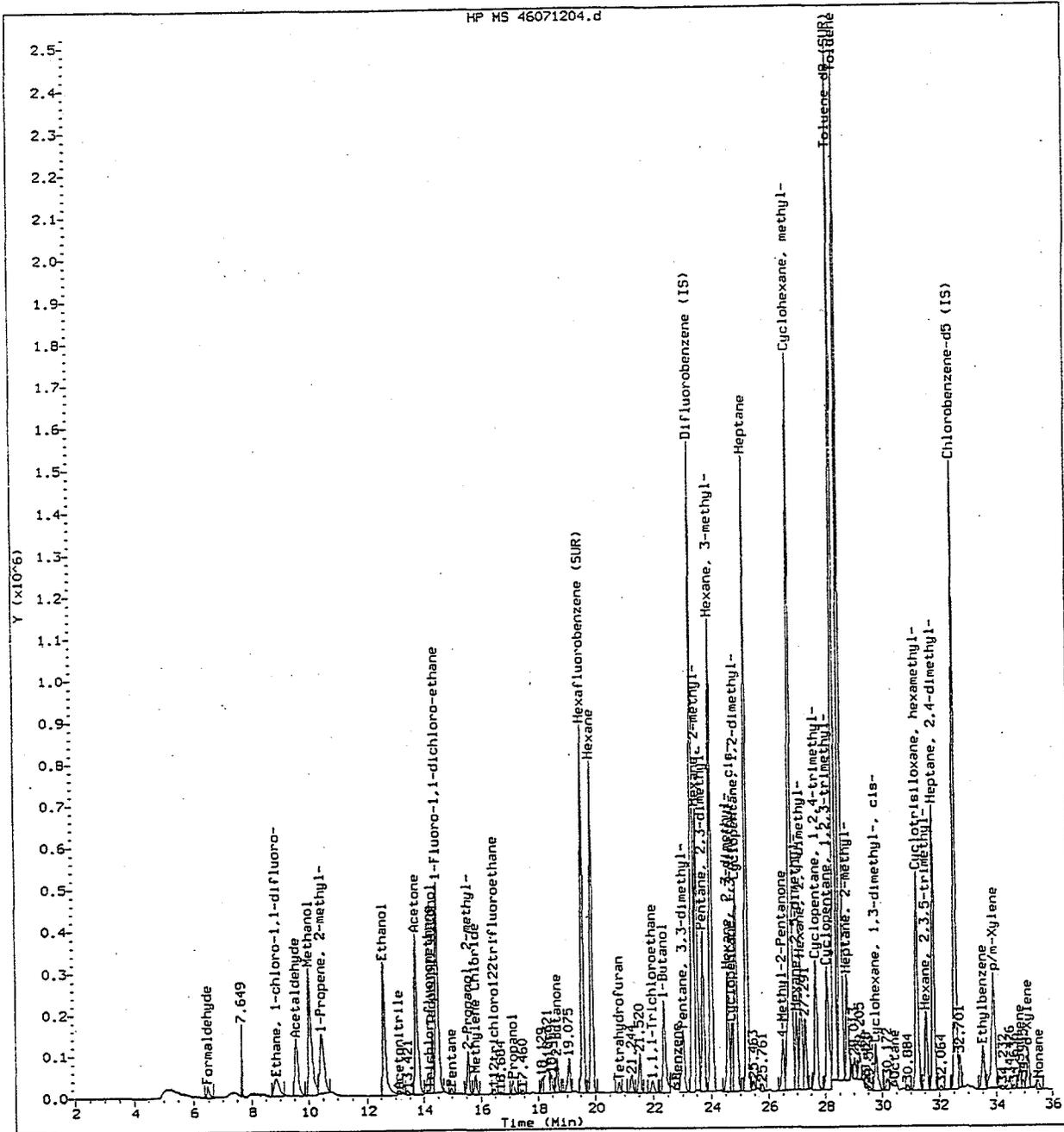


Figure E.1a Total Ion Chromatogram (2 - 36 min) for Hanford Waste Tank S-106 Triple Sorbent Trap Sample S6061-A12-1002 Collected on 6/13/96

Appendix F

Tank Vapor Characterization: Chain of Custody Sample Control Forms

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

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

Project Designation/Sampling Locations 200 West Tank Farm Collection date 06 - 13 - 96
241-S-106 Tank Vapor Sample SAF S6061 Preparation date 06 - 07 - 96
(ISVS Cart)

Ice Chest No. Field Logbook No. WHC-N-697.8

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

S6061 - A07 . S97 Collect NH₃/NO_x/H₂O Sorbent Trap
S6061 - A08 . S98 Collect NH₃/NO_x/H₂O Sorbent Trap
S6061 - A09 . S99 Collect NH₃/NO_x/H₂O Sorbent Trap
S6061 - A10 . 01R Collect NH₃/NO_x/H₂O Sorbent Trap

S6061 - A15 . 02R Open, close and store NH₃/NO_x/H₂O field blank #1
S6061 - A16 . 03R Open, close and store NH₃/NO_x/H₂O field blank #2

[] Field Transfer of Custody		[X] Chain of Possession		(Sign and Print Names)	
Relinquished By	Date	Time	Received By	Date	Time
G W Dennis <i>G.W. Dennis</i>	06-10-96	1130	J A Edwards <i>J A Edwards</i>	06-10-96	1130
J A Edwards <i>J A Edwards</i>	06-10-96	1430	Rm Arnold <i>Rm Arnold</i>	06-10-96	1430
Rm Arnold <i>Rm Arnold</i>	06-11-96	1230	RD Mahon <i>RD Mahon</i>	06-11-96	1230
RD Mahon <i>RD Mahon</i>	06-18-96	0810	GS Caprio <i>GS Caprio</i>	06-18-96	0810
GS Caprio <i>GS Caprio</i>	06-18-96	1044	J A Edwards <i>J A Edwards</i>	06-18-96	1044
J A Edwards <i>J A Edwards</i>	6-20-96	1145	G.W. Dennis <i>G.W. Dennis</i>	6-20-96	1145
G.W. Dennis <i>G.W. Dennis</i>	6-20-96	1530	S.O. Slate <i>S.O. Slate</i>	6-20-96	1530

Final Sample Disposition

Comments:

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

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

POC *[Signature]* POC *[Signature]*

(Revised 05/30/96 PNNL)

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-106 Tank Vapor Sample SAF S6061
(ISVS Cart)

Collection date 06 - 13 - 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

S6061 - A01 . 086 Collect Ambient Air Sample SUMMA #1
S6061 - A02 . 089 Collect Ambient Air Sample SUMMA #2 (through tube bundle)

S6061 - A04 . 097 Collect SUMMA #3
S6061 - A05 . 108 Collect SUMMA #4
S6061 - A06 . 120 Collect SUMMA #5

[] Field Transfer of Custody		[X] Chain of Possession		(Sign and Print Names)	
Relinquished By	Date	Time	Received By	Date	Time
J A Edwards <i>J A Edwards</i>	06-10-96	1430	Rm Arnold <i>Rm Arnold</i>	06-10-96	1430
Rm Arnold <i>Rm Arnold</i>	06-11-96	1230	R D Mahon <i>R D Mahon</i>	06-11-96	1230
R D Mahon <i>R D Mahon</i>	06-18-96	0810	GS Caprio <i>GS Caprio</i>	06-18-96	0810
GS Caprio <i>GS Caprio</i>	06-18-96	1051	J A Edwards <i>J A Edwards</i>	06-18-96	1051

Comments:

Final Sample Disposition

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

Comments:

A diesel crane was running about 20m upwind of the sample collection point before the ambient purge and ambient collection. The VT could smell diesel exhaust while the crane was running. The crane was off during collection of can 086, 089 and off during ambient purges.

POC *[Signature]* POC *[Signature]*

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

(Revised 05/30/96 PNNL)

Custody Form Initiator J. A. Edwards - PNL
 Company Contact R. D. Mahon - WHC
 Project Designation/Sampling Locations 200 West Tank Farm
 241-S-106 Tank Vapor Sample SAF S6061
 (ISVS Cart)
 Ice Chest No.
 Erco Hi/Lo thermometer No. PNL-T-003
 Bill of Lading/Airbill No. N/A
 Method of Shipment Government Truck
 Shipped to WHC
 Possible Sample Hazards/Remarks Unknown at time of sampling

Telephone (509) 373-0141
 Page 85-3009 / P8-08 / FAX 376-0418
 Telephone (509) 373-7437
 Page 85-9656 / S3-27 / FAX 373-7076
 Collection date 06-17-96
 Preparation date 06-07-96
 Field Logbook No. WHC-N-6978
 Offsite Property No. N/A

Sample Identification

S6061 - A11 . 1001 . PNL Triple Sorbent Trap (TST) Sample # 1
 S6061 - A12 . 1002 . PNL TST Sample # 2
 S6061 - A13 . 1003 . PNL TST Sample # 3
 S6061 - A14 . 1004 . PNL TST Sample # 4
 S6061 - A17 . 1005 . Open, close & store TST Field Blank # 1
 S6061 - A18 . 1006 . Open, close & store TST Field Blank #2
 S6061 - A19 . 1036 . Store TST Trip Blank #1
 S6061 - A20 . 1038 . Store TST Trip Blank #2

[] Field Transfer of Custody		[X] Chain of Possession		(Sign and Print Names)			
Relinquished By	Date	Time	Received By	Date	Time		
JL Julia	06-07-96	1425	JA Edwards	06-07-96	1425		
JA 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	0810	GS Caprio	06-18-96	0810		
GS Caprio	06-18-96	1050	JA Edwards	06-18-96	1050		
JA Edwards	06-19-96	0850	JL Julia	06-19-96	0850		

Final Sample Disposition

Comments:

- PNL (only) Checklist**
- Media labeled and checked? Y / N
 - Letter of instruction? Y / N
 - Media in good condition? Y / N
 - COC info/signatures complete? Y / N
 - Sorbents shipped on ice? (<5°C) 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 *(Signature)* POC *(Signature)*

Comments:

While removing SHA from double bagging on 14 JUN 96, it was observed that the plug in effex upstream of TST 1001 and 1004 had fallen out. The upstream side of TST could have been exposed to inside of plastic bag for 20 hrs.

- 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-11260

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